COLLOID CHEMISTRY

THEORETICAL AND APPLIED

BY SELECTED INTERNATIONAL CONTRIBUTORS

COLLECTED AND EDITED BY
JEROME ALEXANDER

VOLUME IV

SECOND SERIES OF PAPERS ON
TECHNICAL APPLICATIONS

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Preface

Since this volume concludes the series, the Editor is enabled to contrast what was projected with what has been accomplished. The preface to Volume I, published in 1926, mentioned that over 175 papers had been promised, but in all 202 are actually published. While it is difficult to draw sharp lines, these may be roughly but coherently grouped thus:

Volume I—Theory and Methods—General, Including Dispersion, 7; Aggregation, Including Surface Tension, 7; Light-effects, 4; Aerosols, Meteorology, Astronomy, etc., 6; Thermal Phenomena, 1; Electric and Surface Structure, 5; Adsorption and Associated Phenomena, 11; Pyrosols, 2; Viscosity and Plasticity, 3; Gels and Associated Phenomena, 6; Methods, Including Ultramicroscopy, Ultrafiltration, Ultracentrifugation and Sedimentation, 7; Chemical Analysis, 1.

Volume II—Biology and Medicine—General, 1; Artifacts, 2; Physiochemical, 8; Proteins and their Behavior, 5; Ferments, Catalysts, Enzymes, 5; Protoplasm and Cells, 6; Ultrafiltrables, 2; Micro-organisms, 2; Fertilization, 1; Plants, 2; General and Internal Medicine, 5; Special Injuries and Diseases, Including Inflammation, Burns, Syphilis, Pneumonia, Concretions, Dust, Fumes and Smokes, Tuberculosis and Cancer, 14; Vitamins, 1; Pharmacy and Pharmacodynamics, 4.

Volume III—Technological Applications (First Series)—General papers, Including Cohesion and Adhesion, X-ray Examination, Catalysis, Grinding and Colloid Mills, 10; Apparatus, Including Electrical Precipitation, Filtration and Flotation, 6; Minerals and Derivatives, Including Glass, Porcelain, Cements and Mortars, Refractories, 7; Metals and Alloys, Including Corrosion, 7; Petroleum, 3; Carbon, Including Fuel, Tar, Asphalt, Graphite, 4; Soils and Agriculture, 4.

Volume IV—Technological Applications (Second Series)—Carbohydrates, Including Cellulose, Wood, Paper, Explosives, Sugar, Starch Products, Sizing, 11; Dyeing, 3; Rubber, Including Latex and Carbon Black, 4; Plastics, 3; Tanning, 3; Photography, 3; Coatings, Including Paints, Color Lakes and Electro-deposition, 6; Foods, 4; Laundry and Dry-Cleaning, 2; Solidified Alcohol and Fire Extinguishers, 2; Water Supply and Sewage Disposal, 2.

Although not *every* aspect and industry has been *directly* treated, so broad a field has been covered that it would be difficult to find any chemist, engineer, biologist, physician, or manufacturer who could not locate much of great interest, and even much of direct application to his problems. To facilitate such use of the books, especial care has been given to the indexes, which are extensive, with cross-references.

The Editor has made a special effort to secure papers from the representatives of as many nations and nationalities as possible, so that the books would be truly international and bring about closer contacts between peoples. If a country is not represented, this does not mean that no one there was competent to contribute. Some asked were unable to accept; with others the Editor could not make contact; and there were limits of space and time. Tabulation by papers shows the nationality of the contributors divided thus: Australia, 1; Austria, 4; Belgium, 2; Canada, 5; China, 3; Czechoslovakia, 2; France, 10; Germany, 26; Great Britain, 25; Holland, 6; Hungary, 3; India, 2; Italy, 2; Japan, 4; Jugoslavia, 2; Mexico, 1; Palestine, 1; Poland, 1; Roumania, 1; Spain, 2; Sweden, 3; U. S. A., 103; U. S. S. R., 5.

The older literature is a rich mine of data for the colloid chemist. In the light of present information the significance of many experiments written in the records far transcends the observations or conclusions there reported. Michael Faraday, William M. Ord, Walther Spring, and Carl Barus are among the many whose work is of importance to colloid chemists. Ord's book, published in 1879, was entitled: "The Influence of Colloids on Crystalline Form and Cohesion"; but colloid nomenclature is not always found in early papers. Subsequent to his splendid research on colloidal gold, Richard Zsigmondy found Faraday's anticipatory work only upon a most thorough search of the literature, where it was buried under a misleading title. It would be of great aid to both science and industry if some of the early important papers in various fields could be abstracted and commented on upon the basis of our now more extensive knowledge.

JEROME ALEXANDER.

March 1, 1932

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Colloid Chemistry of Cellulose.[*][†]

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Introduction.

The term "cellulose" is generally applied to the framework material widely distributed in the vegetable kingdom, which is made up of carbon, hydrogen and oxygen, and which is distinguished, in contrast to most of the other constituents of plants, by a high resistance to hydrolytic agents (acids and bases). In the strictly scientific sense "cellulose" means cotton cellulose, the only type that has been well investigated scientifically; for the other forms of cellulose, the term "zellstoff" is recommended.[1] We are still far from a suitable differentiation between these terms.[2]

There appears to be no fundamental chemical difference between celluloses from different sources (such as pine-wood and cotton),[3] even though optical differences between different celluloses are known.[4]

Wadding and filter paper are regarded as the purest forms of cellulose.[5] Wadding, however, generally contains fatty and minerals acids and is overbleached. In filter paper, flax fibers are to be found amongst the cotton fibers; filter paper is also overbleached and is injured on treatment with strong acids during the removal of mineral substances.[‡]

The great contradictions in the data on the chemical behavior of cellulose are not due, in the last analysis, to the variation in the prior treatment of the material under investigation. Protection of the raw material from damage is assured by cleaning the raw cotton with a 1 per cent solution of sodium hydroxide containing some rosin soap, followed by a sodium hypochlorite bleach.[6] The commercial cottons used for nitration and for certain fabrics to be dyed with alizarin red are very pure.[7]

The purity of the cellulose is controlled by certain "constants" which have the following percentage values in the case of absorbent cotton: Ash, 0.04; hygroscopic moisture, 5.3 to 7.4; copper number,[8] 0.3 to 0.6; cellulose number,[9]

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[*] First section translated by J. Barsha, Dept. of Cellulose and Industrial Chemistry, McGill University, Montreal, Canada.

[†] This treatise was completed and sent to the Editor in 1926; but since it had to go into the fourth volume, publication was delayed. In the meantime, several important publications on cellulose had appeared and research in this field had made great advances. I have attempted to take account of the most important new work, at least in footnotes, but it must be admitted that the new achievements of the past year have necessitated a new conception of individual chapters.

Even more recent publications do not attempt an exhaustive description of the literature having a more or less close connection with the colloidal properties of cellulose, so that the following discussion has a certain *raison d'être.*

I have adhered to the rule of the editor—"as short as possible and as thorough as possible." The reader should bear this in mind, because on looking through the preceding volumes I found that the Editor's rule was variously interpreted.

The derivatives of cellulose constitute special fields which appear to deserve separate treatment. For this reason, no account has been taken of them in the present article.

Ljubljana, October, 1930.

[‡] The wadding here referred to is purified cotton, e.g. absorbent cotton for surgical uses.

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0.25 to 0.32; corrected copper number,[10] 0.04 to 0.25; solubility in boiling 3 per cent alkali after about six hours, 2 per cent; nitrogen content, 0.002 to 0.008 per cent. The form of cellulose which is insoluble in 16 per cent alcohol is called α-cellulose, the soluble portion which is precipitated by acids from solution in alkali is called β-cellulose, while the part which is soluble in alkali but is not precipitated by acids is known as γ-cellulose. The resistance to alkali is actually lowered by prior treatment with acids. According to Haller, the fiber consists of a gum-like portion—the connective tissue material, and a moderately insoluble portion—the skeletal membrane.[11]

The cellulose of plant membranes shows strong double refraction.[12] The orientation of the cellulose molecules to micelles and micellular aggregates is, therefore, vectorial. Hemicelluloses, when present, increase the double-refraction.[13] The double-refraction has been used to determine the kind of fiber[14] and to estimate the strength of the fiber,[15] the latter without any demonstrated basis.[16]

Upon the basis of X-ray spectrographic investigation,[17] cellulose fibers must be regarded, like starch granules, as possessing a crystalline structure belonging to the rhombic system, with the axial ratio of 0.6935:1:0.4467.[18] On esterification or peptization of such structures, the crystalline arrangement of the elementary particles generally remains the same, so that viscose, for example, still exhibits a crystalline structure. It has been concluded, from the X-ray diagram, that there is a repetition of the grouping $(C_6H_{10}O_5)_4$ in the "Molat" (molecular aggregate).[19]

In agreement with this result, the opinion has frequently been expressed that cellulose is a relatively low molecular system in which the larger building units (micelles) are formed through the union of several molecues of the elementary substance. The difference between the basic substance and the associated molecule was first expressed by Stiasny,[20] K. Hess[21] and P. Karrer,[22] and later developed by H. Pringsheim.[23] The researches of K. Hess seem to point to a small molecule. He observed[24] that cellulose, dissolved in copper oxide-ammonia, shows the molecular size corresponding to a formula $C_6H_{10}O_5$ and reversing his former opinion of a "chemical" combination of simple building units in the theoretical cellulose molecule, he concluded that the insoluble cellulose fiber should be regarded as a physical conglomeration. Wislicenus[25] also arrived at a similar conclusion. Cryoscopic molecular weight determinations in glacial acetic acid as solvent, with acetylcellulose, and methylcellulose, also lead to very low values ($M = 280$);[26] however, various considerations, of late, have been adduced against the experiments in question.[27]

Cross and Bevan choose the colloidal nature of cellulose as a working hypothesis. They assume that cellulose does not react as a polymeric structure, with a definite configuration, built up of previously formed hexose groups, but as a labile complex of groups of varying dimensions which is in a state similar, in some respects, to that of the solution of a salt-like electrolyte. Cellulose reacts, therefore, more like a solution-aggregate than a series of molecular compounds; the masses actually reacting follow the stoichiometric relations corresponding to the size of this end group. They retain the affinity of the aggregate which is thus progressively modified by the entry of new groups.[28] Accordingly, the structural-chemical primary valences and possibly also the secondary valences, recede as molecule-binding forces whilst surface energy and electric surface-charges in the form of adsorption, coagulation, agglutination, agglomeration, adhesion, etc., come into full play.[29] It is perhaps possible that the total residual valence of the particles, the energy of the space lattice and the gravitational force contained in it, play an important part.[30]

Through molecular cohesion (*Komolierung*) of chemically condensed hexosans and the molecular adhesion (*Admolierung*) of condensed pentosans, the solid conglomerate of insoluble fibers is built up. It is conceivable that the pentosan mass formed through molecular cohesion and adhesion can be similarly likened to the hexosan-cellulose mass, and that pentosans are actually found to be a building material in the purest technical celluose.[31]

A useful hypothesis, based on von Nägli's micellular theory, has been built up for the colloid-chemical investigation of fiber colloids.[32] Certain conclusions obtained by Gaidukow, with reference to the relation between glossiness and ultra-structure, could not be substantiated by Herzog,[33] even though he, too, sought, in the determination of the ultra-structure, a means for recognizing fibrous material and especially a means for process control in artificial silk plants.

The most widespread view to-day on the structure of cellulose has been developed by H. Staudinger on the one hand, and K. H. Meyer on the other. H. Staudinger [34] advances the view that certain structural units, under the influence of normal covalencies, line up regularly in one direction, so that a fiber-like molecule results. K. H. Meyer [35] believes that these molecules (primary valence chains) unite to form a bundle (the micelle) through reciprocal lateral attraction. Other materials can participate in the formation of such a "bundle," so that mixed micelles can result.

Three methods have been developed for the estimation of the size of the cellulose micelle: (1) Determination of the total surface, from the quantity of swelling liquid taken up at maximum swelling, assuming a monomolecular adsorption layer; (2) determination of the size of the crystallite from the increase in width of the X-ray interference with increase in the angle of diffraction; (3) most careful dissolving of cellulose and determination of its micellular size.

The first of these methods gave a chain length of 100 Å as a maximum.[36] R. O. Herzog and W. Jancke,[37] using the second method, found the chain length of the cellulose crystallite in hemp and ramie to be 117 Å in one direction, and 66 Å in the other; for nitrocellulose 100 Å and 50 Å respectively; for acetylcellulose 110 Å and 60 Å respectively.

The experiments carried out according to the third method gave results having the same order of magnitude; thus there was obtained from the diffusion coefficient of nitrocellulose a chain length of 148 to 300 Å in one direction and 56 to 94 Å in the other.[38]

The observation of J. R. Katz is of interest in this connection. He found that solutions of cellulose derivatives in organic solvents are so finely divided that, when poured onto water, the thickness of the layer attains molecular dimensions.[39]

The ultramicroscopic investigation of cotton shows that the micelles are weakly luminous and are arranged in more or less parallel rows with optically empty spaces between;[40] observation after the action of cuprammonium solution shows that part of the micelles are arranged spirally and part irregularly, thus causing abnormal double refraction of the cotton fiber.[41] Examination with a polarization microscope shows that the longitudinal axis of the elasticity ellipse effective on the surface, makes an angle of 0° to 45° with the direction of the fiber, and that, as a rule, its direction increases from left to right, but is often almost directly turned in the opposite direction.[42] Dead cotton shows a much different behavior.[43]

In contrast to cotton, we find the micelles in the case of many bast fibers (hemp, ramie) to be arranged almost parallel to the fiber-axis; we are indebted to H. Reimers[44] for a closer investigation of the relations actually prevailing. The varying spiral arrangement of the micelles is also brought out clearly in the X-ray diagram.[45]

The difference in the behavior of cotton, flax and hemp is due to the size of the "channel." The widths of the channels of the fibers named are in the ratio of 100:93.6:89.2.[46]

Besides the structural units, cellulose fiber also contains water and ash components;[47] silicic acid cannot be wholly removed by the strongest reagents and apparently has a definite influence on certain properties of cellulose.[48] The mineral constituents certainly cause a variation in the behavior of cellulose in dyeing.[47] G. Malfitano supposes the structure of a colloid generally to consist of the nucleus of an electrolyte ion (SiO_2 in the case of cellulose) around which are arranged the polymers *of polymers* of an organic element, similar to a true Werner complex.[49]

Protoplasmic remains form the wall deposit[50] in the cell lumen which is a hollow space running lengthwise through the fiber. The outermost layer behaves differently[51] from the main portion of the cell membrane towards various reagents (e.g. towards copper oxide-ammonia). While the cell membrane itself gives an indigo blue color with iodine and sulfuric acid, the cuticle is only colored brown.[52] These differences are due, primarily, to the deposition of certain protective substances in the outer layer of the cell membrane;[53] these include pectins, certain substances closely related to cork, natural coloring matters, as well as difficultly saponifiable wax-like substances and fats.[54]

Cellulose as Absorbent.

Water.[55] The average water content of pure, air-dried cotton cellulose at normal humidity is 6.66 per cent.[56] Cotton celluloses from different sources vary in their water content. American cotton is the most moist with 9.5 per cent, followed by Egyptian with 8.5 per cent and Indian with 7.5 per cent of moisture.[57] Since the aqueous extracts of crude cotton are very hygroscopic, it is not impossible that the high hygroscopic moisture of many celluloses is dependent on the presence of accompanying substances.[58]

No conclusive decision has been reached as to the form in which the water is bound in the fiber. F. T. Trouton and B. Pool[59] consider the reason for the fixation of the water to be either chemical combination somewhat like crystal water,[60] or surface condensation on the fiber; other investigators consider it to be a solid solution.[61] All these factors and unquestionably capillary imbibition and osmotic entry of water, besides, are involved in water fixation.

The co-ordinately fixed water (that is hydrate water or water of crystallization) participates in the structure of the *"Cellulose-Protones"*[62] (primary units) and *"Polyones"*[62] (secondary units), and is functionally different from the water present in the cellulose micelle. Observations are lacking on variation in the colloidal structure of cellulose on drying. Since the cellulose fibers, as well as the amorphous *"Viskoid,"* contain water, Beadle thinks that the water in cellulose is to be considered as water of hydration.[63]

It is possible to dry cellulose at 30° to 40° C. under diminished pressure to constant weight. Temperatures from 70° to 100° C. are more useful. On continued drying, the weight decreases continuously, then increases for a short time and then again continues to decrease. Long-continued drying finally causes an increase in weight to set in. These phenomena are apparently due to the decomposition of impurities in the cellulose.[64]

Account should be taken of this in the use of filter paper in analytical chemistry.

If cellulose is heated in a stream of carbon dioxide to prevent oxidation, at 90° to 100° C. it decreases about 6 to 8 per cent in weight and at 100° to 120° C. a further 0.5 per cent. Above this temperature, the loss in weight is only slight, being 0.5 per cent more at 180° C.; the last loss in weight is ascribable to the commencement of decomposition.[65]

H. Ost and F. Westhoff [66] dried cellulose in a stream of dry hydrogen at 120° to 125° C., and obtained a dry residue which corresponded exactly to the formula $C_6H_{10}O_5$. According to K. Hess,[67] a similar degree of dryness is reached at 100° C. over P_2O_5 at a pressure of 10 to 15 mm. of mercury.

Cellulose swollen with water appears to give up the water again in an atmosphere of steam. Thus, damp wood can be dried by heating with steam.

Cellulose loses its firmness on drying. Some workers consider the weakening of the fiber to be due to the fact that the steam loosens the fiber texture [68]; according to the view of others, it is due to the presence of traces of acids which bring about the formation of hydrocellulose and a consequent loss of fiber strength. But little data are available on this loss of strength.

On heating to 100° C. and higher, cellulose is so changed [69] that subsequent chemical reactions are more vigorous.[70] It is unknown whether only loss of water or some other chemical changes are involved. The first assumption appears to be the more plausible, since cellulose, which has become pulverulent and rough by heating to 100° C., at normal temperature recovers its former mechanical properties on taking up the water lost.[71] According to E. Berl [72] the heating of cellulose at 100° C. in inert gases causes a depolymerization. It is possible that the phenomenon involved here is similar to that observed in the case of starch granules, in which a loss of water follows a decrease in the size of the micelle. The change in cellulose on drying can also be very clearly followed by the change in dyeing capacity. The ability to take up water depends quite essentially on the type of pre-treatment the fiber has received. The quantity of water taken up by the dried fiber at first increases with the temperature, but between 70° and 200° C. it decreases with increase in drying temperature.[73] It increases with increasing subdivision [73] [74] and increasing removal of fat from the cotton fiber; the power to combine with water decreases after pre-treatment with acids or bases.[75] Cellulose swollen with strong reagents (acids, bases) contains a relatively large amount of water, even after washing away of the swelling medium. C. von Nägeli [76] ascribes this phenomenon to a decrease in micellular size. It is remarkable that the power to absorb dyes and iodine varies with the power to absorb water.[77] Sindall [78] found greater hygroscopic moisture in overbeaten cellulose than in cellulose ground fibrously or in a Hollander. In agreement with this, we find that parchment papers (papers with a great deal of overbeaten cellulose) are more hygroscopic than papers with little fiber-slime.[79] Possibly, these observations are vitiated through the impregnation of the parchment paper with substances which attract water. Dry ground cellulose also swells more than natural fibers in water and becomes somewhat soluble;[80] similarly freezing of moist cellulose fibers increases their water absorptive power. Perfectly dry cellulose is very hygroscopic and in a desiccator absorbs up to 3 per cent of its weight of moisture from all known drying agents, but not from air-dried cellulose.[81]

The absorption of water vapor takes place according to curves which point to the formation of solid solutions,[82] and is accompanied by an evolution of heat which keeps up for several hours [83] and is approximately equal to the amount of heat liberated by the liquefaction of the water absorbed by the cellulose. The aqueous vapor tension of partially swollen cellulose has been investigated by J. R. Katz.[84] As with other colloids, a decided hysteresis is observed on drying and moistening cellulose. This was investigated by B. O. Masson and T. W. Richards,[85] Kujirai Kotaijshi and Torriyama,[86] and also by A. R. Urquhart and A. M. Williams.[87]

The sum of the volumes of cellulose and water is somewhat larger than the volume of the swollen cellulose. The contraction in volume calculated per gram of dry substance varies, hyperbolically, with the degree of swelling.[88] The ratio *volume contraction/heat liberation* educed on swelling is (for small degrees of swelling) of the order of 10 to 32.10^{4} c.c./calories. The heat liberation observed in swelling and the decrease in free energy are approximately the same.[89]

Cellulose dried at 100° to 110° C. gives up more water when heated to 150° C. but absorbs it again when the temperature is lowered to 110° C.[90] Cellulose dried over P_2O_5 absorbs 12.57 per cent of water in a very slightly saturated atmosphere.[91]

Cellulose is wetted very readily when in contact with water. In order to give it its greatest wetting power, careful purification is required.[92] During wetting, water can enter the capillary spaces by displacing the air, or it can also be taken up in the cell wall itself. The capillaries formed through the juxtaposition of fibers are of greater importance in the absorptive capacity of cotton fabrics and filter paper than the capillaries of the fiber itself.[93]

When aqueous solutions rise in filter paper, the water moves ahead of the dissolved substances.[94] Under the influence of the infiltrating water, the cotton fiber increases in size by about 27 per cent of its original volume and especially in thickness.[95] The fiber becomes softer and more pliable. According to Vignon,[96] 100 grams of cotton absorb 495 to 491 grams of water; Beadle, however, found a water absorption of 100 per cent in the cold and 67 per cent in the warm, and established the fact that the water is absorbed in the cell wall. Natural fibers do not extend appreciably in length (0.1 per cent) on swelling.[97] According to Willows and Alexander,[98] the entire swelling takes place in the breadth (20 to 30 per cent); cross sections of cotton fiber prepared with a microtome, increase in size by 40 to 42 per cent. Artificial fibers swell much more strongly than natural ones;[99] acetate silk swells comparatively the least. The cohesion decreases markedly on swelling. For example, whilst the elasticity modulus of dry *Laminaria* is 430, after imbibition of 50 per cent by weight of water, it drops to 1.5.[100] Many cotton fibers possess their greatest firmness at a certain humidity (70 to 80 per cent).[101] Artificial silks from cellulose hydrate suffer, on swelling, a very great loss in cohesion; when stretched they do not retract.[102] The insulating power of cellulose changes markedly during swelling.[103] The X-ray spectrum does not change after swelling in water,[104] from which one can conclude that in the case of cellulose, the water is fixed intermicellularly. J. R. Katz[105] has developed a more exact picture of the swelling processes by means of X-ray spectrographic behavior. A fiber changes in many respects on aging; it also loses its power to combine with water.[106]

Acids. Cellulose can absorb various other substances just as it does water. In the case of gases, the amount adsorbed is proportional to its solubility in water, so that on arranging these in order of their decreasing adsorption we obtain the following list:—NH_3, HCl, SO_2, H_2S, N_2O, CO_2, C_2H_2, CO, O, N, CH_4, H. Gaseous substances of acidic nature, such as dry HCl, are fixed in well-defined proportions (1 mol HCl to 4 mols $C_6H_{10}O_5$). Of the other gases, only NH_3 appears to follow a similar regularity. In certain respects cellulose shows here a similarity to carbon (charcoal). In both cases, a part of the adsorbed gas is taken up in the atmosphere of another gas. Whereas, with carbon this phenomenon invariably occurs, in the case of cellulose, the adsorbed HCl cannot be displaced by other gases, so that one must regard it as a chemical fixation somewhat in the nature of an oxonium compound or an addition to the aldehyde group.[107] The HCl does not change the cellulose fiber so long as the former is perfectly dry.[108]

Acids are also taken up by cotton fibers from aqueous solutions and an evolution of heat can be observed.[109] However, sulfuric acid, for example, can be easily washed out,[110] whereas volatile acids such as HCl, HNO_3, acetic acid and sulfurous acid remain condensed on the fiber and can be washed out only with great difficulty.[111] Cold dilute mineral acids cause no damage to the cotton fiber, even after long action, if they are so thoroughly washed out that the acid reaction in the fabric disappears. The strength of the cellulose fiber (linen) is very easily changed by HCl.[112] Traces of chlorine appear on treatment of filter paper with hydrochloric acid. Koninck believes that under the influence of moisture and the porosity of the filter paper, there first occurs a combination of oxygen with nitrogen and that the nitrogen oxide formed oxidizes the HCl to chlorine.[113] On beating sulfite-cellulose in the Hollander, the chlorine reaction of the water disappears and the ash content of the cellulose undergoes no change, so that only chlorine but not a chloride is taken up from the water.[114]

The observation of A. Leighton[115] is in direct contrast to the opinion of B. Oddo. The former found the adsorption of HCl, H_2SO_4 and H_3PO_4 to increase with increase in concentration, but that at ordinary temperature none of these acids formed a compound with cellulose. Of the three acids employed, HCl was adsorbed the least and H_2SO_4 the most. The presence of one of the three acids decreased the adsorptive capacity of the cellulose for water. Selective adsorption does not take place with H_3PO_4; it occurs slightly with H_2SO_4 and strongly with HCl; when both acids were used it occurs only in higher concentrations.

Hydrochloric acid having a concentration less than 1 per cent spreads out unevenly on filter paper. The water spreads farther than the acid. The more dilute the acid, the greater the difference in spreading.[116] A similar phenomenon can be observed in the case of other acids.* In $N/10$ solution they generally rise in the filter paper less than does water; in normal solution this phenomenon occurs only with strong acids (HNO_3, HBr, HI, HCl), whereas the weaker acids (formic, acetic and propionic acids) show the same speed in rising as does water. The height of rise of all acids, except boric acid, decreases with continued dilution, which also accentuates differences arising between the individual acids. In many cases, the differences in height of rise are approximately as large as the difference in electrolytic dissociation; still this is not the only reason for the different behavior observed with individual acids, since sulfuric acid has about the same height of rise in dilutions in which it much less dissociated than HCl and HNO_3. Phosphoric acid has a much smaller height of rise than the strongest acids.[117]

The great adsorptive power which cellulose possesses for tannin, which the cellulose can take up from aqueous solution in amounts from 7 to 10 per cent of its own weight, is of particular interest in the technique of dyeing. The adsorbed tannin can be washed out again by vigorous rising. According to Knecht,[118] the absorptive power for tannin increases from unbleached cel-

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* *See* Jerome Alexander, "Selective Adsorption and Differential Diffusion," *J. Am. Chem. Soc.*, 39, 84 (1917). J. A.

lulose to mercerized and then to precipitated cellulose. More tannin is adsorbed from concentrated solutions than from dilute solutions. The adsorption equilibrium is established only after some time.

Georgievics[119] found that the partition coefficient $\frac{\text{C — fiber}}{\text{C — dye bath}}$[120] increases with increasing dilution, but that the expression $\frac{\text{V C — dye bath}}{\text{V C — fiber}}$ remains constant. The optimum temperature for tannin adsorption is about 50° C. Equivalent amounts of formic and propionic acids have the same action as acetic acid; stronger mineral acids or polybasic organic acids decrease the amount of tannin adsorbed[121] but only with higher concentrations of tannin.[122] The adsorption of tannin is also dependent on the presence of salts.[123]

However, the coefficients calculated by Georgievics are not strictly constant, but also show a tendency to decrease with increasing concentration of the tannin solution. The adsorption of tannin by cotton follows, rather, a curve concave to the horizontal axis corresponding to the adsorption formula $\frac{x}{m} = aC^{1/p}$ where $\log \frac{x}{m}$ is 1.37 and $1/p = 0.69$. Tannin is not adsorbed from alkaline solution. At lower concentrations of tannin, the adsorption by the fibers is aided by HCl.[124, 125]

Other substances containing hydroxyl groups show a different behavior from tannin. Phenol, for instance, is retained,[126] whilst gallic acid is not. Of the polyhydroxy phenols, those having orthohydroxyl groups (pyrogallol, pyrocatechol) are not taken up,[127] whilst polyphenols with meta-hydroxyl groups are adsorbed very rapidly. By the action of acetic acid, it is possible, for instance, to cause even gallic acid to be adsorbed.

C. Tanret[128] employed the adsorption of amylose by cellulose to free amylopectin from amyloses, and on the other hand he sought to prove the possible presence of cellulose in this adsorption on account of the strong iodine color of the amyloses.

Sugar is also adsorbed by cellulose from alcoholic solution, a circumstance which can cause large errors in the determination of sugar in beets by alcoholic digestion.[129]

Thorough drying generally lessens the adsorptive power of cellulose.[130] Surface-active non-electrolytes are hardly adsorbed.[131] The fibers, curiously enough, also adsorb suspensions.[132]

Bases. A normal solution of alkali loses 1/20 of its titer by filtering through a well-washed filter paper 15 cm. in diameter. With dilute alkaline solutions the loss in titer is still greater.[133]

Bleached cotton thread takes up acid and alkali in the proportion of 3 HCl; 10 NaOH from equimolecular solutions of dilute NaOH and HCl at 4° C.[134] The adsorption of alkali from cold solutions has also been observed in bleaching.[135] The adsorption of alkali is accompanied by a slight evolution of heat[136] which is greater with bleached cotton than with unbleached cotton. Judging by the external appearance, the fiber is not changed by cold dilute alkali, but its adsorptive capacity for substantive dyes is decidedly increased.[137]

It is possible that even in the low concentration dealt with here, those processes set in which, in concentrated solution, cause a mercerization of the cotton, and which have lead to the assumption of compound formation between the cellulose and the NaOH.

According to Mercer,[138] cellulose should yield a compound $C_{12}H_{20}O_{10}\ Na_2O$ with sodium hydroxide solution. Thiele[139] believes that apparently the soda cellulose is capable of existing only in the moist state, and therefore proposes the formula $C_{12}H_{20}O_{10}.2\ NaOH$. The probable formula for alkali cellulose is written differently in different books.[140] Vignon[141] is of the opinion that strong cold alkali hydrates and polymerizes cellulose; Cross and Bevan[142] consider an alcoholate type of compound in the proportion $C_{12}H_{20}O_{10}.2\ NaOH$.

According to Vieweg,[143] who studied the adsorption by cellulose of different concentrations of sodium hydroxide, two breaks in the alkali absorption curve can be determined with increasing concentration of alkali, one at 16 per cent and the other at 40 per cent. At the concentration of the first break in the curve, the cellulose contains 13 per cent NaOH corresponding to the composition $C_{12}H_{20}O_{10}.NaOH$; at the second break the compound $C_{12}H_{20}O_{10}.2\ NaOH$ is formed.

Vieweg is of the opinion that the absorption of alkali occurs along with chemical reactions, and is not conditioned only by adsorption or by partition of the alkaline solution between water and cellulose. From the fact that the first part of the alkali absorption graph is curved and not a straight line, Vieweg infers that the molecular weight of cellulose is decreased by the action of alkali. Since the alkali absorption curve approaches a straight line at higher concentrations, he concludes that sodium hydroxide solution less concentrated than 16 per cent no longer decreases the molecular weight of the cellulose. The researches of Vieweg have been substantiated by many workers.[144] Because of the inherent difficulties in reproducing exactly the experimental conditions, variations between different authors should certainly not be considered too critically.[145]

O. K. Miller[146] observed with alkali concentrations up to 15 per cent that the equilibrium attained after one-half hour remains unchanged for 24 hours, whereas at concentrations over 20 per cent the solid phase gradually loses alkali. Under the influence of the base, a condensation of cellulose probably sets in, which is directly dependent on the concentration of the alkali solution; the amount of alkali taken up is inversely proportional to the temperature. In his opinion, a chemical combination between NaOH and cellulose does not exist; with alkali cellulose it is rather a case of solid solution. According to Miller, Vieweg's new figures do not justify the assumption of breaks in the curve.[147]

Hübner and Teltscher[148] proved Gladstone's old work.[149] They washed the alkali cellulose with alcohol until a color was no longer given with phenolphthalein, incinerated the product and determined the NaOH in it. According to their observations, the adsorption of sodium hydroxide increases very rapidly at a concentration of 10.6 to 11.5 per cent; the maximum is reached in a 17.7 per cent solution. The alkali-absorption curves give no indication of a chemical compound. A. Leighton[150] arrived at the same conclusion. His researches show that a chemical compound is not formed when using solutions containing up to 500 grams of NaOH per liter. F. H. Thies[151] also obtained the same result. K. Haupt,[152] on the contrary, states that in alkali cellulose we are dealing with a system in which a chemical compound is in equilibrium with physical aggregates. P. Karrer[153] also found that above a certain concentration, the composition of alkali cellulose is constant and that a typical addition compound is present.

J. F. Briggs[154] is of the opinion that the compounds of cellulose with alkali, insofar as they are "addition compounds," constitute equilibrium states of complex nature. Celluloses of different origins have very different adsorption properties under the same conditions. The reason for this is the slight constitutional differences which are conditioned by the origin of the cellulose and by its method of preparation. In alcoholic solutions much more alkali is adsorbed than in aqueous solutions, and the adsorption increases with the concentration of alcohol.

F. H. Thies [155] was also unable to discover a stoichiometric relation between sodium hydroxide and cellulose during the action of alkali.

Despite these various interpretrations of the reaction between cellulose and alkali, the preparation of viscose favors the belief in a cellulose-alkali compound. The variation in the opinions of individual authors is due to the fact that an addition compound, once formed, can still adsorb alkali.[156] In this case, the alkali-adsorption curve overlaps the alkali-compound curve so that the influence of the latter is not sufficiently brought out. We owe a discussion of the alkali-compound curves to R. Wegscheider.[157] According to D. Ans and A. Jäger,[158] the combination of alkali with cellulose is dependent, to a great extent, on the temperature, a fact which constitutes another difficulty in the interpretation of the results of various workers.

The curves obtained by Vieweg show at first (0.16 per cent alkali) no regular curvature such as would be expected with a chemical reaction, where the concentration of one component is constant and the concentration of the other is varying continuously. The section of the curve has an unmistakable turning point. K. Hess' [159] explanation of this is that the concentration of the actual reacting mass of cellulose is not constant, but increases with increase in concentration of alkali owing, possibly, to an increase in surface through swelling. This is the conception of A. Lottermoser and H. Radestock.[160]

The great variation in the observed results is also to be found in the question of the dependence of alkali adsorption on the presence and concentration of salts. According to Miller,[161] carbonates and chlorides which are not adsorbed themselves by cellulose, have no influence, in moderate concentration (4.5 per cent), on the alkali adsorption power; however, saturation of the alkali solution with sodium chloride increases the alkali adsorption.[162] On mercerization with alkali solutions containing salt, the swelling is not as great as in salt-free solutions.[163] Other neutral salts behave in the same way.[164]

Similarly to sodium hydroxide, KOH and NH_3 are also adsorbed by cellulose from cold solution,[165] whilst boiling KOH solution deposits practically no KOH on the fibers.[166] Quantitative researches on the adsorption of KOH lead to practically the same results obtained by Vieweg with NaOH.[167] For this reason, the researches of Mansier, E. Knecht, Taus, E. Ristenpart,[168] which do not appear to fit into this division, lose much of their significance.

Lithium hydroxide is fixed in stoichiometric proportions by cellulose. E. Heuser and R. Bartunek [169] as well as Fr. Dehnert and W. Konig [170] found the stoichiometric relation to be $C_{12}H_{20}O_{10}.LiOH$.

The action of rubidium and cesium hydroxides were investigated by Fr. Dehnert and W. Konig [171] and also E. Heuser and R. Bartunek,[172] but it was not possible to find a distinct reaction relation.

Cellulose is present in compounds in the form of $C_6H_{10}O_5$ units. The work of K. Hess has made it possible to consider the cellulose molecule actually as $C_6H_{10}O_5$, so that the equivalent ratio is also the molecular reaction ratio. P. Karrer [173] hopes to be able to determine the molecular size, as with other insoluble carbohydrates, by the equivalent ratio between alkali and cellulose; but K. Hess [174] has shown this to be inadmissible.

Ammonia is taken up by filter paper from air containing ammonia,[175] in analytically determinable amounts; cellulose takes up 115 times its volume of NH_3 in an ammoniacal atmosphere.[176]

Lime water loses part of its titer on filtration through filter paper.[177] Fabrics heated with lime water in an autoclave have an ash content of 3.13 per cent of which 1.06 per cent is CaO.[178]

The great reducing power of cotton fabric soaked in lime water is remarkable;[179] this is not observed on using an equally strong solution of sodium hydroxide.

Wadding adsorbs from $N/10$ $Sr(OH)_2$ solution at 0° C. 2.18 per cent $Sr(OH)_2$, and from $N/5$ baryta solution, 3.82 per cent of $Ba(OH)_2$; no stoichiometric relations can be deduced from these.[180] The partition coefficient between the baryta solution and the cotton yarn is 2.60 with a 1 per cent baryta solution and 4.127 for a 0.1 per cent solution.[181] Liepatoff investigated the action of $Ba(OH)_2$ on cellulose by Vieweg's method and using the law of mass action came to the conclusion that distribution takes place chemically, since cellulose forms with $Ba(OH)_2$ a compound of the alcoholate type $[2\ (C_6H_{10}O_5)Ba(OH)_2]_2$.[182]

Fr. Dehnart and W. Konig[182] also tried the behavior of strong organic bases toward cellulose and found that tetramethyl ammonium hydroxide, phenyltrimethyl ammonium hydroxide, guanidonium hydroxide and trimethyl sulfonium hydroxide act in the same way towards cellulose. Step-like curves were obtained, which were similar to the curves of alkali action. The equivalent ratio could not, in part, be determined exactly, owing to the bases not always being available in sufficiently large amount; nonetheless, the authors assumed for tetramethyl ammonium hydroxide, a compound of 3 or 4 $C_6H_{10}O_5$ equivalents with 1 mol of base, for phenyltrimethyl ammonium hydroxide the combination of 4 equivalents of $C_6H_{10}O_5$ with 1 and 3 mols of base. For guanidonium hydroxide and trimethyl sulfonium hydroxide there was the combination of 2 equivalents of $C_6H_{10}O_5$ with 1 mol of base.

The heights reached by the capillary rise of NaOH solutions depend on the type of fabric and on the concentration of the solution employed. Above a certain dilution, sodium hydroxide remains below the water, the difference in rise increasing the more dilute the solution. Ammonia, on the contrary, in all concentrations, moves on ahead of the water.[184]

The strong hydroxides, in general, rise higher than the weaker ones. In greater dilution, the hydroxides of the strong alkali metals rise higher than equivalent solutions of the strong acids. However, ammonia and ethylamine rise higher than the alkali hydroxides.[185]

Salts. Neutral salts in aqueous solution are in part reversibly adsorbed and are also partly fixed. However, contradictory results are to be found in the literature owing to the use of different concentrations in the salt solutions.

Thus, according to Knecht,[186] calcium chloride is not fixed, while according to Mansier[187] it is retained. Cellulose is indifferent towards sodium chloride, while 1 gram of cotton takes 0.2 to 0.4 per cent of ammonium chloride from a 0.4 per cent solution.[188, 189] Sulfite cellulose takes up noticeable amounts of chloride from tap water.[190]

In general, salt solutions are quite reduced in concentration by cellulose, but the salts can be completely removed again by rinsing well with water. The adsorption of salts should be taken into account, for instance, in the analysis of water.[191]

Capillary process takes an actual part between cellulose and salts during adsorption and fixation. According to Goppelsroeder,[192] neutral salts rise just as high on filter paper as does water. Mansier[193] and Krulla,[194] however, found that the salts remain behind during capillary rise. Skraup observed that, in general, salt solutions rise much higher than equivalent solutions containing bases or acids. It can hardly be proven, in the case of many salts, that they remain below the water even in very great dilution. Hydrolysis has an actual influence even in the case of very stable salts.[195] In capillary analysis, positive colloids are precipitated at the point of immersion; negative colloids rise upward with the water. The precipitation is due to the electromotive force present in the capillaries.[196]

Cellulose collects iron, cerium and other metal salts from very dilute solutions, and thus permits the analytical detection of traces of these cations.[197] According to C. G. Schwalbe, cellulose takes up from cretonnes, traces of copper which come from the blades of the Hollander, in such amounts that the color reaction with benzopurpurin 10 B is influenced.[198] * Bandage wadding left in $FeCl_3$ solution takes up in several days, 0.112 per cent Fe, which cannot be removed by boiling.[199] Lead salts are retained quantitatively so that wadding can be used for the detection of small amounts of lead in drinking water.[199] Lead is not removed by boiling water but is fixed more firmly.[200]

Titanium chloride is also tenaciously retained so that it remains embedded in the fiber when attempting to remove azo dyes from the fiber with titanium salts. Potassium oxalate prevents this deposition.[201]

Wadding absorbs very little chlorine but much mercury from mercuric chloride solution.[202] It seems that in the presence of water, cellulose splits $HgCl_2$ into HgO and HCl and adsorbs the HgO to the greatest extent. Boiling water can remove only a part of the Hg from the wadding as mercuric chloride. The portion retained as HgO can be removed with acidulated water; a third portion held in the form of Hg_2Cl_2 can be removed with salt solution. The amount of mercurous chloride retained increases with the temperature.

Mercuric cyanide is well adsorbed but not fixed.[203] Copper sulfate is taken up,[204] and copper is adsorbed from Fehling's solution (Schwalbe—cellulose number). The taking up of $Al_2(SO_4)_3$ by cotton fiber has long been known, the mordanting of fabrics being based on this phenomenon. R. Bartunek [205] tried to dye cotton, flax and hemp with a solution of potassium dichromate containing alcohol. The molecularly dispersed particles in the aqueous bichromate solution had no dyeing properties but received these through increasing additions of alcohol. The substantive power of dyeing, so received, increases up to a certain alcohol content of the dye bath, and then quickly decreases. In the case of all three fibers, the best dyeing is obtained with 75 per cent alcohol. The explanation is contained in the fact that the three kinds of fiber swell so in the 75 per cent alcohol that the widths of the channels become equal and the bichromate particles can enter the canals of all three fibers with equal ease.

The salts of organic bases are adsorbed by cellulose both in neutral solution and in a solution containing soda; in some cases the addition of soda has a favorable influence, in other cases an arresting influence, on the adsorption.[206] The strong adsorption of diamine salts (except *o*-phenylenediamine), benzidine and the hydrazines is remarkable. Vignon [207] concludes from this that the atomic grouping $R < \begin{matrix} N < \\ N < \end{matrix}$ or $> N - N <$ has a particular affinity for the cellulose molecule. It is conceivable that the nitrogen changes from a trivalent to a pentavalent form, and then unites in some manner with the cellulose. Tetramethyl benzidine-iodomethylate is not taken up at all by cellulose.

The adsorption of benzidine salts was investigated by Mohlau.[208] Just [209] diazotized the benzidine adsorbed on the fibers, and couped it with β-naphthol; however, Green and Levy [210] disputed the results obtained by Mohlau and Just.

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* Traces of copper in the water of the Great Lakes (U. S. A.) amounting to about one part in 40,000,000 may accumulate on rayon filaments during the washing operation and produce marked discolorations. J. A.

According to Molisch,[211] cellulose requires a pre-treatment with alkali before it is able to fix salts. If this property of salt fixation is shown before such pre-treatment, then it is ascribable to the presence of pectin substances which possess an extraordinary ability to adsorb salts.

On treatment of cellulose with sodium chloride, the remaining solution shows an acid reaction which can easily be determined by titration. The acidity rapidly decreases on repeated salt treatment and falls to zero after 2-3 treatments. If the cotton which has been treated with salt is washed with water, the latter becomes alkaline and its titer is almost equivalent to the titer of the acid determined in the salt solution.[212] There are, therefore, indications that even at ordinary temperature, cellulose causes a splitting of neutral salts into acidic and basic components and then selectively adsorbs the basic component. Similar observations are due also to Jentgen.[213]

This process has a more important action if the salt is dried out on the fibers and then warmed up to 30° to 40° C. in a moist atmosphere.

The acidic components formed in this case cause a marked weakening of the fiber owing to the formation of hydrocellulose. It is possible that the oxidative action of the separated oxides (Fe, Cr, Al) is involved here.[214] * Magnesium salts undergo a similar splitting and cause the cellulose fibers to become tender.[215] From solutions of alum or aluminum sulfate, 12.9 per cent of alumina was fixed.[216]

The ability to split salts depends on the purity of the cellulose.[217]

The problem of fiber damage by metal salts in heat is of fundamental significance in the carbonization of wool. Girard [218] believes the formation of hydrocellulose to be the main reaction in the carbonization and that the charring is a side reaction due to the removal of water. A conclusive explanation of the carbonization process has not yet been made.[219]

Basic salts are retained by cellulose if the fabric is steeped in them and dried with heat in a moist atmosphere. In spite of the easy spontaneous decomposition of basic salts, in these cases too, a splitting action is ascribed to the cellulose, since a highly basic salt or metal hydrate is precipitated on the fiber. The structure of cellulose offers no proof for this splitting.[220]

Salts which are to be used as mordants must possess, according to Cross,[221] the following properties:—they must be derived from a divalent or polyvalent element; they must be split on hydrolysis; their bases must form colloidal or gelatinous hydrates which are soluble in alkaline hydroxides either directly or in the presence of organic compounds.

It is noteworthy that basic lead acetate, for instance, acts on cellulose similarly to a concentrated solution of zinc chloride.[222] Lead is taken up by cellulose from alkaline solution. Mulder [223] has described a compound $PbO \cdot C_6H_{10}O_5$. Plumbates (solutions of lead peroxide in strong potassium hydroxide) can be fixed on the fibers if the latter are placed in flowing water after drying.[224] Mercerization also occurs here as well as the formation of oxycellulose owing to the oxidative action of the alkaline lead solution. Plumbites can also be fixed on the fibers similarly to plumbates.[225]

The Mordanting of Cellulose Fiber.[226] The decomposition of certain salts in the presence of cotton fiber must be ascribed to the colloidal properties of the latter, particularly since many (lead) salts form colloidal solutions themselves.[227] The fixation of the basic component of lead salts must therefore involve colloidal precipitation. The mordants are actually found on the fibers in

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* Absorbent cotton impregnated with $FeCl_3$ solution, to be used as *styptic cotton*, falls to powder on prolonged storage. The iron salt is readily hydrolyzed and the adsorbed components appear to bring about a slow disruption of the cellulose micells. J. A.

the form of oxyhydrates or strongly basic salts. The determination of the amount of mordant on the fiber and its chemical composition involves great experimental difficulties. Schaposchnikoff and Minajeff,[228] in their researches on the quantitative estimation of the mordants, obtained different and contradictory results. Because of the complete ignorance, at that time, of the composition of basic salts in solution, more exact results could hardly be expected; further progress could only be expected when new researches were performed which took into consideration the view of Pauly on the composition of basic salts and metal hydroxide sols. In mordanting, besides the strength of the mordant solution which depends on the composition of the mordant salts, account must also be taken of the surface action of the fiber, its permeability toward the mordant particles, the presence of impurities and many other factors.

Plant fibers display inertness towards the mordant solution when it is taken up without change in concentration. Those processes which lead to the formation of insoluble or very difficultly soluble compounds, take place only on dilution. In many cases, it suffices to hang the fabric, which has been soaked in the mordant, in moist heat, whereupon the salts (acetates and even sulfates) are dissociated, whilst the liberated acids can be removed by dilution or washing. In other cases (e.g. sodium aluminate) the fabric, dried out with the mordant, is drawn through a fixing bath containing a compound capable of double decomposition (e.g. ammonium chloride) and in this way a precipitate of metal oxyhydrate is obtained. Other mordant solutions (such as, for example, those of chromic acid containing chromium oxide, acetates and thiocyanates) are fixed by steam.

The mechanism of mordant fixation is still unexplained. According to Bowmann,[229] the mordant salt is split into a basic salt and an acidic part during the drying of the mordant on the cellulose fiber. If the fabric is washed with water, the crystalloidal part (the acid) of the mordant salt (alumina) diffuses through the outer skin of the cotton fiber into the surrounding water, whilst the colloidal product from the splitting of the mordant salt is retained by the fiber skin which acts as a semi-permeable membrane. [In many cases, differential diffusion decomposes salts. J. A.]

Fluri,[230] who investigated the influence of aluminum salts on the permeability of cells of *Elodea canadensis,* is of the opinion that these salts precipitate the proteins in the cell wall, whereupon the adsorptive power of the wall is so increased as to permit diffusion of these substances. Perhaps the facilitation of the entry of dyestuffs into cotton fiber owing to the influence of mordants is analogous to this phenomenon.

Furthermore, it is not known whether the basic salts are retained in the pores and in the cell channel as insoluble deposits, whether adsorption systems are present, or whether chemical compounds are formed by the cotton fiber and the salt. The last view, which was advanced by Runge,[231] to-day has a few adherents although, to begin with, the formation of chemical compounds cannot be shown.

Dufay, even in his time, observed that even finished lakes can be taken up by the fiber from weak organic acid solution. In connection with this statement, Zacharias [232] has offered the opinion that mordanting does not signify a preparation of the fiber for the adsorption of the dyestuff. In his opinion, Berthollet's theory, that the mordant causes the combination of dyestuff and fiber, is a step backward. The fact that it is possible to bring a color lake on to the fiber from colloidal solution, does not permit the conclusion that in the technical process of mordanting and subsequent dyeing, the separation from the finished lake solution take place through a mechanism other than the dyeing of the mordanted fiber.

At present, the mordant is looked upon as an auxiliary colloid, which favors the adsorption of dyes on the fiber, the adsorption being caused by contact electricity.

According to Languier des Pancels,[233] the mordant colloids are positively charged and favor the precipitation of a negative colloid (the dyestuff) on the negative plant fiber. Similar ideas concerning the action of contact electricity have been advanced by Pelet-Jolivet.[234] C. G. Schwalbe [235] is of the opinion that this theory is not fully proven experimentally for direct dyeing, e.g. the dyeing of wool with acid dyes, to say nothing of its direct application to the complicated field of mordant processes which can hardly be investigated experimentally. The study of mordant dyes, over a period of a hundred years, permits the certain recognition of *one* fact—that very complicated reactions are involved, which are partly chemical and partly physical in their nature.

The mordant is adsorbed by the fiber, fills the cell channel and penetrates the wall of the fiber. If the mordant salt is converted to an insoluble basic salt or oxyhydrate, it remains in the cell channel as well in the cell wall and cell surface. Crum [236] ascribes an important function to the cell channel and emphasizes the fact that "dead" cotton, i.e. fibers which are immature and therefore do not have a clear cell channel, cannot be dyed. Persoz,[237] on the contrary, believes that mordant dyes are to be found only on the fiber surface. In his opinion, the thickened mordant, in calico printing, cannot penetrate inside the fiber. Crum, however, showed that this certainly takes place.

The cell channel of ripe cotton is closed at one end and is filled with air or a liquid, thus rendering difficult both the penetration and filling of the cell channel with the mordant solution. The absence of a cell channel in dead cotton need not be the only reason for this cotton not being amenable to dyeing; the reason for this may more likely be due to a changed structure (porosity, permeability) of the cell wall.[238] According to Bowman,[239] it is possible to fill the cotton fiber with mordant, swelling taking place, even when the torn-off, open end of the fiber is not brought into contact with the mordant solution.

In mordant dyeing, one is frequently concerned not only with the fixing of a mordant, which on dyeing forms a color-lake, but the mordant itself also requires an auxiliary substance. Thus, for example, in Turkey-red dyeing, the fatty acids take a decisive part as auxiliary substances. They are mostly fixed insolubly on the fabric by an oxidative process. It is possible, that the fatty acids combine chemically with the mordant (alumina). The nicest and fastest form of Turkey-red is made when calcium salts also enter into the complex.

Tannin serves to fix the basic dyes on the cellulose fiber. Tannin, in contrast to basic salts, is adsorbed by the fibers but not fixed; however, insolubility is brought about by addition of a metal salt (e.g. antimony) which forms a colloidal compound with tannin. Minaeff [240] has concluded from microscopic pictures of fibers dyed with tannin-tartrate dyes, that the cell wall is completely permeable to the colloidal tannin solution and that the fiber-treated tannin-tartrate is permeable to the solution of a basic dye.

Cellulose and Dyes.[241] The adsorption of the mordant salt and dye and their fixation are largely conditioned by the chemical and physico-chemical state of the dyestuff, but they are also dependent upon the nature of the cotton fiber. The kind of cellulose, its age, maturity and also the ash-content are of great importance. Furthermore, the degree to which the bleaching process has been carried, is of importance as is also the extent of the removal of impurities such as fat, wax, pectin and protoplasm and the amount of impurities which have entered in the form of bleach residues, oxidation products (oxycellulose) and hydrolytic products (hydrocellulose). Bleaching is specially prepared for by the action of dilute alkali under pressure. By this means, the fats of the cuticle are saponified, pectins are changed to soluble substances and the pigments are so changed that they can be removed in the subsequent bleaching processes. Bleached cellulose does not show clay-like (*tonenförmiges*) swelling on treatment with copper oxide-ammonia.[242] The bleached fiber is then chlorinated very carefully so as to avoid the formation of oxycellulose.[243] Haller [244] distinguishes between *apposition dyeing* and *intussuception dyeing.* The latter can only take place with dyestuffs having a degree of dispersion greater than 5 $m\mu$.

The hygroscopic moisture of the fiber, the type of drying (high or low temperature) are of great significance. Furthermore, it is also of importance whether hard or tender spun yarns or strong and close fabrics are being dyed. Chopped up fibers absorb night blue more quickly at first than textile fibers; [245] the fiber pulp absorbs twice as much dye as the uncut fibers, but does not have a deeper shade.

V. Georgievics investigated the absorption of dye by cellulose precipitated from copper oxide-ammonia. The researches, carried out with different dyes, gave no clear result, but the dye was, without exception, fixed better on cotton than on precipitated cellulose. After mercerization, cotton takes up more dye than cellulose precipitated from copper oxide-ammonia. The amount of dye taken up depends to a great extent on the temperature. At lower temperature, the powdered, finely divided material takes up more dyestuff than the whole fiber, because of its greater surface; at a higher temperature, however, the amount of dye retained by the latter is greater because the structure of the dye substance offers a greater resistance to the solvent action of the water. Because of the higher temperature, the fiber swells and, according to Justin-Mueller, changes into "a state closely approaching that of a gel," in which the adsorption power for dyestuff is certainly increased.

After a time in the dye bath, the fiber is rinsed with water; the chemistry of this step may also exert a controlling influence on the process of dyeing. If the fiber is mordanted before dyeing, complex formation takes place on dyeing between the mordant and the dyestuff. It is not known whether this complex is a typical chemical compound. Impurities in the rinsing water may exert an influence.

In this connection, Liebermann [246] states that the quantitative relation between mordant-dye and mordant oxide is not yet known. Liechti and Suida [247] made many analyses of "alizarin red" lakes, but they always started out with mixtures made according to stoichiometric proportions, so that the analyses possess no great significance for either view.

Biltz studied the question of lakes with alizarin in alkaline solution and iron oxide, and measured the dependence of the composition of the resulting lake on the concentration of the components. In the cases studied by him, the existence of a chemical compound was shown. On the other hand, the behavior of alizarin S.W. towards chromium oxide indicates an adsorption compound. In other cases, the investigation provides no clear results. Naturally, the results would be obscured if a chemical compound, formed at first, absorbed additional amounts of dye.*

Direct transfer of the results of Biltz to mordant-dyeing processes is not

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* Color lakes are treated by H. J. Weiser in Vol. IV of this series. J. A.

feasible without further research, since with the cellulose fiber present, another colloid enters the reaction.

In mordant dyeing, Krafft sees an outer coloring of the fiber. In his opinion, the globomorphous separation of compounds of soap-mordants, with dye salts and their tendency to form membranes, is of great significance in dyeing with Turkey red. In the fulfillment of this condition, a membrane of the dye lake separates out on the colloidal surface of the cotton fiber. Krafft obtained this separation of globomorphous (spheroidal) structures, which permit themselves to be compressed into membranes, by double decomposition of 1 mol of sodium alizarinate, 2 mols of aluminum chloride and 2 mols of sodium palmitate in the presence of calcium carbonate. The tendency toward membrane formation is not increased if oleic acid (liquid) or sulforicinoleic acid is used in place of the high-melting palmitic acid. If, on the other hand, the cellulose is treated with oil after the application of alumina or alizarin, then the colloid salt is only a coating and the dyestuff is not changed to a true dye throughout its entire mass. The dye shades, in these cases, are brighter but less fast.

Since the chemical compounds or adsorption compounds formed on the fiber between the mordant and the dye, are completely insoluble and in the form of a cohesive layer which is slightly or not at all permeable to the dye solution, it is conceivable that the surface of fiber appears to be covered over preferentially with the dye lake. If one assumes, with Krafft, that the dye lake is deposited on the fiber surface as a membrane, one receives the same mechanical picture of lake deposition.

Microscopic observation of thread dyed with alizarin red actually shows that the interior of the thread is white, and also that a thread has remained white where other threads lie over it.[248] Only a few threads were colored red in cross section close to the cuticle. In any case, the dye cannot enter the cell channel through the cell wall, but often penetrates into it through the open end of the cell channel.[249] If dyed fibers are dissolved in copper oxide-ammonia, one can see clearly under the microscope the breakage in the cuticle which carries the layer of dye. In contrast to this there are photographs in the article by Crum [250] of cross sections of cotton fibers dyed with Turkey red, which appear to be completely red.

Fibers dyed with tannin-Sb tartrate and basic dyes are colored through the cross section. The color is not only somewhat stronger around the outside but also penetrates into the cell channel. Krafft considers, in the case of the dye-tannates, that the dyeing power depends on the ability of the tannin-tartrate-dye complex used to form membranes. The question has, for a long time, not been completely explained. Thus von Georgievics [251] has shown that the tannates of the dye-bases have a greater ability to form membranes and must therefore possess a greater dyeing power than the lakes from tannin, antimony and the dye base; but experiments show exactly the opposite.

Mineral dyes can be fixed on the fiber by the adhesive action of a gluey substance. Besides this method, which is of less theoretical interest, mineral dyes can be brought on the fiber in very finely-divided state, depending on the type of dyeing. This fact was focussed by the observation of Bloede that the red ocher color of "grounded" cotton is due to mechanical impregnation of the trailing fibers by the ocher-like soil of the cotton field. According to this principle, pigments containing iron, aluminum, chromium, manganese or silicic acid, can be easily fixed; soot is not retained even in the most finely divided condition. Colors produced with mineral pigments are not very fast.

According to Biltz,[252] a large number of amorphous substances, especially metals and metal oxides in colloidal solutions, are absorbed by the fiber; the finished colors, however, are hardly fast to washing and rubbing. A Berlin blue by the two-bath process is much faster than that taken up colloidally. The same is true of indigo.

Furthermore, the mineral dyes can be produced on the fiber by the double decomposition of two components (e.g. chrome yellow) or by oxidation (ferrous sulfate). Color effects so obtained appear superficially to be the same, but microscopic examination shows an actual difference. With chrome yellow, the entire cross section of the fiber is strongly colored; with manganese brown the dye is only on the surface, whilst Berlin blue forms only a loose colloidal skin on the fiber.[253]

The order in which the dye components react is of importance to the fastness of the dyeing.[254] With chrome yellow, satisfactory dyeing is attained only when the fabric is first impregnated with lead acetate and the dye then produced by dipping in chromate solution. It is possible that the special ability of the fiber to accumulate lead comes into play here; this leads not only to the selective adsorption of soluble lead salts but also causes strong adhesion of lead sulfate.[255] According to Persoz,[256] this last occurs only when the fiber has received a lime bath.

Chrome yellow dyeing, according to Vignon,[257] is an adsorption process. He was able to dye all the typical fibers with lead chromate suspensions, but he did not prove that these dyes showed the same fastness obtained with technical dyeing methods. This is a promising field for colloid-chemical investigation.

In the dyeing of wool with organic pigments (vat dyes), the fiber is treated with the solution of the leuco compound of the dye, and after pressing out of the excess solution, is changed to the insoluble dye, either by atmospheric oxygen or by oxygenated water. The fiber absorbs the leuco compound, the extent of the absorption depending upon the fiber and the temperature of the bath. The alkali and salt content [258] of the vat must also be of actual consequence.

According to Justin-Mueller,[259] indigo, the well-known vat dye, is only fixed through adhesion and not adsorption, and is therefore not fast to rubbing. Witt believes it to be a solid solution. The cross section of the fiber is completely and homogeneously dyed and the cell channel is free from dye.[260] The presence of glue in the vat increases the amount of indigo taken up, whilst the dye is better fixed, rubs off less, and the shade of color is brighter.[261] Colloidal indigo and colloidal indigo white have poor properties for technical dyeing, and when applied are not at all fast to rubbing.[262]

The reagents required for the preparation of the pigments of the aniline black type (e.g. for aniline black—aniline hydrochloride, sodium chlorate and potassium ferrocyanide) are not absorbed by the fiber and are not taken up from the solution with change in concentration.[263] The fiber is permeable to this solution and is actually dyed through and through.

A certain adsorption on the part of cellulose fiber appears to take place in the third kind of pigment dyeing, the so-called ice-dyeing. In this method, an azo dye component, generally a solution of β-naphthol, is brought on to the fiber, the latter dried after impregnation, and the color is developed by dipping into a diazo solution. The β-naphthol, according to Minajeff,[264] is adsorbed by the fiber; the fiber is dyed, the cuticle and the layers adjoining it being more strongly colored. Brighter and deeper shades are obtained by this method, through the addition of oil-mordants to the naphthol base. Justin-Mueller [265] assumes the formation of a colloidal combination between the fatty substance and the dye, part of which is adsorbed by the fiber and part adhering to the fiber. C. G. Schwalbe [266] stated that according to this view, the dyed fabric should contain a certain amount of fatty substances, but no experimental evidence has been brought forward as yet, to support this. Colors produced by pigment and mordant dyes can be dyed over with indigo. The microscopic pictures show that normal cotton fiber possesses no porous structure whatever.[267]

The dyeing of cellulose with dyestuffs which exist fully prepared in the solution is, in principle, different from the methods of dyeing mentioned hitherto. The basic dyes belonging to this group give technically utilizable color results in combination with suitable mordants which have already been discussed. Unmordanted cotton fiber adsorbs basic dyestuffs from solution,[268] but the results obtained from such experiments cannot be directly applied to explain real dye processes because the colors obtained are not fast. According to Haller,[269] the cuticle or, in any case, the inner skin of the cell channel, is dyed because of the cutin content; pure cellulose, however, is not dyed. The combination between the fiber and the basic dyestuff is facilitated by the hydroxyl groups of the cellulose.[270]

To distinguish between various fibers, Liebermann [271] makes use of the fact that the colorless fuchsine base dyes wool but not cotton. von Georgievics [272] and Freundlich [273] found that basic dyes (fuchsine, methylene blue, crystal violet) are taken up by cotton as well as by wool. According to C. O. Weber,[274] this absorption takes place in the form of salt, so that no free acid appears in the dye bath. According to Suida,[275] significant amounts of basic dyes are taken up with change in concentration of the bath, by cotton cellulose from a neutral bath, and are fixed, fast to water, so long as the rinse water runs off uncolored. However, particles of dye leave the fiber on pressing and squeezing. The dye vat has a neutral reaction. A dissociation of the dye salt presumably first takes place in the fiber and the acid combines with the ash of the fiber. Michaelis and Rona [276] also believe the absorption of dye to be an exchange adsorption conditioned by the ash constituents. V. Georgievics [277] and Freundlich,[278] on the contrary, found that the dye bath was acidic and that the cotton caused a splitting of the dye salt. The contradiction between these observations may perhaps be caused by variation in the temperature of the dye baths.[279] Knecht's [280] observation also bespeaks a dissociation of the dye bath. Consequently, on dropping a fuchsine solution on filter paper, a red dye spot with a colorless halo is produced, the latter containing half of the acid of the fuchsine salt.

Alkaline solutions of basic dyes form no halo and have no dyeing power. The addition of hydrochloric acid to the solution of a basic dye causes the halo to disappear. When solutions of basic dyes rise in filter paper, the water moves on ahead. The retention of the dyestuff is ascribed to the adsorption of the positively charged dye particles by the negative cellulose.[281] If solutions of dye bases in organic solvents are dropped onto filter paper, the color is changed. The reddish-brown benzene solution of Nile blue produces a blue stain. Michaelis, Weber [282] and Witt [283] believe the formation of a solid solution to be the cause of the absorption of basic dyes by cellulose. According to Heidenhain,[284] the formation of a solid solution does not enter into the matter, since basic dyes color the fabric much better when in alcoholic solution than in aqueous solution, despite the fact that they are more soluble in alcohol. He considers the reason for the change in color to be due to atmospheric carbon dioxide, whereas, according to Michaelis, the reaction also takes place in an atmosphere of hydrogen.[285] Georgievics, Biltz and Freundlich oppose the assumption of a solid solution, because the experimental results cannot be brought into agreement with the regularity of adsorption which can be expressed mathematically. The adsorption of basic dyes by the cotton fibers follows exactly the same formula that holds for wool, asbestos and the absorption of tannin by cotton;[286] still, no general conclusion can be permitted with regard to the similarity of dye processes with wool and cotton, since no account was taken, in the measurements concerned, of the difference in the fixation of the dye and of the difference in the fastness of the colors.[287]

Hübner[288] carried out the absorption of "night blue" with cotton, wool, silk, kaolin and graphite, from cold, hot and re-cooled dye baths, and found the course of dyeing to be similar. The amounts of dye taken up from a water-alcohol solution of "night blue" by equal weights of sand, cotton and silk were in the ratio 1 : 41.83 : 43.40. The process is irreversible.[289] Hübner's researches also show that the influence of temperature on dye absorption by cotton, kaolin and graphite is slight, whereas silk and animal charcoal show an actual increase in dye absorption on rise in temperature. If a cotton fiber is dyed with "night blue," it is possible to dye it green with naphthol yellow S.[290] Weber concluded from this that a loose combination of the dyes had taken place. If, on the other hand, a tannated fiber is dyed with "night blue," it is no longer possible to dye it over with naphthol yellow.

The basic dyes are often very finely divided. In order to fix them on the fiber, use is made of tannic acid to form with the basic dye an insoluble compound which is deposited in the micellular interstices. Outward diffusion of the tannic acid can be prevented by certain metal salts. Dyeing with basic dyestuffs involves, therefore, the formation, in and upon the fiber, of a precipitate which can be produced equally in the absence of fibers.[291]

Acid dyes are absorbed by cotton in the same way as basic dyes and in the same manner as they are absorbed by wool;[292] these results, however, are of no use in the development of a theory of dyeing, since we are not dealing with fast dyeing. Hübner[293] performed quantitative dyeing experiments with cotton, rosin, graphite, wool and animal charcoal, using acid dyes. Naphthol yellow S is absorbed as a nitro dye by cotton from a hot or cold neutral bath. In an acid bath, a trace is absorbed which can be removed by slight washing. Ponceau RR and acid fuchsine behave similarly. From this it is established that cotton cannot be dyed by acid dyes. Filter paper is stained red by a benzene solution of eosin; also the red fluorescent alcoholic solution produces a red non-fluorescing stain. As in the case of the basic dyes, Michaelis[294] points to this phenomenon as being one of solid solution,[295] whilst Heidenhain[296] believes it to be salt formation.

The substantive dyestuffs dye cotton directly. Most of them are coal-tar derivatives and form a sub-division of the acid dyes. They are of considerable molecular size and instead of molecular solutions, often form dispersive systems which can be seen under the ultra-microscope.[297] In general, a definite degree of dispersion of the dyestuff is necessary for the formation of the color. The dyes fixed on the fiber can be re-dissolved. They are absorbed from neutral or acid baths; under all circumstances, a large addition of salts is required for the dyeing of cellulose. According to Gebhard[298] an oxygen "bridge" is essential for the fixation of substantive dyes.

The process of sorption of substantive dyes by cellulose is quite similar to the sorption of basic and acid dyes.[299, 300] The mathematical relations exclude Witt's assumption of a solid solution. Henry's law is not applicable to the dyeing process.

Hübner,[301] on investigating the sorption of substantive dyes by cotton fiber, found that typical cotton dyes, e.g. Diamine Bright Blue F.F. will not dye wool in a neutral or even in an alkaline bath. On boiling a whole week the free dye-acid was fixed on the fiber, the color being that of the dye-salt.[302] A prerequisite of such dyeing is that the fiber shall be practically free of ash (0.04 per cent instead of the usual 0.28). The dye-acid rapidly dyes fiber high in ash, because of salt formation with constituents of the ash. An extremely dilute blue acetic acid solution of Congo Red dyes filter paper red. Heidenhain [303] regards this phenomenon as salt formation with the cellulose. Possibly the ash-constituents of the filter paper play a determining rôle.

Weber [304] also opposes Witt's solid solution theory. For if we assume with Witt that cellulose has a special solvent power for benzidine dyes, it must have a like power for nitrous acid, phenols, and aromatic bases, because the substantive colors are in part developed colors. Furthermore cotton, made water-free and incapable of taking up water, should be able to dissolve dye; but it will not. According to Weber the seat of dyeing is the water in cellular spaces, the dye passing osmotically to this and not to the cellulose. Dyeing ceases when the osmotic pressure within and without the fiber reaches equilibrium. Addition of alkalis or salts to the dye bath reduces the solubility of the dye; the saturation and osmotic pressure of its solution rises. The cellular spaces are filled with the hot dye solution which precipitates the dye on cooling. Behrens [305] reached a similar conclusion regarding the increase of osmotic pressure by alkali. It is more probable that the alkali, rather than affecting the osmotic pressure, swells the fiber so that penetration of the dye is facilitated.

Brilliancy of the color depends on the hygroscopic moisture in the air-dry fiber. If this is removed, the shade becomes dull or changes materially.*

Weber believes that the reason but few of the azo dyes possess substantive properties is that they exhibit very low diffusion coefficients, whereas acid dyes have high coefficients. But his paper gives few supporting data. He believes that his theory is supported by the fact that the rapidly diffusing sodium salt of Crocein B gives a pink color on cotton, whereas the slowly diffusing barium salt gives a fiery scarlet. The microscopic evidence seems to support this view. Many fibers show colorless cell-walls, while the cell-canal is full of dye. This simple picture is, however, often disturbed by the fact that the fiber wall has innumerable transfusion canals. If dye be deposited in these, the fiber substance itself appears as if dyed.

Rötheli,[306] using Congo and Benzazurin, confirmed Weber's observations; but Haller [307] maintained that fixation of the dye within the cell is simulated by dyed protoplasmic residues.

Benzidine colors are in many cases fast against water; but on squeezing the fiber the dye escapes. De Mosenthal [308] found that individual cellulose fibers exert no capillary power, but that, on the other hand, the cuticle is extremely porous. According to Suida and von Hoehnel [309] the cell-wall is equally permeated and out of it the dye solution is squeezed. Minajeff [310] also observed a uniform staining of the cell-wall, the cuticle being somewhat more strongly tinged. But according to his results the cell-canal was free from dye. He believes that the colloidal cell-wall is permeable to the colloidal substantive dye solution. Bowman's [311] microscopical pictures show, with high magnification, a dyeing of the cell-wall, the intensity decreasing somewhat toward the interior. At very high magnification the color becomes specky, a sign that within the fiber the dyeing is uneven.

According to Haller [312] the diameter of a dye particle which is just able to penetrate cotton swollen in water is 5 $m\mu$.

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* This is often observed on ironing fabrics after washing. If the iron is not too hot, the original color, lost on heating, slowly returns as the fabric absorbs atmospheric moisture. J. A.

Von Georgievics[313] opposed the diffusion theory of Weber. He overlooked the proof of the differences in diffusion coefficient and denied the importance of the cell-space. He states that precipitated cellulose and cotton, under like conditions, take up the same amount of dye.

Though Erdmann,[314] R. Meyer[315] and others consider substantive dyeing as chemical, Krafft[316] attributes the fixation of these dyes to their colloidal properties. Such dyes have a very high apparent molecular weight, form slimes with small amounts of water, and can be salted out. On dialysis through parchment the dye salt is split up, only the alkali passing through the membrane. According to Krafft dyeing with direct cotton colors results in a dry membrane on the surface of the fiber. Gnehm,[317] while admitting the importance of the colloid character in dyeing, does not accept the idea of membrane formation.

Biltz[318] believes that the process is an adsorption of the colloidal dye by the colloidal fiber. Knecht,[319] on the basis of conductivity measurements, boiling point increase, and diffusion phenomena, concludes that substantive dyes are normal electrolytes in solution, and believes, therefore, that they cannot be colloidal, a conclusion untenable in this form nowadays. Those dyes which dye membranes (e.g. methylene blue, benzopurpurin) do not pass through them; but others, like Erika, diffuse readily. On measuring the diffusion velocity in pure water, without membrane, benzopurpurin shows a high diffusion coefficient.

The colloidal state of the cotton exerts marked influence on fixation of the dye. Thus according to P. Wilhelm[320] moist vapors cause better fixation of diamine colors printed on cotton with addition of glycerin, the fibers swelling more and taking the dye better than the unswollen fiber.[321]

In the case of substantive colors which must be developed (that is, which are diazotized on the fiber and then coupled with developers), Weber assumes the same fixation in the cell-space as with other substantive colors. But this case Cross and Bevan[322] consider to be one of chemical fixation, since the dye may be diazotized on the fiber without loss. But the diazo compound is supposed to be present in the fiber in solid solution. Dreaper[323] attributes the great fastness and resistance of developed colors to the physical difference of the form in which the dye separates out.

Sulfur colors, which according to Biltz[324] are highly colloidal are taken up according to the adsorption law, like substantive colors. Oxidation by the air converts the sulfhydrate groups of the dye into disulfide groups, whereby the fastness of the color is improved. The sulfhydrate groups enable the dye to react with the cellulose, somewhat along the lines of a xanthate acid ester,[325] which satisfactorily explains the great attraction of cotton for sulfur colors. Subsequent chroming of the dyeing with potassium chromate and acetic acid produces no weakening.[326]

From the foregoing it is evident that in some respects the various theories advanced to explain dyeing are diametrically opposed. The present state of colloid investigation indicates that it is not wise to insist upon a marked opposition between the "chemical" and the mechanical theories of dyeing, since it is to a certain extent possible to effect chemical transformations without changing the external form of the colloid, and on the other hand colloid changes may occur without material chemical transformation. Initially, the dye is unquestionably taken up "mechanically," that is, by capillary imbibition and osmose[327] which is then followed by sorption. According to Kaufler[328] calculation shows that with cotton fiber there is a supersaturation of dye at the interior of the cell, even when the bath is not saturated with dye. Therefore the solubility product may be exceeded and the dye must separate out, and if a chemical reaction occurs the reaction balance must be disturbed.

Differences in electric charge[329] between fiber and dye may give rise to colloid precipitation phenomena, and the formation of a membrane. In certain types of dyeing, no doubt other processes occur, e.g. formation of solid solutions,[330] adsorption compounds,[331] addition compounds (molecular compounds), and chemical combination, which influence the as yet obscure process of dye fixation.[332]

Dyed cotton fibers are dichroic, a phenomenon shown more markedly by flax, hemp and ramie.[333] Artificial silk is always dichroic.[334]

The Swelling of Cellulose.[335] *

Aside from the increase in volume of cotton fibers when immersed in water, which has already been mentioned under the head of "Cellulose and Water," no particular swelling action is brought about by water alone at ordinary temperatures.

Mechanical disintegration of the fibers, however, increases their water-binding power[336, 337] which reaches a maximum in so-called "dead-beaten" pulp. This condition is accompanied by a striking color change, the pulp turning a grayish brown. This highly swollen material is used in the manufacture of grease-proof (pergamyn) paper.

Hot water renders the fibers malleable to a certain extent, as is evident when they are calendered (passed through heated rolls) and especially in super-calendering.[338]

By moist steaming it is possible to set diamine colors topically on the fibers. Justin-Mueller considers this to be dependent on a sort of gel formation.[339]

Cellulose becomes gelatinized when heated to 20 atmospheres pressure with water; after the gel has been pressed and dried it can be pulverized.[340] The powdered, washed and dried substance gives analytical results agreeing well with the formula $C_{12}H_{22}O_{11}$.

Cellulose swells strongly in concentrated solutions of salts such as 40 per cent $ZnCl_2$, concentrated KI,[341] potassium or barium mercuric iodide solutions.[342] The fibers turn glassy and shrink in concentrated KI, very much as they do in caustic soda, as may easily be observed by attempting to filter a concentrated solution of the salt. The iodide is removed slowly but completely by washing. When fibers treated with potassium mercuric iodide are washed, mercuric iodide is at first precipitated on them, but is dissolved by protracted washing.[343]

Sheets of paper gelatinized by means of $ZnCl_2$ remain welded, when firmly pressed together, so that plates of almost any desired thickness may be made, a fact utilized in the production of *vulcanized fiber*. Cellulose gelatinized with $ZnCl_2$ gives a violet color with iodine. When the $ZnCl_2$ is washed out with water, the salt is hydrolyzed so that 18 to 20 per cent of ZnO remains on the fibers.

According to P. P. von Weimarn,[344] it is possible to reduce any sort of cellulose to the plastic gel state by treating with aqueous salt solutions, if care is taken to maintain the proper conditions of pressure, temperature, concentration and time of treatment for the particular salt employed. For

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* This section of the translation has been done by R. H. Doughty, and C. E. Hrubesky, both Assistant Engineers, Pulp and Paper Section, U. S. Forest Products Laboratory, Forest Service, U. S. Dept. of Agriculture, Madison, Wisconsin. To Mr. Barsha, to them, and to Dr. C. E. Curran, in charge of the Section of Pulp and Paper, the Editor expresses cordial appreciation.

instance, LiCl, $CaBr_2$, $Mn(CNS)_2$ will gelatinize cellulose at a concentration of 3 grams per 100 cc. When NaI, $CaCl_2$, $BaCl_2$ or other salts are used the solution must be heated under pressure. Solutions containing as little as 1 per cent of cellulose set, on cooling, to firm, transparent, and frequently very elastic jellies. Other salts which attack cellulose more slowly are NaCNS, KCNS, NH_4CNS, BaI_2, $SrBr_2$, $CaCl_2$, $Ca(NO_3)_2$, NH_4NO_3, NH_4Cl, $FeCl_2$, $CoCl_2$, $CoBr_2$, $NiCl_2$, $MnCl_2$, $MnBr_2$, $CuCl_2$, and $Al_2(SO_4)_3$. Cellulose does not shrink when gelatinized with neutral salts.[345]

The reason that cellulose swells more in electrolyte solutions than in pure water is that one ion of the electrolyte is adsorbed more than the other. This separation of electric charges results in stronger binding of the electric dipole of the water: it also charges all the cellulose micelles in the same sense, thus causing them to repel one another. This repulsion separates the micellar structure and allows water to enter, as it were, passively into the increased interstices.[346]

Like K. Hess[347] we have here assumed the formation of Werner complexes between the cellulose and the electrolyte. This combination is probably formed at the oxygen bond, producing oxonium compounds. Such compounds can be formed on the surfaces of the micelles. It is also possible for the swelled substance to react molecule for molecule, like a zeolite, with the electrolyte throughout its entire structure.

Cellulose swells under the influence of 62 to 70 per cent sulfuric acid.[348] The material produced in this way from filter paper is called *vegetable parchment*. Because it is colored blue with iodine, the substance first formed by the action of the acid is called *"amyloid."* M. Samec and J. Matula[349] have studied the colloidal changes wrought by the action of sulfuric acid.

Strong nitric acid (68.6 per cent) has a similar effect of swelling and parchmentizing, first observed by Cross and Francis.[350] Subsequently mixtures of nitric and sulfuric acids were recommended for parchmentizing.[351] Girard[352] found that the action of strong nitric acid on cellulose formed a gummy, nitrogenous mass.

Concentrated phosphoric acid (sp. gr. 1.7) acts on cellulose in the same way as do sulfuric acid and caustic soda, though the mercerizing action is not so energetic as with the latter,[353] and the swelling and twisting are interrupted by dissolution. The behavior of the jellies produced by phosphoric acid was exhaustively studied by Samec and Matula.[354]

Cellulose is also reduced to a gummy mass by hydrochloric acid of 35 to 37 per cent concentration. Matthews[355] and Bowman[356] report that hydrofluoric acid produces a transparent, tough and water-resistant material which is not, however, identical with sulfuric acid parchment. It has been used for an insulating material and as the filaments of incandescent lamps.

The swelling of cellulose in concentrated salt solutions has been studied by J. R. Katz,[357] with the aid of X-ray methods. If the concentration of the swelling salt is kept below a certain limit the swelling is *inter-micellar,* and no change in the X-ray spectrum is observed. Concentrations above this limit cause *intra-micellar swelling,* accompanied by a change in the interference bands. Often the X-ray diagrams give evidence of a combination between cellulose and the swelling agent. This is most apparent in the swelling of cellulose with nitric acid. If cellulose is swollen in acid of 66 to 70 per cent concentration, washed and pressed out, the Knecht compound,[358] $C_6H_{10}O_5HNO_3$ is obtained, which gives a new and typical fiber diagram.[359] This must be considered as an oxonium compound. The sharp concentration limit above which electrolyte solutions cause a change in the X-ray spectrum, is probably determined by the point at which the cellulose begins to react with the electrolyte throughout its entire structure, like a permutoid.[360]

Technically the most important swelling phenomena are those of mercerization in alkali.

In caustic soda of 16 to 25 per cent concentration the twisted cotton fiber unwinds, swells and shortens by as much as one-fourth of its length. This shortening is at variance with the behavior in water alone, when the fiber becomes thicker without great shortening. In alkaline solutions the cuticle is not disintegrated[361] but stretches, becoming thinner and more porous. The shrinkage attending the diametral swelling may be as much as 20 per cent. The amount depends on the concentration and temperature of the caustic soda solution. The swelling is less the higher the temperature.[362] Addition of alcohol or carbon bisulfide accelerates the process, since it facilitates the penetration of the solutions.[363] Additions of salts are in general undesirable, especially as regards their effect on the gloss of the product,[364] yet there is also no lack of contrary statements.[365]

When mercerized under tension cotton acquires a fine silky luster.[366] The technical development of this particular process is due to Thomas and Prevost.[367]

Gardner[368] states that 40 per cent caustic soda solution wets the fibers with great reluctance, while more dilute solutions have a wetting power greater than that of water. Fatty oils can prevent mercerization.[369] Glycerin prevents shrinkage and development of high luster;[370] glucose has the same effect.[371] It is possible that the caustic is rendered inactive by the formation of glycerin or sugar salts.

After mercerization, the caustic soda may be replaced by ammonia; a gelatinous, elastic, parchment-like substance which may be stretched without breaking is then obtained.[372]

E. Flence, B. Pieus and I. Miller[373] found that cellulose treated once with 17 per cent caustic soda lost about 5 per cent in weight, which was mostly non-cellulose substances. This can readily be verified by measuring the polarization in cuprammonium solution, according to the method of Hess and Messmer.[374]

When cellulose is gelatinized in caustic solution heat is evolved, the quantity being greater the greater the concentration of the caustic.[375] The elasticity of the swollen fibers is comparable to that of rubber, a very striking phenomenon. This matter has been investigated especially by J. R. Katz.[376] [*See also* paper of P. P. von Weimarn in Vol. III, this series. J. A.]

Mercerization increases the absorbing power of the fibers for dyes[377] and other substances.[378] If the mercerization is done under tension the increase in absorbing power for certain dyes is less[379] than when no tension is used. The light-resistance and general fastness of dyes is greater on mercerized than on unmercerized fibers.[380]

The parchmentized fibers produced by treatment with alkali and ammonia lose their elasticity when washed with water. The swelling in alkalis is irreversible, the fibers retain a high water affinity,[381] are thicker[382] and stronger.[383] The Roentgen spectrum is also completely irreversible.

The swelling effect of alkali is greatly increased by a decrease in temperature, at low alkali concentrations; but at high concentrations the temperature effect is very slight.[384] The mercerizing power of hot caustic is vanishingly small. When ordinary or mercerized cotton is treated alternately with hot and cold caustic soda solutions of certain concentrations, the reducing power varies inversely as the swelling or contraction of the fibers; the product of contraction and reducing power has a constant value, the magnitude of which depends on the first treatment given.[385]

Caustic potash gives results somewhat different from those obtained with caustic soda. These differences are especially noticeable in dyeing work.[386] Cotton mercerized without tension gives the Debye-Scherrer ring diagram, while when mercerized under tension it gives a point diagram.[387]

The theoretical meaning of these swelling phenomena is much in dispute. It has been assumed that a cellulose-alkali compound is formed[388] which gives a cellulose hydrate by splitting off the alkali and adding water, when the caustic solution is washed out. At the same time Schwalbe[389] and Ost and Westhoff[390] have shown that mercerized cellulose retains no more water than ordinary cotton. The method used by C. Gladstone and others for isolating the alkali-cellulose, namely precipitation with alcohol, has many times been questioned,[391] but still, the use of other methods than alcohol coagulation have given alkali cellulose of the same analytical composition. Swelling can be produced with strong acids and concentrated salt solutions as well as with caustic, so it might seem that the swelling was purely an osmotic or capillary effect; but salts never give the high luster obtained by mercerizing.

More recently it has been suggested that in mercerization carboxyl groups are formed and lactone formation occurs when the alkali is washed out.[392] R. O. Herzog considers that oxygen bridges are displaced,[393] but Hess[394] has observed that acetyl celluloses carefully prepared from mercerized cellulose have the same optical rotation in various solvents as do acetyl celluloses from natural fiber,[395] which makes Herzog's view seem improbable. Hydrolysis and acetolysis moreover give exactly the same products in the same yields from mercerized and from native fibers.[396] According to Hess and Friese[397] the characteristic change in rotatory power on hydrolysis—or acetolysis—is fundamentally the same for mercerized and natural cotton fibers. The changes caused by the action of strong caustic solutions on cellulose are of the same nature as those caused by strong acids. It is highly improbable that strong acids and strong bases would have identical chemical effects on cellulose.[398] The changes caused by the action of alkali are also essentially the same as those caused by solution in ammoniacal copper oxide, and subsequent precipitation by alkaline, neutral or acid reagents. It has been suggested that the cellulose micelle is broken down during mercerization.[399] If such a breaking down does occur, it certainly has nothing to do with an hydrolysis, since the products have no reducing power whatever. Witz[400] observed that 18.6 or 6.5 per cent NaOH caused no change in the methylene blue absorption, when allowed to act on cellulose for an hour, so the formation of oxy- or hydrocellulose must be excluded. Schwalbe and Neubauer[401] likewise were unable to find any particular change of reducing power due to the action of alkali; Ost and Westhoff[402] and Cross and Bevan[403] arrived at the same conclusion.

Berl contends that the fact that the cuprammonium solutions of mercerized cellulose and solutions of its nitric acid esters have lower viscosities than those of native cotton, is evidence of a gradual molecular degradation during mercerization.[404] Cross and Bevan have conceived that migration of a carbonyl group in the molecule[405] and progressive polarization[406] may occur, in such a way that the positive and negative groups assume positions in fixed relation to one another. The acid nature of cellulose is as a matter of fact strengthened by mercerization. Vignon[407] has also considered the possibility of depolymerization of the cellulose during mercerization, but the increased strength of mercerized cotton is not in accord with this view. Miller[408] has assumed that the cellulose condenses exothermically. According to Gebhard[409] cellulose has the constitution of a cyclic ester, mercerization then becoming a keto-enol transformation.

When cellulose is gelatinized by means of caustic, the characteristic X-ray diagram fades, and two new intense interferences appear at the equator, which J. R. Katz has called "alkali cellulose bands." The alkali concentration necessary to produce this change he calls the Roentgenographic soda swelling number.[410] After the swelling agent is washed away, two strong new bands (mercerization bands) appear at the same points in the cellulose diagram as were occupied by the alkali cellulose bands. The fact that the break in the alkali adsorption curve and the change in X-ray spectrum occur at the same alkali concentration, is very important in establishing a theory of the reactions of cellulose and alkali.[411]

The Roentgen spectrum, finally, agrees with the many analytical results in giving evidence of compound formation $[2(C_6H_{10}O_5)_2NaOH]$ in the Gladstone sense.[412]

The reason why no greater chemical changes occur on mercerization, was established by another study by R. O. Herzog and G. Laske [413] on the infra-red absorption of natural and mercerized cellulose, both of which have absorption bands between 1 and 9 $m\mu$ wave-length. The mercerized cellulose retains its X-ray spectrum even after nitration and denitration.[414] The various phenomena which cellulose shows on swelling are generally roughly parallel, but not in accurate agreement.[415]

It has been found necessary, in order to explain the mercerizing action of salts, to assume a double salt formation between the cellulose and the hydrous salt, or the influence of osmotic processes. It seems, however, that here as well as with concentrated acids, lyotropic effects of the particular crystalloid utilized are of primary importance, since even in ester formation, swelling precedes the chemical reaction. Likewise when pulp is over beaten, it rather seems as if the great change in degree of dispersion and the formation of adsorption complexes with the crystalloids present, must be the conditioning factors for the changes in hydration which occur.

CELLULOSE SOLUTIONS.

In Water. By beating sufficiently long in the Hollander, preferably with the mass acidic, cellulose is brought into a colloidal solution, cellulose slime, and a temperature rise to 40°C. or more is observed. If the solution is permitted to dry in a thin layer, a parchment-like membrane is formed which, as Cellulith, has found technical application. It is very probable that with the slime formation, in addition to an extensive peptization and the accompanying hydration, there is a partial hydrolysis since the slime possesses slight reducing properties.[416] A complete investigation of this interesting colloid chemical process is still to be made. Dry beating of filter paper pulp, also, forms up to 1.2 per cent of water-soluble constituents of chemically undergraded cellulose.[417]

Briggs [418] has collected some observations on pulp slime, which he considers as a hydrogel that may be affected by mechanical and chemical factors. The hydration is to a certain degree reversible by heating or by treating the slime with alcohol. Mechanical fragmentation promotes the gel formation. Increased adsorption capacity and higher hygroscopicity go hand in hand with hydration, whereas the viscosity of viscose solutions prepared therefrom decreases.

Pulp slime retains colloidal copper particles. It is distinguished from hydrocellulose by a greater content of soluble dextrin. It adsorbs more water than cellulose.[419]

In Acids. Concentrated acids, which swell cellulose, dissolve the same, at suitable concentrations initially without material chemical changes. With prolonged action of the acid, however, esterification reactions and hydrolytic degradation take place. Upon dilution or neutralization of the acid, products are obtained which are different from the original material in many colloid-chemical characteristics and which have attained some technical importance. A systematic investigation of these products has been carried out by M. Samec and J. Matula.[420]

These investigations were made with sulfite pulp in sulfuric acid concentrations of 55 to 85 per cent. The iodine color of the reaction mixture changes with progressive acid action, from blue to reddish-brown. The viscosity, during the swelling process, increases to a maximum, depending upon the intensity of the acid action, then rapidly decreases.

With 55 per cent sulfuric acid a product is obtained which is closely related to Guignet cellulose. This can be dispersed in water as a stable white suspension up to a content of 1.3 per cent. The suspension reacts weakly acidic and after a very thorough purification, a 1 per cent solution has an electric conductance of 9×10^{-5} reciprocal ohms and contains 1.7×10^{-4} potentiometrically active hydrogen ions. It appears that we have here a sulfuric acid ester. The dried product can again be completely dispersed in water, as a suspension which upon dilution to 0.1 to 0.2 per cent of the dry material, is changed to an opaque, translucent colloidal solution. The osmotic behavior indicates that the dissolved portion has a molecular weight of about 6,800.

Different salts, especially the sulfates of sodium, magnesium and aluminum, precipitate the substance from solution. Addition of alkali raises the inner friction of the suspension to a certain limit and then depresses it again. Still longer action of the acid yields a product with an average molecular weight of about 2,400. Such dispersed cellulose is partially attacked by diastase. (*See also* the chapter on the degradation of cellulose.)

In Alkalis. Cellulose also dissolves appreciably in cold strong alkalis, the solubility reaching a maximum in approximately 12 per cent caustic soda solution at 23°C.[421] W. Weltzien, likewise, in his investigations on the alkali-soluble constituents of pulp found an optimum solubility with a caustic concentration of 10 to 12 per cent. With artificial silk this optimum is reached with 10 per cent caustic soda solution.[422]

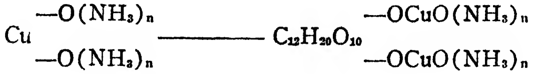
The solubility of the fiber is, however, not attained by a single treatment with alkali. With continued action there is finally a definite approximately constant portion of the cellulose (0.7 per cent) which goes into solution; from which fact, bearing in mind the alkali-soluble modification of cellulose demonstrated by Hess and his co-workers, mercerization can be considered as an initial transformation of natural cellulose to the alkali-soluble form.[423]

In Cuprammonium Solution. Cellulose solutions formed by means of salts and especially by means of alkaline copper solutions,[424] are of great technical importance.

In making these copper solutions, which have been extensively studied,[425] the preparation of the solvent as well as the pre-treatment of the cellulose plays an important rôle. A thorough purification,[426] a suitable bleaching,[427] and a previous mercerization[428] or swelling with sulfuric acid increases the solubility. This aid to solution can probably be traced to the separation of the cuticle by these agents. A similar result can be obtained by digesting the cellulose with a liquor containing 3 per cent sodium carbonate and 5 per cent caustic soda.[429] A content of 12 to 14 per cent water is especially favorable for "solution."

Friedrich substituted alkylated amines for the ammonia of the copper solution [430] whereby the solutions could be obtained in higher concentrations and were less liable to decomposition. A copper hydroxidethylenediamine solution possesses a high solvent power for cellulose.[431] These solutions have a low alkali concentration.[432]

The mechanism of this solution process was explained only recently. Erdmann believed there is a dispersion of the gelatinized cellulose in the form of a highly hydrated solid. Crammer,[433] on the basis of osmotic studies, assumed a complete solution. Linkmayer [434] observed that by the solution of cellulose in cuprammonium solution, ammonia was freed and explained the process by the following formula:



$$\mathrm{Cu}\begin{array}{l}\text{—}\mathrm{O(NH_3)_n}\\ \text{—}\mathrm{O(NH_3)_n}\end{array}\text{————————}\mathrm{C_{12}H_{20}O_{10}}\begin{array}{l}\text{—}\mathrm{OCuO(NH_3)_n}\\ \text{—}\mathrm{OCuO(NH_3)_n}\end{array}$$

The ratio of copper to cellulose must be molecular.[435]

Cross and Bevan held that there is a reaction of the acid and basic groups of cellulose,[436] and metal compounds with the formation of colloidal double salts. Lenher [437] assumed the cellulose to be an alcohol which with metal oxides form alcoholates, which latter then form water-soluble cupramine bases with ammonia.

E. Comerade observed that the fixation of the copper followed the laws of adsorption and the solubility of the cellulose is proportional to the concentration of the colloidal copper-ammonium hydroxide.[438]

E. Berl and A. G. Innes,[439] as well as E. Bauer,[440] also thought of it as an adsorption-like dispersion of the copper in the cellulose and found that this assumption satisfactorily expressed the quantitative facts. K. Hess and E. Messmer [441] demonstrated, however, that the adsorption isotherms do not correspond to the experimental behavior as well as does the law of mass action which they apply.

Lead salts precipitate from the solution residues that contain lead and cellulose. Zinc salts precipitate analogous zinc compounds. If, however, the cuprammonium solution is digested with zinc, the copper of the solution will be replaced by the zinc without any precipitation of cellulose, and a colorless ammonium-zinc-oxide solution will result.[442]

The study of cellulose cuprammonium solutions was greatly promoted by the work on complex copper compounds of tartaric acid and glycerin which Bullnheimer and Seitz obtained in a crystalline state.[443]

The final explanation was brought about by the investigations of W. Traube,[444] and K. Hess and E. Messmer [445] who proceeded from the precipitate, first described by Normann, which was obtained by addition of alkali to a cellulose-ammonia-copper oxide solution and which always exhibited the same composition $[(C_6H_8O_5)_2Cu]\ Na_2$.[446] They concluded that in Schweitzer's reagent, as in this compound, the copper could react in a duplex way: first, with the cellulose to form a complex cellulose-copper anion; and second, as a copper-amine cation $[Cu(NH_3)_4]^{++}$, it combined with this complex to form a salt-like double compound. In this latter form the copper can be replaced by sodium without any influence on the rotatory power of the compound. This action of the alkali explains the technically important fact that, in the presence of a certain amount of alkali with a definite quantity of copper, more cellulose dissolves than without alkali.[447] This conception is in support of the researches of Hess and Messmer who showed that after the addition of alkali copper migrates only to the anode, while without caustic soda, the copper is apparently found only at the cathode.

The viscosity of cuprammonium solutions of cellulose is a good distinguishing characteristic for different celluloses and for the previous treatments they have undergone. This method of investigation, however, suffers from the fact that the viscosity value is not consistent; according to Ost its basis lies in the easy oxidizability of the solution.[448]

The addition of small amounts of cane sugar, sodium chloride or sodium sulfate has no appreciable influence on the viscosity of cuprammonium solutions of cellulose. Greater additions increase the internal friction and make the cellulose insoluble. With increasing ammonia concentration there is a proportional decrease of the logarithm of the viscosity.[449] Joyner assumed two types of cellulose, a cellulose A with high and a cellulose B with low viscosity.[450]

The irregularities of the viscosity of cellulose solutions caused by air occlusion may be partially eliminated by use of the hydrogen viscosimeter. Pretreatment of the cellulose with caustic soda causes a lower viscosity of the cuprammonium solution. It appears that a depolymerization of the cellulose is caused by the lye. Although in general viscosity measurements are not so made that from them we can draw conclusions on the actual internal friction without disturbance by elastic forces, we can assert that the internal friction of a cellulose-cuprammonium solution is greater the purer the dissolved cellulose.

According to Levalois [451] cellulose in cuprammonium solution exhibits a levorotation of — 20°, the rotatory power fluctuating with the concentration and the ratio of copper to cellulose. Bechamp [452] disputed this. The properties of the dissolved substance can be markedly altered by secondary processes, as oxidation and hydrolysis, whereby films and threads obtained from the solution can exhibit great differences, one from the other. K. Hess and E. Messmer [453] found such solutions to be optically active, and considered this as evidence of the asymmetry of the complex water-soluble cellulose-copper compound.

From the definite regularity in the variation of optical rotation of cellulose-cuprammonium solutions, K. Hess concluded that the following compounds occur in Schweitzer's reagent.[454] First, in the absence of alkali $[C_6H_7O_5Cu]_2[Cu(NH_3)_4]$ with high optical rotation; second, in the presence of alkali $[C_6H_7O_5Cu]Na$ but with an excess of alkali the compound $[(C_6H_8O_5)_2Cu]Na_2$ is precipitated.

K. Hess investigated the variation in optical rotation with changing cellulose concentration and constant copper content, as well as with changing copper concentration and constant cellulose content, in order to determine the molecular weight of cellulose. With the assumption that the law of mass action applied, the best agreement between calculated and experimental results was obtained when the cellulose molecule was assumed to be $C_6H_{10}O_5$.[455]

So small a molecule is inconsistent with the high viscosity of the cellulose-cuprammonium solutions, which indicates larger particles. K. Hess explained this on the assumption that each $C_6H_{10}O_5$–group, although in a larger molecular union, reacted with the copper as though it were free.[456]

Upon addition of acids, alkali, sodium carbonate [457] or salts, especially the acid salts and potassium cyanide [458] and dehydrating agents as alcohol and sugar,[459] cellulose is precipitated from the cuprammonium solution in the form of a swollen gelatinized mass. The solution decomposes on standing exposed to the atmosphere so that ammonia can escape, in which case there is precipitated, besides the cellulose, a hydrated copper oxide. After re-dissolving the latter, the cellulose remains in spherical crystals or in the form of needles.[460] The sphero-crystals are conceived of as an aggregate of radial fibers which, contrasted with the cellulose of plant membranes, are very faintly, if at all, anisotropic.[461]

When using alcoholic solvents, frequently an addition of glucose, saccharose, lactose, carbohydrates in general or glycerin is recommended to obtain coagula low in copper, from which the copper is easily dissolved out by dilute acids. If cellulose-cuprammonium solutions of especially high viscosity are pressed through fine nozzles into a precipitating liquid, the cellulose is precipitated as a thread, the technically important cuprammonium silk.[462]

The coagulum obtained with alkalis [463] contains, as expected, about 12 atoms of carbon, 1 atom of copper and 2 atoms of sodium. It gives up most of the metal in water, and the remainder in dilute acetic acid.

Cellulose obtained by precipitation exhibits in general the same chemical properties as the natural fiber, with the exception that in the fresh condition it is very readily dispersable in 8 per cent caustic soda.[464] The coagulum also exhibits the X-ray diagram of mercerized cellulose.[465]

In Alkali and Carbon Bisulfide.[466] Alkali-cellulose, through the action of carbon bisulfide, is made soluble in water, from which it can again be precipitated with its original properties.[467] Cellulose, treated with 15 to 18 per cent caustic soda and then pressed, is converted into alkali-cellulose $C_6H_{10}O_5.2NaOH$. This is then treated with sufficient carbon bisulfide that 1-CS_2 reacts with 1-$C_6H_{10}O_5$.[468] The cellulose forms a gelatinous mass which can be dissolved in water [469] or dilute alkali,[470] giving solutions that are a dirty brown color and more or less viscous

The chemical nature of this reaction has been investigated by C. F. Cross and E. J. Bevan,[471] H. Ost, F. Westhoff and L. Gessner,[472] and E. Heuser and M. Schuster.[473] All of the investigators agree that the preparation precipitated from the solution contains, besides cellulose, sulfur and alkali which decrease in the course of the ripening process. At first the predominating ratio is approximately $C_6H_{10}O_5.CS_2.2NaOH$.

C. F. Cross and E. J. Bevan assume that a xanthic acid ester of cellulose is formed according to the equation:

$$C_6H_{10}O_5 + 5NaOH + CS_2 \text{ ——— } C_6H_8O_3\left\}\begin{matrix} ONa \\ OCSSNa \end{matrix}\right.$$

Because of the instability of xanthic acid toward water,[474] sulfur and alkali gradually split off, so that finally cellulose is deposited again.[475] The ripening of viscose accordingly would be accompanied by a hydrolytic cleavage of the CSSNa-groups.[476]

The exact composition of the product primarily formed is not agreed upon by all investigators. C. F. Cross and E. J. Bevan, as well as H. Ost maintain the formula is $C_6H_{10}O_5.CS_2$, whereas P. Karrer and Th. Lieser,[477] and E. Heuser and M. Schuster believe the ratio to be $2C_6H_{10}O_5.CS_2$. For solution of the cellulose in carbon bisulfide-alkali a strictly stoichimetrical ratio of the reacting constituents is not necessary.[478] The analytical investigations were made in part on the precipitation product formed, for example, upon neutralization of the solution with acetic acid and mineral acids, or by titration with iodine solution which precipitates xanthate solutions by formation of a disulfide-like body.[479] K. Leuchs [480] investigated the aging process by direct determination of the carbon bisulfide, a method which is open to objections.[481]

Viscose solutions are typical colloidal solutions and thus colloid-chemical factors are frequently used for their characterization. The viscosity of freshly prepared solutions decreases during the first 2 or 3 days, reaches a minimum and then increases, at first slowly, then very rapidly to an end point.[482]

According to E. Heuser and M. Schuster, as well as P. Waentig,[483] the primary decrease in viscosity is caused by the cellulose-xanthate gradually going into solution. At the beginning, the particles in solution approximate the fiber particles in size, but these later become smaller.[484] The increase in viscosity is caused by the cleavage of the xanthate-groups whereby the cellulose is regenerated and because of its insolubility, it coagulates and finally solidifies to a gelatinous mass.[485]

The viscosimetric behavior of viscose solutions is dependent firstly on the age of the alkali-cellulose; the more aged the alkali-cellulose, the lower the viscosity of the viscose solutions.[486]

The temporary decrease in viscosity is greater the fresher the alkali cellulose; the increase in viscosity is slower and less marked the older the alkali-cellulose. According to K. Hess the aging of alkali-cellulose is very likely caused by a disarrangement of the crystallites and the formation of impurities under the influence of atmospheric oxygen.[487]

The viscosity of the viscose solutions is further dependent on the previous treatment of the cellulose. Dry beating depresses the viscosity;[488] so does heating the cellulose.[489] The source of the cellulose also influences the viscosity of the resulting solution.[490]

The addition of alkali up to a concentration of 9 per cent depresses the viscosity. At this concentration the solutions are especially stable,[491] probably because the alkali retards the cleavage of the xanthate groups.

Cellulose xanthate can be precipitated by various materials such as alcohol, sodium chloride, ammonium chloride, etc.[492] Magnesium salts, however, give a soluble cellulose compound. Other salts also react with viscose. Thus zinc salts give a white, alkali-soluble zinc salt; mercury salts give a yellow precipitate; lead salts, an orange yellow; iron salts, a brown; bismuth salts, reddish brown; copper salts, chocolate brown; and nickel salts, cherry red metal salts of cellulose-xanthic acid.[493]

Mineral acids in general precipitate hydrated cellulose with the evolution of hydrogen sulfide, while organic acids precipitate the free xanthic acid and act on the impurities so that with their help the raw product can be purified.

The precipitated product can be purified by dialysis with water or alkali.[494] Coagulation by electrolytes results more readily the older the viscose solution.[495] With ammonium chloride as the precipitating agent, the alkali content of the solution is especially important, since under its influence ammonia is set free to form the unstable ammonium cellulose-xanthate.[496]

Fresh viscose solutions under the ultramicroscope[497] with a cardioid condenser exhibit colloidal particles with Brownian movement. On aging, the movement and the number of visible particles decrease. R. O. Herzog and R. Gaebel,[498] however, observed with a paraboloid condenser and azimuth diaphragm no particle decrease. In the coagulation stage a cohering gel structure is observed throughout the entire field of view.

R. O. Herzog and R. Gaebel[499] attempted to explain the aging of viscose solutions by diffusion. The radius of the diffusing particles is constant (1.6 to 3 $m\mu$) for different degrees of ripening, but with ripening, the diffusion is strongly retarded, that is, the gel character of aged viscose solutions hinders the diffusion of the dissolved particles into the caustic soda.

In Salt Solutions. In addition a good solvent for cellulose is concentrated

$ZnCl_2$ solution.[500] For the preparation of this solution the cellulose is permitted to swell uniformly and then solution is effected by heating. The homogeneous syrup obtained finds use in the preparation of incandescent lamp filaments. Grandmougin has demonstrated that the action of zinc chloride is analogous to that of caustic soda. Such solutions were later used for the preparation of artificial silk fibers.[501]

A solution of zinc chloride in double the amount of hydrochloric acid dissolves cellulose without hydrolysis or decomposition,[502] but after prolonged action hydrolysis results.[503] In this case a pre-treatment with alkali favors solution considerably.[504] In order to retard the degradation of the cellulose molecule in the process of solution, Wynne and Powell [505] employ mixtures of zinc chloride and alkaline earth chlorides. Similarly Dreaper and Tomkins [506] use basic zinc salts (chloride or nitrate) mixed with alkaline earth chloride.

Further solvents for cellulose are solutions of antimony trichloride in water or hydrochloric acid, mercuric chloride, bismuth chloride, stannous chloride in hydrochloric acid in the cold, hot aqueous stannous chloride, antimony pentachloride, stannic chloride and titanium chloride mixed with some acid. Less effective are the concentrated hydrochloric acid solutions of cobalt chloride, auric chloride, uranyl chloride, ceric chloride, chromic chloride, cadmium chloride, cuprous chloride, thallic chloride and vanadium trichloride. Ineffective, however, are manganic chloride, cupric chloride, nickel chloride, silver chloride, lead chloride, thallous chloride, thorium tetrachloride, aluminum chloride, phosphorous trichloride, arsenic trichloride, and the chlorides of the alkalis and the alkaline earths.[507]

The action of bromides in aqueous solution on cellulose is mostly masked by the strong effect of hydrobromic acid. Aqueous solutions of zinc bromide, bismuth tribromide and mercuric bromide dissolve cellulose in the presence of hydrochloric acid in those concentrations in which equivalent amounts of hydrobromic acid would decompose the cellulose fibers without dissolving them. Zinc iodide, mercuric iodide in hydrochloric acid, lead iodide and bismuth triodide behave similarly.[507] The solubility of cellulose in neutral salt solutions is in general dependent upon their physical properties. A condition for solution is the presence of a complex salt in the solution.[508]

The salt solutions which P. P. von Weimarn uses to swell cellulose also dissolve it in fairly high concentration.[509] *

According to his experiences, pure cellulose is soluble in dilute salt solutions as a colloid, or better expressed, as a suspensoid. The first stability maximum lies in the sphere of very weak salt concentration. With medium salt concentrations the cellulose is aggregated and precipitates, and with very high salt concentrations cellulose is soluble to a very great extent.[510] Thus sodium iodide, calcium iodide, calcium bromide, strontium iodide, barium sulfocyanide, strontium sulfocyanide dissolve cellulose at atmospheric pressure. For the apparently ineffective salts as sodium chloride, potassium chloride, barium chloride and others, heating under pressure is necessary.

Cellulose precipitates from the salt solutions on dilution or cooling, forming gels which according to the cellulose concentration, are more or less rigid. In general these gels give up their salts in water; only with neutral salts which are split hydrolytically does considerable ash remain in the fiber (with $ZnCl_2$ up to 25 per cent). With sufficiently high concentrations of cellulose the gelatinous mass has elastic properties so that it can be formed into films.[511]

The precipitated and washed neutral cellulose prepared from salt solutions,

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* See also paper by von Weimarn in this volume. J. A.

after drying, is extremely hard, horny and similar to the mass obtained from cuprammonium solution.[512]

Different views are expressed as to the mechanism of the solution process of cellulose in salt solutions. Bronnert [513] is of the opinion that, for example with zinc chloride, there is a depolymerization and hydration of the cellulose. C. F. Cross and E. J. Bevan [514] explain the solution on the basis of the formation of a double salt in which the amorphous character of the cellulose plays an important rôle. H. G. Deming [515] believed that after the resulting swelling, the acid formed by hydrolysis of the zinc chloride initiates an hydrolysis of the cellulose, because zinc chloride solutions in organic solvents do not dissolve normal cellulose unless it has been previously treated with acids. R. O. Herzog and F. Beck [516] believe that the solution power of salts for cellulose is a function of the combined ions of the salt. In agreement with this is the view of P. P. von Weimarn [517] that a loose surface union of the salts with the cellulose micelle is responsible for the dispersing effect.[518]

Cellulose does not undergo any great change upon being dissolved in salt solutions, for according to J. R. Katz and H. Mark [519] there is no change in the X-ray spectrum of ramie fibers caused by swelling in neutral salt solutions. R. O. Herzog,[520] however, has established that the precipitated cellulose product from hot solutions has the diagram of mercerized cellulose.

Under the action of an electric current cellulose up to two-thirds the quantity present, passed into solution in neutral potassium chloride. The residue is soluble in 10 per cent caustic soda but can also, under suitable electrolysis, be brought into a milky colloidal, stable and filtrable solution. Acids and alcohol precipitate a gel from the solution.

CELLULOSE REGENERATED FROM THE SWOLLEN AND DISSOLVED STATE (HYDRATE CELLULOSE).[521]

When the swelling agent or solvent is removed from the sols just discussed, or is altered chemically, the cellulose is regenerated in the form of a more or less hydrophobic gel. This gel differs from the original cellulose especially in possessing a more loose packing of the elementary units. This difference in colloidal structure seems quite sufficient to explain the known differences in behavior. When it is considered that the sols produced by means of different swelling agents and solvents are colloidally and chemically different, it is easy to imagine that the celluloses regenerated from them would show certain minor differences. It is not necessary to assume that no constitutional changes in the structural units [522] occur, but these are not characteristic of the typical hydrate cellulose.

In the development of cellulose chemistry any alteration product of cellulose which, according to C. G. Schwalbe's method [523] shows no change in a copper number from the original material, has been designated as *hydrate cellulose.*[524] This classification includes mercerized cellulose, cuprammonium silk, viscose silk, denitrated nitro silk, deacetylated acetate silk, the products of "wet beating" of wood pulp, of extreme swelling in neutral salt solutions, and others. The β-cellulose of Cross and Bevan (the portion soluble in mercerizing alkali) [525] belongs especially to this class.

Treatment of cotton cellulose with 62.5 per cent H_2SO_4 and precipitation by dilution gives the so-called Guignet cellulose.[526] This material, whether wet or dry, gives a milky suspension with water, the finest particles remaining suspended for days. It can be coagulated, however, by salts, acids, alcohol, etc. Dried in thin layers the colloidal solution gives brilliant films which, however, swell again in water. Iodine-KI solution gives a blue color with Guignet cellulose only in the presence of H_2SO_4. This form of cellulose may also be grouped with the hydrates. The original idea that water is chemically combined in hydrate cellulose, has proven incorrect.[527] More recently attempts have been made to explain differences observed in X-ray spectrograms on the basis of a structural rearrangement caused by the binding of water.[528] A sharp separation has generally been made between hydrate and *hydro-cellulose*. Many attempts have been made to develop methods for following the formation of hydrate cellulose,[529] of which the best early one was Schwalbe's "hydrolysis number." [530] Trouble was encountered because many hydrate celluloses had a low copper number, but still a high hydrolysis number.[531] An important advance was made by *Hess*,[532] who based his method on the change of optical activity with change of concentration of the active complex in cuprammonium cellulose solution. His work led to the conclusion that hydrate cellulose was chemically identical with native cellulose.

The physical behavior of hydrate celluloses is considerably different from that of natural fibers. The regenerated cellulose has an increased water absorption capacity. According to Schwalbe,[533] the absorption amounts to 12 per cent with alkali-mercerized cellulose. Ost and Westerhoff [534] observed an absorption of 10 per cent and Heubner [535] found 8.5 per cent. The differences in absorption between natural and mercerized fibers are considerably decreased by drying.[536]

The water is given up but slowly at 100° C., a temperature of 125° C. being necessary for complete drying. Cross and Bevan suggest that the water which can be driven off at 100° C. be designated *aq.;* that driven off at 150° as *Aq.,* and that the designation H_2O be reserved for water entering hydrolytically.[537] The rate at which mercerized cellulose gives up water decreases regularly with increased time, a behavior parallel to that shown by colloids on drying.[538]

Mercerized cellulose which has been heated to 125° C. shows, after cooling to room temperature, the same characteristics as before heating. However, by heating for a month with strong alcohol, or under high pressure this mercerized cotton can, according to Hübner, be reconverted to normal cotton cellulose.[539]

Cuprammonium hydrate cellulose is manufactured in great quantity as artificial silk (*Pauly silk, Glanzstoff*). This material has a hygroscopic moisture content of 9 to 10 per cent.[540] Upon heating to constant weight at 99° C., the moisture regained in air is reduced to 6.94 per cent.[541] The regain in a moist chamber, of Pauly silk dried at 100° to 115° C. is, however, 23.08 per cent.[542] When immersed in water, 33 to 65 per cent moisture is absorbed, and at the same time the strength is considerably decreased. The drying temperature is indeed an important factor in determining the gloss of artificial silk, and probably also its strength as well. Filaments dried at 400° C. are porcelain-like masses, cloudy and without sheen.[543]

The hydrate water may be separated in other ways. Strong $CaCl_2$ solution, alcohol and superheated steam will serve for this purpose.[544]

Parchment paper, prepared by the action of 75 to 84 per cent H_2SO_4 on filter paper for 5 to 15 seconds, contains about 10 per cent hygroscopic moisture.[545] It has a lower strength in the moist than in the dry condition.

Other members of the group of regenerated celluloses are those prepared from esters, as viscose silk and denitrated collodion cotton. The hygroscopic moisture content of viscose silk varies in the neighborhood of 10 per cent,[546] that of the denitrated cotton from 10 to 11.3 per cent.[547] The artificial silks swell in water, the longitudinal swelling being small in comparison with the increase in thickness.[548]

The increased absorption power of regenerated celluloses for caustic solutions is parallel to their increased sorption power for water. Since the former property increases with degree of mercerization, direct conclusions as to the mercerization can be drawn from the caustic absorption.[549]

The hydrate celluloses obtained from salt solutions,[550] from cuprammonium,[551] from esters,[552] as well as by the action of sulfuric acid,[552] show in general a more or less great alkali solubility. However, when fully dried the cuprammonium cellulose, for example, is strongly resistant to alkalis [553] and may serve as material for alkali storage.

"Hydrate-cellulose" gives characteristic color reactions with iodine-potassium iodide solution,[554] and Hübner showed an increased sorption of iodine by this material.[555]

Pauly silk loses the brown- or blue-black iodine color very rapidly, the fiber becoming white once more.[556] It gives a brownish coloration with zinc chlor-iodide. Parchment is colored blue with iodine-potassium iodide, even in the absence of sulfuric acid,[557] the Flechsig amyloid only in the presence of acid.

The power of mercerized cellulose for taking up tannin is raised considerably above that of the unmercerized material; [558] its power for sorption of alkaline copper solution (hydrate copper number [559]) is likewise increased. With regard to the taking up of mordant salts, there are a number of conflicting observations. Minajeff [560] is of the opinion that the mercerized fiber offers more resistance to the penetration of colloidal mordants (hydrogels) than does the unmercerized material. Chardonnet silk is reported to take up mordants almost as well as ordinary cellulose.[561]

Coloring with mordant dyes goes on in very nearly the same way with both mercerized and unmercerized fibers.[562] Mineral colors dye the mercerized fiber throughout, which they will not do with the unmercerized fiber; the mercerized fiber takes up a considerably larger amount of such dyes.[563] An analogous increased dye absorption has also been observed with developed colors.[564]

Aniline black is taken up in equal quantities by both mercerized and unmercerized fiber, but much less aniline is required to reach a given depth of color with the former fiber.[565] Likewise the iron-grays show a much fuller tone on mercerized fibers, though the amount absorbed is not markedly increased.[566] Very little difference can be detected with basic dyes, but substantive and sulfur dyes are taken up more strongly by the mercerized fibers,[567] so that these dyes may be used to estimate the degree of mercerization.[568]

The degree of tension of the fiber,[569] and any drying treatment given it,[570] have an important effect upon the taking up of dyes by mercerized fiber. These points were not considered in the work of Schaposchnikoff and Minajeff; which explains why Hübner obtained results exactly opposite from theirs; he contended that mercerized fiber required as much dye as the unmercerized, to reach a particular shade.[571]

Chardonnet silk has a great affinity for basic dyes, which may possibly be ascribed to the presence of hydrocellulose.[572] Pauly and viscose silks, on the other hand, resemble mercerized cellulose very closely in their behavior toward dyes. Parchment paper also behaves toward dyes in a manner analogous to that of mercerized cellulose.

The strength of cotton is increased by swelling salts or caustic treatment. The strength of Pauly, viscose and Chardonnet silk is greatly decreased by moistening; this decrease can be limited by treating the fibers with sulfuric acid. Parchment paper retains much of its strength when wet.

The solubility of alkali hydroxide-cellulose is ammoniacal copper oxide solution is greater than that of normal cellulose. Minajeff [573] is of the opinion that the cuticle survives the mercerization treatment; Haller,[574] on the other hand, states that the characteristic cutin substance is removed. Pauly silk is difficultly soluble, Chardonnet silk and parchment paper are very readily soluble in ammoniacal copper oxide.

HYDROCELLULOSE.

Recent research has resulted in modifications in the definition for hydrocellulose, just as has occurred with hydrate cellulose. It is well known that cotton fibers are considerably weakened by the action of dilute acids; [575] the carbonization process for removing cotton from mixtures with wool [576] depends on this fact. According to A. Girard,[577] the best results are obtained by treating the fibers for 12 hours with 55 per cent sulfuric acid, at room temperature. Acid vapors, dilute acids, and easily-dissociable salts work in the same way. at elevated temperatures.[578] The cellulose loses some weight during this treatment.[579] It was at first thought that water combined with cellulose, during this reaction, but later study indicated that this was not correct.[580] The presence of reducing groups has been more definitely determined, so that this property [581] can be taken as typical for hydrocellulose. The reducing part can be removed by boiling with water,[582] so that the residue shows only a trace of reducing power. The fibers of this residue appear on microscopic examination like cotton fibers which have been attacked on the surface.[583] The double refraction [584] agrees with this. The water-soluble reducing part may be glucose,[585] which is removed according to the laws of adsorption. Besides this there is, according to G. Bumcke and R. Wolffenstein [586] a part of the hydrocellulose which is soluble in dilute (2.5 per cent) caustic soda, and may be precipitated from this by acids. Earlier investigators believed this fraction to be very closely related to cellulose, and it received as a consequence a great deal of attention.[587] Finally, K. Hess and E. Messmer were able to show by polarimetric methods that the two do not differ chemically.[588] The alkali-soluble portion of hydrocellulose shows the same X-ray interference bands as normal cellulose,[589] and hence cannot be, as for example Heuser [590] believed, amorphous. K. Hess recommended that the name *cellulose A* be applied to this material.

The behavior of the alkali-soluble part of hydrocellulose on methylation [591] is in agreement with the foregoing. C. G. Schwalbe [592] found that hydrocellulose possessed strong reducing properties, which Knoevenagel [593] and Heuser [594] showed to be characteristic of the alkali-soluble part. It appears that [595] the Schwalbe method was too vigorous, splitting off the cellulose A during the treatment.

To-day we have come to consider hydrocellulose as a colloidal aggregate (collomol) essentially weaker than the unchanged fiber, consisting of glucose, possibly other decomposition products of low molecular weight, cellulose A, and unchanged cellulose.

Characteristic of the washed and dried hydrocellulose is its low hygroscopicity, which varies between 1.2 and 4.7 per cent of bound water.[596] Hydrocellulose binds alkali from dilute solutions; in strong caustic potash it swells and gives a blue color with iodine. It is indifferent toward dilute acids.[597] According to Girard [598] it swells in concentrated acids, giving the blue iodine coloration. Thus hydrocellulose is hydratable, just as hydrate cellulose is readily hydrolyzable.

In contact with hydrocellulose, hydriodic acid is decomposed; the iodine separates on the fibers, turning them brown. On adding water this color changes to blue. Hydrocellulose is not always colored by iodine without some sort of a pretreatment. When coloration does occur it is removed almost at once by addition of water. Zinc chloride solution produces a blue violet color,[599] unaffected by water.

Hydrocellulose forms a milky colloidal suspension in dilute acids, but loses its colloidal characteristics in the presence of alkalis.[600] Ammoniacal copper oxide readily dissolves it,[601] while the solubility in zinc chloride-hydrochloric acid depends on the mode of preparation [602] of the hydrocellulose; zinc chloride alone will dissolve the material, as will sirupy phosphoric acid, according to Grandmougin.[603]

The dyeing properties of hydrocellulose have been little studied—the experimental results available are contradictory.[604]

Oxycellulose. Under the influence of oxidizing agents,[605] aldehyde and carboxyl groups are formed on some of the units in the cellulose structure. The elementary formula shows a higher oxygen content than normal cellulose. The new material is generally insoluble in cold or hot water, alcohol, or ether. Oxycellulose prepared by different means shows different properties. Without any superficial differences being evident,[606] cloth which has been oxidized becomes tendered, loses its strength and can in some cases be rubbed to a white powder. In contact with water vapor the oxycellulose becomes brown. According to microscopic studies, its formation is accompanied by a decrease of 12.5 per cent in the width and size of the fiber.[607] The mordanting capacity for $FeCl_2$ and $FeCl_3$ is retained by oxycellulose prepared with bleaching powder.[608] Chrome alum and chromacetonitrate give an intensive violet color on dyeing with alizarin, while alum, aluminum acetate, and $Al_2(SO_4)_3$ give red lakes. Tin salts, mercury salts, $CuSO_4$, $Cd(NO_3)_2$, and $Pb(NO_3)_2$ combine with oxycellulose, while cuprous oxide is precipitated from alkaline copper solution.[608] It is not impossible that true salt formation occurs between the metal and the oxycellulose. According to Nastjukoff the combination with mordants is not permanent;[609] oxycellulose prepared with nitric acid does not fix mordants.[608]

Oxycellulose shows no affinity for aniline black, although this color can be developed on fibers containing oxycellulose if they have previously been treated with a trace of vanadium salt.

The acid dyes are, like the mordant dyes, not taken up; [608] basic dyes, however, color oxycellulose readily. The reason for this lies in the more acid nature of the oxycellulose, caused by the carboxyl groups. Witz indeed utilizes the formation of oxycellulose to dye cotton cloth topically, or more strongly. Such coloring, however, will not withstand hot water or hot soap baths. It is possible to dye and decolorize the cloth repeatedly without destroying the mordanting power. According to Witz,[610] the counter-effects of capillary action and diffusion are here such that adsorption equilibrium can only be reached after a long time and at an optimum temperature. Saget [611] states that bleaching powder oxycellulose completely repels diamine blue 2B and Erika, while other diamine blue colors behave variously. A considerable decrease in fixing power is apparent when the dyeing is preceded by a light, hot soap washing. No very general differences in dyeing capacity between cellulose, oxycellulose, and hydrocellulose can be determined, though Vignon [612] found a greater affinity for basic dyes in a $KClO_4$—HCl oxycellulose than in normal cellulose. Methylene blue and saffranine color oxycellulose very strongly.

Direct cotton dyes are destroyed by boiling or caustic in the presence of oxycellulose, in greater amounts than necessary to color the fiber, without the fiber becoming in the least colored. Direct dyes which are not attacked by reducing agents color highly oxidized cellulose at once. By treatment with caustic soda, the dyeing characteristics of oxycellulose can be restored.[613]

Oxycellulose gives a violet-blue color[614] with zinc chloriodide, and blue (except when prepared with HNO_3 or $KClO_4$) with iodine-sulfuric acid.[615] It shows an increased neutralizing power for bases,[616] has a high oxygen content,[617] and reacts with phenylhydrazine.[618] A typical property is that of splitting off furfural, which is especially prominent in the case of oxycellulose prepared by oxidation and simultaneous hydrolysis.[619]

There is apparently no great difference in the solubility of oxycellulose and native cellulose in cuprammonium hydroxide.[620] Heated four hours with 15 per cent sulfuric acid, oxycellulose swells to a paste.[621] Nastjukoff has suggested that oxycelluloses be classified on the basis of their solubility behavior[622] as follows:

Alpha-oxycellulose is insoluble in dilute alkalis or in ammonia; beta-oxycellulose is soluble in these reagents; gamma-oxycellulose is soluble in the above reagents, and also in water if not previously dried.

This classification does not, however, seem to have been a very great advance in clarifying the oxycellulose question,[623] since it has never been determined whether there are in fact any oxycelluloses completely insoluble in water.

The solutions of oxycellulose in water have a golden yellow color which suggests an aldehydic nature. In the solution Nastjukoff also found the alkali salts of the acids formed by oxidation of the oxycellulose. He isolated, for example, a barium compound with 4.91 per cent, and another with 5.84 per cent barium

Schwalbe[624] and Heuser[625] consider the solubility in alkali as typical of oxycellulose Heuser considers that glucuronic acid residues are present,[626] and Pringsheim[627] ascribes special formulas to the material.

Some oxycelluloses are incompletely soluble in alkali. The residue remaining after alkaline treatment of such an oxycellulose no longer reduces Fehling's solution, and does not turn yellow with alkalis. This residue resembles hydrate-cellulose quite closely. Schwalbe[628] is of the opinion that only the material soluble in 10 per cent alkali is true oxycellulose.

K. Hess found that oxycellulose washed with 5 per cent bicarbonate solution, gave a cuprammonium solution with the same optical rotation as that of unaltered cellulose.[629] If the bicarbonate wash was not given, the rotation was somewhat more positive than that of natural cellulose. The conclusion may be drawn that the oxidation processes used in preparing oxycellulose give rise to substances with a somewhat greater positive rotation than cellulose. According to this work, oxycellulose is composed of a more highly and a less highly alkali-soluble cellulose and oxidation products of an indefinite nature. From the colloid-chemical standpoint it is inconceivable that the entire molecular complex, completely saturated with aldehyde and carboxyl groups, should be designated as oxycellulose, rather than the fragments which go into solution on treatment with alkali. Faber and Tollens[630] have determined the molecular weight of two alkali-soluble oxycelluloses as 824 and 678 respectively.

The different methods, such as the Ristenpart methylene blue value,[631] Schwalbe's copper number,[632] the permanganate value of Kauffmann[633] and the silver value of Götze,[634] which have been put forward as quantitative measures of oxycellulose content, give a good indication of the relative degree of alteration of the cellulose and the attendant weakening of the fibers.

Products with very different solubility are obtained by varying the intensity of the oxidative treatment. Thus Bull, by the use of 60 per cent nitric acid, obtained a gelatinous, nearly ash-free mass, completely soluble in pyridine, piperidine, Na_2CO_3 and weak caustic alkali solutions. With increasing alkali content, solutions of this oxycellulose became at first gelatinous, then again limpid.[635]

An entirely water-soluble oxycellulose was obtained by Nastjukoff by the action of $KMnO_4$.[636] The solution was opalescent and by transmitted light looked yellow. Polarized light was rotated to the left by this solution. Concentrated solutions were milky, but did not settle on standing and passed readily through a filter. At concentrations of 5 to 10 per cent the solutions were thick as glycerin. On drying, glossy transparent films were obtained; those made from thick solutions were glassy.

These oxycelluloses can be precipitated from solution by the action of NaCl, $BaCl_2$, Na_2CO_3, acids and alcohol. The precipitate obtained with acids is at first water soluble. It loses this property on drying in the air, but can be brought into solution again by heating with soda solution.

The oxycelluloses have a more or less strong reducing power, depending on their aldehyde content,[637] coloring Schiff's reagent red or violet. It is easy to understand that oxidation products without aldehyde groups may be formed from cellulose. To this class no doubt belong the non-reducing products of Bull.[638]

CELLULOSE ESTERS.

Nitrocelluloses. Concentrated nitric acid causes cotton fibers to swell, and if a large amount of very concentrated acid is used, the fibers are decomposed. The acid concentration is very important. Thus 68.6 to 69.8 per cent acid produces swelling of the fibers, with formation of a readily hydrolyzable double compound [639] of low nitrogen content.[640] The stronger acids have a nitrating effect, which sets in quite suddenly [641] with 77.5 per cent acid. The rate of nitration also increases with increasing concentration.

Within certain definite limits of concentration [642] a viscous liquid or gummy mass is gradually formed. If this is plunged into a large volume of water a voluminous, structureless coagulum is produced,[643] which is difficultly soluble in alcohol, and which swells without dissolving in acetone or ethyl acetate. Cellulose is parchmentized and nitrated by 91 to 96 per cent acid.[644]

The products obtained with nitric acid alone have up to the present attained no technical value; those formed by the combined action of nitric and sulfuric acids are, on the other hand, very important commercially.[645]

The degree of esterification depends upon the ratio of the two acids used, and also on the water content of the nitrating bath.[646] Sulfuric acid addition influences the speed of esterification,[647] but not in a simple way.[648] The temperature,[649] and the physical composition of the cellulose,[650] are also determining factors in the nitration.

The NO_3 content is used for a more exact identification of the various nitrocelluloses. One may either use as a basis the C_{12} molecule, designating hexa-, penta-, tetra-, and tri-nitrate, according to Eder,[651] a C_{24} molecule, which will accommodate nine nitrocelluloses,[652] or even a C_{48} molecule.[653] The nitrogen content of 14.14 per cent, corresponding to the hexa- (dodeca-) nitrate, is not practically obtainable. According to Vignon this theoretical value is never obtained because the carbon and hydrogen are disregarded in the analysis, and the fact that the nitrocelluloses are derived from an oxycellulose is neglected. He has set up a formula which does in fact give the theoretical nitrogen content.

An ester structure is generally ascribed to the nitrocelluloses, although some investigations consider them to be adsorption complexes.[654] The entirely continuous change in nitrogen content and hygroscopicity between various nitrocellulose leaves, according to Vieille, no ground whatever for the existence of definite nitration stages in the sense of Eder's cellulose nitrates. Likewise Justin-Müller considers the compounds to be in fact adsorption complexes, basing his conclusion on the relations between the concentration of HNO_3 or H_2SO_4 used, and the composition of the resulting nitrocelluloses.

Certain facts are against this adsorption theory, however. Nitrocelluloses are not reversible toward water. Nitration only takes place with high concentrations of acid, whereas adsorption proceeds relatively most strongly from dilute solutions.[655] Moreover, if the nitrate content of the product is plotted against the molal concentration of HNO_3 in the nitrating acid, a stepwise curve is obtained, which is evidence against adsorption.

Normal nitrated cotton is outwardly differentiated from the natural fiber by a raw feel and by a certain crackling when pressed together. It becomes electrically charged by friction.

The density for any degree of nitration is 1.66.[656] The double refraction of the fiber decreases with increasing nitration, and passes through zero to negative values,[657] so that the course of the nitration can be followed by means of this property. Native fibers are iridescent under the polarizing microscope, and appear brownish-yellow; the nitrated fibers show various colors, the highly nitrated for example, appearing blue. The index of refraction also varies with degree of nitration.[658]

The hygroscopic moisture of nitrocellulose is 1.5 to 2 per cent, decreasing with increasing nitration. According to Will [659] the sum of the percentage nitrogen and moisture content maintains a constant value of around 14.6 per cent. This is independent of the nature of the starting material, and of the course of the nitration. There appears to be an intimate relation between the moisture content and the hydroxyl groups present.[660]

The hygroscopicity of nitrocellulose increases with decreasing temperature,[661] and with increasing relative humidity.[662] Immersed in water for one-quarter to one-half hour, it takes up 25 to 30 per cent.[663]

Fehling's solution is reduced by nitrocellulose; [664] with Schiff's reagent a brighter color is produced the more dilute the nitrating acid.[665]

Nitrocelluloses are colored brown by iodine and sulfuric acid, the color being removed by washing. Iodine—KI solution behaves likewise.

Mordants are but very slightly absorbed by highly nitrated fibers, and such fibers are almost unaffected by subsequent dyeing in madder. Unmordanted nitro fibers, on the other hand, take up much more color from a madder bath than does the original material. Again, if the pyroxylin is partially decomposed, it dyes after mordanting much better than the original fiber.[666] Blodel [667] states that nitrated cellulose refuses to take acid colors.

Partially nitrated fibers, according to Suida,[668] may be dyed with substantive colors, but completely nitrated fibers will not react with these dyes.[669] In general many factors, such as pretreatment, temperature of the bath, particle size, hydration, and so on, influence the dyeing. For this reason, the Lunge and Bebié method for measuring oxycellulose content by methylene blue absorption [670] is not to be especially recommended.

Röntgenographic studies of nitrated and denitrated fibers have shown that these operations do not change the arrangement of the crystals or the microscopic structure.[671] The mechanical properties and swelling power are likewise unchanged.

Considerable differences of solubility exist between the highly and slightly nitrated materials. The former were found by G. Lunge and Weintraub [672] to be insoluble in ether, alcohol, and mixtures of the two, but were soluble in acetone, ethyl acetate and their homologs, in methyl and ethyl glycol acetate, amyl acetate, cyclohexanol acetate, and in fused camphor, and difficultly soluble in nitrobenzene.

The solubility of the less nitrated celluloses in ether-alcohol mixtures is well known. The relative volumes of the two solvents may be varied within wide limits; [673] the membranes obtained by evaporating the solvent vary in their permeability toward colloidally dissolved substances, with the composition of the solvent. The solubility is increased if the ether-alcohol solvent contains water.[674] According to Berl and Klaye,[675] the solubility of the nitrocelluloses depends upon two factors; the chemical union of solvent and solute to form compounds of ether or acetate type, and a physical swelling resulting in colloidal solution. Among other solvents of nitrocellulose not yet mentioned are acetic acid, aldehydes, anilin, alcoholic camphor solution, ether, nitroglycerine, wood spirit, nitrobenzene, and amyl alcohol, acetate and formate.[676] Collodion nitrocellulose is also dissolved by mixtures of alcohol and benzene, and their homologs.[677]

The ether-alcohol solutions of nitrocellulose are dextro-rotatory. The quantitative results of various experimenters are, however, so at variance that it appears constant values cannot be obtained.[678]

It must be remembered that the solubility behavior of nitrocelluloses cannot be defined on the basis of a saturation equilibrium between solid solvent and solution.[679] Rather, the solution is a continuation of swelling and imbibition, the actual change from the latter processes to the former being governed by a variety of factors of which far too little is known.[680]

The viscosity of nitrocellulose solutions is a very characteristic property, which is lower the greater the dissolving power of the solvent mixture.[681] A nitrocellulose preparation is not, according to Duclaux and Wollman [682] a single entity where viscosity is concerned. By fractional precipitation of an acetone solution with water, fractions may be obtained which vary widely in viscosity. A similar fractionation may be brought about by ultrafiltration. The natural conclusion is that a single preparation contains micelles of various sizes.

Any pretreatment of the cellulose with caustic or acids, as used for instance in mercerization and bleaching, is of great effect upon the viscosity of the nitrocellulose produced.[683] Mercerization decreases the viscosity of the resultant nitrocellulose; [684] likewise nitrocellulose prepared from hydro- or oxycellulose has a low viscosity.[685] Since a similar attack may occur during the nitration, it is easy to see why factors such as temperature, time and degree of nitration, and water content of the nitrating solution, have a great influence on the viscosity of the product. A high temperature of the nitrating bath results in increased nitration, and lower viscosity; if the water content of the bath is increased, the degree of nitration is less, and the viscosity is also lowered. A mild treatment of the nitrocellulose itself, such as heating before dissolving,[686] or dissolving and precipitating before final solution, gives solutions of very low viscosity.[687] It may be concluded that these variations in viscosity are evidence of variations in particle size.[688] The viscosity of nitrocellulose solutions depends of course also upon solvent, concentration and temperature at which the determination is made.[689]

Viscosity values obtained by the use of different nitrocelluloses in various solvents do not follow Hatschek's equation, but can be expressed by the empirical formula

$$\eta = \eta_0(1 + ac)^k$$

In this formula η_0 is the viscosity of the solvent, a and k are constants. The variations in viscosity found in certain solvents may be explained on the basis of association compounds between solvent and solute. Nitrated cellulose has a higher viscosity in acetone than nitrated mercerized cellulose, although unnitrated native and mercerized cellulose give the same viscosity in cuprammonium solution.[690]

The viscosity of the solutions decreases on aging.[691] C. Priest[692] explained this on the assumption that a gradual breaking down of originally coarse suspended particles goes on in the solution. Solutions made for spinning show at first a loss and then an increase in viscosity.*

Attempts to determine the molecular weight of nitrocellulose have not given concordant results. C. F. Cross and E. J. Bevan[693] reported that nitrocellulose dissolved in acetic acid gave small and irregular freezing point depressions, not suitable for molecular weight determinations by the Raoult method. G. Bunke and R. Wolffenstein[694] measured the rise in boiling points in acetone solutions equivalent to molecular weights of 1147 to 1487. J. Duclaux and E. Wollman[695] calculated weights of 21,000 for the less viscous, and 70,000 for the more viscous fractions, from the osmotic pressure in acetone across a denitrated collodion membrane, while H. de Mosenthal[696] found no measurable osmotic action.

R. O. Herzog and D. Krüger[697] investigated the diffusion of nitrocellulose in acetone. The molecular weight found in this way for fiber which had not been subjected to any pretreatment agreed with the crystallite deduced from X-ray measurements.[698]

Diffusion coefficients obtained by the Scheffer[699] method were compared with the viscosities of the solutions by N. Yamaga.[700] In general, the diffusion coefficients were higher for nitrocelluloses of low viscosity than for those of high viscosity.

Nitrocellulose may be denitrated by proper reagents. Aqueous alkalis, alkaline earths, ammonia and bicarbonates are not suitable, since the cellulose is decomposed. Sodium methylate solution,[701] acids,[702] and reducing hydrolytic agents are more suitable.[703] Aqueous solutions of the alkaline sulfhydrates, and ammonium hydroxide, are of especial importance.[704] The regenerated cellulosic material can be used to make products similar to hydro- and oxycellulose,[705] and may be considered as chemically identical to cellulose, in a general way. The behavior under polarized light[706] and X-rays[707] also substantiates this view.

ACETYL CELLULOSE[708]

The acetic acid esters of cellulose have acquired great technical and theoretical interest.

Acetic acid or acetic anhydride cannot be directly used for making these derivatives,[709] but acetylation goes on very well in mixtures of acetic anhydride and other substances. Many chemicals have been recommended for this purpose; sulfuric,[710] hydrochloric, nitric,[711] chloroacetic[712] and phosphoric acids,[713]

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* **This probably indicates a zone of maximum colloidality (*see* Vol. I). J. A.**

acetic acid and phosphoric anhydride,[714] phenol or naphtholsulfonic acid,[715] organic sulfonic acids,[716] benzenesulfinic acid,[717] sulfoacetic acid,[718] acid salts such as sodium bisulfate,[719] salts of strong acids and weak bases in general, such as iron, tin and copper sulfates, zinc, tin, antimony and calcium chlorides and ammonium salts.[720] Such salts form, according to H. Meerwein,[721] strong complex acids with acetic acid. Zinc chloride is especially used for scientific purposes.[722] W. L. Barnett [723] states that the acetylation goes very well when small amounts of sulfurous acid and chlorine are added to a mixture of cellulose, glacial acetic acid and acetic anhydride. Acetyl chloride has often been used,[724] with the following added substances: sodium, zinc or magnesium acetate (acetyl chloride diluted with nitrobenzene)[725] pyridine, quinoline (acetyl chloride diluted with nitrobenzene) [726] or without addition.[727] The use of acetyl chloride is also given in the processes of Ballston and Briggs,[728] Z. H. Skraup,[729] and Knoll & Co.[730]

The acetylation may be done in such a way that the fiber structure is not disturbed.[731] This requires the use of a medium in which the acetylcellulose is insoluble, such as benzene or carbon tetrachloride; [732] the acetyl cellulose can also be prepared as a gelatinous flocculate or a pulverulent mass.[733] K. Hess and G. Schultze [734] found that if acetylation was done without destroying the fiber structure, ramie fibers could be split up into small elements.

Acetyl celluloses of lower degree of acetylation can be made either by incomplete esterification or by partial hydrolysis of the triacetate. Cross and Bevan [735] obtained a monoacetate by boiling bleached cotton cellulose with acetic anhydride in the presence of sodium acetate. Acetylation in the presence of much sulfuric acid gives mixed esters; removal of the sulfonic acid groups by saponification gives lower acetates.[736]

A partial hydrolysis of the triacetate in the acetylation mixture itself was accomplished by Miles,[737] by adding dilute sulfuric acid and warming to 50° C. (Other deacetylating methods are, heating the triacetate with aqueous acetic acid in the presence of acid sulfates [738] with phenol containing water,[739] and in the presence of sodium acetate with aniline [740] or 95 per cent acetic acid.) Cellulose hydrolysis products which are formed at the same time [741] may be removed by solution in a 1: 1 mixture of benzene-alcohol.[742]

The less acetylated celluloses are not chemical individuals. This follows from the variable acetyl content (51 to 57.6 per cent acetic acid) and the variable optical rotation in 9: 1 chloroform-alcohol solution.[743]

The characteristics of acetyl cellulose are so dependent on the methods of preparation and isolation that chemical differences were expected,[744] but Hess was able to show on the basis of the polarimetric behavior of the acetate in organic solvents, the cryoscopic behavior in glacial acetic acid, and the polarimetric behavior of the hydrolysis products in cuprammonium solution, that in spite of physical dissimilarities there were no chemical differences.[745] The same was true of the acetates made from hydrocellulose [746] and oxycellulose.[747]

The hygroscopicity of the acetyl celluloses is low. Schwalbe [748] found a moisture content of 0.5 to 1.0 per cent, drying at 30 to 40° C. The acetyl celluloses do not swell in water, but the strength decreases to about 43 per cent of that of the dry fiber.[749] They swell but do not dissolve in cuprammonium solution.

The typical behavior of the acetylcelluloses in polarized light has been thoroughly studied by Herzog.[750] Zinc chloroiodide or iodine-potassium iodide and sulfuric acid impart only a yellow-brown coloration to the fibers.

After drying, the acetates do not dye well. By treating with swelling agents such as alcohols, phenols, glacial acetic acid, aniline or the like, or by dyeing while still moist, the fibers may be made to work well with the ordinary classes of dyes.

Although acetyl celluloses do not swell in water or alcohol alone, they do swell in mixtures of the two. After once swelling, the fibers do not again shrink when thoroughly washed with water.[751] When the swollen acetate is brought in contact with various liquids, solution occurs, without adsorption at the surface.[752] In general, the greater the capillary activity of the alcohol used, the greater the swelling in the alcohol-water mixture. Because of the shrinking action of the alcohol, every binary mixture has an optimum composition for swelling.

When acetyl cellulose is brought into a swelling mixture of nitrobenzene and alcohol, a change in concentration occurs. In the range of composition from 12 to 60 per cent nitrobenzene the alcohol is partitioned in a constant ratio between nitrobenzene and acetate. When the acetate is properly dispersed, the alcoholate is readily formed, and consequently if the alcohol concentration is sufficiently low in the swelling mixture, it is entirely removed.[753] The acetate shrinks but slowly upon dehydration. When dried in the air, the first part of the swelling agent is given up rapidly, after which the drying process becomes slower.[754]

Acetone has been recommended as a solvent for separating the lower and higher acetates;[755] the former are soluble in it. Nitrobenzene, ethyl esters, epichlorhydrin and other chlorhydrins, are also soluble in carbon tetrachloride and in a 4 to 1 pyridine-acetone mixture.[756] It is an interesting fact that cellite is soluble in mixtures of solvents neither of the components of which can alone dissolve it, for example chloroform and alcohol.[757]

By permitting the acetylation mixture to act for a sufficiently long time, alcohol-soluble products are formed,[758] and by considerably increasing the sulfuric acid content of the mixture colloidally water-soluble acetyl sulfates result.[759] The latter compounds are acidic; their calcium, magnesium, and zinc salts can be formed. Acetyl celluloses also are soluble in solutions of some salts. In this case molecular cleavage, but not hydrolysis, takes place.[760]

W. von Neuenstein[761] found that the solubility of cellites in ethyl acetate depends on the quantity of the solid present. Repeated precipitation from acetone results in a decreased solubility.[762] The same is true for glacial acetic acid.[763] On the other hand, the solubility in acetone is increased by heating in neutral organic liquids.[764]

Cellulose acetate solutions are levo-rotatory.[765] They have continuous absorption spectra, which become shorter in the ultra-violet with increasing concentration.[766]

All acetyl celluloses have a high gel-forming power. They gelatinize spontaneously from certain solutions.[767] Examples of this are the acetylating mixture of acetic anhydride, glacial acetic acid and sulfuric acid, and the acetone solutions of the lower acetates. Knoevenagel designates this phenomenon as condensation gelatinization.

By cooling down the cyclohexanol sol to —10° C., for example, or the benzyl alcohol sol to 15° C., the cellulose acetate is precipitated, or if the concentration is sufficiently high gelatinization occurs. The relation between gelatinization temperature and sol concentration[768] is analogous to the solubility curve of a crystallite.

The properties of cellulose acetate in solution depend primarily upon the nature and previous history of the cellulose. Acetates made from wood cellulose have a lower viscosity than those made from cotton, in general. The viscosity is lower, the more drastic the preliminary treatments to which the pulp has been subjected. The size of the particles in the acetylcellulose solution appears to be the same as that of the cellulose micelles. The viscosities of the acetate solutions are parallel to those of the cellulose from which they were made, in cuprammonium solution.[769]

E. Knoevenagel [770] found that in mixed solvents, the mixtures occasioning the least swelling of the acetate gave solutions of the lowest viscosity.

There is no simple relation between viscosity and concentration, in solutions of cellulose acetate in different solvents. The temperature coefficient of viscosity increases rapidly with decreasing temperature and with increasing concentration. In general, the specific natures of the colloid and of the solvent medium have a great effect upon the viscosity.

The ratio of the viscosities of any two acetylcellulose solutions of equal concentration is constant, in various binary mixtures of nitrobenzene and alcohol, whatever the acetate concentration. The viscosity is approximately proportional to the logarithm of the concentration. It is not parallel with the gelatinization tendency of the solution.[771]

The course of the viscosity-concentration curve in alcohol solution gives a measure of the suitability of the acetate for the manufacture of plastic masses. Camphor and triacetin increase the viscosity, while dichlorhydrin and *p*-toluolsulfamide have no plain influence.[772]

From such facts we must conclude that the cellulose acetate is dispersed in micellar form. At sufficiently low (0.1 to 0.6 per cent) concentrations, however, cryoscopic measurements in glacial acetic acid indicate the presence of an acetylated glycosan ($C_6H_{10}O_5$).[773] This molecular-disperse state is reached a few hours after solution, and reverts in a few days to such an extent that the freezing point depression is practically zero. When the acetate has been given pretreatment with glacial acetic, the viscosities of its acetone solutions tend toward a limiting minimum value.[774]

When a very carefully prepared tri-acetyl cellulose is dissolved in carbon tetrachloride, and the solution slowly concentrated, while protected from light and air, definite crystals are obtained,[775] which have the property of swelling. In agreement with this observation, acetyl cellulose made without destroying the fiber structure gives a crystalline X-ray diffraction pattern.[776]

ESTERS WITH OTHER ACIDS.

Cellulose esters of other acids have been less thoroughly studied. By treating cellulose in the presence of sulfuric acid,[777] gaseous hydrochloric acid, or zinc chloride,[778] benzene,[779] chloroform or pyridine, with formic acid, formyl celluloses are produced. By starting with hydro- or hydrate-cellulose, the use of a catalyzer is unnecessary.[780] The esterification is not complete; [781] only 18 to 20 per cent [782] or 23.1 per cent of formic acid combines per glucose unit, while the mono-formate requires 24.4 per cent. A triformyl-cellulose has been obtained by E. Elöst.[783]

The formates are soluble in formic acid, pyridine in such aqueous acids as acetic, lactic, sulfuric and hydrochloric, in aqueous solutions of salts such as zinc chloride and alkaline earth sulfocyanates,[784] and in alkalis.

Propionic and butyric acids form esters of cellulose similarly to acetic acid.[785] Monochloracetic acid, sulfuric acid or zinc chloride [786] can be used as catalyzers. These esters are analogous to the acetates; they are soluble in methyl ethyl ketone, ethyl acetate, benzene and xylene.

Esterification with lauric, palmitic and stearic acids goes on at water-batch temperature, when an excess of the acid chloride is used in benzene solution and in the presence of pyridine.[787] The fiber structure is not destroyed in this case, but the fibers appear somewhat swollen.[788] Lauric and stearic acids give di-esters by this method.

H. Gault and P. Ehrman [789] obtained di-esters by the action of acid chlorides on hydrocellulose at 110 to 125° C. G. Kita and co-workers [790] used acid chlorides and alkali.

When cellulose precipitated from copper solution is finely dispersed in quinoline and treated with acid chlorides at the boiling temperature, tri-esters are formed.[791]

The fatty-acid esters prepared by Grün and Wittka swell in solvents containing chlorine. Their solubility in glycerides increases with increase in size of the fatty acid radicle, so that hot triolein dissolves considerable amounts. On cooling, the solutions set to clear, colorless jellies. The preparations of Gault and Ehrman are soluble in benzene, chloroform, carbon tetrachloride and pyridine, and those of Karrer in chloroform, ether, benzene, ligroin, acetone and carbon tetrachloride. The solutions are levo-rotatory.

Benzoic acid esters are more difficult to prepare. They may be made by the action of benzoyl chloride on cellulose in the presence of alkali.[792] The amount of benzoic acid taken up depends on the alkali concentration. The preparation of homogenous monobenzocellulose has not so far been accomplished.

Tribenzoylcellulose was obtained by H. Ost and F. Klein [793] using benzoyl chloride and pyridine at 110° to 130° C. This ester is soluble in chloroform and nitrobenzene. The chloroform solution has a specific rotation $(d)_D$ of $+26°$ to $27°$.

Carbonic acid esters are formed by the action of chloroformyl methyl ester on alkali-soluble hydrocellulose.[794] They are white, amorphous pulverulent, soluble in pyridine, glacial acetic acid, and chloroform, and insoluble in ether, alcohol, acetone and benzene.

Sulfuric acid esters may be made by grinding cellulose fibers with cold concentrated acid.[795] The esters are separated after dilution as barium salts or by precipitation with alcohol. They are dextro-rotatory in solution, indicating a hydrolytic splitting during esterification. The composition approaches the formula $C_6H_{10}O_5(SO_3H)_2$.

Different authors have reported cellulose esters with oxalic,[796] phthalic [797] aromatic sulfonic,[798] and naphthenic [799] acids, but these have been little studied.

The action of *p*-toluol sulfochloride on mercerized cellulose forms a partially esterified fiber which is practically immune to coloring with substantive dyestuffs.[800] It reacts to some extent with ammonia, giving substances with a small nitrogen content.[801]

Mixed esters of nitric and sulfuric, acetic and sulfuric, acetic and hydrochloric acid are known, and play an important rôle in the production of nitro- and acetylcelluloses.[802]

E. Berl and W. Smith, Jr.,[803] have made nitric and acetic acid esters which are readily soluble in ethyl acetate and acetone, insoluble in chloroform and ether-alcohol. The solution in ethyl acetate gives a very tough, transparent film.

A benzoyl-acetyl ester of cellulose was made by Cross and Bevan.[804]

CELLULOSE ETHERS.

Since cellulose is a polyvalent alcohol, it is able to form ethers. O. Leuchs [805] obtained such by the action of alkyl halides on alkali cellulose, while

L. Lilienfeld[806] describes various alkylating agents and various ethers of all possible natural and alkali-soluble celluloses. Early workers were able to obtain only incompletely methylated products,[807] until K. Hess and W. Weltzien[808] succeeded in producing trimethyl cellulose[809] by the action of dimethylsulfate on alkali cellulose at 50° to 55° C. Similarly, it was at first found possible to introduce only 2 to 2½ ethyl groups per C_6 unit in making ethyl cellulose,[810] but by the use of diethyl sulfate and alkali the triethyl compound[811] was eventually produced.

The methyl ether of cellulose is soluble in cold water, but separates on heating. The reason for this negative temperature coefficient is probably that the solubility is connected with hydrate formation,[812] which is favored by lower temperatures. Besides being soluble in water, trimethyl cellulose dissolves readily in pyridine, chloroform, tetrachlorethane, benzene, glacial acetic acid and ethyl acetate, as well as mixtures of chloroform-alcohol, hot alcohols, hot methyl benzoate and acetate, and malonic acetate.

Triethylcellulose is insoluble in cold or warm water, but readily soluble in chloroform, benzene, toluene, xylene, glacial acetic acid, acetic anhydride, ethyl acetate, ethyl benzoate, dioxan, ligroin and petroleum ether.

Pure trimethyl cellulose is levo-rotatory. The specific rotation $(\alpha)_D^{20}$ is $-18.44°$ in water, $-4.3°$ in chloroform, $-5.08°$ in pyridine, $-18.5°$ in benzene and, $-9.8°$ in glacial acetic acid. Triethylcellulose is dextro-rotatory; $(\alpha)_D^{20}$ is $+26.1°$ in benzene, $+49.1°$ in pyridine, $+24.4°$ in chloroform, $+11.5°$ in glacial acetic.

In water, trimethylcellulose gives very variable freezing-point depressions, which permit no definite conclusions as to the lower limit of the molecular weight.[813] In 0.1 to 0.6 per cent solution in glacial acetic acid, however, it is monomolecular, dissolving as trimethyl glucose. With aging of the solution the freezing point depression decreases. The state in which methylcelluloses dissolve in water varies to a large extent, depending on the previous history of the material.[814] Thus the freezing-point depression shows methylated cuprammonium silk to be only half as great, methylated hydrocellulose only one tenth as great in micelle size, as the methylated native fiber. E. Heuser believes that this shows the extent of depolymerization of the cellulose, which view is, however, opposed by K. Hess.[815]

Triethyl cellulose shows a dissociation and association behavior in glacial acetic acid similar to that of trimethyl cellulose.[816] Trimethyl cellulose purified by repeated precipitation from benzene with petroleum ether can be obtained as birefringent crystals from a 1 : 1 mixture of chloroform and alcohol. If crystallization is rapid, it forms spherolites, while slower separation leads to the production of tufts resembling ice flowers, or of discrete, microscopic needles.[817]

On cooling warm alcoholic solutions, trimethyl cellulose separates in loose flocs, while the hot solutions in ethyl benzoate or amyl acetate set to thick jellies which have good film-forming power. Ethyl cellulose behaves in an analogous manner.

The cellulose ethers cannot be dealkylated without breaking down extensively. Hydrolysis of trimethyl cellulose gives 2-4-6-trimethyl glucose,[818] while triethyl cellulose gives 2-3-6-triethyl glucose.[819]

B. Heferich and H. Koester[820] obtained a triphenylmethyl ester by treating cellulose regenerated from xanthate solution with triphenylchloromethane in pyridine at 200° C. This ester contained one triphenylmethyl group per hexose unit, and was soluble in pyridine and chloroform, giving viscous solutions of carbon disulfide. Tetrachlorethane, benzoic acid ethyl ester and acetic anhydride cause it to swell. Alkali-cellulose reacts with monochloracetic acid with the formation of glycol acid ethers of cellulose,[821] and with chloracetylchloride.[822]

THE DEGRADATION OF CELLULOSE, AND THE COLLOIDAL DEGRADATION PRODUCTS.

It has been repeatedly emphasized that degradation of the cellulose molecular complex may result from a hydrolytic process with the liberation of oxygen compounds, or from a loosening of the crystallization forces or residual valences. Depending on the external conditions, either one or the other of these processes may predominate, so that obviously very numerous derivates may be obtained. Any very small molecular products of the disintegration may be retained in the micellar complex, so that mixed micelles ("Mischmicelle") are formed, differing more or less in properties from the native cellulose. This picture has been kept steadily in view in the discussion of the forms of cellulose (hydrate- hydro- and oxycellulose) already introduced.

It has already been said that sulfuric acid in certain concentrations swells or dissolves cellulose. A few important forms of cellulose are produced by this reaction.

Sulfuric acid of 62 to 71 per cent concentration affects cellulose much as does caustic soda, a fact already observed by Mercer. Similar observations were made by Paumarede and Figurier,[823] Blandal,[824] and Girard.[825] The first two authors named the gelatinous modification obtained from filter paper, "papyrine." The names of "vegetable parchment" and amyloid agree essentially with this.

These forms of cellulose give a typical blue color with iodine in the presence of acids, which slowly disappears on washing with water. Parchmentization can also be recognized readily by means of zinc chloro-iodide or iodine-potassium iodide reagents.[826]

Guignet obtained a form of cellulose by the action of 62.5 per cent sulfuric acid, which is soluble in water and has a slight levo-rotation. The dissolved substance can be precipitated by foreign substances such as sulfuric or hydrochloric acid, salt, sodium, sulfate, lead acetate, and so on, as well as by alcohol.[827] A short treatment with 70 to 78 per cent sulfuric acid renders this "colloidal cellulose" insoluble in water. Iodine does not color this form of cellulose.

We are indebted to C. G. Schwalbe and Schultz [828] for a detailed study of the reducing power and hydrolyzability of amyloid and Guignet cellulose. Samec and Matula [829] studied the colloid-chemical changes of a cellulose solution obtained by the action of sulfuric acid.

During the process of peptization by acid of suitable concentration, the cellulose is transformed to an emulsoid, probably with solvation, without great change in the polysaccharide itself. In consequence of this change of state, the internal friction of the solution increases at first. After a time, the viscosity passes through a maximum, and thereafter decreases, indicating that micellar disintegration has become predominant. During this process the iodine coloration passes from blue, through violet, to brown, and the solubility of the product in water steadily increases. Ester formation accompanies the micelle rupture; the esters formed are at first gelatinized by alcohol, then thrown out as a flocculent precipitate, and eventually become alcohol-soluble with increasing decomposition.

Micelle disintegration prevails at high acid concentration; 65 per cent sulfuric acid forms a gelatinized cellulose which is so highly solvated that a 0.4 per cent solution is entirely stiff.

As a result of the smaller micelle disintegration, cellulose-phosphoric acid gels are much stronger than the sulfuric acid jellies.

The cellulose dextrin and its esters formed in this way were studied very early. They were frequently, though probably wrongly, considered to be adsorption complexes.

The results of Blondeau des Carolles [830] regarding the constancy of the ratio of barium to sulfuric acid in these cellulose derivatives were confirmed by Hönig and Schubert.[831] All their results point to the presence of acid esters of fairly constant composition, but with an optical rotation changing with increased acid treatment from weak laevo to strong dextro. The free dextrin ester acids are amorphous, hygroscopic solids. These results were also confirmed in principle by Stern.[832]

Samec and Matula [833] made colloid-chemical studies on a few of these dextrin esters. They found, for example, that a substance obtained by allowing 55 to 60 per cent sulfuric acid to act on sulfite pulp for three-quarters of an hour gave a white, stable suspension in water, which at 1.3 per cent concentration had a conductivity of 9×10^{-5}mho, and a pH value of 4.2. The substance behaved like a sulfuric acid ester; the saponification could be followed. In the suspension colloidally dissolved and suspended material were in equilibrium; the mean micelle size of the dissolved part was, by osmotic pressure measurements, 6,800. The suspension was acid, and could be titrated using phenolphthalein as indicator, one mol of NaOH combining with 6,700 grams of the substance, agreeing almost exactly with the osmotic pressure results for micelle weight. Apparently the particles correspond to the molecular formulas $(C_6H_{10}O_5)_{40}.H_2SO_4$. However, the maximum caustic-combining power determined electrometrically by these authors was 2NaOH per glucose residue.

The increasing micelle disintegration under long-continued acid treatment can be followed by means of the osmotic pressure. The stoichiometric composition of the product can be obtained by a combination of electrometric titration and sulfur determination. It is worthy of comment that some cellulose dextrins are attacked by diastase, with the production of more highly reducing substances.[834]

By the combined action of sulfuric acid and formaldehyde, products of lower micelle weight are obtained, which resist further attack by sulfuric acid. Formaldehyde acts to decrease the solvation of the cellulose, the viscosity of the sulfuric acid solutions being much less in its presence than when it is not used. Sulfuric acid solutions of cellulose are not colored with iodine when treated with formalin, but show the iodine color once more when the formaldehyde is washed out. The behavior of cellulose toward the formaldehyde-sulfuric acid mixture is best explained on the assumption that the aldehyde adds to the cellulose with the formation of oxymethylene groups.[835]

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Colloid Chemistry of Wood and Wood-Formation.*

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Wood exists in every plant and, from a physiological point of view, in almost every part of the plant. In the typical woody plants (trees) this complex material, in its technically useful condition, is stored chiefly in the stem. The stem takes part in the metabolism of the plant essentially only during the summer vegetative period, when the "annular rings" still contain living cells and permeable channels of the characteristic fibro-vascular system. This woody part is the sap-wood, in which the wood-forming juices are still found in a *reduced* or *reducible* condition. This sap-wood constitutes the so-called soft wood of numerous deciduous foliage trees (maple, birch, beech, hornbeam). In other shade trees (oak, ash, elm) and in most conifers (larch, pine, spruce, fir), the inmost and oldest sap-wood dies either the second year or between the second and tenth years. The fundamental parenchyma and prosenchyma or essels of this portion of the stem are no longer used and become dry. By deposits of colloidal secretions the channels (old ducts and sieve tubes) become narrowed and finally occluded.

Only by diffusion and through drying cracks (microscopic apertures) can juices subsequently force their way through the no longer living woody layer. Air, however, penetrates and its oxygen oxidizes the reduced organic sap and lignin components. In other words, there are leucobases of the plant pigments and tannins which by auto-oxidation produce colored oxidation and condensation products, (such as phlobaphene, anthocyanin, etc.). These substances are stored in the innermost region of the non-living wood, for they are substances of high molecular complexity or are colloids of difficultly soluble nature. Thus it happens that the heart wood, which, in certain species is sometimes highly colored by such oxidation and condensation products of polyoxybenzol derivatives, is stained, preserved and becomes technically of greater value.

On the basis of investigations of the author and his co-workers in the Plant Physiology Institute, High School of Forestry at Tharandt it is evident that the so-called pure soft woods (beech, hornbeam, birch) may, in their advanced age, exhibit a certain *early stage of heart-wood formation*. And, indeed, it is very easy to demonstrate this, if following Kräss,[1] one of the author's co-workers, we quickly char with a blast-lamp flame a fresh cross section of wood; the water-poor, partial heart-wood stage shows up characteristically by being the first area to carbonize. A similar condition of periodic formation of heart-wood substance appears every year at the end of the active vegetation period. The so-called *late wood* or summer wood appears thicker and is light brown in color. It stands out in sharp contrast to the lighter colored early spring wood of the annular rings. That the same oxidation and condensation products as in true heart wood are the cause of this demarcation, is shown by the fact that this dark colored late-wood ring completely disap-

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pears on warming the wood with ammonium bisulfite or sodium hyposulfite solution.

Of what does wood consist, and how does it originate in the plant? Up to the present time only cellulose and "lignin" are classed as organic chemical constituents, and without completely understanding their chemical constitution. The chemical investigation of cellulose has not yet reached an unequivocal opinion, but even much less conclusive is the investigation of "lignin." Little is known of wood-building processes, from the point of view of either pure chemistry or plant physiology. Books of authority on plant physiology admit without question that previous methods of investigation in plant physiology are completely lacking in this respect. (Pfeffer, Jost[2] and others.)

Botany and plant chemistry in their understanding of wood-formation and the chemistry of wood have not advanced substantially any further than the degree of knowledge attained by the work of the plant chemists, *Payen, Schulze, Mohl* and others about the year 1840.

Our knowledge in regard to wood advances only with the slowly progressing chemical investigation of cellulose, and physiological researches concerning the hardening or "lignification" of cellulose with "lignin." Until most recently research workers in this field believed that lignin could be regarded as an essentially homogeneous or uniform substance, and that they could eventually discover a constitutional formula for it. (Klason, Euler, Karrer, Hägglund, Pringsheim, Fuchs, Jonas, Rassow and others.) Such efforts of organic chemists have always been fruitless. On the other hand the fiber or cellulose framework of all plants and parts of plants consists almost exclusively of a definite dextroso-cellulose ($C_6H_{10}O_5$). It is, as far as we know, a simple double anhydride of dextrose. Its exact constitution, especially the size of the molecule, is not even now completely worked out, in spite of the tremendous importance of this substance.* The homogeneous character of cellulose is in accordance with a stoichiometric combination of the elements ($C = 44, 41$, $H = 6, 17$, $O = 49, 39$). On the other hand "lignin," is inhomogeneous, and shows, according to its source from different woods, and according to the method of extraction, a very variable combination of the elements, from over 52 to over 65 per cent of carbon, etc. The elementary organic analysis of *"wood"* shows correspondingly variable values. But we find in *different* species of wood, not typical differences, but rather variations which are not greater than the fluctuations or variants within the parts of a single tree; e.g. the variations between the wood of the stem and the wood of the branches. It is true, however, that the *average* composition, $C = 50$ per cent, $H = 6$ per cent, $O + N = 43.7$ per cent, is typical of what we commonly call "wood." Yet the different species of wood are differentiated materially only by their lignins, and not by their cellulose.

Wood can no longer be considered as a *chemical* compound (of ester-like or of glucoside nature), *a compound of cellulose* and lignin, as Cross and Bevan maintain even today following the precedent of Erdmann and Baltzer, (1873), even if a single ingredient of the complex mixture "lignin" should perhaps have gradually undergone a condensation with cellulose. The *primary* fundamental cell-membrane or fiber is cellulose; then follows its hardening or conversion into wood by "lignin." The concept "lignin" is essentially a collective term, of botanical-physiological character. It is the "wood-forming substance," that is, the sum of all the different substances which have con-

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* Much evidence has recently come from X-ray analysis. See, e.g., Sponsler and Dore, Fourth Colloid Symposium Monograph, New York, Chemical Catalog Co., Inc., 1926, p. 174 *et seq.*; G. L. Clark, *ibid.*, p. 145 *et seq.*, also Clark's recent book, "Applied X-rays," New York, McGraw-Hill Book Co., 1927. *See also* papers by M. Samec and G. L. Clark in Vol. III. J. A.

verted the cellulose cell-membranes or fibers into wood, or using the word introduced by Payen in 1838, which have "incrusted" these cellulose tissues. From the point of view of pure chemistry it is only the constituents of lignin which we can express by structural formulas as individual substances. These "incrusting substances" can be more or less easily differentiated from cellulose. Even the most radical analytical procedures leave residual traces of pentosan and hemicelluloses intimately "combined" with the cellulose. Whether these are chemically bound to the cellulose is not yet determined.[3] It is possible that they may have been gradually converted into glucosides in the growing wood; but more probably by the chemical elaboration of the wood from the cellulose, according to predominating mass action or chemical equilibrium relations, they are transformed either into esters or ethers. A simple adsorptive union of the pentosans and hexosans can equally well result in an (apparently) closer union of an entirely different sort, in which the *complex pentosans and hexosans, because of their state of dispersion and their solubility, more and more "resemble" those of cellulose,* and in this state exhibit a similar resistance to solution.

These pentosans (especially xylan) hexosans and gum-like substances form typical colloidal solutions with strong surface-activity, so long, of course, as they are still soluble. In the typical wood-gums the pentosans (according to the researches of O'Sullivan) are unquestionably bound as glucosides to gummic acids of high molecular weight. They frequently appear as horny gum-like masses, capable of swelling in water, as for example gum-tragacanth. This represents to a certain extent a "pentoso-cellulose," and in its insolubility, swelling-capacity, etc., resembles colloid-chemically the vegetable "reserve-cellulose," mannoso-cellulose. The pentosans and hexosans, together with their pectic acid derivatives, belong to the above-mentioned class of wood-forming or incrusting substances, that is, lignin. According to accepted analytical methods for the determination of cellulose and lignin, these pentosans and hexosans are separated from a lignin residue, which is then designated and estimated as "lignin." If during analysis it is decided to treat these "soluble carbohydrates" as a separate group, this group will nevertheless still belong to the main group of "lignins." Moreover in the extraction of lignin by highly concentrated mineral acid (e.g. HCl, according to Willstätter and others, or concentrated H_2SO_4), they are obviously destroyed together with the cellulose, and this procedure gives not the substance characterized physiologically as "lignin," but rather lignin *components* (aromatic, or more likely, cyclic condensation products). These substances must unquestionably be estimated and identified as two chemically quite different lignin constituents —acyclolignin (carbohydrates) and cyclolignin, with the mental reservation, that they are still mixtures of lignin components.

Up to the present time it has been recognized that lignin comprises three groups of entirely heterogeneous organic substances:

(*a*) Colloid polysaccharides (pentosans, hexosans, hemicelluloses and wood-gums).

(*b*) Colloid calcium salts of pectinic acid and other plant acids of high molecular weights.

(*c*) Colloidal derivatives of polyoxybenzol and cymol, whose next more completely oxidized stages have, by condensation, built up materials of high molecular weight (for example tannins and phlobaphenes, pigments, derivatives of coniferyl alcohol and of anthraquinone, or anthocyanins. These are the same substances which are found in the wood-forming sap of the cambium, partly in lower oxidation and condensation stages, and partly also as the final building stones in wood-formation. *The origin of wood is entirely incomprehensible without taking into consideration colloid chemistry.* The plant body, like the animal body and every living organism, is preëminently a system of colloid materials and reactions. The principal life-functions are bound up with this special state of matter.

The complexity of the vital processes naturally involves the chemical reactions and the states (conditions) of the molecularly and ionically dispersed organic and inorganic accessory substances. Organic colloids and inorganic salts act together. This very wonderful—even in this day of marvels—synthesis of organic substances and of the complicated building-materials of the plant, takes place in the leaves, or in homologous organs, such as needles. This chemical apparatus of the plant obtains from below, from out of the root, in the *ascending* sap, ionically dispersed inorganic nutrient salts in dilute, highly dissociated solution; these serve as the requisite "accessory substances." From the air the leaves take organogenic carbon, in a gaseous state as CO_2, and build up organic matter. They do this with the aid of the radiant energy of sunlight from which the chlorophyll of the leaf absorbs or filters out those rays which lie toward the red end of the spectrum, which are the rays active in phytosynthesis and "assimilation."

Under the catalytic stimulation of molecular and ionically dispersed accessory substances, the chemical synthesis progresses through the stages of formic acid, of formaldehyde, and then through the aldol synthesis of sugar up to the final synthesis or formation of the colloidal building materials. These materials are still partly chemically active, and partly in a reduced condition.

On account of their colloidal state of dispersion these substances have practically lost their ability to undergo ordinary chemical reactions, but have for this very reason *acquired new reactive properties,* especially adapted to the life-functions of the plant, namely *typical surface-activities.* They have become "surface-active." But now, as the plant physiologist knows, they are withdrawn from the leaves, and distributed *via* the sieve tubes and cambium layer which lies between the cortex (bark) and the wood, to their storage depots (e.g. in the inner bark). Physiology designates these substances secreted by the leaf as "forming sap." It is the downward-moving sap transferred by the sieve tubes, in contrast to the raw materials transported upward from the roots through the ducts. This sap contains chiefly *sucrose* or its hydrolyzates, namely dextrose and levulose. From these substances there are built in the cambium association complexes of increasingly high molecular weight which are finally soluble only colloidally ("cambial sap"). In the sieve sap and the cambial sap the building materials for the woody-tissue make their way downward by slow movement to the stem and roots. Here, coincident with the vital process of cell division, by adsorption and by deposition, or "intussusception" of the molecular aggregates, they produce the thickened "secondary" growth.

We must therefore distinguish between the sap containing the nutrient salts, which rises at a comparatively rapid rate from the roots through the ducts, and the more slowly *descending* sap of the sieve tubes and cambium. This sap distributes the colloidal building materials through the vessels and open medullary rays, partly by diffusion, to the interior regions of the stem where the heart-wood is being formed. These substances (still in a reduced condition, e.g. as leuco-compounds) are in part capable of diffusion through thin membranes (e.g. through the pits of the pitted-tracheids of the conifers). During their migration further synthetic and aggregative changes occur and also simple associations of molecules into groups appear to take place. Such chemical and physical building-up processes are brought about by the synthesizing and coagulating influence of *multivalent* salt ions which diffuse through all the tissue with the ascending mineral-containing nutrient sap; or under the influence of the capillary electric charges in the tissues (Nathanson) they keep on moving or are precipitated.

The exterior thin cambium layer during the summer builds the youngest wood ring toward the center of the stem and the youngest layer of bark towards the outside, accompanied by peculiar oxidation transformations, under the influence of the oxygen which penetrates through the lenticels of the bark. Thus are formed in the layers of the bark high-molecular, wax-like substances, e.g. suberin, as esters of high-molecular, monovalent alcohols with high-molecular acids, besides tannic acids and their phlobaphenes. The nearer these building materials, still dissolved in the sap, attain typical colloid dimensions—that is, a particle size of 1μ to 0.1μ, or thereabouts—the more readily they undergo adsorption on an adsorbing surface, that is a solid material with a greatly extended surface, and more or less pronounced electrostatic charge; but the adsorption is often irreversible on account of the primary adsorption of ions. Furthermore, the chemical nature of the solid surface is a determining factor. Thus fibrous aluminum oxide[4] is an amphoteric substance, and cellulose a weakly acid (electronegative) adsorbent. In *adsorption* is to be sought the *first and determining step in wood-building or lignification.*

"Wood is primarily the result of a colloid adsorption synthesis."

The adsorbent in wood is the cellular matrix existing in a state of dispersion called by Nägeli "micellæ." This micellar structure, the original profoundly dispersed membrane- and fiber-cellulose, or "skeletal material" (E. Schmidt) secreted in an insoluble state out of the chemical reaction system, is in this special condition capable of little further *chemical* reaction. Instead of synthetic or analytic *chemical* reactions, there take place typical colloid chemical surface reactions. And these are relatively more effective in dilute solutions of the adsorbate.

The *adsorbate* consists predominantly of the components of lignin, colloidally dissolved substances of high molecular weight, which, as before stated, were built up in the cambial sap. "The 'lignin' or the wood-building, 'incrusting' substance is, in other words, the *sum-total of all the colloid building-constituents precipitated primarily by adsorption from the cambial sap hydrosol upon the surface particles of the cell and fiber membranes.*"

The adsorption is, no doubt, brought about partly by an equilibrium of electrical, surface charges and partly by simple mass attraction (gravitation). The effect of the residual valence resulting from the molecular lattice also plays a part.

According to the chemical law of mass action the thickening or solidification of the tissue facilitates the slow reactions of the particles of high molecular weight.[5] *Chemical after-effects* of adsorption may follow. Incidental or gradual chemical reactions may also take place between the cellulose and easily reacting mono-molecular sap constituents (glucosidic, acetal- and ester-formations).

Although the nature of adsorption is not yet entirely clarified, yet it may be measured quantitatively, whether the process is reversible or irreversible. The statements advanced above are the results of such measurements made by the author, by means of a carefully worked out method of *absorptio-metric colloid determination.*[6] The measurements were made to answer the following basic questions from the point of view of colloid biochemistry, that is, of physiology.

Does the wood-forming cambial sap contain more colloid-building materials than the ascending nutrient mineral sap, and how does the colloid content change during the course of the summer wood-building?

Since in the wood itself the sap which rises during the summer cannot by any practical method be separated from the sap which at the same time descends from the leaves and is distributed by diffusion into the wood, there was used for the analysis of wood-sap, only the rising sap of the transition period from winter to spring, till the unfolding of the leaf-buds, the "early spring sap" or so-called "bleeding sap." This flows out upon wounding certain barks and sap-woods. Besides the nutrient mineral salts and organic acids, it contains, for almost every kind of wood, a special monosaccharide or disaccharide sugar. (Maple: cane sugar, Birch: a honey-like mixture of dextrose and fructose, Hornbeam: much pentose, etc.).

The cambium sap, on the other hand, was obtained about every month by scraping the sap-containing cambium from the barked wood, and from the inner surface of the bark, the thick, viscid mass being transferred to a little water. The filtrate from this was diluted with water until (according to determinations) the content of organic material was about 0.5%, and this solution was quickly subjected to the absorptio-metric analysis. For adsorbents, in addition to purified cellulose, and fat-free cotton-wool, there was employed the fibrous aluminum oxide, mentioned above. This fibrous aluminum hydroxide adsorbs the colloids from cambial sap much more effectively than does cellulose, but in a rather different manner because of its amphoteric nature. However, it serves excellently for the estimation of adsorbable colloidal material.

If cellulose were to adsorb as powerfully as this, a diffusion of the colloids into the wood would hardly be possible, because then the cambium sap-ingredients would overload and clog the first cellulosic tissue with which they came in contact.

In accordance with the established laws of adsorption equilibrium, the woody tissue appears initially to take relatively little out of the *concentrated colloid saps,* so that the saps upon distribution dilute out gradually, and hence, in as diffused a state as possible, are distributed until adsorption is complete, and thus carry the zone of liquefication further and further into the stem.

The three subjoined graphs show the characteristically different amounts of colloid adsorbed by the two different types of sap on fibrous alumina.

The *spring saps* of different species of wood show typical differences, but for the most part, a low amount of adsorbable colloid material and high amount of crystalloid material (especially the varieties of maple). In white beech only is this ratio altered. The birch occupies a middle position with an almost equal amount of colloid and crystalloid matter. In general, however, the colloid content of the spring saps fluctuates very little from a constant *low* level.

Biochemically, the early spring sap may be regarded as a partial reversion of the adsorption synthesis of wood. The reversible, stored and hydrolyzed carbohydrates (reserve starch), in the form of a sugar solution (starch-free), are again mobilized and transported with the nutrient salts for the development of the assimilation organs of the buds.

The *cambial saps* of different species of woods show a much higher content of colloid wood-building constituents during the early summer months, from about the middle of May on. This depends entirely upon the summer vegetative season. It holds true for the central European climate, and applies to those trees where the sap-containing cambium layer is separable from the bark. At the beginning of August the content of soluble colloids drops suddenly, and by

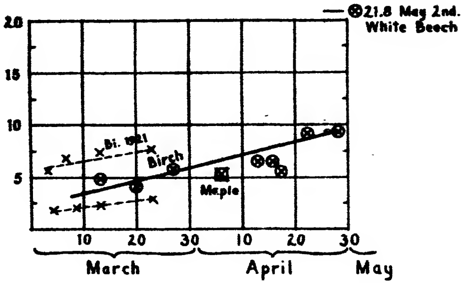

FIG. 1.—Spring sap, 1908.

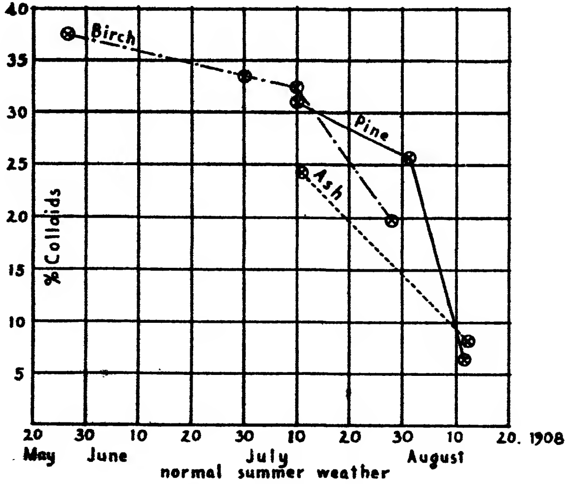

FIG. 2.—Colloids in cambial sap, 1908.

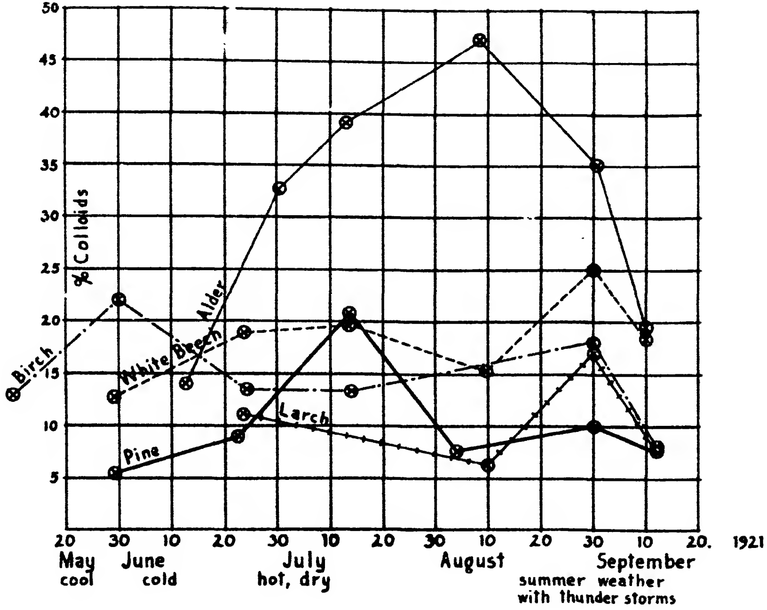

FIG. 3.—Colloids in cambial sap, 1921.

the middle of August the cambium adheres so firmly that one can no longer separate the bark from the wood. The life-activity of the tree ceases at the beginning of August, in central Europe, and awakens again from the dormant period in earliest spring, as the sap rises. This normal course of vegetative activity is shown in Figure 2, based on experiments made during the climatically normal summer of 1908. Even more convincing are the results from the abnormal summer of 1921 (Fig. 3). The vegetative development began with a cool May, after a cold spring, and was followed gradually by somewhat warmer, rainy weather. Then instead of the temperature continuing to rise to warm summer weather, because of a wet spell it fell till the middle of June to almost winter frigidity, and remained so several weeks. Only very gradually did it rise again until there was a definite increase the middle of July. Now instead of a damp, chilly summer season, a short hot spell followed, becoming in the middle of August, practically a drought, during which the life activity of the tree rose abruptly to a normal maximum, and quickly dropped again at the beginning of August to normal. Now there came a most interesting period. In the year 1921, at the beginning of August a warm and fresh vegetative summer period set in with summer-like thunder-showers; and this weather lasted about two and a half weeks, and changed over to nice dry autumn weather only about the last of September. All this is reflected in the graphs representing the colloid content of the cambial sap. In the cool early summer (May, June) the life-activity of the tree rose only gradually from a low rate of metabolism. At the beginning of August a second, but evidently normal, minimum can be recognized. In the cool late summer, during August, according to the curve of cambium colloid content, there occurred a second maximum of wood formation. The firm adhesion of the cambium layer to the bark with consequent loss of function, thus occurred at the end of September instead of at the beginning of August, as normally.

The unusual curve of the alder has a very typical course. During the hot, dry period this tree responded with especially vigorous wood-formation. This is because the usual habitat of the alder is along a water course and hence it suffers from no lack of moisture.

It follows, therefore, that there is a complete correlation between climatic influences upon life-activity, and the content of colloid-building materials in the cambial sap.

The experimental picture establishes the theory of wood-formation briefly outlined above, and serves to supplement dormant chemical and physiological investigations on the nature of wood. The material for this has already been presented in several articles and addresses in the journals,[7] and will be supplemented by further contributions.

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[1] Diploma thesis, Tharandt 1922, and Wislicenus, Cellulose Chemistry, 1929, X, 206.

[2] L. Jost, Lectures on Plant Physiology, Vol. 3, 350.

[3] Recently Erich Schmidt of Munich believes that he has established the presence in the framework-cellulose, or skeletal substance, of a chemical esterfication of pure cellulose with glycuronic acid, which undergoes further esterfication with pentoses and hexoses, or with pentosans and hexosans (hemicelluloses).

[4] This series, Vol. 1, p. 628.

[5] "Concerning the extension of the laws of mass reaction to colloid reactions," by Rudolph Lorenz, Wochenblatt f. Papierefabrikation, 1925 (Habilitationsschrift Tharandt).

[6] Kolloid-zeitschrift, **2**, 8 (1907); "Collegium" No. 255/6 (1907).

[7] *Tharandter Forstl. Jahrb.*, **60** (Leipziger Jubiläumsband), 333-358 (1909); *Kolloid-Z.*, **6**, 87-94 (1910); **27**, 209-232 (1920); *Papier-Ztg.*, **29**, Febr. (1910); *Cellulosechemie*, **6**, 45-58 (1925).

Colloid Chemistry in the Paper Industry.

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A widely used textbook of paper technology opens with the sentence: "Papermaking is essentially a mechanical process." Although it is true that all kinds of paper-making machines are built on the principle of a mechanical contrivance for the dewatering of paper pulp, the water dropping down through a wire screen known as the Fourdrinier, on which the fibers form a mat of paper, as against this merely mechanical explanation, I believe I am right in asserting that paper-making is essentially a capillary-physical and colloid-chemical process.

CAPILLARITY AND SWELLING IN PAPER MANUFACTURE

The mechanical processes of suspending and screening the ground fibers are not the prime essential to the formation of a moist web of paper; otherwise it would be possible to produce a mat like paper out of mineral suspensions on paper machines equipped with very fine-meshed wires.

The mechanical power driving the paper machine does not produce paper; this power does nothing but pass the web of paper over the different parts of the machine and over and under the drying cylinders.

On the contrary the web or matted sheet of paper is built by the *surface forces of vegetable fibers.* The best paper machine would be useless if the fibers did not adhere together in a sheet capable of being pressed by rollers and carried on felts.

On the so-called *Cylinder Mold Machine* cellulose is dewatered, paper board being manufactured from repulped waste paper or largely from groundwood. Advantage is taken of the variations in capillary adhesion as a means of conveyance; that is, for the automatic carrying of the moist mat from the wire-covered drum to the felt belt and from there to a polished metal cylinder at the dry end of the machine.

This transfer, or act of "couching" as it is termed by papermakers, must be regarded as a capillary-physical action. There is no molecular attraction, the couching effect depending chiefly upon the condition of the surfaces pressed together and on the water content of the fiber mat as induced by the swelling of the fibers.

Wolfgang Ostwald states in his *Treatise on Dispersoidological Chemistry of Peat:*[1] . . . "just as water in *immovable* capillary spaces is drawn up the higher, the narrower these spaces are, so, on the other hand, *movable* capillary walls are pressed against each other the more vigorously, the smaller the water space is between them. . . ." It is possible from this to deduce hypothetically that with a distinctly small proportion of water on the surface of the web a maximum of adhesion is attained while couching. If the moist network of fibers is dewatered to a still greater degree, so that between the couching surface and the surface of the paper texture no capillary space of water is to be found at all, then the adhesion must again diminish. The small air-bubbles that are present between the rough surface of the moist web of paper and the couching surface are very important in this transferring process, for the power of capillarity has its effect on the interface between the fluid and the vapor sphere.

It is necessary that the couching surface be smoother than the surface from which couching is to be done; for the smoother this surface is, the smaller is the volume of the capillaries filled with water and air, which means that they have more activity. By the pressing of the couching surface upon the rough surface of the moist paper web, almost always a hollow will meet a hollow and only very seldom will the high spot and hollow come into apposition. The roughest part is the wire cylinder with its relatively large openings; the felt being in a finer capillary condition, pulls the web of paper away from the cylinder, but subsequently transfers it to the smooth-polished drying roll.

Let us try to estimate the extent of the capillary forces effective in couching. In a treatise published in the *Kolloid-Zeitschrift* under the title "Capillary Phenomena"[2] K. Schultze defines a rough surface, like a moist web of paper, as a "system of *open* capillaries." By pressing the couch roll on it *closed* capillaries will result. Schultze has made measurements on open and closed capillaries made of glass and of equal width, the height of suction being the measure of the activity of capillarity in *unmovable* capillary spaces. Corresponding to this height of suction, between *movable* capillary walls there acts the pressure by which these walls are drawn together; that is, by means of capillary action. The data, according to Schultze, show an increase of the capillary activity from 100 to 150 per cent upon closure of open capillaries about 0.5 to 1 mm. in diameter with an opening from one-fifth to one-sixth of their circumference. The open capillaries determining the roughness of the surface of the paper texture will, in most cases, have wider openings than one-fifth to one-sixth of their circumference; by pressing them to the couching surface their capillarity will increase easily up to several hundred per cent. What considerable forces are brought into play are shown by some experiments which I undertook. I pressed moistened strips of filter paper to a piece of paper machine felt which I stretched vertically; I then loaded the paper strips with weights. Strips having a contact surface of 15 square centimeters would bear a load of 100 grams; that is 7.5 grams per square centimeter. Smaller surfaces of contact showed still higher relative values, e.g. a single square centimeter bore a load in excess of 10 grams for a period of several minutes.

In addition to the cylinder board machine, capillary physical phenomena are also found on the Fourdrinier machine which is so generally used in papermaking operations, especially on the endless wire which corresponds to the wire-covered drum of the cylinder mold machine. In this machine the water which is held only by *occlusion* and *capillarity* drops down, while the swollen layer of fibers is being formed into the web.

Wolfgang Ostwald states the following concerning peat pulp: "In a movable capillary system, a closer packing of the solid parts will appear automatically and permanently during drying. . . . Movable particles surrounded by capillary water spaces of unequal thickness, will move until they attain the most uniform and the closest position." A. Hausding is of the same opinion. In his *Handbook of Producing and Using Peat*[3] he speaks of a "strange *natural* desire of pappy, tenuously subdivided cellular and fibrous stuffs to arrange their tiny particles close together while the water is evaporating, and of reducing their volume; that is, of shrinking or shriveling together, at a rate equal to that at which the water evaporates."

With paper a similar process takes place on the carrying felts and on the heated drying cylinders where the sheet is finished by further reinforcing of the shrinking fibers. The hot dryers induce a heat coagulation of the gel-like cellulose, which is only slowly reversible; they thus free and evaporate the colloidally combined water, which cannot be expelled either by pressure of the dandy roll on the Fourdrinier, of suction by the vacuum boxes below the wires, or by means of the capillary action of suction of the felts carrying the web of paper. Overdrying is to be avoided; indeed, the paper is sprinkled before it is reeled at the end of the machine. An overdried mat of fibers could not be evened out by the succeeding calendering to obtain a well-glazed sheet; the papermaker says that "well damped is half way glazed."

Care must be taken of the shrinkage which ensues when a strip is spread out. This, according to experiments reported by P. Klemm, may account for a decrease in length up to 30 per cent. It can be overcome to a certain extent by regulating the speed of the single cylinders of the paper machine. By failing to do this it may happen that the sheet of paper will snap and be torn on the machine. The better fibrillated and hydrated the sheet is, the more it will be capable of taking on a good formation during the process of manufacturing, and the more it will be capable of stretching. Of course this extension in length will partly reduce the width.

As is well known in practice the degree of shrinkage varies according to the thickness of the paper and the conditions of the mixtures of fibers employed. The speed of rotation of the single rolls must therefore be adjusted by means of conical pulleys or, as it is done with modern machines, by regulating the sectional electric drives which move the single cylinders. It is interesting to note that the colloidal processes in the web of paper necessitate certain types of mechanical construction in papermaking machinery.

Having studied the workings of our paper machines we have seen that capillary-physical and colloid-chemical phenomena are the principal factors of papermaking. However an old saying of the papermaker is: "Paper is made in the beater," where the stuff is prepared for the paper machine and takes up the water to be removed again on the Fourdrinier wire.

This beater consists of a large oblong tub or vat with a central partition called the midfeather, around which the stuff in water is propelled by a roll equipped with iron bars or knife projections for cutting and beating the stock on the bed-plate of standing bars or knives. By means of lowering or lifting the roll to a lesser or greater degree to or from the standing knives of the bed-plate, the circulating fibers of the stock are more bruised, frayed or cut. Therefore by regulating the space between the revolving and standing knives or bars it is possible to vary the degree of beating and swelling of the fibers, and thus produce different kinds of paper.

C. G. Schwalbe[4] made the first systematic colloid chemical research on the "hydration" of paper stock in the laboratory, using a small model beater. R. O. Herzog and J. R. Katz[5] followed the swelling of the cellulose by taking X-ray spectrograms. Swelling begins on the surface of the fibers, and gradually on the *interior* surface also, that is in the tubular spaces of the cellulose fibers when they absorb water and the enclosed air bubbles are driven out. Swelling proceeds on mere contact of the fibers with water. As an example it may be noted that pulp left in the beaters over the week-end always works "slower" on the machine on Monday than similar pulp produced without such storage. According to Schwalbe the maximum of swelling is reached in from six to nine hours.*

If at the same time intensive mechanical work with a lowered roll is going on in the beater, the fiber becomes "dead beaten," being gradually converted into a homogeneous mucilage which becomes hard and horny while drying to a structureless material. This mucilage or mucus is technically important, because, if it is mixed in certain proportions with the pulp, it increases the strength and the resistance of the resulting sheet of paper to the penetration of writing and printing inks. Cellulose mucilage, when dried, is water-repellent and effects selfsizing of paper, making rosin sizing for certain kinds of paper unnecessary; hard-beaten paper of this type is also grease-proof. While it is impossible to produce a paper from cellulose mucus alone, the mucilage provides a good agglutinating material for selfsizing, but uninjured fibers must be present to assure good strength. Schwalbe has given special attention to research work on cellulose mucilage. The formation of the mucilage is furthered by the addition of acids, acid salts, sulfocyanates in alkaline solutions, undercooked fibers containing incrusting materials and by similar substances that accelerate the beating process in a chemico-colloidal way. Schwalbe has been granted patents on a cellulose-mucus former that goes by the name "Mucigen," which, added to the beater in the proportion of 1 to 3 per cent, shortens the time of beating to a considerable extent.

The papermaker has always known that an alkali will assist in swelling or hydrating the pulp. In the production of certain Swedish kraft papers (which means *strong* papers) made of soda sulfate cellulose, part of the alkaline cooking liquor used for boiling the wood is left in the fiber pulp, instead of being washed out or neutralized by sulfuric acid as is usually done, to assist the disintegrating action of the kollergang or edge runner † which grinds the pulp ready for the beater. Neutralization is effected subsequently. The papers made by this process have the advantage of extraordinary strength. Apparently the rosin and fatty substances of the half-stuff are peptized by this treatment, and improve the quality of these papers.

Schwalbe attained the maximum swelling of cellulose by beating in a 0.1 per cent solution of lactic acid; cellulose fibers impregnated with such a liquor retain five times their own weight of water after being centrifuged, whereas cellulose swelled in water alone does not bind more than one and a half times its own weight of water. Dilute acetic acid, too, swells the cellulose fibers to a marked extent. With reference to the influence of electrolytes in water, it has been found that a relatively small proportion of salts, as found in hard waters, increase the time of beating and demand perhaps a greater expenditure of energy. This is explained theoretically by the cations coagulating the negatively charged cellulose, and thus opposing in colloid chemical fashion the mechanical disintegration.

P. P. von Weimarn[6] made important researches in the dispersoidological chemistry of cellulose, especially on the influence of concentrated solutions of salts. Such high salt concentrations are not commonly found in the beater, and so had no direct application in the paper industry. But these investigations are nevertheless useful and interesting for the papermaker, who esteems science and research and desires to acquaint himself with the behavior of his raw material, the vegetable fibers. In making parchment paper and vulcanized fiber strong zinc chloride and sulfuric acid are used.

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* Rowe (Technical Section, Papermakers Association of Great Britain and Ireland) reported contrary effects. Bacterial action must also be considered as a factor. J. A.

† This is the so-called chaser or Chilian mill. Alkali affects different pulps differently. J. A.

Our knowledge of the colloid chemical relations of the raw material should not be limited to fibers of half-stuffs, but must start in the forest where are found the supplies of wood for papermaking. H. Wislicenus has shown that the growth of wood is typically a colloid chemical adsorption process. The first technical treatment of the cut wood that interests the papermaker also has a colloid chemical basis, that is, the barking of the wood. Ready and complete barking without loss of ligneous substance is closely dependent on the condition of swelling of the cambial layer. While the ascent of the juice is going on, from May to June or July, the bark is easily removed. This refers not only to logs cut in summer, but also to timber cut in the fall or winter and subsequently stored. These are also easily peeled and in a shorter time.*

The wood digesting processes also involve in colloid chemical phenomena, such as wetability, surface tension, diffusion, osmosis, swelling, adsorption. At first a saturation of the wood chips is caused by the digesting liquor diffusing through many of the overlaying films of the wood fibers. This diffusion is accompanied by swelling or distension. It has been found practical to effect these saturations and distensions at a rather low temperature, say, 100° C., especially in the soda and sulfate processes. The mucus substances set free during the cooking of the wood, the pentosans, appear to retard the dissolution of the incrusting nonfibrous parts of the wood, by gluing up and closing the diffusion membranes on the surface of the chips. Faulty digestion will therefore take place and undercooked stuff will be obtained if the alkaline lye is not used in sufficiently concentrated form to dissolve the incrusting material and the mucus substances as well.

On the other hand, trouble will ensue from shrinking or "dehydration"; thus if mechanical pulp is exposed too long to the rays of the sun during storage, it will become unfit to produce paper of good translucency. Prolonged soaking will not remedy the condition, as the shrinking becomes partly irreversible. Similarly, a chemical pulp which has been stored for any length of time in a moist place, will, because of excessive swelling, produce a rather opaque paper, as compared with cellulose freshly prepared in paper mills having a chemical pulp plant of their own.

It is advantageous to accelerate the swelling by the aid of heat, when grinding wood. By means of so-called "hot grinding" at a temperature of 70° to 80° C. fibrillation is effected lengthwise of the fibers, thus favoring the production of a "wetter" pulp of increased pliability, felting quality, toughness and strength. In producing brown mechanical woodpulp, the sticks are steamed in closed boilers before being ground. In this way the incrusting lignin and resinous matter are partly swelled up and partly dissolved, the fibers being loosened so that they readily grind to pulp under the action of the grinding stone, and produce a very long-fibered, strong stuff, well adapted for use in manufacturing leather board.

At the same time it is interesting to note that the cellulose fiber itself is shrunken or dehydrated by heat; the frictional heat generated in the beater causes wood fibers to shrivel and give up water.† Advantage is taken of this by the paper machine man when the stuff is "too wet" beaten, when the sheet adheres to the couch and press rolls. In such cases it has been found practical in some mills to inject steam into the stock before it flows over the wire, which serves the purpose of making the pulp "freer" and enables it to pass over the machine without sticking or picking.

* Waste sulfite liquor aids decortication in the Thorne barking machine, where logs roll against each other.

† Increase in kinetic activity is a factor. J. A.

METHODS FOR DETERMINING THE SWELLING DEGREE OF ORGANIC FIBER GELS

A brief survey of methods for determining the degree of swelling of vegetable fibers may be given. Similar to F. Hofmeister's *weight method* for measuring the swelling of gels, well known to those engaged in colloid chemical research, is the method of Carl G. Schwalbe, already referred to. The loosely held water of absorption is removed by centrifuging in a small wire basket. The paper stuff in the basket is weighed in the moist state after being centrifuged and later after having been dried. The difference in weight affords an idea of the proportion of water of turgescence. I found the results obtained by this method too high, some water being occluded and held by capillarity. Perhaps the use of a very high speed centrifuge would give better results.

Martin H. Fischer's volumetric method resembles that of P. Klemm, who measures the height of the sediment of two grams of fiber contained in a cylinder having a perforated bottom, from which the water drops. The results indicate the degree of swelling and beating, but show difference too trivial to serve as a basis of mill control. Klemm therefore recommends microscopic examination as the most reliable method to enable the beaterman to follow the progress of his work. He uses a projection apparatus in order to show more distinctly the condition of the fibers. Klemm believes the measurement of shrinkage of moist sheets to be useful for test data; but since the drying is time-consuming, this method can only be used in research work. I should also advise the use of drying diagrams similar to those used by Wolfgang Ostwald in his studies of peat. When constructing a diagram of this kind by drying a part of the paper sheet in a drying oven, I found the curve characteristic for adsorbed water. The test occupies about twenty-four hours and requires considerable control, so that it is not practicable for mill work and is applicable only in research investigations.

R. Fournier gives a convenient volumetric method for the determination of water in fiber stock. A flask with a graduated upright tube fitted with a ground glass stopper is charged with a measured quantity of moist cellulose; air bubbles are expelled by vigorous shaking, and the flask is filled to a determined point with water. The proportion of water in the stock is calculated according to the weight of the moist pulp and by the amount of water needed for filling up, as the specific gravity of the absolutely dry cellulose is known to be 1.5. The usual drying process at 105° C. until the weight is constant is thus avoided, as well as any further measurement. This method assumes that in the swelling process cellulose and water combine in a purely additive way, without any contraction or expansion of their volumes; but it is necessary that this be tested before using the method.

Schwalbe found measurements of viscosity unsatisfactory. But curves of freeness of the pulp seemed practicable in research experimentation. A measurement of the freeness with which water leaves the pulp is, so to say, an inverse method of determining the viscosity. Viscosity is generally measured in apparatus employing a capillary of fixed diameter, variable viscosities being shown. With capillaries of variable diameter, such as exist in the pulp, we have water, a fluid of constant viscosity; and its velocity of efflux measures the freeness of the pulp.

The skilled beaterman dispenses with the use of a freeness test. He "feels" the stuff by continually squeezing it through his hands, and is able not only to gage the degree of "wetness," but also the length of the fibers. The Schopper-Riegler freeness (or slowness) tester is, however, commonly used in most mills. The degree of hydration or swelling of the stuff is estimated on the ratio of the amount of water which is freed from beaten pulp quickly, representing "free" or "quick" beaten stuff, against the amount which is liberated slowly, indicating "wet" or "slow" beaten stuff. Free beaten stock consists of elastic fibers of a low degree of swelling, whereas wet beaten stock is very pliant if not smeary stuff, being swelled to a high degree.

A measured amount of the fiber stock is taken from the beater and put into a container having an open end that is closed by a conical valve, the bottom of which is covered with a fine wire gauze sieve. The upper part of the apparatus fits tightly into a funnel-shaped chamber having two openings in its lower part, one vertical, the other slightly higher up, running off at about 45 degrees. Below the two openings two graduated glass cylinders are placed. The lower vertical opening is thin, like a nozzle. If the water is running down quickly it cannot pass rapidly through the nozzle and flows through the upper neck into the graduated vessel below. If the water drops slowly it will fill up the other graduated standing below the nozzle. A comparison of two levels in each of the two graduates gives an idea of the freeness or slowness of the stuff in conventional figures.

The methods mentioned above are colloid-physical in character. The attempt has also been made to measure the swelling of the fibers in a colloid-chemical way.

Vieweg immersed weighed quantities of different cotton celluloses for a specified time in soda lye of uniform concentration, keeping the temperature constant. The decrease in the alkalinity of the lye caused by adsorption of sodium hydrate at the fibers indicates the swelling capacity of the cellulose. A similar method is to soak the fibers in Fehling's solution, and then determine the amount of copper incapable of being washed out; this measures the degree of swelling. The copper method gives erroneous results with stuffs containing incrusted ligneous materials, e.g. ground wood. Schwalbe and his collaborators Behringer and Becker, as a third adsorption method, determined the fixing capacity of the fibers for hydroxides of chromium, iron and aluminum from solutions of their acetates. Color experiments, especially with diamine blue and methylene blue, serve to make visible the formation of mucilage while beating; the shade darkens in proportion to the slowness of the stock.

A. W. Schorger attempted to determine chemically the degree of swelling of the fiber. He hydrolyzed swollen and unswollen sawdust into sugar by dilute sulfuric acid. The method failed because the differences obtained were too small.

From what has already been said, it is obvious that papermakers may gain much from colloid chemists. Those engaged in paper research are bursting the trammels of orthodox organic chemistry and are taking up, wherever necessary, physico-chemical modes of approach to problems, which, as we hope to show in the next section, have already been successful in coloring, loading and gluing or "sizing" paper.

LOADING, COLORING AND SIZING OF PAPER.

In the beater additions of fillers, colors and gluing or sizing substances are made to the fiber stock.

Minerals are used for loading paper to attain special qualities of characteristics. Thus the so-called "noiseless" paper for concert programs is made smooth and pliant in order to avoid a crackling noise while folding or turning the pages in a concert hall. This is effected by the addition of fillers which reduce the natural harshness of the fibers. Loading is also essential for improving the color, and the printing qualities of the paper.

As fillers the papermaker uses china clay, talc, asbestine, gypsum and barytes. These substances are suspended in water. Protective colloids, assisting in suspending the fillers, consist of admixtures of waterglass (sodium silicate), starch, etc. The suspended fillers must be fixed on the fibers so that they cannot be washed off by the water. This typical colloid chemical problem has not yet been solved satisfactorily in practice, and there is still considerable loss of fillers in the waste water.

Together with Otto Seiderer and Robert Stopp [7] I have made investigations of paper loading and of the suitability of the different fillers used in Europe. Their fineness is of great importance, but is not the sole factor in their fixation on the sheet; the form and the surface conditions of the small mineral particles is also of importance. We must not forget that there are at least two additional factors that exert an influence on the completeness of retention of pulverized minerals in the fiber mat. There is, for instance, the size of the meshes of the fiber network, which depends on swelling and beating conditions and varies from one paper stock to another, and also the binding of the fillers to the fibers by adsorption and by cementing preciptations. The former is favored by coarseness, whereas adsorption is favored by fineness. As a general rule loading material of medium fineness will give the best results, so far as china clay is considered, the results depending on the colloid chemical character of the stock. A wet beaten or smeary stock will retain rather small particles, down to 1 micron and less, in a larger quantity than a comparatively wide-textured, elastic network of a free beaten stuff. If a free beaten stuff is filled with a very finely subdivided clay, there is apt to be a high loss on the wire. Another disadvantage is that the filling material will be shaken out of the dry sheet in the form of clay dust, which leads to trouble on the modern high-speed printing presses by mixing with the printing ink to form a smeary paste that blurs the type and illustrations so that they are not clearly outlined.

It is different with clays, gypsum and barytes which are used as fine as possible so that they may be aggregated while in aqueous suspensions.

The colloid chemistry of paper coloring is quite similar to cotton dyeing and will therefore be only briefly mentioned. In general wool and silk exhibit greater adsorption than cellulose fibers, e.g. linen, cotton, woodpulp, etc. Many dyes used by papermakers are colloids and can accordingly be fixed by electrolytes. The fiber is charged negatively in water. Acid coloring materials, as Congo red, being negatively charged colloids, are repelled by the fibers. Basic dyes, e.g. night blue, being positively charged are attracted and adsorbed by the fiber. The adsorption itself reduces the electric charge of the fibers and will cease after the charge is neutralized. If there is a neutral salt electrolytically dissociated in contact with the fibers, the cation (whose effect increases with the number of the electric charges), will diminish the potential difference between the solution and the paper stock. In consequence neutral salts reduce the repulsion of the negatively charged coloring material, and thus favor adsorption, whereas the adsorption of positively charged substances is diminished.

Experience has, however, demonstrated that adsorption in paper containing any considerable amount of ash is greater than in a paper rather free from ash. Rona and Michaelis [8] assume the adsorption of dyes to be an exchange reaction with the ash of the paper, an opinion which harmonizes with facts established by H. Weyl,[9] showing that the adsorption of dyes by paper pulp diminishes when colloids, e.g. gelatin, serum, glue, etc., are present.

According to tests reported by Fichter and Sahlbom[10] the height of capillary rise of colloid dyes in strips of filter paper determines whether the dyes are positively or negatively charged. If negatively charged, the dye will rise with the water; if positively charged, it flocculates closely above the fluid surface and forms a sharp boundary, clear water rising in the strip above.

By impregnating paper with a sol of aluminum hydroxide, Lorenz succeeded in charging paper positively so that positively charged dyes rose in it, while negatively charged dyes flocculated.

Lorenz conducted several theoretical and experimental investigations[11] on paper sizing, and was often able to aid in the solution of sizing difficulties.

The following are used for paper sizing: rosin size, animal size, vegetable size, gum arabic, viscose, casein, starch, dextrin, rubber latex, hydrated silica (from waterglass), hydrate of alumina from alum or sulfate of aluminum, etc. These are all colloidal substances and possess considerable surface area which renders them particularly well adapted for sizing paper. Sizing serves the purpose of filling up the minute pores of the paper and of covering the fibers by a thin protective film so that their attraction for water is diminished and the paper made ink resistant. The sizing varies according as to whether the paper is to be used for writing or for printing. Usually printing paper is not required fully sized. The following is a good test for the quality of the sizing: Draw some lines on the paper with writing ink, and allow them to dry; the absence of all penetration of ink indicates perfect sizing, whereas in case of defective sizing, even light pen lines "bleed" or run to some extent, so that the lines become indistinct at the edges.

Rosin size, with or without admixtures of the other colloids mentioned, is mainly used.* It is most interesting from the colloid chemical standpoint. In the preparation of rosin size it is customary to digest the rosin with approximately half the amount of alkali that is required to effect saponification. The other half of the rosin, which remains in the unsaponified state, is dispersed throughout the solution as free rosin in the form of a colloidal dispersion. This gives rosin solution a milky appearance, whence the name, milk of rosin. But the saponified rosin, which is in the state of a true solution, is gradually converted into the colloidal condition in the beater, which means that the rosin particles increase about one hundred times in size. In fact, the resinate of soda is rather completely hydrolyzed as a consequence of the great dilution that ensues in the beater when the rosin size is added thereto. The abietic acid liberated as a result of hydrolysis is insoluble in water and aggregates to colloidal dimensions. Lorenz found that the formation of the dispersion and the changes following hydrolysis of the milk of rosin can be measured by stalagmometric methods and expressed in graphs.

The next point to be taken into consideration is what happens to the colloidal rosin solution when sulfate of aluminum is added to the beater. I believe that no appreciable precipitate of aluminum resinate is formed, for that would demand the presence of ionized abietic acid. But resinate ions are not present to any appreciable extent in the sizing solution after it has been hydrolyzed in the beater. What is found are aggregates of rosin in the colloidal

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* The *purpose* of sizing must always be borne in mind. Thus with ordinary writing papers the object is to prevent the writing ink from running or "bleeding," and the discovery of blotting paper is said to have been due to the accidental omission of sizing. Prior to that time, fine sand was generally shaken from a sifter onto the wet ink, whence the German saying to denote finality: "Punktum! Streu Sand darauf." Rosin sizing tends to make the paper resistant to moisture, but for writing papers glue, gelatin, starch, etc., are more desirable as they "take" writing ink better; they also tend to make paper resistant to grease.

While the rosin soap may be largely in true solution when hot, the conditions referred to in J. W. McBain's paper in Vol. I of this series must also be considered, especially as the solution cools and is diluted. J. A.

condition, each particle of which is at least one hundred times larger than abietic acid molecules or ions.

It may be thought that resinate is formed on the surface of these colloidal rosin aggregates, by reaction with aluminum ions. However, even if this be so, the reaction is necessarily limited, because most of the rosin located within the colloidal particles is inaccessible.

On the other hand, if the rosin dispersion is left in the beater as such, the rosin particles being of colloidal dimensions, are largely washed away in the waste water. Sulfate of aluminum acts as a flocculating agent. Quantitative laboratory tests showed that the trivalent aluminum ion in aluminum sulfate possesses approximately five thousand times the coagulating potency of the univalent sodium ion in common salt, and fifteen hundred times that of the divalent magnesium ion in magnesium sulfate. Schulze's law as to the coagulating potency of ions was thus checked on rosin sol.

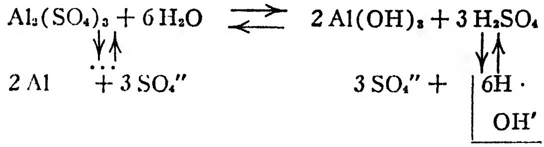
The fact that salts possess a flocculating action on the rosin suspensions is often very clearly and inconveniently manifested when the addition of a hard mill water to the rosin dispersion produces deflocculation or coagulation of the size, or at least makes a clear size cloudy or muddy in appearance.

When other colloids are added in the proper proportions to the rosin, as is the rule with commercial sizing preparations, it is possible to regulate the flocculating action of the electrolytes, that is, accelerate or reduce the speed of the coagulating process so as to maintain the particles of rosin in the most advantageous condition of dispersion. The character of the colloid that is added to the rosin suspension is not the only factor to be considered, for it is necessary to take into account the conditions under which these colloids exert their respective actions on the milk of rosin; there are frequently small changes in the method of their use which, while all other conditions remain unchanged, reverse results. Thus in the case of the addition of casein to the rosin emulsion, the circumstances under which the addition is made may result in complete inhibition of flocculation or may cause it to take place immediately.

This very interesting, and at the same time very important bit of colloid chemical knowledge, has not been given any attention at all in the practical application of the sizing process. Whenever casein was added to the rosin size, the addition was always made in an empirical manner, without any very definite knowledge of exactly what was going to ensue or without any real understanding of what did take place or any suspicion that different actions could be produced by the addition of this colloid under suitable controlled conditions.

In the foregoing, the flocculating action of the cations, aluminum, sodium, magnesium, for example, has been discussed. On the other hand, the anions, for instance the sulfate ion and the chloride ion, possess a dispersive or peptizing action on rosin suspension. This dispersive action varies in intensity with the number of electric charges on the anion. Thus, for example, the singly charged chloride ion has a lesser dispersive potency than the doubly charged sulfate ion. In the preparation of rosin soap, the hydroxyl ion of the alkalis acts as the peptizing agent, dispersing the free rosin and stabilizing the suspension.

The conditions of flocculation with the aid of sulfate of aluminum are particularly adapted to the reaction. Not only does the aluminum ion possess a high electric charge, and therefore great coagulating potency, but the stability of the rosin dispersion is considerably reduced at the same time because the hydroxyl ions, which are derived from the alkali added to make the rosin soap, are neutralized by the sulfuric acid which is liberated as a consequence of the hydrolysis of the sulfate of aluminum. The neutralization of the hydroxyl ions removes the peptizing agent, which tends to keep the rosin in a state of suspension. The following equation illustrates the manner in which the reaction takes place:



$$\begin{array}{lcl} Al_2(SO_4)_3 + 6\,H_2O & \rightleftharpoons & 2\,Al(OH)_3 + 3\,H_2SO_4 \\ \downarrow\uparrow & & \downarrow\uparrow \\ 2\,Al^{\cdot\cdot\cdot} + 3\,SO_4'' & & 3\,SO_4'' + \left|\begin{array}{l} 6H^{\cdot} \\ OH' \end{array}\right. \end{array}$$

The hydrolysis of the sulfate of aluminum is promoted by the removal of the hydrogen ion from the system; this is in accordance with the law of mass action. At the same time aluminum hydrate is formed continuously and on account of this, the concentration of aluminum ions steadily decreases. Inasmuch as the white water from the paper machine is practically free from aluminum, the hydrolysis must be almost complete.

As all the aluminum ions are converted into aluminum hydrate, their flocculative action, which is known to be very powerful, ceases. This action takes place within the time that is consumed between the beginning of the hydrolysis of aluminum sulfate and its completion. After hydrolysis is effected, the hydrogen ions can at best complete the flocculation of the rosin in the slightly acid bath.

The aluminum in final analysis is found in the state of colloidal hydrate. What, then, is the action of this colloid on the sizing process? Does it merely play the rôle of a mineral filler in the finished paper and can it be replaced by other mineral substances with just as good results, or is it indispensable to successful sizing of the paper?

Experience has shown that when coagulating reagents are used which are absolutely free from aluminum, such as magnesium sulfate, sodium sulfate, or dilute sulfuric acid which may, at first glance, be expected to give just as good results as aluminum sulfate because of their powerful coagulating action, the sizing of the paper is not stable, that is, papers sized in this manner, after being stored for a short time, act as though not properly sized.

This seems to justify that the old resinate theory which is made untenable by our previous observations, showing that there was no proof of any considerable formation of aluminum resinate in the beater. But this apparently contradictory phenomenon can be explained colloid-chemically. It is known that cellulose is negatively charged when dispersed in water, and that the rosin sol is also negatively charged. Particles of these two substances should, therefore, repel each other electrostatically. On account of the mechanical agitation in the beater, the rosin and the cellulose fibers are intimately matted together.* Hence, when the fritting of the rosin size is carried out on the drying cylinders of the paper machine under correct conditions the network of fibers are covered with an even coating of rosin. But the electrical repulsion that ensues between the cellulose fiber and the film of rosin, occasioned by the similar charges on both, causes a disruption of the extremely thin rosin coating. The structure of the rosin film is loosened from the underlying cellulose, with

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* It must be remembered that although a particle *as a whole* may be negative (or positive) it may also have and usually *does* have a high degree of *surface specificity* involving a "checker-board" of plus and minus areas; so that particles of the same *gross charge* (due to ion adsorption) or of the same *net charge* (due to excess of plus or minus areas), may readily adhere providing oppositely charged areas come into contact. Particles have *individuality;* although in *some cases* they may be mathematically treated as uniform spheres; in *other cases* their shape and surface peculiarities are dominant. Agitation aids surfaces to find their mates. J. A.

the result that fissures are formed in it and the paper is "desized." Ink and other liquids penetrate the paper and the writing or printing runs.

On the other hand, when a positive colloid is distributed throughout the paper, this will about balance the negative charges on the rosin and the cellulose, and the paper becomes approximately isoelectric. The aluminum hydrate colloid plays this rôle in being positively charged, as is always the case when oppositely charged colloidal substances are mixed. In other words, the hydrate of alumina acts as an "electrostatic cement" between the rosin and the cellulose.

This is Lorenz' colloid chemical theory of rosin sizing, which he found helpful in correcting sizing difficulties in paper mills.

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Cellulose Esters.

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The cellulose esters, of which many are known besides the familiar cellulose nitrate (nitro, cotton, pyroxylin, etc.), cellulose acetate (acetyl cellulose) and so-called cellulose xanthate (viscose), behave as typical colloidal materials in common with cellulose, their parent substance, although during the process of esterification the cellulose, either cotton or purified wood pulp, is degraded and modified.

In the preparation of the formates of cellulose this degradation proceeds to a marked extent, partly due to the high reactivity of formic acid and the product, which is soluble in many salt solutions but not in the usual organic solvents of cellulose nitrate or acetate, is friable and of no technical importance.[1] Similarly, if the action of sulfuric acid and acetic anhydride be carried too far in the preparation of cellulose acetate, the ultimate product is a crystalline octo-acetate of a biose sugar.

The modification or degradation which the cellulose undergoes, either before or during esterification, plays a profound part in fixing the strength and mechanical properties of fibers or films prepared from the cellulose esters and accordingly of their commercial values. Gault and Ehrmann[2] report from their investigations on the preparation of cellulose tripalmitate, etc. from hydro cellulose "Girard" (cellulose dipped in diluted sulfuric acid and dried slowly at 30° to 35° C.) that films of the di- and tri-esters obtained by the spontaneous evaporation of benzene solutions were remarkably supple but did not possess the toughness and durability shown by films of cellulose nitrate or acetate. They attribute this behavior to the advanced degree of degradation experienced by the cellulose during the preliminary acid treatment.

W. L. Barnett[3] has made an interesting attempt to determine the degree of degradation in the case of some cellulose acetates by calculating the value of n in the empirical formula $[C_6H_7O_2(OCOCH_3)_3]\ n$, corresponding to the triacetate, from the estimation of the nitrogen content in the phenylhydrazones and bromine in the *para*-bromophenylhydrazones, assuming that a single complex has one ketone group available.

His results show that for the phenylhydrazones, n varied from 2 to 12, and for the bromo derivatives from 7 to 36, according to the original cellulose used, solvent, and time of heating.

It has been found impossible to introduce more than three acyl or other groups into the cellulose molecule of empirical formula, $(C_6H_{10}O_5)n$ where n is taken as unity, so that the triacetate represents the fully esterified material. Actually, commercial cellulose derivatives are not usually completely esterified; thus, the cellulose acetate used in industry has, when anhydrous, a formula corresponding to $C_{12}H_{15}O_5(O.CO.CH_3)_5$.[4]

Similarly, the cellulose nitrates used in industry vary in nitrogen content;

the chemical composition of explosive insoluble guncotton approaches that of cellulose hexanitrate, whilst the ether-alcohol soluble pyroxylin is formed chiefly of the tetranitrate $C_{12}H_{16}(ONO_2)_4O_6$ and the pentanitrate $C_{12}H_{15}$-$(ONO_2)_5O_5$. There seems, however, to be no break in the curve representing the amount of nitrogen introduced by different concentrations of acid. The benzoate of cellulose which has been prepared corresponds to about 2.5 benzoyl to one simple $C_6H_{10}O_5$ molecule, whilst the tripalmitates, etc. of cellulose also contain small amounts of di derivatives.

Not only is it possible to vary the character of the cellulose ester, especially with regard to its solubility in organic liquids by preparing modifications of different degrees of esterification, but mixed esters can be made. Mixed acetates of nitrates, sulfates, benzoates, butyrates and palmitates of cellulose have been prepared and described as well as phospho-formates and nitro-sulfates of cellulose, lauro-diaceto-cellulose, etc.

Solubility is also affected by the degree of modification which the cellulose undergoes. An interesting example of the influence of the preliminary treatment of the cellulose on the solubility of the derivatives, is afforded in the case of the cellulose laurates and stearates. Grün and Wittka [5] prepared these from unmodified cellulose, and found them to be characterized by their insolubility in organic liquids, whereas the same esters prepared by Gault and Ehrmann from modified cellulose (hydrocellulose of copper number 3 to 5), dissolved freely in benzene, chloroform, butyl acetate and other well known solvents of cellulose esters.

Usually, any special property of the original cellulose, e.g. high or low viscosity, is transmitted in part to the derivative, so that it is necessary for technical purposes to select suitable quality cellulose for the particular purpose required. For nitrocellulose finishes a low viscosity is advantageous since it means economy in solvents.

One of the most important properties of cellulose and its esters from the point of view of colloid chemistry and technology is the viscosity of their solutions. According to Worden [6] the viscosity of solutions of fully purified cellulose is held to be a measure of the chemical quality of the cellulose in the sense that solutions of modified celluloses are extremely deficient in "body."

It would appear that, with certain reservations discussed later, a close relationship exists between the viscosity, toughness and mechanical properties of fibers and films, and the degree of complexity or colloidality of the cellulose derivative. Any factor which causes a breaking down of the colloidal complex of the original cellulose also reduces the viscosity and the degree of toughness of the cellulose ester. It has been recorded by Sir R. Robertson [7] that it is necessary to control by means of viscosity measurements the boiling of cotton in the manufacture of cordite, since faulty boiling resulted in lack of coherence in the threads of cellulose nitrate.

Cellulose esters are heterogeneous solids which, like cellulose, can be "purified" or fractionated into a number of fractions of similar chemical composition but different solubility, viscosity, etc. From the appearance of X-ray diagrams, Herzog and Von Naray-Szabo [8] concluded that nitrated cotton and ramie fiber are composed of cellulose trinitrate and cellulose, but this conclusion has been disputed by Miles and Craik,[9] and others.

Further data is required to account systematically for the chemical heterogeneity of cellulose esters.

There is at present a good deal of mystery with regard to the physical structure of cellulose and its derivatives, and it is not known what exactly endows them with their remarkable properties, although it is realized that these properties are intimately associated with the physical structure. Until more recently the value of *n* in the empirical formula $(C_6H_{10}O_5)n$ was considered on chemical grounds to be very large, but Cross[10] put forward the view that celluloses do not necessarily consist of large molecules in the strict chemical sense and can be regarded as liquid (supercooled) systems or solution aggregates.

There is no doubt that cellulose is in different colloidal states in different parts of the fiber, the outer portions being more solid than the inner, and this heterogeneity is transmitted to its derivatives. Nägeli (1862) found that the cotton hair was composite, consisting of a large number of fibrils winding in different directions and he used the word *micelle* to denote the ultimate cell of the cellulose tissue. Recent investigations on the physical structure of cellulose and other naturally occurring colloidal substances, especially by means of X-ray spectroscopy, have led to the idea that they are built up of colloidal units, which are not necessarily single molecules but are molecular aggregates or polymers. The word "micelle" has been adopted for this unit and is used in the combining sense rather than with its botanical meaning. Information has recently been obtained with regard to the form of the micelles. The X-ray diagrams show that the celluloses and many of their derivatives possess a crystalline character, the position of the lines being explicable upon the assumption of a rhombic space lattice.

Sir William Bragg, in a discourse at the Royal Institution, London, on cellulose in the light of the X-rays[13] summed up in saying:

(1) Cellulose contains crystals which may be invisible in the microscope but are clearly indicated by the X-rays: they are usually termed crystallites.

(2) These crystallites are partly oriented, having one direction in common, more or less.

(3) In each crystallite there is a periodicity in this special direction of 10.3 Å. This is often called the "identity period."

It may not be safe to say that the whole of the cellulose is composed of crystallites, but there is a strong temptation to assume that this is so. Cellulose is a multiple, as regards content, of the unit $C_6H_{10}O_5$, as we have seen reason to suppose that this unit forms a ring which is the basis of the structure. The X-rays do not suggest the presence of a second structure, having any real difference from the first: and we suppose, therefore, that the ring structure pervades the mass.

Ambronn[11] concluded from investigations on the double refraction of gels that cellulose probably consists of anisotropic particles, the longitudinal axis of which coincides with the axis of the fiber. Results obtained by Hess[12] and his co-workers on the study of cellulose and derivatives also tend to confirm the micellar theory. They have prepared crystals of cellulose triacetate from tetrachloroëthane solutions in the form of beautiful, needle-shaped crystals, which spontaneously passed into well-defined rhombs. These contained solvent, were brittle and readily decomposed in the air.

Progress in knowledge of the physical structure of cellulose ester films and fibers must necessarily follow that of gel structures in general and considerable work is necessary in order to establish clear ideas with regard to correlation of the mechanical properties of films with the size, shape and disposition of the micelles.

The vast industrial uses of cellulose esters depend entirely upon the preparation from them of plastic masses and solutions or varnishes. The artificial silk industry depends on the preparation of suitable solutions which are squirted through dies into a precipitation bath of a non-solvent where fine threads of cellulose acetate or cellulose in the cases of viscose and nitrocellulose when the ester part is removed, are formed and subsequently dyed and woven.

B. Campbell[14] in reviewing the historical development of nitrocellulose finishes states that after the discovery of nitrated cellulose by Schönbein in 1845, early efforts were devoted to the application of the product for military purposes.

It was noticed, however, that certain types of nitrocellulose having a nitrogen content below 12.5 per cent were readily soluble in organic solvents such as acetone, ethyl acetate, or mixtures of ethyl ether and ethyl alcohol, and that such solutions when poured upon smooth surfaces gave continuous films when the solvent had evaporated.

No important industrial developments resulted immediately, owing to the fact that films from the solvents mentioned shrink badly on drying, tending to wrinkle and turn white.

With the discovery of the value of amyl acetate in preventing these effects, real progress in solution development began. In 1882, Stevens obtained a series of patents in one of which amyl acetate was mentioned as a solvent for nitrocellulose.

With the advent of this solvent into the art, many of the difficulties which had prevented rapid development of the use of solutions for coatings were eliminated, and the foundation for the present cellulose finish industry was laid.

For the next thirty years a steady growth began. The number of experimenters increased. Knowledge of the solubility factors of different types of nitrocellulose was broadened, new solvents were found and their methods of manufacture cheapened, methods of combining nitrocellulose with various resins, vegetable oils, etc. were worked out. In this pioneering work mention may here be made of the valuable contributions of F. Crane as given in various British Patents from 1889-1892. To this investigator must be ascribed the credit for the discovery of the value of many of the solvents for nitrocellulose used in the industry at the present time. These include the methyl, ethyl, propyl and butyl acetates, acetone oil and ketones. F. Crane also patented the use of gums (or resins), linseed oil and pigments in nitrocellulose coating compositions.

As further instances of the dependence of the modern industry on these pioneers it is of interest to observe that several of the most efficient solvents and plasticizers of nitrocellulose were patented by Alfred Nobel in 1894. These include the methyl, ethyl, propyl, butyl, and amyl esters of lactic, phthalic, oxalic, tartaric, citric, succinic, benzoic and salicylic acids.

A comprehensive account of various solvents and solvent mixtures proposed for technical applications is given by Worden in "Technology of Cellulose Esters." (See Ref. 1.)

The first important step in the celluloid industry can be traced to Alexander Parkes, who, in 1864, disclosed the strong solvent power possessed by solutions of camphor in wood spirit * or oil of turpentine.[15] In a lecture given before the Royal Society of Arts in 1865, he describes the use of camphor as an important improvement in the manufacture of solid masses from pyroxylin, since it renders them more uniform and less contractile. Pellen's patent 1856 (Eng. Pat. 2256/1856) for the use of collodion for covering toys and balloons is of interest in view of the immense development of aircraft dopes later.

A description of aircraft dopes and varnishes has been given by Deschiens.[16]

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* The "wood spirit" was not pure methanol, but contained considerable amounts of ketones, etc. In reading patents raw materials of their period must be considered. J. A.

He states that in 1896 a cellulose nitrate dope was used to cover Andree's balloon for his exploration of the North Pole. In 1911, the house "Leduc and Hertz" introduced "Emaillite," a cellulose acetate dope, which, on account of its property of tightening fabric and being of low inflammability, was immediately adopted in aeronautics.

The manufacture of artificial silk made by the nitrocellulose process has been long established. Swann exhibited some silk, denitrated, as early as 1882. In 1884, Chardonnet took out his first patent in France; in 1897, Pauly repatented the process for making filaments from cuprammonium cellulose solutions, originally patented provisionally in France in 1890 by Depisses.

The history of viscose silk dates from the discovery of viscose solution by Cross and Bevan, and many of the important details of manufacture are disclosed in Stearn's patent 1898.

Empirical knowledge of cellulose esters is in advance of the theory. It is not known what exactly happens when cellulose nitrate plastic masses set or harden to ordinary celluloid or why cellulose nitrate is readily dispersed by a mixture of ethyl ether and ethyl alcohol, but not in the liquids taken singly.

The study of the action of organic liquids on cellulose esters forms an important contribution to the theory of colloidal chemistry, especially with regard to the mechanism of swelling and gel formation. Knoevenagel and co-workers[17] have carried out an extensive investigation on the swelling of cellulose acetate in mixed organic liquids and have arrived at a number of important conclusions. They found that the constituents in the swollen mass were often in stoichiometric proportions whilst thermal studies showed that the ratio of kg.-calories liberated per molecule of cellulose acetate during swelling to the total molecules of absorbed liquid was always a constant.

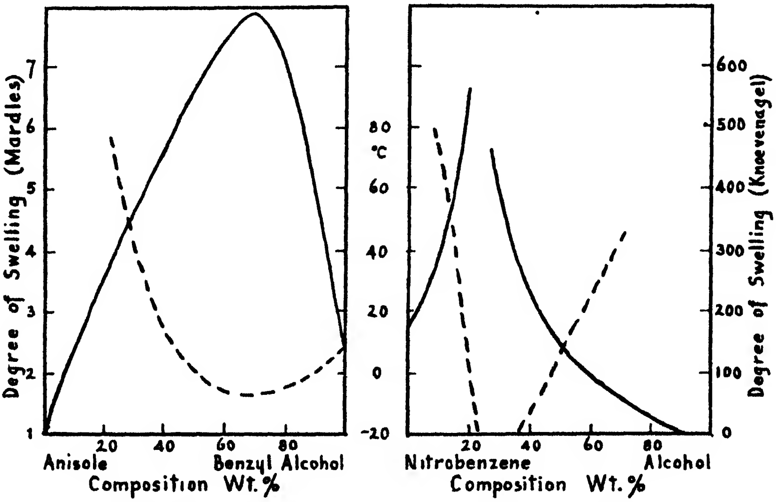
It is important to bear in mind with regard to the theory of solvent action that the dispersion of a cellulose ester in any solvent is subsequent to its swelling, and when precipitation from solution occurs it is the swollen mass which separates, usually in the form of a clear jelly.

When cellulose nitrate is soaked in dry ether or absolute alcohol, there is little apparent change even if the temperature be varied from —80° to +100° C., but a slight amount of swelling occurs. On mixing the liquids there is a rapid increase in the degree of swelling. For example, a film of cellulose nitrate, after immersion at the ordinary temperature for a few days, increased 28 per cent in weight in dry ether and 68 per cent in absolute alcohol; in ether containing 5 per cent (vol.) of alcohol the increase was 75 per cent, and any further addition of alcohol resulted in a very high degree of swelling. Similarly, the addition of 2.5 per cent of ether to alcohol increased the swelling nearly five-fold whilst dispersion of the more soluble constituents began.

Fibrous cellulose nitrate absorbs the vapours of both ethyl alcohol and ethyl ether in considerable quantities, and the absorption reaches a maximum for the proportion—1 mol. alcohol : 1 mol. ether.[18] It has been known for some time that the best dispersing mixture, i.e. the solvent mixture which disperses most rapidly forming the clearest and least viscous solutions, for cellulose nitrate has also a composition which is nearly equimolecular.[19] There is an interesting correlation between the degree of initial swelling and the dispersing action of mixed liquids. This is seen in Figs. 1 and 2, which give the relative swelling and solvent action of mixed liquids for cellulose acetate.

The very marked influence of swelling on dispersion is shown by the study of the binary mixture anisole-benzyl alcohol. Cellulose nitrate becomes swollen but is not dispersed by this mixture, and it is possible to plot the whole of the swelling curve. The swelling of cellulose acetate in this binary mixture is considerable and dispersion occurs on warming, so it is possible again to note the relation between degree of swelling and solvent action. Towards the copal resins, this binary mixture behaves similarly to cellulose acetate. It was found during the study of swelling in mixed liquids[20] that the rate of swelling was highest when the swelling was greatest. This is of importance in explaining why the "best" solvent mixture disperses the most rapidly; for not only does the optimum solvent mixture often form the least viscous sol, so that the resistance to the diffusion of the colloidal particles from the surface during dispersion is at a minimum, but also the initial swelling of the colloid is most rapid.

The important influence of swelling on dispersion can be shown equally well with other binary mixtures, e.g. alcohol and water. Knoevenagel and his co-workers have measured the swelling of cellulose acetate in a number of binary mixtures, and the solvent action of many of these mixtures on the same substance has been determined.[21] There is a close correlation in most cases, although different varieties of cellulose acetate were used.



FIGS. 1 and 2.—The correlation of the swelling of cellulose acetate in binary mixtures with solvent action.

——— = degree of swelling.
- - - - - = temperature of precipitation (Mardles).

The methods of determining the solubility of cellulose esters in organic liquids call for some attention, since it would appear that cellulose esters dissolve in all proportions in their solvents and in this way seem to be different from the ordinary crystalloids of limited solubility. However, there is evidence of a saturation concentration for cellulose esters even in acetone, so the difference is one of degree rather than of kind.

Cellulose esters form viscous solutions and when the concentration is over ten grams per 100 cc. of dispersing medium the sols tend to become intractable with regard to further dispersing action, and it is not possible to determine readily whether the cellulose ester is in true solution or whether a part is merely gelatinized and dispersed as such.

Viscosity measurements are sufficient to determine whether the system is really macro-heterogeneous, since, with a true solution, the law of Poiseuille is obeyed, but with the heterogeneous system the rate of flow varies with the pressure.

The following viscosity results were obtained with a sample of commercial cellulose acetate dispersed in pure solvents at 25° C.[22] and illustrate the rapid rise of viscosity with increase in concentration:—

TABLE 1. *Increase in Viscosity of Cellulose Acetate with Increase in Concentration.*

(a) Viscosity of cellulose acetate in acetone at 25° C.

Concentration (grams/100 cc.) ..	0	4.8	9.5	19	30
Viscosity (poises.)	0.0032	0.35	4.85	148	3500

(b) Viscosity of cellulose acetate in benzyl alcohol at 25° C.

Concentration (grams/100 cc.) ..	0	2	10	15	22
Viscosity (poises.)	0.053	0.37	70	550	6500

There does not appear to be any simple relation between the viscosity and the concentration.

The empirical formula proposed by Baker[23] for cellulose nitrate solutions, namely,

$$\eta/\eta o=(1+ac)^k$$

where η is viscosity of sol; ηo is viscosity of medium; c is concentration in grams per 100 cc. and a and k are constants although applicable to cellulose acetate solutions of concentrations below 10 per cent[24] fails over wider ranges.

With the higher concentrations, it was found that there was a steady and regular increase in viscosity with time and in some instances a jelly was formed. This transition from sol to gel[25] indicates an upper limit to the solubility if it be regarded that gelation is a consequence of the saturation concentration having been exceeded[26] and the curve connecting gelation temperature or "setting" point with concentration is analogous to the solubility curve of a crystalloid.

It does not appear possible to determine the solubility of cellulose esters directly, not only because of the high viscosity but also because of the heterogeneous character of cellulose and its derivatives.

By fractional precipitation, cellulose derivatives can be separated into fractions of different viscosity such as with cellulose acetate from acetone solution. (Table 2.)

TABLE 2. *Fractional Precipitation of Cellulose Acetate.*

Fraction	a	b	c	d	e	f	g	h
Percentage weight ..	2.3	10	4.6	26	5	14	25	5
Relative viscosity ...	300	107	100	80	50	34	25	3.8

Fraction "a" gave the highest content of ash.

Clearly, a measure of solubility cannot be accurately made by determining the amount of undissolved material, although usually the best solvents give the clearest solution so that in one sense it is a rough guide in appraising solvents.

A much more useful and accurate method, which is used in industry, is to determine the solvent power number or dilution ratio.[27] A non-solvent such as hexane or water is added to the solution of known concentration and the proportion of diluent required to begin precipitation is noted. The underlying principle of this method is that the better the solvent the greater the amount of non-solvent is required to cause incipient precipitation. Several objections which have been raised against the use of this method have been met by

Davidson and Reid,[28] who claim that the dilution ratio is a reasonably accurate measure of solvent power.

The method of procedure is to add the "non-solvent" e.g. the heptane fraction of petroleum spirit, from a burette, to about 5 cc. of the sol contained in a test-tube and to note when the incipient turbidity persists. The temperature is kept constant, usually at 20° C. A suitable concentration of the sol is 5 grams per 100 cc., this sol not being too viscous. Several minutes of shaking is required after each addition of "non-solvent" in order to dissolve the clot of precipitated cellulose derivative. Towards the end of the determination, a drop is sufficient to cause a faint turbidity throughout the sol, and if this remains, after an interval of two or three minutes, the volume of the non-solvent added is read off.

Larger quantities of benzene and alcohol are required to cause precipitation than petroleum spirit and it would appear that neither benzene, alcohol, water, nor any other lower member of a homologous series can be classified as inert diluents since, as is shown later, under certain conditions they can contribute to the solvent power.

Acetone and other lower molecular weight solvents have in general a greater solvent power number than the higher members of the homologous series,[29] although with esters and the ethers of the glycols, especially in the case of cellulose nitrate, there is a slight departure from the rule. Davidson and Reid [30] point out that as far as the dilution ratios with gasoline are concerned, the normal propyl and butyl ethers of glycol are better solvents of cellulose nitrate than the ethers of lower molecular weight.

McBain, Harvey and Smith conclude from their investigations on the solvents of cellulose nitrate that the fundamental fact operative in the behavior of solvents is the direct combination between solvent and suitable complementary chemical groups in the cellulose derivative. The best solvents are those which most effectively combine with these bonds and, by themselves satisfying the residual affinities, dismember the aggregates. It thus appears on these grounds that the more active and smaller molecular weight solvents would naturally be the best.

Deschiens, Guilleminot and Gault [31] have found that 1 gram of cellulose acetate did not dissolve in 0.5 gram of acetone, but the solution in 1 gram of acetone could be diluted with 0.45 gram of water before precipitation occurred. It would appear from this observation that cellulose acetate has a limited solubility in acetone. A characteristic behavior of many cellulose acetate sols on cooling is the precipitation from them of a gelatinous mass; thus, in nitrobenzene or benzyl alcohol, the cellulose acetate first swells considerably and then, on warming, dissolves to form a clear solution, which becomes opalescent or turbid on cooling with separation of gelatinous clots.

Observations of this transition temperature from solvent to non-solvent afford another method of determining solvent action on the principle that the lower this temperature the better the solvent. The following precipitation or transition temperatures for cellulose acetate given in Table 3 were observed by noting when a 5 per cent sol became opalescent or turbid on cooling:—

TABLE 3. *Precipitation Temperatures.*

Dispersion Medium	Temperature of Precipitation, °C.
Benzyl alcohol	25
Tolyl alcohol	47
Cyclohexanone	—17
Cyclohexanol	95
Phenyl acetate	33

Cyclohexanone can be regarded as a better solvent than benzyl alcohol since its solutions are stable to —17° C., whereas, with benzyl alcohol, they gelate or become opalescent at 25° C. separating into swollen cellulose acetate and a superincumbent liquid of benzyl alcohol containing only a small amount of dispersed material.

It is possible to prepare a solubility curve of cellulose acetate in a liquid by noting *the temperatures of precipitation* with different concentration sols. Some results are given in Table 4:—

Table 4. *Solubility of Cellulose Derivatives—Method of Precipitation by Cooling.*

(a) Cellulose Acetate in Benzyl Alcohol		(b) Cellulose nitroacetate in Benzyl Alcohol		(c) Cellulose Acetate in Benzyl Acetate	
Concentration	Temperature	Concentration	Temperature	Concentration	Temperature
%	°C.	%	°C.	%	°C.
0.05	14	0.25	89	0.05	35
0.1	16	0.5	92	0.1	39
0.25	19	1.0	100	0.25	42
0.5	20	2.5	106	0.5	48
1	21	5	106	0.75	50
2	21.5	12.5	109	1.0	51.5
5	22			2.0	52.5
				4.0	54

When a solution of cellulose acetate in benzyl alcohol is placed in a thermostat at about 25° C., it slowly sets to a clear jelly and the changes can be followed by measurements of viscosity, elasticity and volume, etc. The falling sphere viscometer is suitable for following the viscosity changes with time until no movement of the sphere is discernible. Thus, with sols of concentration, 7 grams/100 cc. and 10 grams/100 cc. respectively at 25° C., the following results were obtained. (Table 5.)

Table 5. *Increase of Viscosity with Time During Gelation of Sols of Cellulose Acetate in Benzyl Alcohol at 25°C.*

(a) Concentration 7 Grams/100 cc. Original Viscosity $\eta_o = 14.8$				(b) Concentration 10 Grams/100 cc. Original Viscosity $\eta_o = 70$			
Time Interval		η	Log $(\eta - \eta_o)$	Time Interval		η	Log $(\eta - \eta_o)$
Hrs.	Min.			Hrs.	Min.		
0	15	19.6	0.68	0	10	70	—
0	30	21.3	0.81	0	25	83	1.11
1	0	21.3	0.81	0	45	90	1.30
2	0	29.4	1.16	1	25	108	1.58
3	30	33.6	1.27	2	5	133	1.8
5	15	91	1.88	2	55	149	1.9
5	45	126	2.05	4	5	207	2.14
7	30	210	2.29	6	20	707	2.8
9	30	560	2.74	7	5	2307	3.35
10	20	700	2.84				

When the value log $(\eta - \eta o)$ is plotted against the time interval a straight line is obtained; this can be expressed by the empirical equation,

$$\eta - \eta o = a\ e^{kt}$$

where k is rate of gelation, t time and a is a constant. Now, if the sols are allowed to gelate at another temperature the rate of gelation is different and another value for k can be determined experimentally. The following values were obtained for k (table 6) at different temperatures:—

TABLE 6. *Rate of Gelation at Different Temperatures.*

(a) Concentration 7 Grams/100 cc.		(b) Concentration 10 Grams/100 cc.	
Temperature, °C.	$k \times 10^4$	Temperature, °C.	$k \times 10^4$
25.6	0.48	25	1.78
25	1.45	24.3	4.3
24.3	3.9	23.3	13.5
23.75	7.7	22.3	34.6
22.8	38.6	21.3	53.3

At the higher temperatures, the rate of gelation becomes small and above a certain temperature referred to as the maximum gelation temperature no apparent change occurs. The curve relating the maximum gelation temperature and concentration is analogous to a solubility curve since gelation is a consequence of condensation or separation of the dispersed cellulose ester from solution.

At a temperature below 12° C. benzyl alcohol practically ceases to be a solvent of cellulose acetate, whilst intermediately to the maximum gelation temperature only a portion is dissolved and the remainder aggregated in the gel structure. Aggregation is a kinetic process with regard to time, and its rate must depend on the collision frequency and be in accord with the aggregation formula, established upon the fundamental Einstein-Smoluchowski expression for Brownian movement. The relative number of aggregating particles can be obtained both from the solubility data and from elasticity data since the modulus of elasticity of the gels is a known function of the numbers of particles aggregated in the structure.[32]

TABLE 7. *Proportion of Cellulose Acetate Aggregated in Gel Structure at Different Temperatures.*

(Concentration 15 grams/100 cc.)

Temperature °C.	Relative Modulus of Rigidity of Gel	Percentage of Cellulose Acetate Aggregated in Gel Structure		
		Calculated from Rigidity	Calculated from Solubility	Average
12	250	99.9	99.9	99.9
20	70	96	96	96
22.5	28	85	87	86
25	12	72	67	70
27.5	3	50	33	42
30	0.75	41	13	27
31	0.25	19	About 7	13

It is interesting to compare the rate of gelation at different temperatures with the proportion of condensed material, relative distance between the particles and the viscosity of the medium. The data is given in Table 8.

TABLE 8. *Conditions of Aggregation.*

Temperature °C.	Proportion of Cellulose Acetate Aggregating	Viscosity of Medium	Relative Distance Between Particles	Rate of Gelation *k*
20	96	0.06	0.19	Very high
22.5	86	0.11	0.2	400 × 10-4
25	70	0.98	0.28	60 "
27.5	42	19.2	0.33	11.8
30	27	63	0.45	1.1
31	13	135	0.66	About 0.3

It might be argued that with clear, fine-textured jellies, the whole system is homogeneous (one phased) in the sense that both constituents are within the range of molecular attraction.

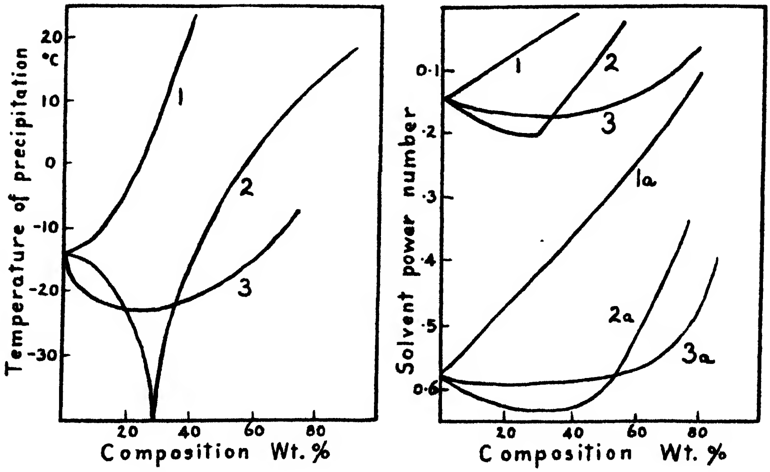
Against this view must be placed the experimental finding that there is a volume and refractive index change in the system during a short time preceding the slow jelly formation, indicating that condensation has occurred although the system remains clear.

The view has been expressed that cellulose derivatives and their solvents are miscible in all proportions since, if the cellulose derivative is in predominance, it absorbs the liquid, forming a gel, whilst with excess of solvent the derivative is dispersed spontaneously. The view that solubility is infinite swelling cannot be entertained in the light of modern researches, neither can absorption with gel formation be regarded as solution any more than the hydration of anhydrous copper sulfate into blue copper sulfate crystals be regarded as ordinary solution.

The changes in volume and refractive index associated with the solution of cellulose derivatives in organic solvents are much smaller than those for the formation of hydrosols of gelatin: the changes are usually greatest with the best solvents and with the less concentrated sols.[33] Also, the best solvents usually yield sols of relatively low viscosity and this behavior affords another method of appraising solvents. Thus, Baker [34] found that the observed values for the viscosity of cellulose nitrate solutions were qualitatively in agreement with the view that the better the solvent the less the viscosity. More recently, McBain, Harvey and Smith [35] have carried out investigations to test the theory that comparative fluidity is a criterion of solvent power. They concluded that the viscosity of the solutions of one definite sample of nitro cotton in various solvents under definite conditions is inversely proportional to their solvent power. The close correlation of solvent power with the physical properties of the sols is best seen with binary mixtures of liquids discussed later. A simple explanation of the observed phenomena is that with the best solvents there is a very high degree of dispersion so that there is an approach to ordinary solution, with the characteristic low viscosity and high stability.

In Figs. 3 and 4 are shown the increased solvent action of cellulose esters in some mixed solvents and the effect of adding so-called diluents, such as benzene, alcohol, etc., on the solvent action of acetone. In the industrial preparation of cellulose varnishes, benzene and industrial spirit are used in large quantities in conjunction with acetone and amyl acetate or butyl acetate.

The explanation of the high dispersing action of mixed liquids must be sought in the cause of the increased swelling; also the specific characters of the liquids and colloidal substances are evidently of primary importance. Cellulose nitrate in an ether-alcohol mixture probably attaches to its particles both kinds of molecules from the dispersion medium, and these attracted molecules may bind additional ones. Esselen,[36] discussing the characteristic solvent action of mixtures of chloroform and alcohol on cellulose acetate, puts forward a possible explanation based on the fact that cellulose and its compounds have marked affinities for the hydroxyl group of alcohol. Mixtures of liquids containing as one constituent a substance with reactive groups, such as an alcohol, ketone, or acid, especially if this constituent is the first member of a homologous series, usually have markedly high solvent action. A liquid, such as hexane or xylene, which is not particularly reactive and is a high member of a homologous series, behaves like a diluent or inert component in a binary mixture.



The solvent action of cellulose esters in mixed liquids.

FIG. 3.—Binary mixtures of cyclohexane and cellulose acetate with
1. ethyl alcohol
2. benzyl alcohol
3. methyl ethyl ketone

FIG. 4.—Binary mixtures of acetone, cellulose acetate (curves 1, 2, and 3) and nitrate (curves 1a, 2a, and 3a) with
1 and 1a. benzene
2 and 2a. ethyl alcohol
3 and 3a. equal volumes of benzene and ethyl alcohol.

The effect of the addition of a colloidal substance on the viscosity of a binary mixture of liquids is, in general, such that the shape of the viscosity-composition curve becomes exaggerated and any special feature of it is developed.[37] These effects are produced when cellulose nitrate is added to ether-alcohol mixtures. The sag in the viscosity curve for the pure liquids is exaggerated and, for the sols of higher concentration, there is a minimum point, which occurs at a composition near that of the optimum solvent mixture.

From the differences in density between the dispersion medium and the sols, it was found that the greatest volume changes occur when the compositions of the mixed liquids are near that corresponding to the maximum sag in the viscosity curve and when the solvent power of the mixed liquids is high.

McBain and co-workers[38] report from their viscosity measurements that the evidence is overwhelming: that in almost all cases a mixture of solvents in suitable proportions has greater solvent power than that of the mean of the two solvents, and they quote a large number of non-solvents of cellulose nitrate which form a solvent mixture when taken together. They suggest that the explanation lies in the direction of assuming that certain molecular groupings in each substance have a specific power of combining with definite groupings in the cellulose nitrate complex, differing from substance to substance.

Highfield[39] in a study of the solvent action of ether-alcohol mixtures on cellulose nitrate concluded that the best solvent mixtures contain polar and non-polar groupings balanced in optimum proportions.

With some solvents it is possible to find diminished solvent action on mixing,[40] e.g. with aniline and acetic acid or acetone and phenol for cellulose acetate. This effect is due to complex formation between the different molecules of the mixture, a part of their attraction for the cellulose derivative being lessened in proportion to the amount of complex formed. In general, any change which tends to increase the molecular complexity of the dispersion medium causes a decrease in solvent action, and therefore when compound formation occurs between the components of a binary mixture loss of solvent power is to be expected. In cases where mixtures containing molecular complexes are good solvents, the effect of the complex formation is masked by that due to the molecular dissociation of the liquids.

The attraction between the cellulose derivative and the molecules of the mixed dispersion medium, due to the presence of mutually reactive groups, appears to reach a maximum with certain combinations of liquids, because of the special spatial arrangement and interlocking of the various molecules in the complex with the cellulose derivative.

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Smokeless Powder.*[1]

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All modern military smokeless powders are colloids of nitrocellulose.[2] They vary in composition from a simple colloid prepared with a volatile solvent to colloids containing both nitrocellulose and nitroglycerin and more complex mixtures with or without nitroglycerin, in which are incorporated materials which serve as stabilizers, flash reducing agents, non-volatile colloiding agents, etc.

The change from black powder, which had for centuries been universally used as a propellant explosive in firearms, to colloidal smokeless powders was necessitated not only by the objections to the obscuring smoke clouds produced by black powder, but by the rapid strides which were made in the improvement of both small arms and artillery. The development of rifled guns and rapid fire guns caused a demand for increased propellant energy without corresponding increase in the capacity of the powder chamber of the gun or in the size and weight of the ammunition. The high concentration of energy in guncotton appeared to offer promise, but attempts to use fibrous guncotton resulted in failure because this energy was liberated so suddenly by the rapidly burning charge that the gun was burst before the inertia of the projectile could be overcome. Efforts to control the rate of liberation of this energy by compressing the finely pulped guncotton into masses of greater density were without success, and it was not until Vielle in France in about 1886 demonstrated that the rate of burning of nitrocellulose could be controlled by forming it into dense colloidal grains, that the way was paved for the development of satisfactory smokeless powders.

The smokeless powder used by the Army and Navy of the United States for both cannon and small arms is an ether-alcohol colloid of nitrocellulose containing approximately 12.60 per cent N. The particular grade of nitrocellulose used, known as "pyrocellulose," "pyrocotton," or "pyro, is almost completely soluble in a mixture of 2 volumes of ethyl ether to 1 volume of ethyl alcohol. Different grades of nitrocellulose are used in the smokeless powders of certain other countries. Thus, the French Poudre B (named after General Boulanger) is an ether-alcohol colloid of nitrocellulose of about 12 per cent N, in which is incorporated a large proportion of insoluble nitrocellulose containing about 13.40 per cent N; British Cordite is a mixture of nitrocellulose of about 13.0 per cent N with nitroglycerin, colloided with the aid of acetone; Italian Ballistite contains nitrocellulose of 12 per cent N, together with nitroglycerin.

It is the object of this paper to discuss from the manufacturing standpoint some of the factors which exert an influence on the colloidal properties of

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the types of nitrocellulose used in the manufacture of smokeless powders, and to indicate the possibilities in the use of new colloidal mixtures for this purpose. No attempt will be made to consider the theoretical side of the subject, and details of the manufacturing process will be omitted, as they may be found in numerous textbooks and published articles.

NITROCELLULOSE—MANUFACTURE.

Nitrocellulose containing about 13.0 to 13.4 per cent of nitrogen, and practically insoluble in ether-alcohol (2:1) is generally known as guncotton, although this term is often improperly used to cover all varieties of nitrocellulose. The term pyrocellulose applies to the product between 12.50 and 12.70 per cent nitrogen, soluble in ether-alcohol; while the terms soluble cotton or collodion cotton are usually applied to products with 12.0 per cent or less of nitrogen. Nitrocellulose of appreciably lower nitrogen content than 12.0 per cent is not used in military powders, but enters into the composition of some of the pyroxylin plastics, lacquers, blasting gelatin, etc.

Raw Materials.

Nitrocellulose is usually manufactured, in the United States, from purified cotton linters. Frequently the linters is mixed with the still shorter hull fiber obtained from the cotton seeds after the long fiber cotton and linters have been removed. The use of purified wood pulp as a substitute for all or part of the cotton has been demonstrated to be entirely feasible. Beyond doubt practically all of Germany's production of nitrocellulose for smokeless powder during the World War was from wood pulp.

The cotton is first freed from oils and other impurities by digestion under pressure with dilute caustic soda solution. After washing it is next given a mild treatment with bleaching solution, again thoroughly washed, and dried at about 100° C. to a moisture content of about 1.0 per cent. Weiszenberger[3] states that any influence which increases the colloidal characteristics of the cellulose adversely affects the homogeneity of the nitrocellulose; hence digestion of the cellulose at excessive temperatures and pressures, and drying at too high a temperature should be avoided. The use of excessive amounts of alkali or of bleaching powder, especially at excessive temperatures and pressure, causes the formation of oxy- and hydrocellulose,[4] resulting in increased solubility of the nitrated product with lower viscosity of its solutions, and in the formation of unstable materials which add to the difficulty of purification of the nitrocellulose.

Nitration.

Weighed charges of the dried cellulose are nitrated by immersion in a mixture of strong nitric and sulfuric acids. Numerous types of nitrating apparatus are used in different factories, and the method of procedure varied according to the grade of nitrocellulose desired. The process may vary as regards composition of nitrating bath, ratio of cotton to acid, temperature of acid and time of immersion of the cotton. Since water is liberated by the reaction of the nitric acid on the cotton, it is obvious that efficient agitation of the mixture is an important factor in increasing the uniformity of the nitrated product. This principle applies in general to all reactions between any two materials and particularly to substances so widely differing in physical structure as cotton and acid.

The principal properties of the nitrated product which depend upon definite conditions of nitrating are nitrogen content, solubility and viscosity.

Chandelon has shown[5] that other conditions being constant, increasing the HNO_3 content of the mixed acid causes an increase in the viscosity of the nitrocellulose. Leysieffer[6] found that by increasing the time of nitration decreased viscosity resulted. Increase in temperature of the mixed acid beyond proper limits causes the formation of oxidation products which render the nitrated product difficult to stabilize and lower its viscosity. It is beyond the scope of this article to discuss the numerous theories that have been proposed regarding the nitration of cellulose or the effects of the variations in procedure on the properties of the various types of nitrocellulose. In products intended for use in the manufacture of lacquers, artificial leather, etc., solubility and viscosity are naturally of much greater importance than in the nitrocellulose used in the manufacture of smokeless powder, although it must be remembered that the consistency of the smokeless powder colloid, the facility with which it is mixed and pressed through dies, the shrinkage of the grains in the drying process, etc., depend largely on solubility and viscosity, and that these factors must be kept constant if a uniform powder is to be obtained.

Nitrated Cellulose a Complex System.

It is generally admitted that the nitration of cellulose invariably produces a mixture of nitric esters, although much difference of opinion exists as to the propriety of the arguments offered in support of this theory. Duclaux and Wollman[7] have shown that by fractional precipitation with water a solution of a sample of nitrocellulose in acetone may be separated into a number of fractions, each having a different degree of viscosity but practically the same nitrogen content. Breguet,[8] however, states that there is a recoupling of the colloidal particles when they are thrown out of solution by water. Koehler and Marqueyrol,[9] as well as McBain,[10] have also claimed that there is a change in the properties of nitrocellulose on precipitation from solution.

Various investigators have claimed that the variation in color observed when nitrocellulose is examined under the polarization microscope indicates different degrees of nitration in individual fibers.[11] Phillips[12] takes strong exception to such a conclusion and states that "The colors shown by nitrocelluloses of varying degree of nitrogen, in polarized light, are a function of the dispersion of the nitrocellulose." Also, Tissot[13] states that the colors do not depend solely on the nitrogen content of the nitrocellulose but appear to be linked with the composition of the nitrating bath.

Extraction with various solvents may remove from a sample of nitrated cellulose portions of the product with different nitrogen contents,[14] and varying widely in other properties; e.g., extraction of highly nitrated guncotton with pure ethyl alcohol removes a small fraction containing approximately 10 per cent nitrogen, while further extraction with a mixture of ether and alcohol dissolves a portion containing 12 per cent or more of nitrogen, the residue having a nitrogen content of about 13.0 to 13.4 per cent. There is, furthermore, no doubt that even in the most carefully prepared nitrocellulose the presence of unnitrated fibers can be demonstrated.[15]

Brunswig[16] dissolved a nitrocellulose containing 12.25 per cent nitrogen in acetone and precipitated it in three fractions by successive additions of water. These fractions had nitrogen contents of 12.43, 12.28 and 11.92 per cent, respectively. He states that the existence of a heterogeneous chemical equilibrium between product and nitrating acid is shown by the fact that products of the same chemical and physical characteristics (per cent N, solubility, hygroscopicity, etc.) result from either nitration or denitration under appropriate conditions.

Weiszenberger[17] regards nitrated cellulose as a disperse system in which exist various nitric esters, unaltered cellulose, oxy- and hydrocellulose nitrates, sulfuric esters and mixed esters. Complexes of varying composition may exist in different parts of the mass, and free acids may be held in such complexes by the formation of adsorption compounds.[18]

In opposition to these well-founded ideas as to the nature of nitrocellulose, Herzog and von Naray-Szabó[19] concluded from X-ray studies that the various cellulose nitrates are in reality mixtures of cellulose trinitrate (guncotton) and unchanged cellulose.

While it is probably possible, by proper care in the purification of the cellulose used for nitrating and proper control of the nitrating process, to obtain a product in which an individual cellulose nitrate predominates, there is no good reason to believe that a homogeneous nitration product composed of a single individual nitrate of cellulose can be obtained.

Preliminary Purification.

After the nitration of the cellulose is complete, the acid, now known as "spent acid," is removed as much as possible by means of a centrifuge and the nitrated product transferred to a large volume of cold water in which it is quickly immersed or "drowned" in order to avoid local heating. Such heating would cause denitration, as is evidenced by evolution of brown nitrous fumes, and would also lower the viscosity of the product. The nitrocellulose, from which the major part of the free acid is thus removed, is now transferred to boiling tubs and boiled for a long time with several changes of water, the mass being heated by the injection of live steam from beneath a perforated false bottom in the tub. The purpose of this boiling is to hydrolyze and thus remove the unstable esters, probably products of low nitrogen content, and sulfuric esters. No alkali is used in these boilings, the water being allowed to remain slightly acid, since it has been found that acid hydrolysis has less effect on the stable nitrocellulose than has alkaline hydrolysis. The time of this so-called preliminary boiling is usually at least 40 hours for nitrocellulose intended for use in smokeless powders. Because of the fact that long boiling is well known to materially lower the viscosity of nitrocellulose, products which are intended for use in the manufacture of blasting gelatin, gelatin dynamites, pyroxylin plastics, lacquers, artificial leather, etc., are given little or no boiling treatment in their purification. In some materials high viscosity is considered of greater importance than careful stabilization. When low viscosity is required, special treatment is given.

Pulping.

The nitrocellulose is next pulped for the purpose of facilitating the removal of the last traces of free acid from the cellular fibers and increasing the uniformity of the product. This operation is usually carried out in either the Jordan engine or the Hollander beater, in either of which the nitrocellulose in water suspension is forced to pass between two metal surfaces, one of which moves, with relation to the other, and between which there is a clearance of only about 0.0001 inch. The general effect of the Jordan engine is to cut the fibers into shorter lengths, whereas the Hollander combines a shearing effect with a brushing or bruising treatment of the fibers. Other types of machines, especially the Colloid Mill and the Rod Mill, have recently been experimented with and found to offer considerable promise.

The pulping process is entirely mechanical and produces no change in the chemical characteristics of the nitrocellulose. Traces of acid liberated during this process are neutralized and removed partly by washing in the pulper and partly in the subsequent purification process. Undoubtedly some traces of acidity are left, held by adsorption within the cellular fibers. Any improvement in the pulping process which would more completely open up the fibers and permit the complete elimination of free acid would no doubt greatly improve the stability of the finished product.

It has been claimed by some manufacturers that too great a degree of fineness of pulping of the nitrocellulose renders the colloided powder more brittle. As the fibrous structure of the nitrocellulose is largely destroyed in the colloiding operation, it would appear that there is little foundation for such claim.

Final Purification.

The final purification or "poaching" treatment consists in boiling the nitrocellulose with live steam, first with water made slightly alkaline with sodium carbonate, then with pure water. The total time of boiling is usually 12 hours with 6 changes of water. Finally the product is given at least 10 cold water washings. Mechanical agitation in the poachers is provided. Additional boilings and washings are given if the material fails to pass prescribed tests for stability. The alkaline boiling is intended to neutralize all free acid and hydrolyze unstable esters that have not been removed by acid hydrolysis in the preliminary boiling, while the subsequent boilings and washings are for the purpose of removing all alkali and other soluble impurities. The purified nitrocellulose is next freed from the final wash water by means of centrifugal wringers, the centrifuged pulp retaining about 25 to 30 per cent of water.

MANUFACTURE OF SMOKELESS POWDER.

Pyrocellulose Powders.

While the general methods of manufacture and purification of nitrocellulose described above apply with certain modifications to all grades of nitrocellulose used in various military smokeless powders, the subsequent operations involved in the manufacture of the powder vary with the type of powder to be produced. The processes involved in the manufacture of the pyrocellulose powder used by the United States Army and Navy, by Russia and certain smaller countries, are (1) dehydration, (2) mixing, (3) graining, (4) drying.

Dehydrating.—The 25 to 30 per cent of water left in the nitrocellulose by the centrifugal wringers must be removed before the nitrocellulose is colloided with ether and alcohol. Because of the dangers involved in actually drying nitrocellulose in warm air dryhouses, the method used consists in extracting the water with alcohol in a suitable press called a dehydrating press. This method has the advantage that it leaves the pyro wet with the alcohol necessary in the subsequent colloiding process. The pyro from the wringers is pressed in the form of a block in the press, and alcohol (95 per cent ethyl alcohol) forced through this block by means of compressed air, thereby displacing the water. The diluted alcohol is recovered and rectified by distillation. Final pressure is applied to the block so that the pyro is left with as nearly as possible the proper proportion of alcohol required in the mixing process.

It is well known that the addition of sufficient water to a solution of nitrocellulose in ether and alcohol precipitates the nitrocellulose from its solution. Similarly, the gelatinization of nitrocellulose by ether-alcohol is hindered by the presence of more than an allowable content of water, therefore the alcohol used is generally required to be at least 95 per cent (by volume), and the water in the pyro must be practically entirely displaced by this alcohol. The presence of excessive water in the colloid is indicated by a peculiar milky appearance of the finished powder grains. Besides interfering with the proper colloiding of the nitrocellulose, it is probable that a portion of the water from the alcohol may be retained in the interior of the dried powder grain and tend to develop porosity and instability.

The dehydration process may also be regarded as a supplemental purification process in that it effects the removal of a certain amount of nitric esters of low nitrogen content which are soluble in alcohol. Evaporation of the spent alcohol in the rectification process always leaves a colloidal residue of incompletely nitrated cellulose containing about 9.5 per cent nitrogen, which is of much lower stability than the finished pyro. The dehydrated pyro is therefore of increased homogeneity and stability.

The removal of lower nitrates by extraction is illustrated by experiments conducted by the writer in which samples of nitrocellulose of different nitrogen content were extracted with 95 per cent alcohol in order to remove all soluble material. The amounts soluble were as follows:

Sample	N of Sample Per Cent	Soluble Material Per Cent
1	11.85	15.50
2	12.48	5.37
3	12.50	4.32
4	12.54	4.05
5	12.60	1.48

It is apparent that dehydration with alcohol will therefore tend to increase the nitrogen content of the pyro. The stabilizing effect of the treatment was shown by extracting all soluble material from an unstable sample of pyro with 95 per cent alcohol. The original KI-starch paper heat test of 6 minutes was increased to 30 minutes. The amount of alcohol used in dehydration should be at least equal in weight to the dry weight of the pyro in the charge.

Mixing and Colloiding.—The blocks of alcohol-wet pyro from the dehydrating press are usually put through a so-called "block breaker" in order to obtain a uniform mixture, and this material charged into the mixer together with the proper amount of ether. A small amount of diphenylamine which is to serve as a "stabilizer" in the finished powder is previously dissolved in the ether. The mixers ordinarily employed are of the common type of dough mixer and are usually provided with a cooling jacket in order to minimize loss of ether and promote gelatinization, it being well known that the solubility of nitrocellulose in ether-alcohol increases as the temperature is decreased.

The charge for the usual type of mixer is approximately 100 lbs. of finished product. The total amount of solvent (combined alcohol and ether) used in mixing varies somewhat according to existing conditions—atmospheric temperature, nature of the nitrocellulose, size of powder grain to be manufactured, etc. It is usually approximately equal in weight to the dry weight of nitrocellulose in the mixer charge. Not less than 64 per cent of this total solvent should be ether.

The mixing is continued until the solvent is uniformly distributed throughout the mass, usually about one-half to three-quarters of an hour. At the end of this mixing the material is by no means gelatinous, because of the limited amount of solvent used, and its colloidal nature is apparent only on applying pressure, as by pressing a small portion between the thumb and finger. It is transferred to a blocking press when pressure of 1,000 lbs. or more per square inch converts it into a partially colloided block of more or less translucent appearance. This block is usually placed in a strainer press and forced through a perforated brass plate at a pressure of about 3,000 lbs. per square inch. The strands issuing from this press are quite flexible and plastic, the mass having been formed into a good colloid by the effect of the pressure. These strands are reformed into a solid block by another pressing and this block is ready for charging to the graining press.

An effort is being made to reduce the number and time of the operations at present involved in mixing the dehydrated nitrocellulose with the solvent and forming a colloided mass. With this object in view, a study is being made of the application of proper kneading and mixing machines which are being used in the rubber industry. These mixers have a special form of broad blades which force the material against the walls of the mixing trough under great pressure. It is also provided with a weighted piston-like lid which rides upon the mass being mixed. Under these conditions more than a mere mixing of the nitrocellulose and solvent is accomplished. Within as short a time as 15 minutes a clear colloided mass, apparently free from fibrous structure, is produced, requiring only a final blocking before it is transferred to the graining press. In the event that a mixer of this type is found to have a practical application in the manufacture of smokeless powder, it is expected that it will replace not only the present type of mixer, but also the preliminary blocking press and the "macaroni" press or straining press.

Graining.—The usual form of grain of smokeless cannon powders manufactured in the United States is a cylinder of length about 2½ times its diameter, provided with 7 longitudinal perforations, six of which are arranged symmetrically about the center one. Rifle powders are usually made in the form of single perforated cylindrical grains. The reason for a perforated grain is that it affords a greater burning surface, since combustion takes place on the surface of the perforations as well as on the outer surface of the grains, the colloid burning in parallel layers. The above number of perforations is selected so as to afford an *increasing* burning surface as the grain burns, this condition giving a higher velocity to the projectile. The size of the grain, or more particularly its minimum dimension,—the thickness of the "web,"—is regulated to suit the gun in which the powder is to be used. Thus, caliber 0.30 rifle powder averages approximately 350,000 grains per pound, as compared with only about 15 for powder for a 16-inch gun, the corresponding burning surfaces per pound of powder being respectively about 4,000 square inches and 150 square inches.

The blocks of colloid referred to above are granulated by forcing the colloid through one or more dies in a suitable press, the pressure on the block varying from about 2,500 to 3,000 pounds per square inch, or more, depending on the size and proportions of the die and the stiffness of the colloid. Usually the dies are kept cool by means of water jackets. The colloid issues from the dies in the form of perforated strands, which are fed to mechanical cutters adjusted to give the desired length of cut

Drying.—The "green" powder grains obtained from the cutters are first subjected to a preliminary drying process in which a large part of the solvent (ether and alcohol) is recovered and subsequently rectified for further use. An additional amount, which cannot economically be recovered, is then removed by one of several drying processes. The methods that have been employed in drying nitrocellulose powders are (1) air-drying, (2) water-drying, and (3) alcohol-drying.

In the air-drying method the closed circuit or "dead-air" system is generally employed, the maximum temperature allowed being about 45° C. If the powder is placed in an open current of fresh warm air, the rapid removal of solvent from the surface of the grains causes the formation of a hard "skin" which greatly retards the escape of solvent from the interior of the grains. The time required to reduce the amount of solvent to the desired percentage is therefore greatly reduced by a closed circuit, in which the air coming in contact with the powder contains sufficient solvent vapors to prevent too rapid drying of the surface of the grains. The powder is placed in the dryhouse in large bins with perforated bottoms. From a few weeks to several months, depending on the size of the grains, is necessary for drying powder by the usual air method. The amount of solvent left in the grains varies from approximately 1.5 per cent in small granulations to as much as 7 per cent in powder for the 16-inch gun. The allowable amount depends on the average web thickness of the grain, and is fixed at such a figure that further loss will not take place under storage conditions. The ballistics of the powder are, of course, affected by the content of solvent and moisture, and after the proper charge for the gun is determined by firing tests, and charges assembled and issued to the service, proper precautions must be taken to keep these factors constant. It is not practicable to reduce the content of solvent below a definite amount because continued drying would be injurious to the stability of the powder and would tend to render the colloid brittle. The finished grains are tough and hard and can be cut with a knife only with difficulty. It is required that sections cut from the grains, having length equal to diameter of grain, may be compressed between parallel surfaces until the length has been reduced an average of not less than 35 per cent without the appearance of cracks.

In the water-drying process, the major part of the solvent remaining after the recovery process is removed by soaking the grains in water. The powder is placed in large wooden tanks through which the warm water, at a temperature of 40° to 50° C., is circulated. By this method, the solvent is removed much more quickly than in the air method,—from a few days to about two weeks,—and the subsequent removal of the water by drying in warm air requires only a few days.

The water treatment undoubtedly has, however, a marked influence on the colloid. The grains lose their translucence and assume a "muddy" lighter color, and their brittleness is appreciably increased. There is every reason to believe that water-dried powder is more porous than air-dried powder, and that it will therefore lose its residual solvent more readily and develop a condition of instability more quickly. Water drying of powder is therefore undesirable except in an emergency when time is an important factor. A "continuous water drier" was developed and constructed at one of the largest War plants in 1918, which was capable of drying to the proper moisture and solvent content as much as 100,000 lbs. of 75 mm. powder in 24 hours.

The alcohol-drying process was developed and used to a limited extent during the World War. It combines the solvent recovery and drying treatments, the "green" powder from the cutter being immersed directly in dilute alcohol of the proper strength, which absorbs the excess solvent from the grains in such manner that it can be recovered. The alcohol treatment is followed by water treatment and final air drying.

After removal from the dryhouses, the powder is made up into blends of 50,000 to 100,000 lbs. each, in large blending towers, in order to minimize the unavoidable variations in nitrogen content, solubility, viscosity, stability, etc., of the product and ensure that each charge for the gun will give as nearly as practicable the same ballistic results.

The blended lot is packed for storage in hermetically sealed metal-lined boxes or metal tanks until it is to be made up into charges for ammunition.

French "Poudre B."

The smokeless powder used by the French Government, designated as Poudre B, although also a nitrocellulose powder, differs from the pyrocellulose powder of the United States in that it is prepared from a mixture of two different grades of nitrocellulose rather than from one grade of as nearly as possible a uniform nitrogen content. It contains about 60 per cent of nitrocellulose known as CP_1 (coton poudre 1), which is ordinary guncotton having a nitrogen content of about 13.2 per cent, and about 40 per cent of nitrocellulose known as CP_2, which has a nitrogen content of approximately 12 per cent. The CP_1 is practically insoluble and the CP_2 soluble in a mixture of ether and alcohol. The two grades are prepared separately by suitable modifications of the process already described, and mixed in the desired proportion.

The nitrocellulose is dehydrated and incorporated in mixers with ether and alcohol together with diphenylamine (usually 2 per cent) as a stabilizer, and the mixture of colloided and uncolloided nitrocellulose pressed through dies in the form of flat strips of desired thickness, which are cut into strip grains of suitable length. For use in small arms the strips are usually cut into small square flakes. The French powder is dried by the water-drying process discussed above.

It is important to note that Poudre B is not a completely colloided powder, but that it contains a large part of its nitrocellulose, (the CP_1) mechanically incorporated in the colloidal material (CP_2).

Russian Pyrocellulose Powder.

Mention has already been made of the fact that Russian smokeless powder is similar to the pyrocellulose powder used by the United States. This type of powder was originally developed by Mendeléeff, in 1890. At present the Russian powder is made in the strip form of grain.

British "Cordite."

The service powder of Great Britain, known as Cordite from the fact that it is granulated in the form of cord-like strands of usually the full length of the cartridge case or powder chamber of the gun, is essentially a colloided mixture of nitrocellulose and nitroglycerin. Because of the fact that it contains both of these explosives it is classed as a "double base" powder, as distinguished from the nitrocellulose "single base" class which includes pyro powder and Poudre B. This powder was developed by the British Government and adopted as their service propellant in 1889. The nitrocellulose used is ordinary guncotton, with a nitrogen content of about 13 per cent or more, usually at least 85 per cent insoluble in a mixture of ether and alcohol. Cordite originally contained 58 per cent nitroglycerin, 37 per cent guncotton and 5 per cent vaseline or mineral jelly, the mixture being made into a uniform colloidal paste by the assistance of acetone as a solvent. This "dough" is pressed through dies in the form of solid strands or cords of varying diameter, which are wound in coils or cut in suitable length and dried for several weeks or months to eliminate the solvent. The colloid is much softer and more pliable than pyrocellulose powder because of the large content of nitroglycerin.

Cordite of the above composition had the disadvantage that it caused excessive erosion of gun barrels owing to its high temperature of combustion. There was also a tendency for the nitroglycerin to exude, especially when the powder was stored in a warm place. The original Cordite was therefore displaced by M.D. Cordite, which contained 30 per cent nitroglycerin, 65 per cent guncotton and 5 per cent vaseline. This type of Cordite is still used by the British service. The vaseline was originally added to reduce erosion. It probably accomplishes this to a considerable extent, not by any lubricating effect, but by lowering the temperature of combustion of the explosive mixture. Another very important part played by the vaseline in Cordite is its action as a stabilizer. It is assumed that unsaturated hydrocarbons in the vaseline absorb the oxides of nitrogen liberated by decomposition of the nitroglycerin or nitrocellulose and thus prevent or retard further decomposition. An entirely analogous rôle is played by the diphenylamine used as a stabilizer in other smokeless powders.

A modification of Cordite, known as "R.D.B. Cordite," was used extensively during the World War. This was made from a nitrocellulose containing only about 12.2 per cent nitrogen, together with the usual admixture of nitroglycerin, the nitrocellulose being colloided by means of ether and alcohol instead of acetone. This modification was presumably made necessary by the scarcity of acetone. In this powder the nitroglycerin does not play a part in the colloiding of the nitrocellulose, this effect being accomplished by the ether-alcohol. Gibson and McCall[20] found that the addition of nitroglycerin to an ether-alcohol solution of the nitrocellulose did not affect the solubility, but tended to increase rather than decrease the viscosity of the solution.

There has been much controversy as to the relative merits of the double base nitroglycerin powders represented by Cordite, and the single base nitrocellulose powders such as United States pyro powder and Poudre B. Cordite undoubtedly produces a higher temperature with greater erosion of the gun barrel; but, on the other hand, it has the advantage of being practically nonhygroscopic, and owing to its higher energy content a smaller charge can be used to produce a required velocity in a given gun.

Italian Ballistite.

This type of powder used by the Italian service is also of the double base or nitroglycerin type, but differs from Cordite in that it contains nitrocellulose soluble in ether-alcohol instead of high nitration guncotton. This soluble nitrocellulose contains only about 12 per cent nitrogen, and in addition to being soluble in ether-alcohol is soluble in nitroglycerin. The proportions of nitroglycerin and nitrocellulose are usually about 40 per cent and 60 per cent, respectively. Less than 1 per cent of diphenylamine is also added as a stabilizer. The ingredients are mixed in an excess of hot water, the whole being thoroughly agitated by means of compressed air jets. The resulting mixture is freed from most of the water and colloided by rolling between large heated iron rolls at a temperature of about 60° C., the remaining water being evaporated by the heat from the rolls. By means of repeated rollings the material is formed into plastic translucent sheets of colloid, which are finally cut up into strips or square flakes, the dimensions of these grains varying with the gun for which they are intended. Ballistite powder of the same general type as that used by the Italian Government is largely employed in sporting rifle ammunition.

The method of mixing the nitroglycerin and nitrocellulose under water offers marked advantages over the process generally employed in the manufacture of blasting gelatin in which the nitrocellulose is dried and then incorporated with the nitroglycerin in mechanical mixers provided with warm water jackets. The mixture, under the influence of the heat, forms a clear plastic colloid. By mixing under water the dangerous drying of the nitrocellulose is avoided, as well as the obvious dangers of mechanically mixing the two components in a heated mixer.

There is, of course, some danger of ignition of the colloid during the rolling process, but this is chiefly a fire hazard, as the unconfined powder merely burns rapidly when ignited. All unnecessary accumulation of powder around the rolls is, of course, avoided.

German Powder.

Germany uses a nitroglycerin powder of the Ballistite type for its Navy and a nitrocellulose powder for its Army. The nitrocellulose powder is, like Poudre B, composed of a mixture of soluble and insoluble nitrocellulose. Some of it contains several per cent of a tetrasubstituted area as a surface coating to serve as a retarding agent. One type of this powder is made in the form of long single-perforated tubes. The nitroglycerin powder usually contains about 25 per cent nitroglycerin and is made without a volatile solvent, the ingredients being mixed under water and the mixture gelatinized by pressing in heated cylinders, then grained by forcing through a heated die. Some of it is granulated in the form of tubes as much as two meters in length.

SOLUBILITY AND VISCOSITY OF NITROCELLULOSE.

The principal solvents used commercially in the preparation of various nitrocellulose products are ether-alcohol, acetone, ethyl acetate, amyl acetate, and various mixtures of these solvents. Practically all grades of nitrocellulose are soluble in acetone or in amyl acetate and all except the more highly nitrated products are soluble in various mixtures of ether and alcohol. The last-mentioned mixtures are the only solvents of importance in the manufacture of nitrocellulose smokeless powders, although, as has been mentioned, acetone is sometimes employed as a solvent in double base powders like Cordite, containing high nitration guncotton. Single base nitrocellulose powders made with acetone as the solvent or colloiding agent are impracticable on account of the brittleness of the resulting colloid.

The important work on the solubility of nitrocellulose in ether-alcohol carried out by Lunge and his associates may be summarized as follows: [21]

(1) As the temperature of nitration is increased, the solubility of the product increases and the viscosity of its ether-alcohol solutions decreases.

(2) For a given nitration product the viscosity is a direct function of the concentration of the solution.

(3) The viscosity of the solution bears no direct relation to the nitrogen content of the nitrocellulose, although it reaches its maximum with the highest nitrogen content.

(4) For a product of given nitrogen content, the viscosity of solutions falls as the time of nitrating is increased, and as the water content of the nitrating acid is increased. These influences are greater in the case of concentrated acid mixtures than in more dilute mixtures. The explanation is offered that the original cellulose molecule is broken up into smaller ones, or that possibly esters of oxy- or hydro-celluloses are formed.

(5) Nitrocellulose which contains traces of acid as a result of incomplete purification undergoes a gradual loss of viscosity on storage for a short time.

T. Chandelon [22] has described a process for increasing the solubility of nitrocellulose, consisting in heating the material with water containing 1.5 to 3.0 per cent of mixed nitric and sulfuric acids in an autoclave at 1.5 to 3 atmospheres pressure. The nitrocellulose does not suffer any apparent change in nitrogen content but its solubility is greatly increased and its viscosity appreciably reduced. Filaments produced from the treated material were found to have superior strength and elasticity. Chandelon considers that the change taking place in the nitrocellulose is purely physical, probably a decrease in size of the molecule.

Various processes have been patented for decreasing the viscosity of solutions of nitrocellulose, such as heating under pressure in a non-solvent liquid.[23] Such methods are, however, of chief importance in the manufacture of nitrocellulose solutions for lacquers, artificial leather, etc., and not in the manufacture of smokeless powder.

F. Baker [24] found that the viscosity of nitrocellulose of various grades in different solvents might be expressed by the equation, $n = n_0 \ (1 + ac)^k$, where n_0 is the viscosity of the solvent, c the concentration, and a and k constants depending on the nature of both solvent and solute.

The usual methods of determining the viscosity of nitrocellulose involve tests of a rather dilute solution (as low as 2 per cent in some types of viscosimeters). The principles involved in the various types of viscosimeters used for this determination are: (1) measurement of flow of solution through a small orifice, as in the apparatus of Engler, Saybold, Redwood, Ostwald and others; (2) measuring the rate of rise of a bubble of air of definite size through a fixed height of solution, as in the apparatus of Cochius; (3) measuring the rate of revolution of a paddle in the solution under fixed conditions (Stormer viscosimeter); (4) measurement of time of fall of a spherical weight through a definite height of the solution (falling ball viscosimeters). Most apparatus involving the outflow method is suitable for use only with dilute solutions. Results by this method are more or less affected by evaporation of the solvent and consequent clogging of the orifice. The falling sphere method [25] is particularly adapted to viscous solutions and has been used to a considerable extent by the British Government in tests of viscosity of guncotton solutions, as well as in the United States.

Mention has been made of various factors in the process of manufacturing nitrocellulose for smokeless powder, which have considerable influence on the solubility and viscosity of the product. It should also be mentioned that even when manufacturing conditions are kept as nearly uniform as possible, there is good evidence from practical powder men that the nature of the colloid is affected by weather conditions. It is claimed that cotton nitrated in clear dry weather will give a tougher and more viscous colloid than that nitrated in very damp weather. It should, of course, be understood that variations in the properties of the colloid affect the shrinkage of the powder grains during the drying process. This shrinkage amounts to about 10 per cent in length and 30 per cent in diameter, of the usual type of multiperforated cylindrical grain used in the United States. Water-dried and alcohol-dried powders show a greater shrinkage than air-dried powders. Since the amount of shrinkage determines the final dimensions of the dried powder grains, and since these final dimensions determine the rate at which the charge of powder burns in the gun, it is obvious that care is necessary to ensure that the colloidal properties of the daily production of a powder plant be kept as nearly constant as possible.

Reference has been made to the work of Gibson and McCall [20] on the viscosity of ether-alcohol solutions of the nitrocellulose, containing about 12.2 per cent nitrogen, used in the manufacture of R.D.B. Cordite. In order to ascertain the properties of ether and alcohol having the maximum solvent action on this grade of nitrocellulose, a series of determinations was made with 4 per cent solutions at a temperature of 20° C., using the falling sphere viscosimeter. The specific gravities of the ether and alcohol were 0.72 and 0.817, respectively, at 15°/15°, and the nitrocellulose was thoroughly dried. The results obtained were as follows:

Solvent Mixture		
Ether (Per Cent by Vol.)	Alcohol (Per Cent by Vol.)	Viscosity (Time in Sec.)
80	20	160.7
75	25	59.6
70	30	39.9
60	40	28.8
50	50	23.1
45	55	26.1
40	60	30.5
30	70	90.4

The 80:20 and 30:70 mixtures gave distinctly jellied solutions. Additional tests showed that a mixture of 55 per cent ether and 45 per cent alcohol gave minimum viscosity in solutions varying from 3 to 6 per cent nitrocellulose.* As the nitrogen content of the nitrocellulose increases, the percentage of ether in the mixture must be increased to obtain a minimum viscosity, and this minimum viscosity also varies appreciably with the nitrogen content, as shown in the following table:

EFFECTS OF VARIATIONS IN PER CENT N.

N Per Cent	Minimum Viscosity (Seconds)	Optimum Ether : Alcohol Ration (by Vol.)
11.8	31.8	50 : 50
12.2	23.1	53 : 47
12.55	7.6	70 : 30

J. Desmaroux [26] found 2 parts ether to 1 part alcohol (by volume) to be the best gelatinizant for the CP_2 (approximately 12 per cent N) used in Poudre B. He found that substituting alcohols of higher molecular weight for the ethyl alcohol gave decreased solubility. The 2:1 ether-amyl alcohol mixture was used in a study of factors influencing solubility. The presence of 1 per cent of water increased the solubility to a marked degree, e.g., from 16.5 to 100 per cent on one sample of nitrocellulose. The influence of temperature was also found to be very great; 2 samples 16.5 and 38.8 per cent soluble at 20° C. were respectively 82.5 and 100 per cent soluble at 12° C. A gelatinization test developed and used during the World War at French powder factories was based on the use of such an ether-amyl alcohol mixture, the per cent of soluble material determined by an empirical method being designated as the coefficient of gelatinization of the nitrocellulose sample.[27]

TEST FOR PLASTICITY OF COLLOID.

The French also devised a method for the determination of the plasticity of the mixer charges in plants manufacturing Poudre B. The mixer charge, as already noted, is a mixture of two grades of nitrocellulose (12.0 and 13.2 per cent N), of which one is soluble and the other insoluble in the mixture of ether and alcohol used as the solvent.

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* This indicates a zone of maximum colloidality. *See* Vol. I of this series. J. A.

The test[28] was made to ensure uniformity in the plasticity of the various mixer charges, and the procedure was briefly as follows: A sample of the mixture was pressed into a block by means of a plunger in a metal cylinder, and a round metal rod 10 mm. in diameter, held vertically by a clamp and provided with a 2 kg. weight, was inserted through the top of the cylinder and allowed to rest on the block of colloid. The clamp was then released for exactly one minute and measurement made of the depth to which the rod penetrated the block. This measurement was designated as the "coefficient of plasticity."

Abderhalden[29] studied Poudre B colloids by this method of test, and found that the coefficient of plasticity reached a maximum when the proportion of soluble to insoluble nitrocellulose was 40:60, using amounts of solvent up to the maximum ever used in practice. The plasticity increased uniformly as the amount of solvent used was increased.

Changes in Smokeless Powders During Storage.

It appears to be a more or less general characteristic of organic nitrates to undergo a gradual decomposition on long storage. This decomposition is usually assumed to be the result of hydrolysis from the action of moisture. Undoubtedly the presence of traces of free acidity which have not been removed by the purification treatment play a large part in this slow decomposition, and it is probable that smokeless powder absolutely free from acidity and properly protected from absorption of moisture would have an indefinite stability life. Some lots of smokeless powder have been kept in service for 25 to 30 years without marked loss of stability, while other lots have developed instability in 5 years or even less. Stabilizers such as diphenylamine retard this decomposition and materially increase the average life of powder, by combining with the oxides of nitrogen liberated in the initial stages of decomposition, thereby preventing these gases from acting as catalysts to induce decomposition at an accelerated rate. Alcohol in the solvent undoubtedly acts as a stabilizer, by combining with liberated oxides of nitrogen, the odor of ethyl nitrate being frequently noted in smokeless powder long before there are other indications of decomposition. Excessive moisture in the powder has the opposite effect, the life of powder being materially shortened by storage in a hot damp climate. It is therefore essential that smokeless powder be stored in hermetically sealed cases and protected from abnormal temperatures. Loss of solvent from the grains might be expected to increase their porosity, thus exposing more surface for the absorption of moisture.

Tenney L. Davis[30] has advanced the theory that the absorption of moisture by colloided nitrocellulose powders partially separates the nitrocellulose from its solution in the ether-alcohol, producing minute pores or cracks which facilitate the escape of the solvent. He showed that powder exposed to moisture loses its residual volatile solvent more readily than before such exposure. By alternately exposing samples of powder to saturated atmosphere until equilibrium was reached, then drying for 6 hours at 100° C. to remove moisture, he found that the loss on drying was at first materially greater than the gain on exposure, the difference gradually becoming less and finally increasing again, due to decomposition from the repeated heating.

In addition to the effect of moisture on the stability of smokeless powder, its effect on the ballistics of the powder is also an important consideration. Increase in the moisture content produces a decrease, while decrease in moisture causes an increase in the velocity and pressure given by a fixed charge of the powder. Hence uniformity in moisture content is essential to accuracy of firing, and this constitutes another important reason for keeping smokeless powder hermetically sealed.

COATED "PROGRESSIVE POWDERS."

For a given weight of powder charge, the maximum velocity is obtained when the powder burns "progressively," that is to say, when the ratio of burning surface to weight of unconsumed powder increases as the grains are consumed in the gun. This condition is obtained by the use of the multi-perforated cylindrical grain employed in the United States. Various other methods are successfully employed to accomplish this result. Thus, powder of flake granulation, which is normally "degressive" burning, may be made "progressive" by a surface treatment of the grains, which lowers the rate of burning of the outer layers without affecting the interior of the grains. Coated powders of this type (both flake and single perforated grains) have been successfully and extensively used for both sporting and military purposes, particularly in small arms. The coating material is usually a colloiding agent for the nitrocellulose, such as a tetrasubstituted urea, nitrotoluenes, or other nitrocompounds, camphor, etc. The depth to which this coating penetrates depends upon the nature and amount of the coating agent used. As a result, the grain of powder is not of uniform composition throughout; the outer layer has a lower rate of burning than the interior of the grain, so that as the charge burns in the gun there is an acceleration in the rate of increase of pressure after the projectile has begun to move through the barrel.

COLLOIDING AGENTS FOR NITROCELLULOSE.

Marqueyrol and Florentin[31] tested a large number of esters, amines, chlorine derivatives, ketones, alcohols, etc., the use of which for the coating of "progressive" powders has been covered by numerous patents. In addition to dimethyldiphenyl urea (commonly known as Centralite) and camphor, which were the first substances to be used for this purpose, they tested phenylcarbonate, dimethylphenyl o-tolylurea, dimethyl di-o-tolylurea, ethyl sebacate, diethyldiphenyl urea, cyclohexane, turpentine monochlorhydrate, phenyl acetate, phenyl carbonate, borneol, ethyl succinate, ethyl phthalate, ethyl citrate, benzyl benzoate, ethyl malonate, triphenyl phosphate, ethyl oxalate, ethyl stearate, acetophenone, benzyl acetate, ethyl acetoacetate, and ethyl ricinoleate. Many of these substances were found to give very incomplete gelatinization of both soluble and insoluble nitrocellulose (CP_2 and CP_1 respectively). The tests were made by treating the nitrocellulose with the material in alcoholic solution at 35° C., determining the proportion of active ingredient required to give gelatinization of the nitrocellulose on evaporation of the alcohol. Ethyl sebacate and dimethylphenyltolyl urea were found to be the most efficient of all the substances tested, 70 parts and 75 parts respectively being required for the complete gelatinization of 100 parts of soluble nitrocellulose (CP_2).

Tenney L. Davis[32] investigated 16 colloiding agents, most of which are not included in the above list, using alcohol, benzene and ligroin as media for bringing together the nitrocellulose (pyro) and the colloiding agent. He found the tetrasubstituted ureas, especially s-dibutyldiphenylurea, to be the best colloiding agents, particularly when applied in benzene solution.

IMPROVED SMOKELESS POWDERS.

Most nitrocellulose smokeless powders possess the disadvantage of hygroscopicity, partly because of the hygroscopic nature of nitrocellulose itself, and partly on account of the hygroscopicity of the solvent. As already mentioned, the amount of residual solvent left in the powder grains may vary from about 1.5 to 7 per cent, depending on the size of the grain. This hygroscopicity of the powder and the volatility of the solvent, require that special precautions be taken to ensure tightness of packing and storage containers. The desirability of satisfactory non-volatile colloiding agents in smokeless powders is therefore clearly apparent, and the volume of patent literature on this subject is evidence that much effort has been and is still being exerted in this direction. Certain types of coated progressive burning powders, already referred to, are less influenced by exposure to moisture, because the coated surface is naturally less hygroscopic and protects the interior of the grain from absorption of moisture.

Another disadvantage possessed by all of the usual types of smokeless powders is that the large brilliant muzzle flash of the gun, especially at night, reveals the location of the battery and attracts counter fire. Much effort has been concentrated on attempts to produce powders of sufficiently low temperature of combustion so that the combustible gases will not ignite on mixing with air at the muzzle of the gun, while at the same time avoiding any marked reduction in the energy of the powder, so that the charge to give the desired velocity will not be too large for the chamber of the gun.

It is not the purpose of this article to discuss the methods employed in the development of improved flashless, non-hygroscopic smokeless powder, but it may be mentioned that the difficulties encountered are numerous. A substance which may be very effective as a colloiding agent, in lowering hygroscopicity or in eliminating muzzle flash may so greatly lower the potential of the powder as to render its use impracticable.

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Structural Variations in Smokeless Powders *

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The questions have sometimes been asked, What is the average structure of smokeless powder grains? How do powders of varied compositions vary in structure? Is it not true that microscopic examination simply magnifies microscopic impurities which are relatively unimportant; and finally, What is the practical significance of such variations as may be found?

Taking the last question first, the ballistic characteristics of a powder are of primary importance. A powder is fitted to a gun rather than the gun being fitted to the powder; that is, a powder is designed, tested, and calibrated to produce a desired muzzle velocity and pressure. These requirements must be met by the ballistician without exceeding the permissible pressure or density of loading for that gun. The cost of the powder, its stability, etc., come in as secondary considerations, the primary one being—how does it shoot?

The factor of chief importance with regard to pressures developed in the gun barrel is the rate of burning of the powder. In the case of a multi-perforated grain, the rate of burning is largely controlled by the surface exposed per unit weight of powder. This ratio is controlled by the length and character of the powder grain, and the size and arrangement of the grain perforations. These last changes are said to control the grain web (the initial minimum burning surface).

A factor of considerable importance in connection with the web is the viscosity of the nitrocellulose employed. When use is made of two different grades of nitrocellulose of the same nitrogen content, but of very different viscosities, the higher viscosity material will require more solvent to produce a mass of a given plasticity, than will the nitrocellulose of low viscosity. A die designed to give a desired web thickness and size of grain will not produce a similar grain from the other plastic mass, because of the difference in solvent content and consequent variation in shrinkage. That is, the one with the larger amount of solvent will shrink more during drying, will have a thinner web, burn at a different rate and develop a different pressure within the gun barrel, from that of the one made with the smaller amount of solvent. Hence, the structure of the powder which is influenced by the viscosity of the nitrocellulose is a factor in establishing its ballistic properties.

Two factors which influence viscosity are the state of aggregation of the nitrocellulose micelles and the degree to which the material is dispersed in the solvent employed. By using materials of the same nitrogen content, but which are not dispersed to the same degree in the solvent, the material with the lesser degree of dispersion will have a lower viscosity and a different shrinkage, so that dispersion and shrinkage bear a relation to each other. The distribution of undispersed, presumably high-nitrated nitrocellulose will affect the pressure developed within the gun, because the normal rate of burn-

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ing of a powder will be affected by the uneven distribution of highly nitrated nitrocellulose, within the body of a grain of lower nitrated material.

The distribution of dispersed and undispersed material is revealed by a microscopic examination of the structure of the grain. As will be shown, structural variations may be linked with shrinkage, rate of drying, web thickness and ballistic properties and these variations are paralleled by changes in velocity, pressure and uniformity.

DISPERSION.

In considering structure it must be remembered that a grain of smokeless powder is composed of nitrocellulose in an incompletely gelatinized condition. Manufacturing conditions are such that complete gelatinization is not obtained and therefore the important consideration is the structure of a powder grain, which may contain ungelatinized or gelatinized but undispersed nitrocellulose, rather than the fibrillar, filamentous, brush-heap, granular, honeycomb or meshwork structure of a nitrocellulose gel.

One of the most important factors affecting the structure of a powder grain is the dispersion of the nitrocellulose employed. For the sake of simplicity, the structure of a grain made of 12.6 per cent nitrogen nitrocellulose and gelatinized with ether-alcohol, will be considered. The propelling power or potential of the powder is primarily regulated by the nitrogen content, but the nitrogen content does not necessarily indicate how well the nitrocellulose will be dispersed by the solvent employed.

Pyrocotton, or 12.6 per cent nitrogen nitrocellulose, is dispersed to a clear liquid in a mixture of 2 parts of ether and 1 part of alcohol. Brunswig[1] has shown that there is a region between 10.2 and 12.8 per cent nitrogen where complete dispersion may be attained. However, Worden[2] points out that a 12.5 per cent nitrogen nitrocellulose may be entirely undispersed in ether-alcohol or may be dispersed to a clear fluid, and Craik[3] has discussed the mechanism in connection with the production of non-dispersed or completely dispersed nitrocelluloses of the same average nitrogen content.

Commercial pyrocottons vary widely in their dispersibility as evidenced by the films shown in Figure 1. This is a photograph by oblique, transmitted, illumination, of films 0.0023″ thick. These were made from 8 per cent dispersions of pyro in ether-alcohol which were allowed to stand for 16 hours at 0° C., poured on a chilled glass plate and spread with a film spreader. The films were first air-dried and then vacuum-dried at 55° C. They represent commercial samples of pyrocotton which are commonly used for the production of smokeless powder. By using oblique, transmitted illumination, the undispersed material is made to stand out as white areas on a black background. The two extremes represent low and high viscosity nitrocelluloses of the same nitrogen content, the very well dispersed sample at the right having the high viscosity.

Figure 2 is an enlargement of some of the undispersed material in the films, which had the characteristic high double refraction of unaltered nitrocellulose.

In addition to variations in the dispersion of the pyrocotton, there is encountered the influence of the amount of solvent. Although sugar is very soluble in water, if several spoonfuls are dropped into water, stirred for a moment and the water poured off, some undissolved sugar will be found. This same condition with regard to time of mixing applies to the treatment of pyrocotton with ether-alcohol. In commercial practice approximately equal weights of solvent and nitrocellulose are employed. The conditions permitting the formation of a transparent film are not present because of the small amount of solvent and short time of mixing used.

Now the nitration of cellulose is a continuous reaction and as far as is known, no individual ester is formed or has been isolated. A mixture results, the sum total of the nitrogen being 12.6 per cent—in the case of pyrocotton. A portion of the mixture has a lower and another portion a higher nitrogen content than 12.6 per cent, which accounts for the presence of material which is not dispersed in ether-alcohol. Desmaroux[4] has shown that in guncotton * containing ether-alcohol soluble material, it is not a question of partially soluble fibers being present, but rather a mixture of soluble and insoluble fibers. The same condition is probably present in pyrocotton.

Pyrocotton may, therefore, contain material which is soluble, relatively insoluble, and entirely insoluble in ether-alcohol—that is readily, slowly, or not at all dispersed, even under the most favorable conditions. If the amount of solvent is reduced, as in the case of a nitrocellulose dough for powder making, the amount of slowly dispersed material is enormously increased, and no indication of the amount of this type of material present, is given by the ordinary solubility determination in which a large excess of solvent is employed.

FIG. 1.—Films from different brands of commercial pyrocottons, showing varying amounts of undispersed material. —2 X

FIG. 2.—Undispersed nitrocellulose in pyro film. —30 X

As has been pointed out by many investigators, the gelatinization and dispersion of nitrocellulose is a time reaction involving the depolymerization of large aggregates, which is accompanied by swelling and disper ion. Two processes are working against each other. One is a tendency toward increase in size of the aggregates as the nitrocellulose swells in contact with the solvent and becomes gelatinous. The other process is a tendency toward decrease in size of the aggregate as the gelatinized material is dispersed. The dispersion process is triumphant in the formation of a sol—that is, in the preparation of a nitrocellulose dispersion; however, little dispersion is effected when the volume of solvent is reduced as in smokeless powder manufacture. Dispersion is effected by a type of mixer in which the gelatinized material is rubbed and kneaded, or by blocking—that is, forming the plastic mass into a block and subjecting it to pressure.

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* In this paper the term pyrocotton is embraced by nitrocellulose containing 12.6 per cent nitrogen ± .15 per cent, while guncotton embraces nitrocellulose containing over 13 per cent nitrogen.

The usual manufacturing processes do not afford sufficient time for this process of gelatinization and dispersion to be completed. This is shown by the opacity of the extruded cord and the cut grains. But a marked change in translucency takes place if the specimens are stored for 24 hours under conditions which hinder or prevent the loss of volatile solvent from the grain. A clearer gel results as the nitrocellulose particles become more completely gelatinized.

This gelatinization on storage is somewhat analogous to the ripening of viscose, the souring of clay in clay pits, the aging of hydrated lime in protected containers, etc. The increased translucency of the grains while green is merely an indication of better gelatinization but not necessarily dispersion; for if there is no further mechanical working to disperse the gelatinized material, it will partially revert to its original condition when the solvent dries out. Mechanical working of the gelatinized material is, therefore, a prerequisite for the production of powder of uniform ballistic characteristics.

VISCOSITY.

In the making of a multiperforated powder grain, extrusion takes place through a die and pin plate such as is shown in Figure 3. Extrusion occurs in the direction indicated by the arrow, the pin plate *A* being seated in the die body *B*. The nitrocellulose dough is forced through the perforated plate and appears like vermicelli strings, which are compressed about the pins, forming the grain perforations. The dough appears at the exit as a multiperforated cord, which is then cut into individual grains. A grain with its perforations is shown beside the die and pin plate in Figure 3.

FIG. 3.—Die, pin-plate assembly and multiperforated grain.

FIG. 4.—Lateral section of a fresh powder grain—300 X.

In extruding the continuous cord from which the grains are to be cut, there is encountered the effect of variations in dispersion and viscosity which are found to have an effect upon ballistic properties. Depending upon the viscosity of the extruded cord, the vermicelli strings are compressed into a continuous cord or matrix, in which there is no visible structure, or else the welding is such that materials of differing viscosities remain segregated. This results in irregular shrinkage and portions or whole sections of the vermicelli strings remain visible, under the microscope. Such an effect is shown in Figure 4, which is a lateral section of a freshly extruded grain. The dark areas are portions which have lost solvent and shrunk more rapidly than the surrounding light areas. This difference in rate of shrinkage is attributable to differences in viscosity in portions of the plastic mass. As the grain dries there is a continuation of the shrinkage which does not eliminate the effect of the variations in viscosity. Even in dried grains there is usually some trace of these viscosity differences. This is especially true of powders containing a non-volatile gelatinizing agent. There does not appear to be any relation between the viscosity of the original nitrocellulose and the structure previously discussed. It appears to depend solely on the viscosity of the plastic dough, which is largely controlled by the amount of solvent used and the variations in the degree of dispersion effected.

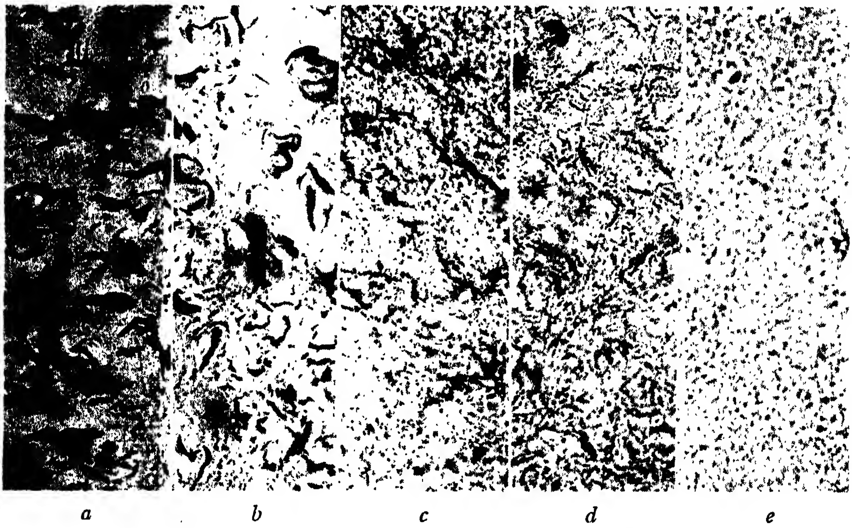

FIG. 5.—Lateral sections of dried grains—300 ×.

The variations in structure resulting from irregular shrinkage are shown in Figure 5. This is a series of lateral sections from dried grains. The first, *a,* is from a grain containing 17 per cent of a non-volatile gelatinizing agent. The addition of such gelatinizers always has a tendency to increase the viscosity of the mixture. In agreement with this fact are the recorded experiments of Gibson and McCall[5] and Mertz,[6] who show that with increasing molecular weight of the added gelatinizing agent, more viscous solutions are obtained at ordinary temperatures. Davis[7] has pointed out that gelatinizing agents with heavy hydrocarbon radicals are superior at high temperatures and inferior at low temperatures. By inferior is meant, that at low temperatures there is much swelling, but little dispersion. Evidently, in *a* (Fig. 5) segregation of high and low viscosity material took place. In *b,* which contains 15 per cent of non-volatile gelatinizers, there was less of this segregation. The same considerations apply to *c.* These three sections were made from powders in which nitrocellulose of a nitrogen content of 13.2 per cent was added to the 12.6 per cent pyro, in order to increase the potential of the mixture. The next section, *d,* is from a straight pyro powder—a powder without added non-volatile gelatinizer. The peculiarity here is, that it was made from very high viscosity nitrocellulose, for instance a 1,000 second pyro, as compared with 50 seconds for the other pyros. In spite of the viscosity of the raw material, a dough was obtained in which no segregation of high and low viscosity material took place. The last section, *e*, is that from a reworked grain. That is, dry 75-mm. powder grains were crushed and ground under water until the material passed a 60-mesh sieve. This sieved material was then incorporated with ether-alcohol and manufactured into powder in the usual manner. An extremely satisfactory material, with respect to structure, has been obtained—a fine-grained uniform structure.

It might be suggested that more solvent should be added to the very viscous masses, in order to facilitate welding. This, however, is objectionable, for addition of more solvent will increase the amount of shrinkage, alter the web dimensions and the rate of burning of the finished powder. In addition, if the die was redesigned, a separate die would be necessary for each different grade of nitrocellulose and considerable time would be lost, while a pilot lot of powder was being made and dried.


a *b* *c* *d* *e*

Fig. 6.—Longitudinal sections of dried powder grains—300 ×.

Now it is evident that if lateral sections of the grains show evidences of segregation, then longitudinal sections will likewise show something of the same sort. A number of these longitudinal sections are shown in Figure 6. The first is a section of a pyro powder containing a small amount of a non-volatile gelatinizing agent. The second, *b*, is a straight pyro powder section, made from high viscosity nitrocellulose, a lateral section of which is shown in *d* (Fig. 5). The middle section, *c*, is from a straight pyro powder 22 years old, which was a translucent amber yellow, while *d* is a section of a grain from the same lot which was beginning to show signs of decomposition. The grain is no longer a translucent amber, but an opaque brownish gray. There is no development of acidity, but the grain is brittle and the volatile content is only 4.3 per cent as compared with 5.1 per cent in the translucent grain. A breakdown in structure is taking place, in between the strings previously mentioned.

This structure would perhaps be unimportant were it not for the fact that it has been found associated with that of grains stored under water.

Instead of using magazines for the storage of powder, it has been found feasible to store the powder containers in concrete vats filled with water, or even in natural lakes. Periodical examination has shown that some of the powder grains stored under these conditions are gradually losing volatile solvent and becoming faster burning. In addition, they are developing the structure shown in *d*. The last section, *e*, is an illustration of what is meant. This is a section of a straight pyro powder, water-stored. It is opaque instead of being translucent and therefore any changes in its internal structure are not so readily seen as in the case of a transparent grain.

Associated with the structures noted in *d* and *e*, there is a development of brittleness which is of interest in connection with the structure of the powder grains. Brittle grains may break up into fine fragments within the gun and develop pressures sufficient to burst the barrel and are therefore highly objectionable. Brittleness is associated with loss of solvent. The loss of solvent may be considered an effect, the cause being a decrease in dispersion with aggregation and agglomeration of the nitrocellulose micelles. This decrease in dispersion results in a diminution of solvent carrying capacity, by the nitrocellulose.

In attempting to develop this idea, the fact is encountered that brittleness is an ageing phenomenon which is not specific for smokeless powder. Any material which is dispersed to the colloidal state is in an unstable condition. A slow and continuous transformation tends to take place with agglomeration of particles, coagulation and finally crystallization. Von Weimarn,[8] from the fact that he was able to obtain in the crystalline condition, several hundred compounds such as alumina and gelatin which are usually considered to be amorphous, considers that the crystalline condition is the normal condition for all compounds and that they are continually striving to reach this condition. Clark,[9] from a wide experience in X-ray analysis, speaks of "the inevitable urge of all things in nature, whether they be non-crystalline or not, to become crystalline." In addition, the opinion is frequently encountered that clear transparent gels are composed of ultramicroscopic crystals, which have a tendency to grow until the crystals are of microscopic size.

The ageing process in colloidal materials, which is the result of agglomeration and coagulation, takes place in human beings, in animals, plants and minerals. Old age is, therefore, connected with the formation of colloidal aggregates of increasing size. Because of aggregation, the surface is cut down, which results in a decreased adsorption of solvent or a decrease in the ability to retain solvent. According to Dhar and Chakravati,[10] who worked with sols and gels of silicic acid, the particles in a highly dispersed system, like a sol, gather to form larger particles. In the case of gels, the elasticity decreases and they become optically inhomogeneous or turbid, as the result of agglomeration.

In considering nitrocellulose products, there is considerable evidence to show that this same process takes place, first an agglomeration and second a loss of solvent because of the decrease in surface. Chandelon[11] has found that if nitrocellulose is heated under pressure, a physical change takes place, which is shown by a decrease in viscosity and an increase in solubility. Such a change, however, is not permanent. The nitrocellulose loses its acquired solubility on standing for one year in a moist condition, in the absence of light. This is due to aggregation and agglomeration of nitrocellulose particles. Freundlich[12] postulates the presence of primary, secondary and tertiary particles in a nitrocellulose solution. That is, after gelatinization and dispersion takes place, the nitrocellulose micelles undergo a continuous process of aggregation and disaggregation. Large and small aggregates are present in solution and they are continually changing in size. McBain, Harvey and Smith[13] point out that nitrocellulose recovered by precipitation from solution is more difficult to dissolve than the original nitrocellulose. They state that this is due to a recoupling of colloidal particles which were separate in the original solution, with the formation of very dense aggregates—a physical change.

Goldsmith,[14] in reporting on the behavior of celluloid films, states that the nitrocellulose which dissolved completely, gradually reappeared as ghosts of nitrated cotton fibers, the sheet becoming more and more turbid. Finally, Breguet[15] has shown by very elaborate experiments, that the ageing of nitrocellulose films which is associated with increasing turbidity, is consequent upon changes in the aggregation of the nitrocellulose particles. The low viscosity nitrocellulose, which is most mobile in either the sol or gel condition, is responsible for the agglomeration and turbidity in the film.

From the above considerations it is believed that the same process is taking place in the materials from which *d* and *e* were prepared. They are becoming turbid and brittle. The coagulation and agglomeration result in decreased surface and decrease in ability to bind solvent. The latter is therefore lost. A powder grain will not necessarily be brittle because it is low in solvent, but when it is brittle, solvent has been, or is being, lost.

A connection may thus be established between viscosity, structure and stability, which is of importance for the following reason. Comparatively little attention is paid to the viscosity of the nitrocellulose used for smokeless powder, since variations are ascribed to unavoidable variations in the viscosity of the cellulose from which the nitrocellulose was prepared. Blending is resorted to in order to bring the nitrated material to any specified viscosity. Given a nitrocellulose with a certain viscosity, the solvent ratio may be varied, within limits, to regulate the plasticity of the dough. Or given a fixed solvent ratio, because of die dimensions, nitrocellulose of a desired viscosity may be specified. This variation is further complicated by variations which set in, as soon as solvent and nitrocellulose are brought together.

The increased gelatinization on storage has been previously referred to, the dough becoming more viscous because of this increased gelatinization. There are a number of factors which have considerable influence on this increase in viscosity. They may be classified as follows: (*a*) Time factor; (*b*) swelling of material by gelatinizing agent; (*c*) variation from optimum solvent composition; * (*d*) influence of non-volatile gelatinizing agent on optimum solvent ratio.

(*a*) *Time factor.* The formation of a nitrocellulose sol, which involves swelling, gelatinization, dispersion, etc., of the nitrocellulose aggregates, is a process which involves considerable time before an equilibrium is reached. McBain[16] has shown that a 1 per cent nitrocellulose solution required two weeks at 55° C. before equilibrium was attained, as measured by viscosity changes. The first portion of time involved an increase in viscosity, while the latter portion involved a slight decrease. The process of attaining viscosity equilibrium is likewise retarded when a plastic dough is employed instead of a thin solution. A freshly made, opaque powder grain becomes translucent if stored for 24 hours in a closed container. This is an evidence of increased gelatinization.

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* The optimum solvent composition, is the particular mixture of ether-alcohol-water, or acetone-water, etc., in which the nitrocellulose has its lowest viscosity.

(*b*) *Swelling of material by non-volatile gelatinizing agent.* In the making of powders by the addition of a non-volatile gelatinizing agent, any nitrocellulose present which is unaffected by the ether-alcohol will be, at least, partially if not completely gelatinized by the non-volatile solvent.

It has been observed visually, that when material similar to that shown n Figure 2, is dissolved in ether-alcohol, the undispersed material becomes visible as very fine fibrils clinging to the sides of the containing flask. If 5 to 10 per cent of a non-volatile gelatinizer is added, the fine fibrils swell laterally but show no further tendency toward dispersion. At the same time the solution transmits less light and becomes noticeably more viscous.

(*c*) *Variation from optimum solvent composition.* Masson and McCall[17] state, that in a solution of nitrocellulose, the more widely the composition of the solvent varies from an "optimum" ratio, the longer is the time required for the solution to arrive at its highest viscosity. In addition, Mardles[18] points out that the optimum solvent mixture disperses the cellulose ester most rapidly because the least viscous solutions are formed and the particles diffuse most rapidly away from the dissolving material. This means that there is a definite ratio of ether-alcohol and water which is superior to any other ratio, for rapidity in gelatinizing nitrocellulose. The ratio will vary with the nitrogen content of the nitrocellulose. If this optimum ratio is not secured, viscosity variations in a nitrocellulose sol or gel will be prolonged over a considerable period of time.

(*d*) *Influence of gelatinizer on optimum solvent content.* Highfield[19] has adopted the polar-non-polar theory in discussing the solubility of nitrocellulose. That is, nitrocellulose contains strongly polar groups (hydroxyl) and weakly polar groups (hydrocarbon chains). The best solvents for nitrocellulose will therefore contain these two classes of groups, in suitable proportions. Sheppard, Carver and Houck,[20] in discussing the action of mixed solvents on nitrocellulose, conclude that although the polar-non-polar theory does not completely explain some observed cases, yet it is by far the best theory developed to date.

If this theory be applied to an optimum ether-alcohol-water ratio, then it appears obvious that the addition of any other solvent will disturb the balance between polar and non-polar groups. This happens when any non-volatile gelatinizer is added to the volatile solvent and the increased viscosity of masses containing non-volatile gelatinizing agents may be attributed, in part at least, to this upsetting of the balance between polar and non-polar groups in the solvent.

An effect on structure caused by increase in viscosity is shown in Figure 7. These are non-hygroscopic powder grains from the same lot of powder, which are characterized by hairlike, fibrous incrustations. They were found to be present on the surface as the cord issued from the die of the graining press. In addition, a great many of these hairs were scraped off the surface and fell in a pile on the floor, under the graining press. The effect was found to be due to pressure and motion in connection with materials of varying viscosities. The pressure used in graining the plastic mass was sufficient to force the low viscosity material through the high viscosity material, in the form of fine hairs.

For all practical purposes the scraping of a slight amount of material from the surface, with resulting change in the web dimensions, has no serious effect upon ballistic properties. But the varying amounts of fuzz on the grain surfaces would result in variations in ease or rate of ignition and be a hazard in plant operations. Consequently, these grains would "shoot all over the lot" and give non-uniform results, as far as velocity is concerned.

In concluding this discussion of viscosity, it is safe to state that the differences observed are not microscopic, as evidenced by operating reports. In a comparison of two lots of pyro of different viscosities, it was found that one lot required more time in the beater for reduction to the required fineness. When gelatinized with an equal weight of solvent it required 125 to 150 lbs. pressure per sq. in., more than for the other, for extrusion in the graining press; it was much harder to cut, which involved frequent sharpening of the knives and tended toward the formation of speckled, cloudy surfaces on the grains.

Fig. 7.—Surface variations in powder grains due to viscosity variations in the plastic dough—2 ×.

Polarized Light Structures.

The combination of examination in polarized light with crossed nicols and the determination of refractive indices, suffices to show abnormal conditions in the grains, which are not readily revealed by other methods.

Those sections which show a pronounced structure with transmitted light, like *d* and *e* in Figure 6, will reveal a corresponding structure in polarized light with crossed nicols. Those like *a*, *b* and *c* in Figure 6, which have no pronounced structure, may or may not be structureless in polarized light. For instance in Figure 8, *a* is the structure in transmitted light of a longitudinal section of the reworked material, which has been previously referred to. Two dark patches in it represent undispersed nitrocellulose. With polarized light and crossed nicols, the two dark patches are revealed as white spots which retain some of their original double refraction, as shown in *b*. The majority of grain sections, irrespective of their appearance in transmitted light, reveal structures somewhat similar to those of *c*, *d* and *e* of Figure 8. The doubly refracting areas correspond to the strings in *d* and *e* of Figure 6, the grain sections being made up of strongly doubly refracting, weakly doubly refracting and non-doubly refracting areas.

There are a number of interesting characteristics in connection with these doubly refracting areas, for they show great variations with regard to size and color. Section *c* is from a grain containing 13.2 per cent nitrogen guncotton and 12.6 per cent nitrogen pyro with a non-volatile gelatinizer. Any mixture containing guncotton and a non-volatile gelatinizer gives a very viscous dough. It might, therefore, be reasoned that the strings through the pin plate (Fig. 3) were not sufficiently worked and welded to form a homogeneous whole, and that these white areas were most viscous and therefore least susceptible to welding. But as a matter of fact, *e* is a pyro-guncotton powder with more non-volatile gelatinizer than *c*, so that wide doubly refracting areas should likewise be obtained here. In contradistinction *d* is a section from a straight pyro powder without any added gelatinizer. It is to be presumed that such material would have a lower viscosity and be welded into a homogeneous whole, yet some very wide doubly refracting strings are found to be present.

If it be admitted that a certain amount of work is done on the nitrocellulose in forcing it through the perforations of the pin plate shown in Figure 3, then some additional work is done on the pin-plate strings in welding them about the pins of the pin plate. That is, the pin-plate strings which retain, more or less, their original form as shown in Figure 4, are subjected to this additional working. The areas which retain their double refraction are the areas which have not been completely dispersed and fused into a homogeneous whole, in spite of the work that has been done on them. But by reason of the work done on them they are very dense and impermeable. Probably the doubly refracting strings are denser at the centers than at the edges.

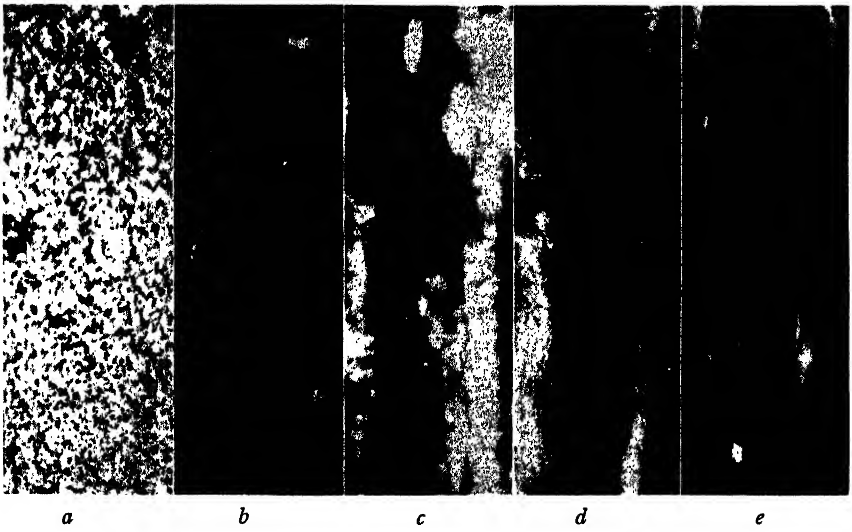


FIG. 8.—Longitudinal sections of dried powder grains in polarized light with crossed nicols—300 X. *a* and *b* are photographs of the same section. *a*—with transmitted light, *b*—with polarized light and crossed nicols.

The density and impermeability of these strings has been demonstrated by staining freshly cut grains with methylene blue in alcohol. The effect is best secured with small caliber grains which dye rapidly. By sectioning and drying them, relatively permeable and impermeable areas are disclosed, which follow the outline of the strings in polarized light with crossed nicols. Figure 9 is a photograph of one of these strings from a straight pyro powder. It is visible as a pale blue streak on a black background, with polarized light and crossed nicols. By staining one of the fresh grains with methylene blue, the strings become visible by transmitted light as gray-white streaks on a deep blue background. If staining is prolonged, the white area is likewise dyed blue, but by stopping the process at the proper time the permeable and impermeable areas are disclosed.

It appears probable that differences in degree of dispersion exist within and at the borders of these strings, since they vary in color from blue white through blue and purple to brown, when examined in polarized light. There are likewise color variations within these strings which are similar to those noted by Phillips [21] in the examination of nitrocellulose fibers in polarized light. Figure 11 is taken from a section of a powder in polarized light with crossed nicols. It shows the varying width of the strings and the variations in color from dark blue to yellow within the strings.

It should perhaps be emphasized that these streaks which display colors in polarized light are not the residual skeletons of nitrocellulose fibers. They show no central canals such as are found in ungelatinized fibers, are in the majority of cases invisible by transmitted light and do not have the high double refraction of ungelatinized fibers. They are viscous, impermeable masses which are drawn into strings by passage through the perforations of the pin plate. They usually lie parallel to the direction of flow of the material through the die and are not so well dispersed as the material which surrounds them.

A further illustration of what size and color variations may be encountered is provided by the three photographs in Figure 10. The first, *a*, is a powder containing a non-volatile gelatinizer. The strings are characterized by their width and brilliant blue-white color. The second, *b*, is a straight pyro powder containing no non-volatile gelatinizer. These strings are narrower, rounded and are of a deep blue color with pale blue centers. The third section, *c*, is a powder containing a non-volatile gelatinizer. It is structureless by transmitted light and in polarized light with crossed nicols shows brown strings which merge into the background.

The last two photographs show a characteristic which is commonly encountered in polarized light examinations but whose significance has not yet been correlated with the behavior of the powder. This characteristic is the color of the background. In the first photograph the background is black. This is common with specimens of well dispersed nitrocellulose which have lost their double refraction during gelatinization. They are optically inactive and thus appear dark when examined in polarized light. The double refraction of cotton fibers and of nitrated cotton is assumed to be due to strains set up in the fiber by spiral twists during growth. If this strain is removed by even incipient swelling, the double refraction is lost.

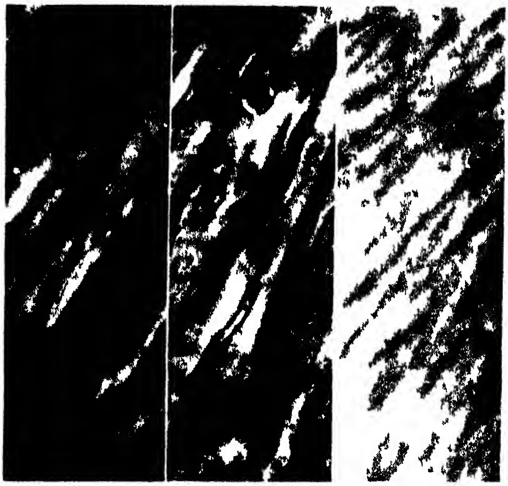
DOUBLE REFRACTION.

There are in general two types of double refraction, "orientation double refraction," due to the arrangement of micelles in a colloidal aggregate, and "tension double refraction," due to stresses set up as in the case of a sheet of celluloid which exhibits interference colors when strained.

It is known that when green timber is dried rapidly it may check and crack. This is because the exterior at first dries more rapidly than the interior, so that the surface is under tension and the surface shrinkage puts the interior under compression. At a later period the inside dries and tends to shrink, but is prevented to some extent by the dried exterior. The stresses are then reversed, placing the surface under compression and the interior under tension.

It is entirely possible that it is this "tension double refraction" which is

FIG 9—Impermeable, undyed string in pyro powder section—500 ×



a *b* *c*

FIG 10—Structural variations in dried grains, polarized light, crossed nicols—150 ×

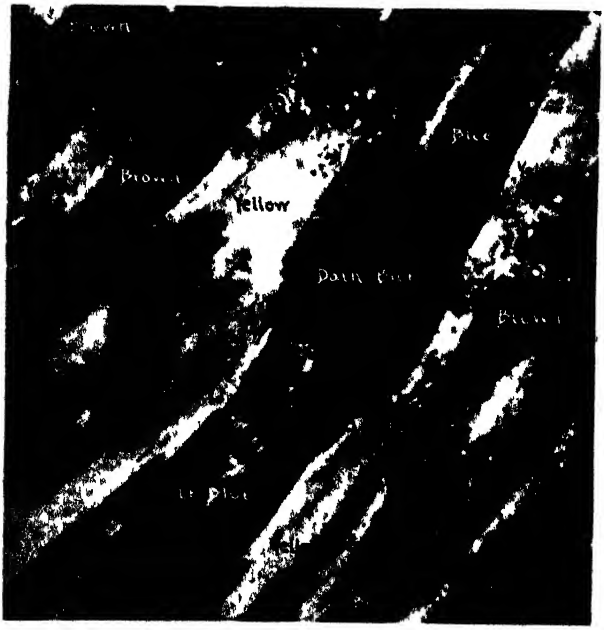


FIG 11—Variations in color and width of strings in powder section Polarized light with crossed nicols—500 ×.

present in the sections under discussion, the strains being the result of the drying treatment given the grains. The light-colored backgrounds in the last two photographs will extinguish in certain positions, when the stage of the microscope is rotated. The background of the first section remains dark during a rotation of the stage through 360° C.

This type of double refraction is more frequently met with in straight pyro powders than in the pyro powders containing a non-volatile gelatinizing agent. An illustration of the difference is shown in Figure 12. The first photograph is that of a lateral section from a dried straight pyro powder. The section was examined in polarized light with crossed nicols. It shows the characteristic highly doubly refracting bands, not only about the periphery of the grain but also about the perforations. The second section is from a pyro powder containing a small amount of non-volatile solvent, dried under the same conditions, but showing only a slight amount of localized double refraction. No connection has yet been established between these drying strains and the stability of the powder. They are simply an added complication in the interpretation of the composite picture.

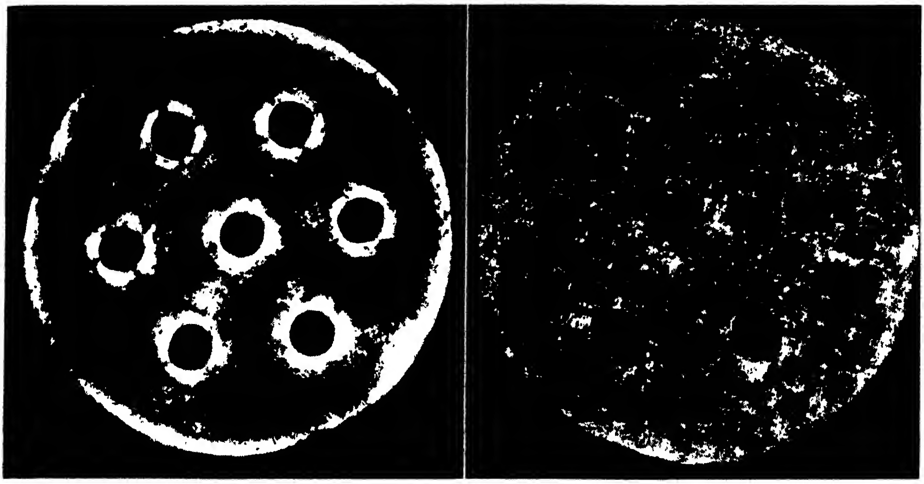


Fig. 12.—Lateral sections of dried grains, showing the variations in the amount of double refraction—8 X.

An interesting connection between double refraction, structure, percentage of gelatinizer, and time of drying is shown in Figure 13. These are longitudinal sections of pyro powders made with increasing amounts of a non-volatile solvent and dried under identical conditions. They were examined in polarized light with crossed nicols. It was desired to dry these powders to approximately 1 per cent solvent and a very good relation was found between increasing amounts of non-volatile solvent, improvement in structure and decrease in drying time. The last four sections are practically structureless by transmitted light and even with polarized light the last two show little or no structure. All of these sections show the "tension double refraction" in the background, previously referred to. In no case is the background black, but a clear brownish yellow. These sections show the value of polarized light in indicating a connection between structure and rate of drying which cannot be observed with transmitted light. The more rapid drying with increasing

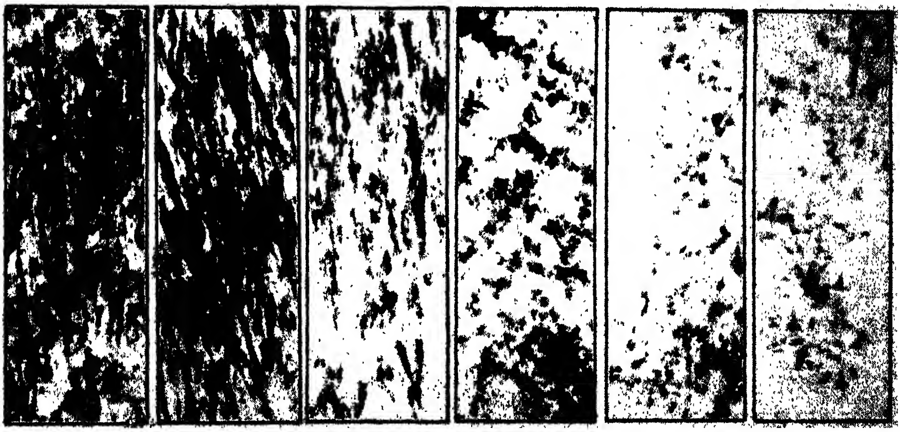


Fig. 13.—Powder sections in polarized light with crossed nicols—50 ×.

Drying time—days	154	136	27	27	41	20
Total volatile	1.09	1.07	.88	1.03	.98	1.12

amounts of non-volatile solvent is due to the dispersion of the strings shown in the first two sections. The strings are richer in solvent than the surrounding areas, as shown by refractive index determinations; and by their dispersion an opportunity is offered for more rapid removal of solvent.

Distribution of Insoluble Material.

The undispersed nitrocellulose, which was previously considered in connection with shrinkage and alteration in web dimensions, also plays a considerable part in connection with uniformity in ballistics and with rate of drying. The connection with ballistic uniformity is revealed by an inspection

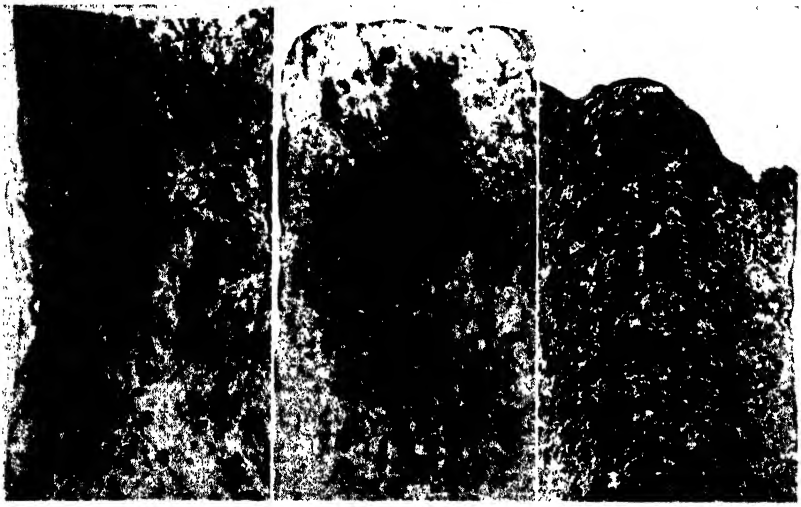


Fig. 14.—60-40 pyro-guncotton compositions showing non-uniform distribution of guncotton—50 ×.

of the reactions in Figure 14. These are sections of powder grains made from 60-40 pyro-guncotton mixtures. The guncotton is opaque, ungelatinized and readily recognizable. In the first section it has piled up along one side of the grain. In the second it has aggregated into large lumps. In the third a shearing has taken place, which has resulted in telescopic flow. The mechanical mixture of guncotton and gelatinized pyro is more viscous than the gelatinized pyro alone. The application of pressure has a tendency to cause the pyro to flow faster and flow through the pyro-guncotton mixture. However, friction is encountered at the walls of the die, which retards the passage of material at the point of contact. The result is the formation of a series of arcs, as shown in Figure 14.

It is obvious that these grains would burn in entirely different manners and would develop dissimilar pressure curves. The distribution of the ungelatinized high-nitrated material is therefore of importance in connection with burning characteristics and this distribution is readily revealed by microscopic examination.

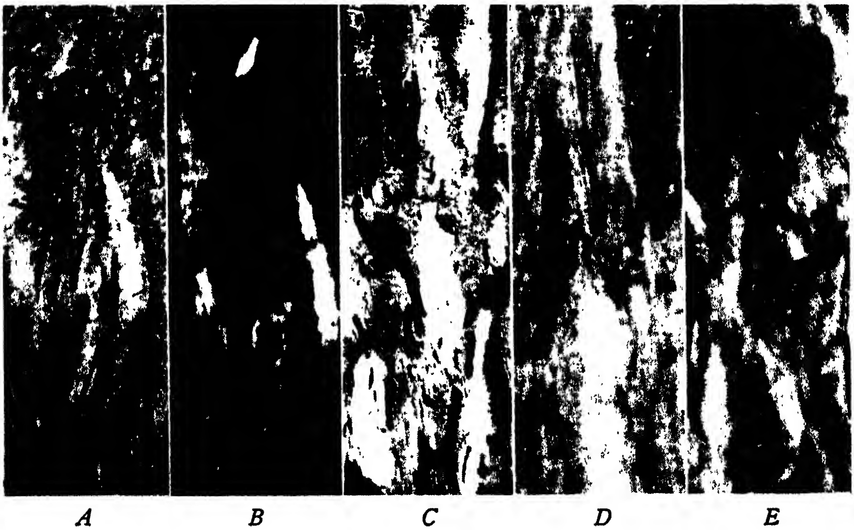


FIG. 15.—Longitudinal sections with partially crossed nicols, showing distribution of insoluble outside the white strings—300 X.

In cases where guncotton, or pyro-containing material which is not dispersed by ether-alcohol, is used in connection with a non-volatile gelatinizing agent, some dispersive action will take place. It is of interest, therefore, to note the location of the undispersed material. It is seldom found within the white strings, which are revealed by polarized light. There is a decided tendency toward non-uniform distribution. A few examples are shown in Figure 15. With polarized light and crossed nicols, the doubly refracting structures are readily observed, but the ungelatinized material, which has lost its double refraction, is invisible. This is shown in section *b*. If transmitted light is used, the white, doubly refracting strings become invisible. By partially crossing the nicols, however, both strings and ungelatinized areas may be seen. The characteristic location of the undispersed material is shown in sections *a, c, d* and *e*. It is generally just outside of the viscous, doubly refracting white areas. Undoubtedly, this is due to differences in viscosity. Sections *c* and *d* were manufactured to the same formula, but with different raw materials.

A characteristic of the ungelatinized nitrocellulose, in these powders, is the absence in it of double refraction. Being ungelatinized and undispersed, this material should show, at least, a portion of its original high double refraction. However, it has been found that by macerating guncotton in a pyro solution and drying it thoroughly, the double refraction of the guncotton is lost. Thorough penetration, which requires working and kneading, is necessary in order to achieve this result. The penetration of ungelatinized by gelatinized material, is shown in Figure 16. This is a section from an 80-20 guncotton-pyro powder grain, by transmitted light. The light reticulated areas are the gelatinized pyro, while the darker areas are guncotton. Close inspection shows that the darker masses are interpenetrated by the reticulated material.

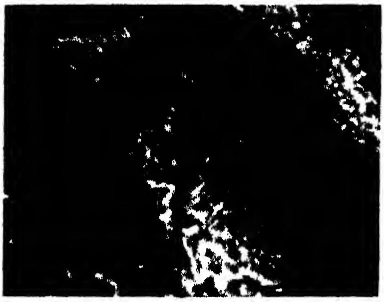


FIG. 16.—80-20 guncotton-pyro composition, showing dark guncotton areas interpenetrated with reticulated pyro—1200 X.

FIG. 17.—Dried grain section immersed in liquid of 1.48 refractive index—50 X.

Abderhalden [2] has called attention to the fact with mixtures of dispersible and undispersible nitrocellulose, the former gelatinizes the latter in the sense that the dough becomes plastic and the white spots of unaffected guncotton are removed. This increase in plasticity has been found to be of importance in the extrusion of a coherent cord. In high-percentage guncotton mixtures, it has been found occasionally, that blocking and extrusion resulted in the formation of a sandy cord, which would not hold together after extrusion from the die. The material was "short," but by increasing the time during which the block was held in the blocking press, the coherence of the cord was materially improved and a "long" cord was secured.

The process of blocking and screening the plastic dough has been followed microscopically and it has been found that the squeezing of the dough not only causes penetration of the ungelatinized by the gelatinized nitrocellulose, but also causes a marked reduction in the size of the aggregates. Their increased plasticity makes them pure susceptible to mechanical working. By impregnating the ungelatinized with gelatinized material, the ungelatinized takes on a characteristically gray color which is readily recognized in polarized light with crossed nicols. There is no change in the color of this material during a complete revolution of the stage of the microscope. The films shown in Figure 1 will therefore represent the amount, but not the condition of the ungelatinized, undispersed material, because the mechanical working, to which it is subjected, affects its optical characteristics.

DRYING PHENOMENA.

Refractive Indices. The material of intermediate dispersion, which becomes gelatinized only with passage of time, forms undispersed, jelly-like masses which are rich in solvent. They do not give up their solvent content and dry as rapidly as the surrounding, well dispersed material. Prolonged drying then becomes necessary in order to reduce the solvent content of the grain to a low figure. The addition of a non-volatile gelatinizer not only causes a swelling of the ungelatinized material, but also facilitates the dispersion of the material of intermediate dispersion, so that there is less tendency for the formation of areas rich in solvent and consequent slow drying of the powder.

Considerable information as to degree of gelatinization is obtainable by refractive index determinations made on thin sections of the dried powder grains. Dry pyro powder specimens have an index of approximately 1.48, while the pyro itself is approximately 1.53. Where spots in the section have an intermediate index, it is an indication of incomplete gelatinization. Where the index is below 1.48, an excess of solvent is indicated. A solvent-rich area of undispersed material is present. If double refraction and refractive index are high, it is an indication that little or no gelatinization has taken place. If double refraction is high and refractive index is low it indicates that one of the areas rich in solvent, in which there was gelatinization without dispersion, is drying out to leave a porous spot. This combination of high double refraction and low refractive index is usually indicative of drying stresses. The variations in dispersion are indicated in Figure 17. This is a photograph of a straight pyro powder section immersed in a liquid of 1.48 refractive index. The focus is first found and the draw tube of the microscope raised. The white halos move toward the material with the higher index, and away from the material of lower index. It is thus indicated that the small black patches have a lower index than 1.48.

SKIN EFFECT.

In the process of solvent recovery and drying of smokeless powder grains, the ideal condition for drying is established when solvent diffuses from the interior to the exterior of the grain at the same rate at which it leaves the grain. This is a theoretical condition which is never maintained throughout the drying period, for each individual grain. Consequently, there is a current belief that during drying a skin is formed about the exterior of the grains, which rapidly becomes impervious. It dries out to a hard, dense mass which prevents the evaporation of solvent from the interior of the grain.

If such a skin was formed it is to be expected that on account of drying stresses it would be doubly refractive in character. Thus its presence would be shown by a band of doubly refracting material about the periphery of either a lateral or longitudinal section of the grain.

In agreement with this idea Figure 12 shows one of the lateral grain sections with a doubly refracting band about the periphery of the grain, as well as the perforations. The other section from a grain containing a non-volatile gelatinizer, does not show these bands. This is in accordance with the statement of Bittner,[28] that the addition of plasticizers to wood oil varnishes, prevents the formation of a skin.

Figure 18 is a photograph of a section of a freshly made grain, taken from the solvent-recovery bin, just before heat was applied in order to drive out the solvent. It was sectioned with a razor and photographed by reflected light. It shows the so-called "skin effect," in that the material around the edges had lost more solvent, was denser and took a higher polish, than did the material within the grain.

As opposed to this, there have been found a sufficient number of facts to disprove the "skin effect" theory, as follows:

1—Grains taken from the solvent-recovery bin during the process of solvent recovery and sectioned as shown in Figure 18 revealed no differences in structure which could be attributed to a skin effect.

2—The presence of a doubly refracting ring about the periphery of a grain is not sufficient to indicate the formation of a skin, since in very many cases the doubly refracting material has been found to have a lower index of refraction than the material within the grain. This indicates that more solvent is present at the exterior than is in the interior of the grain and therefore an impermeable skin cannot be present.

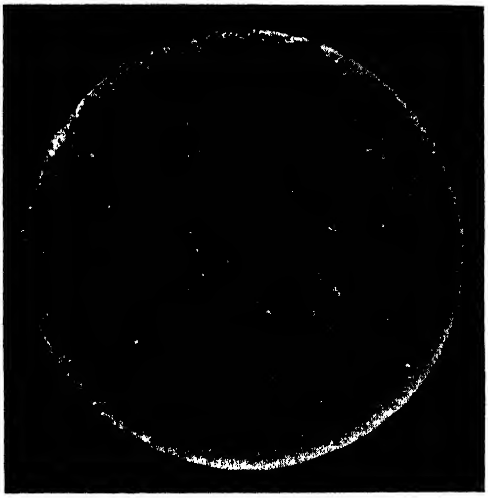


Fig. 18.—Lateral section of an undried powder grain, showing the "skin" effect—8 X.

Fig. 19.—Section from 30 caliber powder showing the presence of ungelatinized lumps rich in solvent —250 X.

3—Grains given a solvent recovery at 65° C. and an air dry at 65° C. have developed no doubly refracting ring, while those given an identical solvent recovery at 65° C. and an air dry at 55° C. have developed the ring. The latter is therefore an indication of the production of drying stresses and not necessarily an indication of impermeability.

4—A definite connection has been established between slow drying powder grains and lumpy material of the type shown in Figure 19. These lumps were found in slow drying 30 caliber powder grains, while fast drying grains from the same lot did not show the presence of these lumps. They were identified as non-doubly refracting masses of gelatinized, but undispersed nitrocellulose which were relatively rich in solvent and had a refractive index below 1.48. It is not necessary that these lumps should be aggregated in large masses in order to give the slow-drying effect, for in many cases the material has been found well scattered, as shown in Figure 17.

In view of the repeated confirmation which has been obtained, of the fact that slow-drying powders invariably contained non-dispersed material with a low index of refraction, it is believed that the theory of the formation of an impermeable skin about the grain being responsible for slow drying, is untenable. It appears preferable to assign the cause of slow drying to a structure which has been observed under the microscope, rather than to a hypothetical structure which has not been definitely proven to exist in any dried powder.

SUMMARY.

Microscopic examination is of value in establishing a relationship between the amount and distribution of insoluble material and variations in the viscosity, shrinkage, rate of drying, uniformity, velocity and pressure characteristics of smokeless powder.

Viscosity variations affect the amount of solvent required, shrinkage and wet dimensions, which are reflected in variations in loss of solvent, stability, velocities and pressures.

The development of brittleness is linked with changes in the micellar structure of the powder. Polarized light examinations are of particular value in showing the presence of variables which affect shrinkage, rate of drying, drying stresses and ballistic uniformity.

The structural goal with relation to ballistic uniformity is absence of visible microscopic structure with either axial transmitted light or polarized light with crossed nicols.

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Colloid Chemistry in the Sugar Industry.

By R. T. Balch *

and

H. S. Paine.**

Introduction.

Wolfgang Ostwald in one of his lectures delivered some years ago in the United States (*227*)† called attention to the importance of colloid chemistry to the sugar industry. It is a strange fact that, although colloid chemistry and the science of sugar manufacture have made great advances during the past twenty-five years, it has only been during the last few years that any systematic study of the relations between these two fields of scientific endeavor has been made. Up to the present this knowledge has been scattered through the chemical literature, which has been reviewed from time to time (*37, 56, 84, 102, 155, 223, 262, 298*). None of the several books dealing with the technical applications of colloid chemistry makes more than a passing mention of the sugar industry; and yet this industry for a very long time has unconsciously applied various colloid-chemical principles successfully to actual practice.

Here and there voices were raised by sugar men years ago, inviting a study of the various processes used in sugar manufacture from a colloid-chemical point of view (*118, 221, 246*), but it is only recently that increased impetus has been given this subject in widely separated parts of the globe. Three factors especially have contributed to this newly awakened interest: first, the advent of highly activated decolorizing carbons; second, certain technical difficulties experienced in sugar manufacture and more clearly recognized in the various sugar industries, these difficulties being evidently connected with colloid phenomena; and third, increased knowledge of colloid-chemical principles.

Considerable progress has been made in such studies, and this chapter represents an attempt to bring together all available information, as well as to point out the gaps in our knowledge and to indicate the possibilities for further research. Although it was intended originally to deal only with colloids as pertaining to the cane and beet sugar industries, the manufacture of corn sugar and sirup has grown so tremendously during the past few years that it seems desirable to include here also a discussion of colloids in relation to this industry in so far as information is available. Data on sorgo and maple sirups will also be included as being of some interest.

Colloidal Constituents of Sugar Products.

The colloidal substances encountered in various sugar-house products may be considered under two groups: (1) those which occur normally in the sugar-

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† The authors are indebted to Dr. F. W. Zerban, Chemist in Charge of the New York Sugar Trade Laboratory, New York City, for placing at their disposal his bibliography through the year 1925 and a manuscript on this subject written in 1923, which have been consulted in preparing this article.

producing plant; (2) those which are derived from external sources or result from influences which are preventable to some extent.

Although the principal sources of commercial sugar are not related botanically, the approximate chemical composition of the parts used for the manufacture of sugar is similar. The structural material of both the beet root and the sugar cane (also the sorgo) stalk consists of cellulose, hemicelluloses, pentosans and lignin. The juices consist essentially of a solution of sugars and of salts of inorganic and organic acids, molecularly dispersed, but contain also small quantities of material of colloidal dimensions. This material includes several groups of substances such as proteins, fats and waxes, gums and pectins, coloring matters, inorganic constituents such as lime and silica, and occasionally starch.

In the group of sugar-liquor colloids which are not normal constituents of plant saps, but are frequently encountered in practice, may be included coarse dispersoids and colloids derived from the soil and not removed by the washing process, if practiced at all; colloids extracted from or produced by the action of heat and lime upon fine particles of fiber or marc, which are not screened out by the mechanical devices used; and colloids produced by fermentation, as a result of unsanitary conditions within the sugar factory or of storing the sugar-containing plants under unfavorable conditions, as well as those produced by injury to the sugar plants from abnormal cultural and climatic conditions, such as are caused by various pests and diseases and by freezing.

Proteins.—Of the nitrogenous material occurring in sugar plant juices (a total of about 0.5 per cent) (*64*), only about 20 per cent may be considered as being colloidal; namely, the proteins and certain of their degradation products. Albumin is the principal protein constituent, and on account of the ease with which it is coagulated by heat, it contributes but little to the difficulties of sugar manufacture. Those proteins and degradation products which escape the clarification processes do frequently, however, have serious effects. They are regarded as molasses formers, and contribute to pan-boiling difficulties; they are also responsible, partly at least, for the very troublesome froth "fermentation" (*63, 70, 129, 186, 261, 321, 327*). Of consequence, too, is the contamination of the sugar by nitrogenous substances, these being either constituents of the molasses film on the sugar crystals or else are actually adsorbed by the growing crystals. Their presence in commercial sugars increases tremendously the susceptibility of the sugar to deterioration by microorganisms; in addition they are undoubtedly partly responsible for certain objectionable properties of some direct consumption sugars, such as that of causing dark-colored candy and yielding sirups that are more susceptible to fermentation.

Fats and Waxes.—The natural fats of the cane and beet plants are present in such small quantities, and are so overshadowed by the intentional and frequent addition of various oils (rape and lard) for the purpose of reducing foaming in the evaporators and vacuum pans, that they are of negligible importance. Waxes form a protective coating on the sugar-cane stalk and are encountered only in the cane sugar and sirup industries. Fine milling of cane coupled with hot maceration removes a large proportion of the wax from the stalk. The wax may thus be considered a normal constituent of factory cane juice, although not a component of the plant sap. Fats and waxes constitute about 0.3 per cent (*64*) of the sugar cane, while beets contain about 0.16 per cent of fats (*245, 272*). Clarification processes remove a large proportion of the wax, but a small quantity usually remains emulsified in the defecated juice in raw sugar manufacture and is found in all subsequent products (*27, 28, 29*). Poor filtration of raw sugars is due to some extent to the presence of wax (*170, 206, 248, 299*).

Gums.—Considerable attention has been paid during recent years to the "gums" occurring in beet and cane products. This term is generally understood to denote various complex polysaccharides which are soluble in water but which are readily flocculated by strong, acidulated alcohol (*142, 173, 269, 346*). In this group are also included the pectins (*103, 107, 109, 112, 220, 303*)* which are somewhat similar in physical and chemical characteristics. Mature cane has been reported to contain about 0.20 per cent (*64*) of these substances, whereas immature cane is considerably richer therein; furthermore, the gum content is increased by the effect of incidental stimuli such as freezing, burning or action of microörganisms (*143, 144, 205, 338*). A gum of the latter type, the result of Cobb's gumming disease of sugar cane, has been isolated and purified by dialysis. It is levorotatory and upon hydrolysis yields a product which also is levorotatory (*339*). A gum which was prepared from beet molasses by dialysis had a specific rotation of —28.7° (*244*). Water-soluble colloids from beet sugar, separated by ultrafiltration, had a specific rotation of —30.5° (*239*), indicating the presence of substances of a nature similar to, if not identical with, that of the gums in molasses. A similar levorotatory gum has also been found in decayed beets (*311, 334*). All these gums are probably closely related to levan ($[\alpha] = -40°$) found in raw cane sugar as a result of the action of microörganisms (*133, 176, 230, 319*). Other gums of similar origin, sometimes encountered as unwelcome guests in the sugar factory or refinery, are dextrans ($[\alpha] = +200°$) (*15, 99, 355*), and levulans ($[\alpha] = -221°$) (*195, 334*).

Coloring Substances.—The coloring substances of beet and cane products are usually regarded as colloids, because it has for a long time generally been assumed that they are essentially polymerized and dehydrated products of sugars and hence have been classified under the name of caramel (*79*), which is known to diffuse and dialyze slowly. Recent investigations have shown, however, that the assumption that caramel is the principal coloring substance is more nearly correct in the case of maple products (*25*) and of bone char filtered refinery liquors (*341*) and the products derived from them, whereas in raw cane sugar and in sugar beet products other coloring matters are of far greater importance than caramel (*65, 124, 126, 158, 183, 186, 197, 198, 199, 213, 315*).

It is now known that the natural coloring matters in the cane may be divided into four different groups (*352, 354*). The first of these comprises the green and yellow pigments of the rind which belong to the chlorophyll group. These substances do not dissolve in the juice and only the small quantity which passes mechanically into the juice may later give rise to secondary coloring matters through the action of the chemicals used in clarification. The second coloring matter, saccharetin, is, like chlorophyll, insoluble in the juice but may in a similar way contribute later to the color of the products, as it becomes intensely yellow upon contact with lime. To the third group belong the red and purple coloring matters of the rind of certain varieties of cane. These are soluble in the juice and, while the color apparently bleaches out shortly after the expression of the juice, it is nevertheless a well-known fact that red and purple canes yield a much darker clarified juice and sirup than yellow or green canes. These red coloring matters are polyphenol compounds, somewhat resembling, but not identical with, anthocyanins (*55*). They probably contribute to the color of the juices in much the same way as

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* *See* paper by Johnston and Griggs in this volume. J. A.

does the fourth group of coloring substances, which are formed from true tannins found throughout the cane stalk, but particularly in the tops and rinds (*55, 136, 141, 142, 287, 350, 351*).

These tannins, closely related to oak tannin, are derived from pyrocatechol and give a green color with ferric salts (*351*). Fresh cane juice, expressed without use of iron apparatus, soon turns brown, through the effect on the tannin of an oxidase contained in the juice, but if iron is present, as is always the case in the factory, the juice turns green, through the interaction of the tannin and iron and possibly oxygen (*6*). The dark color which beet juice assumes soon after its extraction is due to a similar phenomenon, the effect of tyrosinase on pyrocatechol contained in the juice, also in the presence of iron (*131, 132*). The pyrocatechol is probably a secondary product, being derived from the tyrosine of the beet. It is also interesting to note that a tannin-like substance has been isolated from sorghum (*306*).

During the process of manufacture, at least two new groups of coloring matter appear: first, those consisting of caramel or similar products formed by the action of high temperatures on the sugars and by reactions between reducing sugars and alkali (*79, 124, 140*); second, products resulting from reactions between reducing sugars and amino acids (*5, 124, 140, 186, 201, 229, 258, 352*). These substances evidently constitute an important part of the coloring matter in final beet and cane molasses (*119, 229, 258, 308, 309, 310, 315*). From beet molasses an acid containing nitrogen and possessing extremely dark color has been isolated and termed "fuscacinnic" acid (German—Fuskazinsäure) (*61, 308*). So far, it has not been definitely ascertained which of the various coloring matters are colloidally dispersed in the sugar products, but it seems certain that some of them, such as the polyphenols and their iron compounds, as well as the polymerization products of sugars, belong in this category (*5, 79, 208, 208a, 250, 271*). When sugar products are dialyzed or ultrafiltered, only a very small proportion of the coloring matter is retained in the colloid fraction; a portion is adsorbed by the membrane (collodion) for it soon becomes colored, but by far the greater proportion of the coloring matter passes through the membrane, and is probably molecularly dispersed.

A difficult colloid chemical problem has lately arisen in efforts to measure accurately the color of sugar products. In all older work on this subject the presence of colloids was entirely disregarded, and the usual colorimetric methods were applied to sugar factory products without paying any attention to the state of dispersion. It has been found, however, that in such determinations great care must be taken to remove all suspended matter (*329*). Careful work done in connection with spectrophotometric measurements on sugar products has shown that even more rigorous precautions are necessary (*26, 199, 254, 255*). It was found that coloring matter does not follow Beer's law (*282*) when the particles are beyond a certain range of size, but the dividing line has not yet been accurately determined. It is necessary, therefore, in spectrophotometric work to permit only the faintest Tyndall effect in the solution to be examined. Even solutions of purified sucrose have been found to exhibit a Tyndall effect (*66, 75, 123, 228*).

Starch.—Traces of starch may be considered a normal constituent of young sugar cane, but as it reaches maturity the starch usually disappears from that portion used for sugar manufacture. It has been reported, however, that Uba cane grown in Natal contains a sufficient quantity to cause difficulties in factory operations (*137*). Juice from this variety of cane is noted for its refractory properties as regards clarification and, although confirmation is lacking, it is possible that starch is partially responsible for factory-operating difficulties in districts other than Natal. Starch occurs more frequently in sorgo juice (*285, 346*) than in cane, but its source may at times be in doubt since incomplete removal of the seed heads makes contamination of the juice with starch rather easy. The concentration of starch in sorgo sirup may be sufficient to render the sirup jelly-like in consistency, rendering manufacture difficult and the quality of the sirup very inferior. A single investigator has also reported the presence of starch in beets (*251*).

Inorganic Constituents.—It is difficult to determine just what proportion of the ash constituents is colloidal. The strictly inorganic compounds are believed to be molecularly dispersed. Some of the mixed compounds, such as the organo-silicon compounds (*39, 40, 41, 108, 113, 215, 216*), calcium salts of certain organic acids and organic phosphorus compounds (nuclear substances) are probably colloidally dispersed, since they are always found associated with the colloids separated from sugar liquors by either dialysis or ultrafiltration. A portion may, of course, be held by adsorption on the colloid particles, but undoubtedly by far the greater quantity is retained by the dialyzing or ultrafiltration membrane by virtue of its colloidal condition. From Table 1 it may be noted that the ash content of these colloids ranges from about 9 to 56 per cent, depending on the type of colloid, its source and method of isolation. The water-soluble portion of the colloids contains the least ash. Colloids from cane sugar factory products contain about the same quantity as similar products of a beet sugar factory, whereas the greatest proportion of ash in colloids is found in those from maple sirup. [Seasonal and specific variations are to be expected. J. A.]

Miscellaneous Constituents.—Among the constituents which may be considered colloidal, and which at times may be responsible for certain sugar manufacturing difficulties, may be mentioned saponin (*7, 175, 280, 293, 324, 325*) and another glucoside, coniferin, which has been isolated from woody beets (*194*).

An interesting constituent of both sugar beets and sugar cane is the so-called "colloid water," which has been the subject of much controversial literature (*46, 98, 128, 145, 151, 188, 196, 214, 253, 260, 317*). It is evidently water adsorbed by, or water of hydration of, the saccharo-colloids of the fiber or marc, and is distinct from water contained in the sweet sap.

METHODS FOR DETERMINING COLLOIDS—QUANTITATIVE DATA.

It is to be noted from the preceding sections that the colloids of sugarhouse products consist of a heterogeneous mixture of substances in admixture with crystalloids and with materials of greater than colloid particle size. It is a difficult problem, therefore, and one yet to be solved, to effect a precise separation of the colloids from this other material. Various means such as centrifuging, dialysis and ultrafiltration have been used, but all are open to certain objections, with the result that the quantitative data on colloids can only be considered as approximate.

*Dialysis and Ultrafiltration.**—The methods usually employed for the approximate quantitative separation of colloids are dialysis and ultrafiltration through semi-permeable membranes of collodion. Theoretically, dialysis is more suitable and is less subject to objection than ultrafiltration, especially in view of the unknown effect on permeability of the relatively high pressures employed in the latter method. However, ultrafiltration appears to be preferable from the standpoint of greater ease of preparing membranes of rea-

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* *See* paper on Ultrafiltration by H. Bechhold in Vol. I of this series. J. A.

sonably constant permeability and also from the standpoint of time required for separating colloids.

The preparation of dialyzers and ultrafilters has been described in detail elsewhere (*4*, p. 820). It is desirable to emphasize the importance of adopting a standardized procedure for their preparation in order to obtain as nearly constant permeability as possible. It is also desirable to determine the approximate pore size of the membranes, since the size of particles retained by the filter or dialyzing sac is largely dependent upon this factor. This point is too frequently overlooked.

During ultrafiltration or dialysis, a portion of the colloids becomes flocculated, due, it is believed, to the removal of the peptizing and stabilizing influence of sugar and certain electrolytes. If a water dispersion of the colloids so separated is evaporated to dryness, an additional quantity of the material becomes incapable of being redispersed. This property of the colloids has served as a basis for classifying them into two groups—"reversible" and "irreversible" colloids. Although it is not possible to make a sharp distinction between these two types, because a portion of the reversible colloids becomes irreversible each time a water dispersion of them is evaporated to dryness, the procedure can be standardized sufficiently to give valuable information, particularly from the viewpoint of sugar technology. Colloids of the irreversible type and those which exhibit a tendency toward the properties of this type are the ones which are most easily removed from sugar-plant juices by the defecation and clarification processes now in use. These are also probably responsible to some extent for the formation of scale on heating surfaces and for the formation of precipitates in sirups after concentration and standing. In addition, the reduction in solubility of crystalloidal non-sugar compounds as a result of concentration of the juice plays a part in these well-known phenomena.

Electro-dialysis.—Some of the disadvantages of dialysis in comparison with ultrafiltration may be overcome by employing an electrical potential to accelerate diffusion of salts through the membranes. This process is termed "electro-dialysis," the principles of which and the apparatus employed have already been discussed (*4*, p. 937). This method has found application in many colloid researches, but, unfortunately, has not been applied from a quantitative standpoint to studies of sugar-factory products. It may have some interesting possibilities in this respect. The practical application of electro-dialysis to the purification of sugar juices, which has aroused considerable interest, will be discussed later.

*Super-centrifuging.**—The method of centrifuging at very high speeds (super-centrifuging) has recently been advocated for the separation of colloidally dispersed material (*4*, p. 846). Such a method is of course satisfactory for eliminating particles of relatively high density, but its use for removing very highly dispersed colloids, or those, such as gums, which are highly hydrated, is open to some question. The density of the colloidal particles in many cases probably approximates closely that of the sugar solution, so that their removal is impossible with the centrifugal force ordinarily obtainable, particularly when high viscosity effects are also encountered. There appear to be no data available regarding the proportion of colloidal material which can be removed from sugar factory products by such means.

Electrical Properties of Colloids and the Dye Test.†—As is the nature of many colloids dispersed in water, the electric charge of the colloids in sugar

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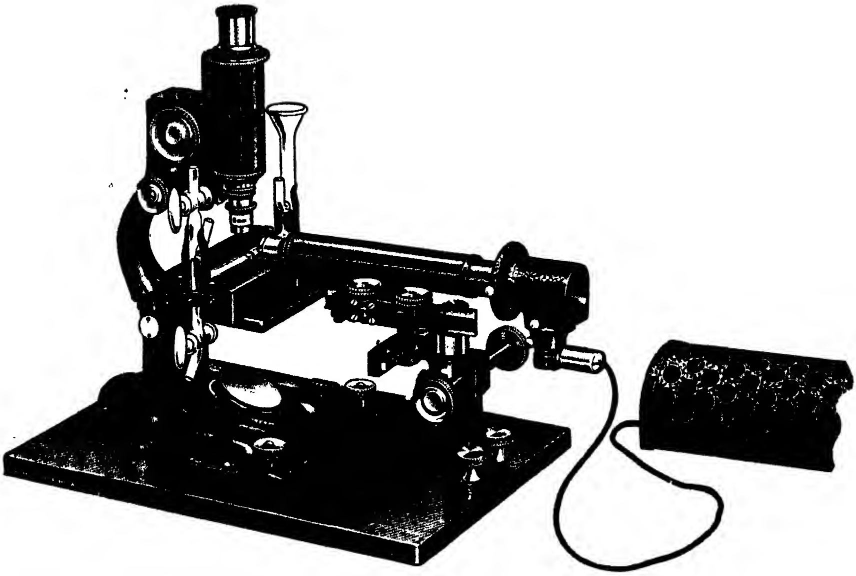
* *See* paper on the Ultracentrifuge by The Svedberg in Vol. I of this series. J. A.

† *See* paper by L. Michaelis and H. Freundlich on Electrical Properties of Colloids in Vol. I of this series. J. A.

beet and sugar cane liquors is negative (*20, 97*) over a very broad hydrogen-ion concentration range (*24*), indicating that these colloids as a group exhibit no normal isoelectric point. This is contrary to the belief of various investigators who, without making cataphoresis measurements (which is the surest method of proving the existence of such a property), have attempted to show from theoretical considerations (*134, 139, 286*) and from factory or laboratory observations that there exists a definite isoelectric point.

In contrast to the colloids of sugar-beet and sugar-cane products, the colloids of converter liquors in the corn sirup and corn sugar industry normally have a positive electric charge and show a definite isoelectric point, which varies from 3.37 to 5.29 pH (*23, 235*). The difference in the isoelectric point of these colloids is probably due to relatively small variations in composition of the converter liquor dependent upon the purity of the starch used and the conditions of conversion, particularly the concentration of acid and the time and temperature of heating.



Courtesy of Arthur H. Thomas Co., Philadelphia, Pa.

FIG. 1.—Cataphoresis apparatus.

Advantage has been taken of the electrical charge of colloids for devising a semi-quantitative method for their estimation. This method has been termed the dye test (*20, 21, 22*), and is based upon the property of mutual electrical neutralization and coagulation of the sugar colloids and a dye possessing an opposite charge. The quantity of dye solution (such as 1 gram per liter) required to neutralize exactly the electric charge on the colloids contained in a definite weight of sugar product, as determined by cataphoresis measurements,* is taken as an approximate measure of the quantity of colloidal material present. It has also been proposed to weigh the precipitated colloids and to subtract from this weight the quantity of dye used for neutralization (*268*), but apparently this method has not found extensive application.

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* A very satisfactory cataphoresis apparatus for performing the dye test is now manufactured by the Arthur H. Thomas Co., Philadelphia, Pa. See Fig. 1.

As the electric charge on the colloidal particles varies with such factors as the nature of the colloids, the treatment to which they have been subjected, the hydrogen-ion concentration of the solution, and in general the concentration and nature of the electrolytes present, it is obvious that an electrical neutralization method can be only approximately quantitative and that care must be taken in conducting the tests and in interpreting results.* It is necessary also to use a dye which has a definite chemical structure and which can be prepared reasonably uniform and pure. Water-soluble Night Blue has been found to be very satisfactory in this respect and has been used for the approximate estimation of colloids in cane and beet sugar products (*20, 21, 22, 23, 62, 235, 240, 243, 294*), but since this dye has a positive electric charge it cannot be used for estimating colloids in starch conversion liquors.

There is some question in regard to the specific influence upon the dye itself of the various non-sugar compounds normally present in sugar products. It is an interesting fact that ultrafiltrates and dialyzates are usually dye-reactive to a considerable degree, which indicates either the non-retention of a large proportion of colloids by the membranes or the presence of other substances which react with the dye. The colloids remaining after removal of crystalloids by ultrafiltration or dialysis show typical emulsoid characteristics in that they are dye-reactive but do not flocculate readily with the dye (less readily than in the original liquor). These facts bring up interesting questions regarding the source and quantity of the electric charge and the chemical reactions involved during neutralization of the dye by the sugar colloids, which should be investigated further if the dye test or a similar method is to be applied in a more definitely quantitative way.

Surface Tension.†—Surface tension is usually considered in connection with colloids owing to their characteristic effect upon this physical property. A number of investigators (*3, 82, 94, 165, 191, 192, 237, 238, 242, 265, 281, 323, 326*) have measured the surface tension of sugar products in an attempt to correlate such data with colloid content. Data of this character are presented in Table 2. These investigators have apparently overlooked, however, the probability of contamination by oil or grease which may be present in many sugar-factory products. This possibility has been pointed out in the more recent investigations (*153, 276*). Correlation with colloid content of much of the surface tension data pertaining to sugar liquors is therefore open to much doubt.

Quantitative Data.—In the accompanying tables are given much of the available pertinent data relating to the colloid content and dye test of various sugar products derived from sugar cane, sugar beets, sorgo cane and maple trees. Many variations in the data pertaining to similar products are to be noted, but this is not surprising in view of the variation in colloid content to which these products are subject and the opportunity for errors in making colloid determinations, particularly since no uniformly satisfactory procedure for the preparation of the sample has yet been devised. The ash content of the total colloids ranges consistently between 4 and 20 per cent for all products with the exception of the colloids of maple sirup. In this case the average ash content of the colloids was 56 per cent, and 85 per cent of this ash was silica. In all products the ash content of the reversible fraction is low in comparison with that of the irreversible fraction. In cases in which the composition of the reversible fraction of the colloids was investigated it was

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* The reader should consult the original articles for detailed directions and precautions.

† Papers by W. D. Harkins, Sir W. B. Hardy and other papers in Vol. I of this series deal with surface tension. J. A.

found to contain considerable quantities of araban, strongly indicating the presence of "gums."

The colloid content of beet diffusion juice as determined by the dye test is about twice as great as that of raw cane juice (*cf.* Tables 2 and 3). Greater extraction by the diffusion process probably accounts for a part of this difference. Owing to the more rigorous clarification of beet juice, the colloid content is, nevertheless, reduced below that of lime-defecated cane juice and is about equal to that of cane juice clarified by the double carbonatation process. As is to be expected, the colloid content and dye value increase in almost direct proportion to the degree of concentration resulting either from evaporation of water or from removal of sugar by crystallization. This relationship is especially striking in the data given in Table 4 showing the dye test values of cane sugar refinery products.

COLLOID ASPECTS OF JUICE EXTRACTION.

Milling of Sugar Cane.—Since the beginning of the cane sugar industry, the process of juice extraction has consisted in crushing the cane and pressing out the juice. When this separation is made by using light pressure, the juice is richer in sugar and contains less colloids than when the cane is subjected to high pressure in multiple mills, as is customary in modern factories. This greater pressure, coupled with high maceration, liberates an increased proportion of the cell sap and colloidal constituents with the result that colloid problems have increased greatly with such modernization. The compensating factor is of course greater extraction of sugar and more sugar bagged per ton of cane. There is a limit, however, where the increase in sugar extraction is overbalanced by the increase in extraction of colloidal substances which have a detrimental influence on the factory process. Although sugar factory managements desire as high an extraction as it is possible to obtain with their equipment, there are undoubtedly many superintendents who would welcome a decrease in the colloidal as well as the other non-sugar constituents of their cane juices.

Colloid chemistry plays little part in the milling operation itself and is confined almost entirely to the maceration process, the principle of which is replacement of the original cell sap liberated by a previous mill, with dilute juice or water which is then expressed in the mill following. The absorption, diffusion and dilution effects are largely responsible for the efficiency of the maceration process. Conditions should be maintained whereby the blanket of cane bagasse will quickly absorb all the applied liquid so that diffusion of the cell sap into the added juice or water will be possible during the period required for the bagasse to pass between the two adjacent mills. The bagasse is in ideal condition for absorption of liquid just as it emerges from a mill, for it then expands from the high pressure exerted on it by the mill and is capable of absorbing water (comparable to releasing a squeezed sponge) very much more quickly than when mixing of the maceration liquid with the remaining cell sap is dependent on diffusion alone.

Diffusion of Sugar Beets.—During the infancy of the beet sugar industry, the juice of the sugar beet was extracted by rasping and pressing, but this method has long since been superseded by the "diffusion" process. In its original form it was more nearly a dialysis process, with the cell walls of the beet acting as membranes. Investigations on the speed with which various constituents of the beet migrate through membranes have shown that the inorganic salts pass out of the cell more quickly than sugar, and that proteins, gums and other typical colloids dialyze very slowly (*8*). At higher temperatures the sugar passes out relatively more quickly and salts relatively less quickly, so that the use of heat is advantageous up to a certain point. The modern process, however, is not by any means a pure dialysis. The cell walls are frequently ruptured or weakened by the high temperatures often used to speed up operations with the result that actual leaching of the cell contents by the hot water occurs. This causes a higher colloid content of the diffusion juice than was the rule in the early days of the industry.

During recent years considerable attention has been given to procedures for drying beets prior to diffusion (*14, 127, 231, 232, 233, 297, 333*). The underlying thought prompting these investigations was the possibility of storing the raw material for longer periods of time in order to extend the sugar factory operation over the entire year instead of the customary two or three months. As drying must produce rather profound changes in the behavior of some of the colloidal constituents of the beet, this subject deserves at least passing mention.

It is apparent that, during the drying operation, a considerable proportion of the colloidal matter is denatured and consequently is not redispersed during diffusion of the dried chips. This results in a juice which is claimed to be superior in quality and which may be clarified by rather simple procedures. A more thorough investigation, from a colloid viewpoint, of the diffusion of dried beet chips and the clarification of the resulting diffusion juice is very desirable.

Osmosis.—A more typical dialysis procedure has been used intermittently in the beet sugar industry since 1887 (*190*) for the extraction of sugar from beet molasses. In the diffusion of sugar beets a separation of sugar from colloids is an important object, whereas in the treatment of molasses it is desired to make a separation of the more readily dialyzable inorganic salts from the sugar, the colloidal material being thereby retained with the sugar. This is properly known as the "Osmose" process, and was revived for a short period in the United States (*80*) during the period of high price of sugar following the World War, the only essential modification of the earlier procedure apparently being the addition of a small quantity of hydrochloric acid to the molasses, which it is claimed gives a more favorable separation of salts from sugar. A more recent use of osmosis has been made in Europe (*120, 121*), but apparently with no particular success. Membranes of parchment were used in the "Osmose" process, but collodion has been suggested not only for this purpose but also for purification and sterilization of beet juice and similar products (*117*).

COLLOID ASPECTS OF CLARIFICATION PROCESSES.

The primary object of clarification processes in sugar manufacture is to eliminate as large a quantity of colloids and other non-sugar compounds from the sugar plant juice as possible, in order that the greatest recovery of sugar may be obtained with the least operating difficulties. The processes used vary considerably and depend upon the type of sugar to be produced; that is, whether raw, "direct consumption," or refined sugar.

Clarification in Raw Cane Sugar Manufacture.—In producing raw cane sugar the clarification process consists, in brief, of adding milk of lime to the screened cold raw juice until some definite titration or pH value is reached, heating, and allowing the coagulated material ("muds" or "cachaza") to settle and the scums to rise, either in tanks or in continuous clarifiers (Deming, Dorr, Rückstuhl, Gilchrist). The "clear" juice drawn from the defecators is pumped to the evaporators and the "muds" and scums are usually filtered, with or without the use of additional lime. In the Petree-Dorr process, the "muds" are returned to the mills, thereby eliminating the filter-press station. The filtered juice is added either to the unclarified or the clarified juice, depending on factory equipment and other conditions. There are some variations in this process, such as heating the juice before liming, using calcium sucrate (*294, 314*) instead of milk of lime, etc., for which certain advantages are claimed but which have not been widely adopted.

The action of lime is, for the most part, purely chemical in that it unites with phosphoric acid and certain organic acids to form insoluble compounds of a flocculent character. A precipitate of this type is usually highly adsorbent, and being formed directly in the cane juice it adsorbs and occludes the major portion of the suspended material, including on the average about 20 per cent of the colloids (*241, 242, 243, 294*) as determined by the dye test. Double defecation of cane juice apparently increases colloid elimination (*243*), which is to be expected from theoretical considerations.*

As indicating that the mechanism of colloid elimination is primarily by adsorption there may be cited the observations that the P_2O_5 content of the juice is closely correlated with the effectiveness of clarification (*12, 13, 49, 207, 211, 242, 243, 247, 301, 302*) and that increasing the phosphate content of the juice increases the elimination of colloidal material and improves the appearance of the juice (*42, 43, 49, 50, 163, 185, 211, 243, 247, 270*). It is interesting to note, too, that the calcium phosphate precipitate removes from the juice substances which otherwise would remain peptized by the sugars. It is well known that iron in the quantity usually present in cane juice cannot be precipitated as the hydroxide with alkalis in the presence of sugar, but that calcium phosphate adsorbs very appreciable quantities of iron and, therefore, must be largely responsible for the removal of iron during clarification (*49, 218*). In all probability numerous other substances are eliminated from the juice in a similar manner. The action of lime and phosphoric acid, "black paste," which was used for a great many years in sugar refineries for clarifying affined sugar melt, depends upon the same principle of adsorption and occlusion of the various impurities present. The adsorptive property can undoubtedly be ascribed to the physical character of the phosphate precipitate rather than to its chemical composition, since the ratio of CaO to P_2O_5 varies with the quantity of lime added (*45, 115, 185*).

The degree to which cane juice is limed varies considerably in different factories. Precipitation of acid calcium phosphate begins at a pH of about 6.0 (*115, 240*), but for maximum elimination of impurities the cold juice should be limed to a pH of 8.0 or above (*47, 154, 159, 207, 240, 242, 301, 302*). The reaction of the juice at this point should be sufficiently alkaline to prevent the evaporator sirup from becoming acid enough to cause inversion of sucrose, but on the other hand it should not be so high as to result in formation of an excessive quantity of soluble and partly colloidal lime salts (*168*) which are the cause of factory-operating difficulties at subsequent stages, nor to destroy, appreciably, reducing sugars with resulting formation of decomposition products, some of which doubtless have colloidal properties.

The application of heat in the clarification of cane juice causes coagulation of certain normal constituents of the juice, particularly albumin, and flocculation of the precipitate produced by lime. It has been stated that 72 per cent of the non-sugar substances in cane juice, which are eliminated by ordinary

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* *See* paper by H. J. Weiser in Vol. I of this series. J. A.

lime defecation, can be flocculated by the application of heat alone or can be removed by filtration through asbestos, whereas the removal of the remaining 28 per cent is ascribed to the action of calcium phosphate formed in the juice (*97, 111*). This indicates that a considerable proportion of the material eliminated from cane juice by lime defecation consists of particles of greater than colloidal dimensions which can be removed by such means as simple straining or filtration. There has been a tendency during the last few years toward fine screening of juice and even filtration of raw juice has been recommended. This latter process, however, has not yet found application in the manufacture of raw sugar. The removal of small particles of bagasse or bagacillo from the juice is desirable, because lime, especially when present in excess, peptizes a portion of the cellular tissues (*109*), which are believed to contribute to certain factory difficulties, and because a portion of the very fine particles of un-peptized material passes through the entire sugar manufacturing process and is finally present in the sugar (*257, 335*). This material is a portion of the non-settling matter which is regarded as being responsible for retarded filtration of raw sugars (*106, 172, 178, 206, 209, 210, 249, 299, 300, 335, 336, 337, 342*), an important difficulty experienced by the refiners of raw sugar.

The optimum temperature for heating limed juice is still a debated question, but general practice indicates that the boiling point, or a temperature very close to it, represents the best condition for producing flocculation. There are cases where heating to the boiling point or superheating the juice under pressure before liming is claimed to be of assistance in eliminating albuminoids and in decomposing organic silicon compounds (*39, 40, 41, 108, 110, 113, 182, 215, 216, 217*). Although it has not been definitely proven, it is probable that compounds of the latter class are colloidal in character and are a source of the silica present in colloids separated experimentally by means of dialysis or ultrafiltration. Scaling of heating surfaces and slow formation of silica-containing precipitates in cane sirup (*38, 74*) are probably also caused by such organic silicon compounds. [Possibly silicon is present as colloidal silicic acid, *protected* by organic colloids. J. A.]

Clarification in the Manufacture of Direct Consumption Sugar.—In making direct consumption sugar, that is, a "white" sugar produced directly from sugar cane or sugar beets, it is necessary to obtain greater elimination of colloids and other non-sugar substances from the juice than can be accomplished by use of lime alone. The carbonatation process is used exclusively for direct consumption beet sugar, whereas for cane sugar of a similar type three methods are in vogue, viz.: (1) a carbonatation process which is the same in principle as that used for beet sugar, except that the temperatures employed during clarification are considerably lower; (2) the sulfitation process using sulfur dioxide and lime; and (3) the lime and phosphoric acid method. From the standpoint of colloid chemistry there is nothing particularly different in these processes from that involved in simple lime defecation, with the exception that greater care must be exercised in controlling the processes to prevent the re-solution, peptization or freeing of precipitated or adsorbed substances which may occur when the proper limits of saturation are exceeded. This is particularly the case when the carbonatation process is employed. These processes have become fairly well standardized through many years of use, and have been improved as rapidly as chemistry has yielded additional knowledge regarding the reactions involved. Both the sulfitation and the carbonatation processes are more effective in removing colloidal material (*113, 242, 331*), coloring matter, etc., than ordinary lime defecation, which in these cases, also, is brought about principally by flocculation, occlusion and adsorption effects (*296*) facilitated by heat.

It is apparent that the best clarification and filtration are obtained when a large quantity of precipitate composed of rigid particles is produced in the juice. Microscopic observations have shown that the particles of slimy coagulum and the rigid particles of the inorganic precipitate become attached firmly to each other (*44, 53, 60, 71, 100, 307, 330*). It is fortunate that this is the case, for with the carbonatation process much depends upon the ability to filter the juice efficiently after each saturation. Although suitable indexes (titration and pH determinations) have been adopted for fixing the end-points of the second and third saturations, skill in judging the manner in which the precipitate in the first saturation juice settles, is still the usual means of controlling this process. As a result of experience, the operator can determine very closely when the stage is reached at which the coagulum is in a condition to filter readily, this condition apparently being directly correlated with maximum adsorption of colloidal material (*18*).

Clarification Processes Using Filter Aids and Decolorizing Agents.—It is natural that a very large number of agents for clarifying beet and cane juice (*304*, p. 535) should have been proposed and tried during the many years that sugar of a high degree of purity has been produced. Many of these agents possess considerable merit, but owing to their cost in relation to the benefits derived, as compared with lime, sulfur and carbon dioxide, and to some extent phosphates, practically none have survived the test of time. Mention should be made, however, of two agents which have come into wide use within the last decade—diatomaceous earth and vegetable decolorizing carbons.

The use of diatomaceous earth in conjunction with mechanical press filtration has displaced the lime-phosphoric acid clarification of affined sugar melt in sugar refining; this material is also used to some extent as an aid to filtration of beet sugar sirups and of muds in the manufacture of raw cane sugar. Filtration of the entire volume of cane juice has been suggested as a means of improving clarification and hence the quality of the sugar, but as a considerable quantity is required for efficient filtration, the method has not advanced beyond the experimental stage.

The first view taken of the action of diatomaceous earth was to regard it as an adsorbent for colloidal and other substances; in fact, data have been given which were assumed to prove this contention (*57, 168, 225*). However, more recent work strongly discredits this theory and makes it appear that the action of this material in the filtration of sugar solutions is primarily that of a mechanical straining medium and that adsorption of colloids plays little part (*24, 26*). This conclusion is based on the observations that: (1) the dye test value of raw sugar solutions is changed very little, if at all, by filtration through diatomaceous earth; (2) the filtered raw sugar solution may have a filtration rate approximating that of a pure sugar solution (*11, 24*) (depending upon the quality of diatomaceous earth and manner in which the filter aid is used) in spite of the difference in the quantity of colloids present in these two solutions; and (3) the material removed from sugar solutions by diatomaceous earth can be largely separated from the latter by suspending the disintegrated filter cake in water and centrifuging at low speeds to remove the diatomaceous earth (*24*).

If this separated material is re-suspended in a pure sugar sirup, in the same proportion as in the raw sugar sirup, the filtration rate is practically the same as that of the original raw sugar sirup (*24*), indicating that the material which retards filtration consists for the most part of suspended, "non-settling" particles retained by the diatomaceous earth when present as a cake in a filter press. The quantity of material removed from a sugar solution by diatomaceous earth is dependent not only upon the quantity but also upon the quality of the diatomaceous earth used. The more rapidly filtering grades generally remove less suspended material from the sugar melt than those of slower filtering characteristics, with the result that the sugar producer often suffers loss of clarity of filtered sirup in order to obtain an increased filtration rate. It has become the practice, therefore, to select a filter aid of such grade as to give the desired balance between clarity and rate of filtration. One reason for the diversity of opinion regarding the action of diatomaceous earth is probably the fact that a considerable quantity of the material separated and weighed as colloids in laboratory measurements may consist of suspended particles larger than colloidal size, that is, about 200 $m\mu$. There is no satisfactory method available whereby it is possible to make a close separation of non-colloidal particles prior to separation of colloids by ultrafiltration or dialysis; hence a more precise determination of the question must await the development of more accurate methods.

Diatomaceous earth does not remove coloring substances from sugar solutions except possibly when these substances are present in a state of relatively gross dispersion. Therefore other agents are required for the removal of color. These are available in the form of highly activated vegetable decolorizing carbons which have been on the market in commercial quantity since about 1909 (*202*), and which have since aroused great interest among sugar technologists, as is evidenced by the voluminous literature bearing on this subject.* Interest in these carbons may be attributed to their high decolorizing efficiency, to their possible use for producing refined sugar directly on the plantation, and their use as an aid in improving quality when supplementing the usual processes employed in making direct consumption sugars or sirup.

The nature and properties of activated chars used for gas defense during the recent war, as well as the properties of decolorizing carbons, have been studied quite extensively. It is well known that activated carbons show selective adsorption properties (*32, 124, 150, 169, 187, 212, 252, 263, 264, 267, 298, 316, 326, 332, 344*). For instance, good gas absorbing carbons are generally poor decolorizers, and a decolorizing carbon that is particularly efficient for sugar products may be very mediocre for use with oils, and vice versa. The reason for this must probably be sought in differences in the size and perhaps the shape of the ultramicroscopic pores of these carbons (*1, 19, 60, 125, 316*). It has been definitely proved, at least for sugar products, that the decolorizing effect of these carbons is due to true adsorption, following the well-known experimental formula (*90, 150, 277, 278, 279, 318, 353*). Since adsorption is a function depending on two (and perhaps even more) constants, it is evident that it is impossible to express the comparative decolorizing power of a carbon for a certain sugar product by one simple figure. For the same product one carbon may, at a certain concentration and using a certain proportion of carbon, be better than another carbon; whereas under changed conditions the reverse may be true (*52, 73, 90, 277, 278, 279, 320, 322, 353*). This undoubtedly accounts for the widely divergent opinions of various investigators regarding the comparative efficiency of different carbons. The proper way to evaluate the efficiency of a carbon with reference to a given sugar product is to determine the two constants in the adsorption formula by establishing a sufficient number of points on the logarithmic curve.

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* No attempt has been made to present a bibliography on carbons, but instead there are given references to reviews (*9, 33, 54, 81, 83, 162, 203, 348, 349*).

It might be expected that the adsorption formula holds true for all nonsugars as well as for coloring substances; unfortunately, there is little published data at hand regarding this point (*328*). It is well known, however, that adsorption of colloids and ash constituents occurs when sugar liquors are treated with either bone char or vegetable decolorizing carbon (*45, 57, 72, 85, 87, 92, 95, 96, 116, 130, 152, 161, 164, 169, 181, 182, 221, 222, 318, 343, 345*). That there is a difference in the behavior of carbons of these two types is also well known, but when their chemical composition is considered the difference is really not unexpected (*72, 160, 161, 174, 181, 187, 273, 343*). The superiority of the vegetable carbons as decolorizers is due to the high percentage of active carbon, whereas the efficiency of bone black in adsorbing ash constituents, particularly calcium salts (*91, 267*), is to be credited largely to the calcium phosphate which constitutes 75 to 80 per cent of the char, as would be anticipated from theoretical considerations. The peculiar structure and hardness of bone black offer great advantages from the standpoint of handling. Vegetable decolorizing carbons also have special advantages because of their enormous power of adsorbing coloring substances.

The efficiency of decolorizing carbons is governed by a number of factors such as the hydrogen-ion concentration, temperature and density of the sugar liquor, time of contact, etc. (*33, 51, 58, 193, 332*), and all of these factors are of practical importance. In general, it may be said that maximum decolorization with vegetable carbons as applied to sugar manufacture occurs in an acidified sugar solution of low concentration and at elevated temperatures. Unfortunately all of these conditions cannot be met in practice, but can of course be compensated by the use of a greater proportion of carbon, if by no other means. It is probable that the total benefit obtained with bone char and vegetable carbons is not due entirely to adsorption effects; in addition to decolorization, clarification of the sugar liquor may result in part at least from filtration and ultrafiltration effects.

Clarification by Skimming.—There is another type of clarification which is widely applied in the production of cane, sorgo, and maple sirups, and to some extent in the production of cane sugar; that is, clarification by skimming (and heating). Regardless of whether the juice is limed or not, a part of the coagulum adsorbs the dissolved gases expelled by heating, and the entire mass, having a lower specific gravity than the juice, rises to the surface and can be removed by skimming or brushing. In open evaporators, so widely used for production of edible sirup, the material flocculated by heat is continuously conveyed by the foaming juice to a certain section of the evaporating pan which varies with its construction and is there removed by skimming. A high degree of clarity of the juice may be obtained in this manner. Since the concentration of colloids tends to increase at air-liquid interfaces, one would expect that by repeatedly brushing off the foam which forms on juices when heated, it might be possible to eliminate colloids to an extent comparable to that obtained by the action of lime and heat. The data available do not, however, sufficiently indicate the extent of elimination of colloids by this procedure. To have wider application in sugar manufacture, the benefits derived must, of course, be sufficient to justify the required expenditures for heat, labor, and equipment. Possible loss of sucrose by inversion is also an important consideration.

Clarification of Corn Sirup and Corn Sugar Liquors.—Colloid chemical principles are displayed in a more obvious and more definite manner in the clarification process used in the manufacture of corn sirup and dextrose than in that used in cane or beet sugar manufacture. The colloids in the converter liquor" resulting from the hydrolysis of starch by acid are charged positively and exhibit true isoelectric properties. In neutralizing the acid with alkali, a pH value is reached at which the charge on the colloids becomes neutralized and maximum flocculation occurs. If additional alkali is added, the charge on the colloids reverses and the colloids again become dispersed. The effectiveness of the clarification process therefore depends essentially upon adjusting the pH of the liquor to the isoelectric point. [The presence of other ions is also a factor. J. A.]

Sodium carbonate is the alkali customarily used for neutralizing converter liquor. Recently, however, it has been found that certain colloidal reagents with a negative electric charge may be used to advantage for neutralizing the charge of "converter liquor" colloids and causing their flocculation. The clay, bentonite, a colloidal aluminum silicate, and sodium aluminate have already found practical application (*23, 68*).

Miscellaneous Methods of Clarification.—A clarification process of another type which may possibly have some value in sugar manufacture is that based on the principle of electro-endosmosis, i.e., diffusion through semi-permeable membranes under the influence of an electric current. The purpose at first was to improve the extraction of sugar from beet slices by the use of charged diaphragms (*259*); however, this process has never been developed to the commercial stage. Although a large number of patents relating to electro-endosmosis have been issued during recent years (*35, 76, 77, 104, 105, 259, 347*), information as to results obtained is very meager (*167*), particularly from a colloid standpoint, so that it is difficult to ascertain the extent of elimination of colloids from sugar-plant juices and the feasibility of such processes.

Although centrifugal force has been employed for years in other industries as a means of clarification, its application to the clarification of sugar-plant juices has been extremely slow. Considerable interest has been aroused recently as a result of the development of apparently practical centrifugal machines (*2, 8a, 138, 157, 177, 179, 204*). However, these machines are still relatively inefficient from the standpoint of removal of colloids because of the relatively slow operating speed and the short time cycle employed. The beneficial results claimed must therefore be attributed to the removal of non-colloidal suspended material. By increasing the centrifugal force very greatly, as with a supercentrifuge (*4*, p. 846; *36*), it should be possible to remove a portion of the colloids, particularly those of the suspensoid type. It is probable, however, that colloids of the emulsoid or highly hydrated type cannot be removed to any material extent by supercentrifuging as now practiced and the benefits resulting from supercentrifuging would not be adequate under present economic conditions.

Of interest and possible importance, too, is the Hele-Shaw "Stream-line" filter (*10, 16, 122, 148, 256*), which, it is claimed, removes coloring substances, gums, pectin, and other colloids from sugar solutions. Unfortunately, pertinent data are not available. The filter consists of a pack of perforated discs of specially prepared paper with a matt surface which leaves minute passages for the liquid. The dimensions of the passages are governed by the pressure upon the pack of sheets. The liquid is pumped into a large channel and forced between the layers of paper (so-called "stream-line" effect) into small channels which conduct the filtered solution. Experiments have been made in the West Indies and Hawaii on the possibility of applying the filter to sugar manufacture, but only meager reports (*16, 256*) have been published.*

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* *See* papers by A. J. Pickard and Wm. James in Vol. III. J. A.

Colloid Aspects of Evaporation and Crystallization Processes.

During evaporation of clarified sugar juices, various phenomena occur which undoubtedly are of a colloid chemical nature. Foaming during evaporation is a difficulty frequently experienced in beet and cane sugar factories, and is probably due to the presence of such colloids as plant gums, peptones, saponins, etc. (*135, 149, 215, 356*). From surface energy considerations, frothing of solutions and the formation of emulsions is made possible by the lowering of the surface tension, but apparently other contributing factors are involved in a predominant way in the case of beet diffusion juice. This is known to contain considerable quantities of colloidal material and foams very copiously, yet its surface tension, as determined by various methods, approximates the value for pure water (*82, 94, 265, 281*).

Frothing, which makes its appearance at times in cane molasses during storage, is caused by evolution of gases resulting from decomposition reactions such as the reaction between amino acids and reducing sugars. The froth is stabilized by the presence of colloidal substances. Frothy sugar products often cause considerable inconvenience in chemical control work and serious errors resulting from incomplete removal of air may result, particularly in the determination of density with a hydrometer (*146, 184*).

It is not known whether scaling of the surfaces of juice heaters and evaporators in sugar factories involves colloid chemical factors, but theoretically it is possible that a portion of the colloidal material, particularly that of a highly hydrated gum-like nature, may tend to act as a preventive of hard scale formation, whereas those colloids which are dehydrated and flocculated most easily may become attached to the heating surfaces and eventually form a heavy crust. It may be possible, too, that colloidal material becomes attached to the heating surfaces as a result of electrical neutralization, the colloid particles and the heating surfaces bearing opposite charges; however, there are no observations in the literature which directly substantiate this theory. The tenacious attachment of scale to heating surfaces in a manner somewhat similar to electro-deposition of metals is suggestive of phenomena of this character. Adsorption of other substances would also be expected and this is in harmony with the somewhat varied chemical composition of the scale. It is interesting to note, also, that the nature of the surface influences the composition of the incrustations (*312*).

An investigation, from a colloidal viewpoint, of the factors which influence scale formation is very desirable. It would be necessary to make a distinction between incrustations of various types, for cause and remedy would probably vary. For instance, heavy incrustations due to the use of an excess of lime in clarifying cane juices and as an aid to filtration of cane juice muds and poor carbonatation work in beet sugar manufacture can frequently be remedied by more efficient chemical and mechanical control of the clarification process. Sugar-factory heating surface incrustations of the more common type contain a high proportion of silica (*283, 305*), which is probably derived from the organic silicon compounds previously mentioned as being of a colloidal nature. Scale formation during superheating of the raw juice in order to decompose these organic silicon compounds has been advanced as the principal objection to this method of elimination.

The flocculation of colloids from juices and sirups on concentration is of considerable practical importance. The behavior of cane sirups is worse in this respect than that of beet sirups, probably due to the fact that the juice has been subjected to less efficient clarification. The chemical composition of this flocculated material is somewhat similar to that of the incrustations on heating surfaces (*38, 59, 74*), indicating possibly that it is produced by the same process, i.e., slow dehydration and flocculation of "irreversible" colloids. The flocculent precipitate which forms in sirups of fairly high density on standing is detrimental in sirups such as cane, sorgo and maple sirups designed for marketing purposes, because it renders the product less attractive in appearance. In raw sugar manufacture such material is undoubtedly responsible to some extent for sugars of poor quality and contributes to such characteristics as dirtiness and poor filterability; in the manufacture of refined and other granulated sugars an off-colored and dull-appearing product usually results (*13, 48, 158, 222, 224*).

The quality of sugar is influenced by various other factors in addition to the presence of suspended material in the sirup and other liquors from which the sugar is produced. Probably of greatest importance from the colloidal standpoint is the adsorption of colloids, coloring material and other substances by the growing sugar crystals (*30, 34, 78, 87, 93, 156, 180, 200, 239, 274, 275, 284*). The presence of this material in sugar crystals, although amounting to only a few hundredths of one per cent, is responsible for the difference in behavior of various commercial granulated sugars when used in certain industries (*67*). This difference is particularly noticeable when granulated sugar is used for making hard candy (*cf.* the so-called "candy test" for sugar).

That sugar crystals are capable of adsorbing substances from the mother liquor during growth is indisputable. Differentiation must be made, however, between adsorption on the one hand and occlusion of the mother liquor and suspended particles between the interfaces of crystal aggregates on the other. By ultrafiltration of a series of beet sugar samples it has been shown that colloids are distributed rather uniformly throughout the sugar crystals (*239*). The ash constituents usually are present in higher concentration on the crystal surface, probably being derived to a great extent from the film of mother liquor which may not be entirely removed by washing in the centrifuge. The data pertaining to one sample in this series of beet sugars strongly indicated the presence of more grossly dispersed suspended material at the center of the crystals, and it is probable that this acted as a nucleus for crystal formation.

Since it is characteristic of colloids to increase in concentration at liquid-solid interfaces, which are immeasurably extended in a massecuite by the innumerable sugar crystals, adsorption of colloids on the crystal surfaces should not be unexpected. Electrical effects may also play a part in this phenomenon, for constituent crystal particles in changing from molecular dispersion to the solid phase may possess an electric charge. This electric charge, if present, is probably very feeble and, if it is a factor in adsorption, is positive, for the quantity of adsorbed colloids is usually very small and the charges of these colloids have always been found by cataphoresis measurements to be negative.

Coloring substances are usually not as serious a problem in beet sugar manufacture (*86*) as in the making of direct consumption cane sugar. This probably may be attributed to differences in the composition of the coloring substances of sugar beets and sugar cane. The pigments in cane juice appear to be of more intense color and apparently are more readily adsorbed by the sucrose crystal. Raw cane sugars possessing a greenish gray coloration are not as suitable for refining purposes as those which are golden brown to red (*31, 189, 340*) in color, since these latter pigments, whatever their source, are more easily adsorbed by the large proportion of bone char used.

An important phase of colloid chemistry in relation to sugar manufacture is the effect of colloids on the viscosity of sirups and molasses, for high viscosity retards the rate of crystallization (*88*) and frequently makes pan-boiling a difficult task (*89*). The effect of suspensoids upon viscosity is usually small, whereas emulsoids may increase viscosity greatly, and in some abnormal beet and cane juices it may even approach the plasticity of a jelly. The effect on viscosity of the colloids of sugar factory products, which contain colloids both of the suspensoid and the emulsoid types, has not been adequately investigated, owing partly to uncertainty regarding the influence of various non-colloidal constituents on viscosity. Viscosity data pertaining to beet molasses and sirups indicate that the relative effect of the non-sugar substances as a whole is to decrease viscosity (*44, 67, 69, 226*); in other words, when sucrose is partly replaced by non-sugar substances and a constant solids-water ratio is maintained, the viscosity is decreased. This effect is particularly noticeable in solutions of low water concentration.

In these experiments there was obtained only the total viscosity effect and not the individual effect of various non-sugar components. The viscosity of Steffenized beet molasses is in general higher than that of non-Steffenized molasses, but, as there is so much variation in viscosity in molasses of both types, it is difficult to derive definite conclusions. Additional knowledge of the identity and properties of both colloidal and non-colloidal non-sugar substances is required in order that a better understanding of the specific viscosity effects of colloids in sugar liquors may be attained.

The viscosity of cane molasses is generally greater than that of beet molasses (*67, 147, 171*), and extrapolation of sugar concentration-viscosity curves indicates that it usually exceeds the viscosity of pure sugar solutions of equal solids concentration. This indicates that the viscosity of the non-sugar constituents is greater than that of the sugars present. It is not known what proportion of this effect may be ascribed to colloids. In experiments in which colloids were separated from molasses and then added to pure sucrose solutions, little effect on viscosity was observed (*67*). The viscosity of cane molasses is materially lessened by filtration through diatomaceous earth or by treatment with decolorizing carbons (*24, 147, 171*). Evidence of appreciable adsorption of colloids from sugar factory liquors by diatomaceous earth is lacking and adsorption apparently does not explain the decrease in viscosity resulting from filtration through this material.

There is some evidence that cane molasses may exhibit plastic rather than true viscosity effects (*24*). Since cane molasses usually contains a large quantity of material which flocculates and settles out upon dilution, it is possible that this material may form a kind of continuous (gel) structure in the undiluted, high density molasses, thereby producing plastic effects and causing erroneous and high viscosity results. If this structure is broken up, or if the material is removed by filtration through diatomaceous earth or otherwise (after dilution of the molasses), a drop in viscosity should result, as is actually the case (*67, 147, 171*). Decolorizing carbons should remove this material as well as adsorb a portion of the colloidal and other non-sugar substances from the molasses, thus causing a still greater decrease in viscosity, and this has also been found to be the case (*67, 147, 171*). It is possible that the beneficial effects which are reported to result from centrifuging molasses (*177*) may be due to the removal of suspended material or to the breaking up of a gel-like structure formed by such material at low water concentrations. Slow boiling and poor vacuum pan circulation may also be explained by the presence of this material. Extreme effects of this kind are sometimes observed in Louisiana, when frozen and deteriorated cane (*338*) is being ground.

TABLE 1. *Colloid Content of Sugar Factory Products.*

Product	No. of Samples	Colloids										Basis of Calculation	Source of Data
		Reversible			Irreversible			Total			Ash Per Cent in Colloids		
		Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.			
Raw cane juice	6	—	—	—	—	—	—	0.244	0.484	0.373	9	Grams/100 cc.	*(57)*
(centrifuged)	4	—	—	—	—	—	—	0.130	0.226	0.173	9	Grams/100 cc.	*(57)*
(filtered through diatomaceous earth)	7	—	—	—	—	—	—	0.023	0.046	0.035	14	Grams/100 cc.	*(57)*
	—	—	—	0.20	—	—	—	—	—	—	—	Grams/100° Brix	*(243)*
	1	—	—	—	—	—	—	—	—	0.234	—	% on solids	*(20)*
(hand mill juice)	1	—	—	—	—	—	—	—	—	0.21	10	Grams/100° Brix	*(111)*
	4	—	—	—	—	—	—	1.36	2.19	1.81	—	% on Brix	*(114)*
(filtered through diatomaceous earth and carbon)	7	—	—	—	—	—	—	0.011	0.034	0.020	17	Grams/100 cc.	*(57)*
Defecated juice (lime)	1	—	—	—	—	—	—	—	—	0.058	—	Grams/100° Brix	*(111)*
	5	0.261	0.367	0.331	0.147	0.292	0.227	0.451	0.624	0.558	—	Grams/100° Brix	*(168)*
	6	0.206	0.407	0.342	0.013	0.054	0.027	0.224	0.441	0.315	—	Grams/100° Brix	*(243)*
Filterpress juice	5	0.421	0.548	0.485	0.027	0.131	0.087	0.540	0.672	0.572	—	Grams/100° Brix	*(168)*
Defecated juice (SO_2 and CaO)	3	—	—	—	—	—	—	0.039	0.052	0.047	11	Grams/100 cc.	*(57)*
	2	—	—	—	—	—	—	0.14	0.26	0.20	—	% on Brix	*(114)*
Raw sugar	6	—	—	—	—	—	—	0.124	0.240	0.175	—	% on sugar	*(21)*
Cane molasses	2	—	—	—	—	—	—	—	—	1.63*	20	% on molasses	*(111)*
Filtered raw sugar melt	1	—	—	0.045	—	—	0.057	—	—	1.02	—	% on sugar	*(21)*
Granulated sugar	4	0.003	0.076	0.034	0.004	0.014	0.011	0.017	0.080	0.044	4–20	% on sugar	*(238)*
	3	0.007	0.012	0.009	0.003	0.007	0.006	0.010	0.018	0.015	10	% on sugar	*(239)*
Beet molasses	3	0.060	0.229	0.167	0.149	0.215	0.180	0.201	0.444	0.347	10	% on molasses	*(238)*
	6	0.44	0.74	0.58**	0.17	0.35	0.23	0.61	0.94	0.81	5.3–7.6	% on molasses	*(61)*
(Steffen)	2	—	—	—	—	—	—	1.60	2.4†	—	4.2–5.6	% on sucrose	*(238)*
Sorgo sirup	13	0.142	0.874	0.377	0.087	0.590	0.351	0.230	1.463	0.728‡	4.7–15.2	% on solids	*(24)*
Maple sirup	2	—	—	0.027	—	—	0.037	—	—	0.064	56§	% on solids	*(24)*

* Wax—37 per cent; Pentosans—8.5 per cent; Protein—1.4 per cent.
** 25 per cent araban.
† 27 per cent araban.
‡ Pentosans—5 per cent.
§ 85 per cent SiO_2.

Miscellaneous Aspects of Colloid Chemistry.

In sorgo sirup production, jellying is a well-known phenomenon, but in this case the effect is due to the presence of starch which has become gelatinized during evaporation of the juice to sirup. Treatment of such juice with a diastase preparation results in hydrolysis of the starch to a sufficient degree to eliminate the jellying properties (*295, 346*). Similar treatment of certain starch-containing cane juices has also been recommended (*137*).

The use of pepsin has been proposed as an aid in clarifying beet and cane juices (*289, 290, 291, 292*). From a colloid standpoint the effect of the action of pepsin is to hydrolyze protein juice constituents to a stage at which colloidal properties are largely eliminated. The application of enzymes as an aid in sugar manufacture constitutes an interesting field for investigation, but the economic value of the benefits obtained is still a matter of some uncertainty.

In connection with the subject of enzymes, it is pertinent to note the application to the sugar and sugar-consuming industries of the widely distributed enzyme invertase, which is prepared (*17, 266*) as a colloidal dispersion. Its well-known property of hydrolyzing sucrose has been turned to advantage in the manufacture of fondant-type confectionery and of noncrystallizing high density sirups such as cane, maple, and soft or raw sugar sirups in which the use of acid reagents for inversion would adversely affect the flavor (*234*). This enzyme has also become of considerable value in the analytical determination of sucrose (*17*, p. 185), particularly in products of low purity or in those containing interfering substances such as invert sugar, amino acids, and acid-hydrolyzable sugars or gums.

Table 2. *Dye Value and Surface Tension of Beet Products.**

Product	Dye Value	Surface Tension (dynes per cm.)
Diffusion juice	1790–2600	61.1–67.8
1st carbonatation juice	320–455	59.2–61.0
2nd carbonatation juice	280–550	57.6–60.0
Thin juice	350–700	56.6–58.5
Thick juice	330–600	57.6–59.5
White fillmass	540–900	57.2–58.7
Raw sugar	155–380	56.2–60.0
White sugar	12–25	65.7–68.2
Molasses	1366–3150	53.2–56.9

* Source of data—Reference (82).

Table 3. *Raw Sugar Factory Products* (*Cane*).

Products	Dye Value	Source of Data
Crusher juice	386–548	241
1st mill juice	1208–1530	
2nd mill juice	3077–3529	
3rd mill juice	3228–4000	
4th mill juice	3397–3710	
Unlimed primary juice	989–1600	
Clarified juice	915–1121	
Clarified secondary juice	2262–2509	
Evaporator sirup	883–906	
1st molasses	1757–1884	
2nd molasses	3601–4618	
Final molasses	5645	
Defecated juice	850–1196	168
Filterpress juice	1336–2637	
Raw juice	868–1454	243
Defecated juice	689–1274	

TABLE 4. *Comparative Dye Values of Vegetable Carbon and Bone Char Refinery Products.*

Product	Vegetable ‡ Carbon	Bone Char §
Raw sugar	239	263
Affination sirup	1052	1394
Melted sugar	74.7 *	67 **
Sweet water to melter	28.1	67
Char liquor	11.9 *	9.6 **
1st massecuite	14.1	7.2
2nd massecuite	23.9	14.4
3rd massecuite	45.2	24
4th massecuite	64.9	48
5th massecuite	128	†
Granulated sugar	5.0	9

* Elimination by carbon treatment = 84 per cent.
** Elimination by carbon treatment = 86 per cent.
† Repassed over bone char.
‡ Reference (241).
§ Reference (237).

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Applied Colloidal Chemistry in Confectionery Manufacture

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Promotion or prevention of crystallization is behind every process in which sugar is employed. Some products must grain out but still retain sufficient moisture to make them acceptable, while others must show no grain if they are to meet with public approval. India is accredited with being the birthplace of the sugar industry, for here sugar was first prepared from sugar cane by the expression of juice and subsequent evaporation until sugar crystals began to form. The resulting mush was then poured into earthenware pots, with a hole in the bottom, and syrup was allowed to drain off. In some cases this crystal-syrup mush was poured into conical shaped holes in the ground and allowed to drain. It was early discovered that such crystals became very hard upon drying out, so in the natural course of events a search for materials which would prevent hardening was instituted.

Sugar was looked on first as a medicine and its sale confined to the apothecary shops. In its incorporation with medicinals crystallization caused disintegration of the product and, to prevent such an occurrence, the incorporation of gum arabic was common practice. It seems that pills which carried the name "dragee" were composed largely of gum arabic and sugar, along with some mystic potion. Gum arabic will prevent strong sugar solutions from crystallizing, so the first application of colloidal chemistry to the manufacture of confectionery dates from its first use. As time moved forward there were places which were not situated properly to obtain gum arabic; therefore other gums were looked for as a substitute. This led to experimenting with plants, fruits and general gummy exudations. A direct outcome was the production of marshmallow, which was first prepared from the root of the mallow plant. When this root was ground up with water the starch and gums formed a sticky sort of mass which would dissolve in hot water, and could be combined with sugar and beaten to incorporate air. Marshmallows of today do not contain any extract from the mallow root, since this has been entirely replaced by better and more convenient colloids.

After sugar passed through its stage as a medicine and became a popularized food, it was combined with milk which contains casein. As milk and sugar were boiled to a satisfactory consistency, caramels, toffees, fudges and the like were prepared. The consistency of these products will vary from the grained fudges into non-crystallizing caramels and toffees. Casein exerts a colloidal action and, when coupled with corn syrup, prevents the graining out or crystallization of sugar.

The next colloidal material of importance to be introduced into confectionery manufacture was egg albumen. Nougat, with its many modifications, originally depended upon egg white entirely for its consistency. It is customary to cook two batches in its preparation, one at a higher heat than the other. In the high cooked batch most of the sugar, corn syrup, milk and invert sugar is used. In the lower cooked batch small quantities of sugar, corn syrup and invert sugar are employed and, when this batch has reached the proper temperature, albumen, previously whipped to a froth, is incorporated, and the mixture allowed to beat until such time as it has reached the proper height. This whip is then stirred into the higher cooked batch, where it is gradually coagulated and causes the light fluffy character so familiar in nougat. Marshmallow is of a different type, in that it is generally of such a nature that gelatin only can be used. This is not true entirely for there are times when marshmallow whips are required and these contain albumen. There are mixtures, all the way from the soft whip to the hard marshmallow, which depend upon varying percentages of albumen and gelatin in combination. Products made from albumen remain soft and somewhat liquid, while those from gelatin will set up and assume a rigid shape. If products in which albumen has been used are heated high enough, the albumen will coagulate, just as it does when eggs are prepared in any conventional manner. Gelatin products, such as marshmallow, become liquid with heat and set up when cold. It may be added that the jelling power of gelatin, as used in confectionery, is gradually broken down by excessive heat, which is to be avoided.

In the preparation of fruit jellies, it has been customary to boil apricot or apple pulp, add sugar and cook to a string, after which the material may be cast in starch molds. Pectin is the colloidal principle involved in this operation and it, like gelatin, gradually breaks down with heat. Since the commercial production of pectin, it has become a familiar article in the confectionery plant, and finds uses in the production of materials wherever a fruit jelly consistency is desired.

No review of the application of colloids would be complete without giving due consideration to lecithin. This product has long been recognized as being of value in the formation of emulsions, as well as a desirable addition to the food value of products, in which it is used, since it contains notable quantities of phosphoric acid in organic combination. It was first discovered in brain tissue, later in egg yolk and then, after extensive investigation, it was found to be present in almost every seed and reproductive germ. The present commercial supply comes largely from Soya beans, from which it is extracted along with the oil, and it may be obtained in appreciable quantities from the press cake, where oil has been removed by mechanical means. Lecithin is of interest largely because it is a fat-soluble colloid, which also has great attraction for water. Such a compound may bring about ideal conditions in the production of chocolate coatings, if small amounts of moisture has caused thickening. It is further claimed that the emulsifying action of lecithin causes fat particles to be distributed more uniformly and that the resulting product will be more easily digested. This principle has been applied in the production of special chocolates recommended for those whose digestive organs do not readily assimilate fat. Not only is lecithin of value in the manufacture of chocolate products, but it also finds use wherever fat is to be distributed through a confection of any character. A notable example is butter-brittle, in which large percentages of dairy butter are distributed through a syrup composed of sugar and water and cooked to a temperature high enough to develop desired color and taste. Without an emulsifier, such as lecithin, this product may become coated with a thin film of grease, which oxidizes readily in the air and develops rancidity. In the production of taffies, caramels, nougats and the like a fat-soluble colloid of the lecithin type is also very desirable.

The remaining colloidal material of importance is seldom recognized by the industry, although used more often than any of those already mentioned. All converted starch products will contain dextrins in proportions varying with their method of preparation. A high-converted corn syrup will show a low dextrin content, while the low-converted product will show an increase in dextrin. In the production of marshmallow, nougat, whips of all kinds, fondants, caramels and the like corn syrup is generally employed. The presence of dextrin helps in the prevention of sugar grain, and may be considered as an auxiliary colloid. Perhaps all manufacturers do not realize the rôle played by dextrins, and it is suggested that different types of corn syrup be tried and results carefully noted. Undoubtedly results will be convincing.

Starch itself is one of the most widely employed colloidal materials and each modification in process of preparation produces changes in physical characteristics.* These variations start with starches as they are obtained from natural sources and progress through several intermediate steps until the extra thin boiling starches are obtained. Fluidity of the starch solution will be directly dependent upon the type used and subsequent treatment given. It does not stop here, for the use of a starch, with the same fluidity, does not always mean that the same physical characteristics will be found in a finished product of which it is a component part. There are chlorinated starches, phosphatized starches and starches modified by acid and alkaline treatments. There are also many other modifications, which have been practiced at one time or another to produce a satisfactory type for a particular purpose.

Plant processes also have their effect. The longer a batch of starch confections is boiled, the greater the change in physical characteristics of the starch itself. Assuming that the cooking time is the same, which does not always follow if the same quantity of moisture is to be removed, it can be seen that a starch which thickens faster, will retain moisture longer than one which boils thinner. If a thermometer is placed in such a cooking batch, the temperature may be apparently the same in the two cases due to loss of conductivity, while the actual moisture contained may vary greatly. After the batch is finished, the temperature of the starch molds into which it is cast, should be carefully regulated. Particularly is this true of confections which are not placed in a drying room. If it is necessary to use a drying room, the temperature, humidity and time of drying play an important rôle and should be standardized. Where products are dried too fast, the starch jellies have a tendency to skin over on the outside and to retain large quantities of moisture, and if they are dried slowly, further conversion in the confection itself may take place and produce a thinner consistency. Quite recently it has become common practice to employ a type of starch for boiling which will allow sufficient water to be removed from the confection, so that it may be cast into molding starch, whose temperature may reach as high as 190° F. Here no drying room time is required, for the boards, in which the molding starch is placed, may be stacked in a room with average temperature and humidity conditions until the jellies have sufficiently set up to be removed. By such a procedure the action of starch in the confection itself is different than where the finished product is placed in a drying room and the water removed by heat and air circulation.

It was mentioned earlier that gum arabic was perhaps one of the earliest colloidal materials to be used and that it had been replaced by starch in many later day confections. Wherever such substitution has taken place, a thin-boiling starch is desirable, for in it gel formation is not strong enough to

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* *See* paper on Starch by M. Samec in this volume. J. A.

retain an unnecessarily large quantity of water. If, after boiling, starches are substituted, it will be almost impossible to remove the necessary quantity of water during the boiling process unless fruit acids or an acid salt are added. Such a procedure is subject to variation and becomes a matter of personal judgment; therefore it is far better to use a properly processed starch in the beginning, so that a definite number of pounds in each batch will always produce uniform results in the finished product. An example of the use of thin-boiling starches may be found in the familiar gum confections of the chewy type, which are generally made into small shapes in order that drying time may be shortened.

Fruit slices have quite recently become popular and in the production of such confections a thick-boiling or modified thick-boiling starch is generally used. There are starches, processed so that they boil thin in the beginning but thicken during cooking, which also produce satisfactory confections of this type. The familiar orange slices, made by boiling starch, sugar, water and corn syrup to the proper consistency and then adding color and flavor, have attained great popularity. In some cases small quantities of a neutral vegetable fat has been emulsified through this confection to produce a cloudy effect. This cloudy effect is thought to be desirable, since it reminds of the cloud naturally present in fruit juices, particularly those of the citrus type. The colloidal nature of starch in the sugar solution makes this effect possible without the addition of any other protective colloid. There are almost unlimited possibilities in the production of individual type confections when the proper starch is selected, and if we follow through the effect of converting agents, either on the starch before it is used in the confection or in the confection itself of which it forms a composite part, it will be seen that consistency of such products may be varied at will.

The application of all colloidal materials in the manufacture of confectionery are for the same purpose, regardless of their sources. To preserve gloss and prevent crystallization, which is attended with drying out, many fondants which are used for dipping should contain small quantities of some colloidal material. It has been pointed out that nougat depends largely on the properties of egg albumen, while marshmallow will vary from whips which require albumen, to the cast type in which only gelatin is used. Fudges keep much better when milk is incorporated, for casein acts to retard crystallization and keeps the product in better condition. A greater quantity of milk will produce caramels and toffees, where no grain is apparent, provided the balance between corn syrup, invert sugar and sugar is proper. Thus we see that in many familiar confections colloidal materials have their constant application.

There is also a wide application in the production of raw materials to be used in confectionery manufacture. Flavoring extracts, which originally required the use of alcohol as a diluent, may now be prepared satisfactorily and at a far lower cost. Common procedure indicates that essential oils should be dispersed in sugar solutions of proper strength to permit fluidity, and that such dispersion be maintained by the incorporation of a fraction of a per cent of gelatin or other satisfactory colloid. Not only is this process applicable to the manufacture of flavoring emulsions, but also finds extensive use in the distribution of fats. It has been possible to disperse fifty per cent of cocoanut fat in a like amount of invert syrup, provided one per cent of gelatin is incorporated. If either the flavor emulsions, or those used for distribution of fat, are desired in transparent form, it becomes necessary to match the refractive indices of the sugar solution with that of the oil or fat, and then to disperse this mixture properly.

A Summary of the Colloid Chemistry of Starches *

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INTRODUCTION.[1]

Starches occur in the form of morphologically well-defined granules, whose shapes vary from one type of plant to another and whose constituents themselves are differentiated from one another by many physiological and physico-chemical characteristics.

Between the spherocrystalline form of starch and the elementary molecule itself which is the same in all starches, there are a series of aggregation states (gels, solutions, dextrins) which have particularly formed the basis of colloid-chemical investigations.

From the results obtained with starch solutions, numerous conclusions have been drawn as to the constitution of the starch granule itself, introducing, however, the undemonstrated assumption that the picture found in starch solutions preexists also in the starch granule. Despite this uncertainty, we definitely accept today the view that several different substances or different aggregation states of one and the same fundamental substance exist in the starch granule; their separation is possible by virtue of their varying resistance to diastatic ferments, acids, or water.

Recent X-ray investigations have given material support to the view that the starch granule has a crystalline structure.[2] Even although it has not been possible to make so complete an analysis as with cellulose, nevertheless the X-ray spectrograms disclose two types (potato groupings and wheat groupings).[2a]

The more resistant portion has been designated by the names farinose,[3] starch cellulose,[4] α-amylose,[5] and the less resistant portion by the names granulose,[6] β-amylose [7] or briefly as amylose.[8] The amyloses turning blue with iodine are termed amyloamyloses, those turning red with iodine are termed erythroamyloses.[9] The paste-forming substance has later been termed amylopectin.[10]

Sufficiently definite conclusions have not yet been formed as to the elementary molecule of the starch substances. The more recent investigations [11] indicate, on the one hand, that a polymerized maltose anhydride, of the polymerization grade of a hexa- or octa-amylose, and, on the other hand, that a polymerized triamylose is to be considered as the building unit of the starch substances. In the following treatment the magnitude of the elementary molecule itself is not of the first importance, our principal consideration being that in aqueous solutions and in starch pastes the existing particles are molecular groups, micelles,[12] or molecular aggregates (= molates).[13] In such aggregations, not only the disperse phase, but also particles of the dispersion medium and even other substances are associated, such as non-carbohydrate constituents. These latter are of particular significance in the characteristics of the

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* **Translated by Dr. Milton Levy, New York.**

starch granule. Phosphoric acid exists partly as an ester and partly as an associated complex.[14] Silicic acid is likewise in partial esterification [15] as well as also fatty acids.[16] C. Malfitano considers that in the arrangement of the building stones in the starch micelles, polymers of an anhydrosaccharide are stratified around a phosphate or silicate ion, something on the order of Werner complexes being formed.[17] K. H. Meyer [18] assumes a chain-like arrangement of the elementary building units united by primary valences, these chains being collected into bundles (micelles) by means of secondary valences. These molecular groups, and not the elementary molecules as such, determine the technically significant properties of starch pastes and starch solutions, and only the consideration of such systems offers a means of understanding correctly the nature of starch substances.

Starch Granules and Water.

As might be expected, water is always present in the starch granule, the quantity, however, in air-dried starches varying from sample to sample.[19] So long as the temperature has not reached a certain limit (the gelatinization temperature) the water content varies with the water vapor tension of the medium in which the granules are present.[20] Thus, it is possible, by keeping the starch in a vacuum over P_2O_5, to dehydrate it to the same degree as obtained by heating it at 120° to 130° C.[21] Alcohol of specific gravity 0.833 ($T = 12\frac{4}{9}$° C.) will abstract water from starch until about 11 per cent is left; starch with a lower water content will, however, dehydrate the alcohol and thus change its concentration. By determining the specific gravity of the alcohol, which has stood in contact with starch, it is possible to determine the water content of the starch with moderate accuracy.[22]

Upon lowering the exterior water vapor tension, the water content of the starch granules decreases. On the other hand, if the dehydrated granules are brought into a moist room, the water content will increase. The equilibrium value of the water content which is obtained upon dehydrating, is consistently higher than in the subsequent hydration, a phenomenon which has been designated as chemical hysteresis and investigated in careful detail.[23]

The curves expressing the relation of the vapor pressure in the atmosphere and the water content of the starch granules are combined sinusoids of the general formula $y - a = b \sin (\sigma - \beta) + c \sin (\sigma - \beta)$.[24] When partial or totally dehydrated starch granules take up water, heat is liberated, more being liberated the drier the starch. Thus, 1 gram of air-dried starch (water content of 16.33 per cent), after a loss of 16.14 per cent water, liberates 23.57 calories upon subsequent saturation with water. Upon later saturation with water, following a loss of 0.91 per cent water, only 2.96 calories are liberated. The specific volume decreases with the hydration. Thus, starch has a specific volume of 0.67273 when it has stood in contact with water at 0° C.; it has a specific volume of 0.72585, however, after a loss of 16.33 per cent water.[25] The hydration-dehydration values for volume contraction and energy loss are practically proportional. The heat expansion coefficient increases directly with the water content of the starch. The average pressure under which water exists in completely gelatinized starch amounts to —561 atmospheres, the maximal pressure with which water is drawn into completely dehydrated starch is —2073 atmospheres.[26]

Even though these observations on hydration and dehydration indicate that the process is smoothly continuous, it must be remembered that the mechanism is of several types, i.e., there is hydrate water, capillary-imbibed water and adsorptively retained water. The tenacity of water-binding may be variable and all observations regarding hydration and dehydration can only be the result of numerous individual mechanisms.

A partial differentiation of the individual mechanisms requires first a consideration of the variations which the starch substance undergoes on drying.

The mechanically and chemically intact starch granules in water at the ordinary temperature do not give up any substances belonging to the starch groups. When, however, the starch is freed from water, it is converted partially at the ordinary temperature into a water-soluble form. The X-ray spectra are blurred.[27] The solubilized fraction increases with increasing intensity of drying, however, only up to a certain point at which water of constitution is driven off by decomposition of the $C_6H_{10}O_5$ groups. The removal of water of constitution diminishes the solubility.[28] These results, obtained in a starch purified by freezing,[29] have subsequently been extended to observations using native starch granules. By determinations of osmotic pressure and of the fractions filtrable through a collodion membrane, it can be established that the degree of dispersity decreases with increasing intensity of drying.[30] An energetic drying of the starch granule also diminishes the adhesiveness of the paste prepared therefrom.[31] Since variations of the adsorptive or capillary-bound water are not associated with fundamental variations in the constitution of the molates, we are led to the view that part of the water contained in a starch granule is concerned with the structure of the starch micelle, playing something of the rôle of crystal water. By grinding the granules the linkages between the molates are severed, leading to finer dispersion upon subsequent solution. Hydration subsequent to drying brings the water back into the starch granule, but it is not known to what extent a reconstruction of the original molates is obtained.

THE STARCH GRANULE AS ADSORBENT.

The fact that certain salts exert an influence on the gelatinization temperature of starches, led A. Meyer to the hypothesis that starches take up salts from salt solutions. This takes place according to the relations between the various quantities of water, salt and amylose, corresponding to the condition of distribution.[32]

Such an absorption of dissolved materials by the starch granules can actually be demonstrated by means of dye solutions.[33] Dyes of one group do not enter the starch granule, for example, carmine, Congo red, Hessian purple. Another group colors starch granules slowly, as tropäolin, picric acid, methylene blue, indigo carmine, and Bismarck brown. Again another group colors starch rapidly, as fuchsin, neutral red, saffranin, methyl green, etc. The alcoholic solution of fuchsin dyes much more faintly than the aqueous solution.

Acids and salts dissolved in water are only slightly adsorbed by starch granules.[34] The adsorption varies with different types of starches, however, not so much according to mass as according to surface.[35]

Starch takes up bases[36] and basic dyes[37] much more strongly. The absorption of bases follows the law[38]

$$\frac{x}{(n-x)\,(a-x)} = K_n$$

The relatively strong binding of alkalis by starch is to be explained by assuming an acid nature of starch[39] or by assuming an alcoholate-like linking.[40]

Besides various mineral components which arise partly from the plant and partly from the manufacturing process, the starch granule contains phosphoric acid[41] in the form of amylophosphoric acid salts.[42] This amylophosphoric acid, which is liberated from its salts by acids, can react with bases and salts to form salts. Various substitutions of this nature naturally must have a certain influence on the adsorption of electrolytes by starch granules. Dried starches also adsorb gases; for example, 5 to 6 volumes of carbon dioxide can be taken up.[43]

GELATINIZATION.

If starch is heated to a certain temperature in the presence of water or brought into sufficiently concentrated solutions of certain crystalloids,[44] gelatinization (swelling) occurs.[45]

A small cavity first appears in the starch granule and as the resulting hollow spheroid continues to expand, the wall becomes thinner and the granule loses its double refraction. Finally the wall breaks into segments which agglutinate to form the ordinary starch paste if the original starch suspension was of sufficient concentration.[46] The gelatinization temperature varies for different species of starch[47] and different authors have reported different values for starch from the same species. This variation is due to the fact that the gelatinization temperature does not represent a transition point between two phases, but is a zone in which processes which are practically dormant at ordinary temperatures begin to show increased velocities. Different "gelatinization temperatures" must therefore result from the application of different methods of determination. Gelatinization has been followed by the microscopically observable changes in the form of starch granules,[48] by microscopic inspection of the starch suspension,[49] by the disappearance of the double refraction[50] of the granules, by the change of the optical properties of the starch suspension[51] as well as by the change in viscosity.[52]

An interesting study of the gelatinization of starch is due to J. R. Katz, who treated the problem in connection with the staling of bread.[53] The dynamics of gelatinization has been investigated by Wo. Ostwald and G. Fränkel.[54]

The gelatinization temperature is changed by the presence of crystalloids in relatively low concentrations. The anion of a salt determines primarily the direction of the change, while the cation has a more quantitative influence on the swelling process caused by the anion. The influences of salts and organic crystalloids on the swelling of starch and gelatin are identical except for slight variations. The influence of the simple ions (cations and anions) on swelling is a periodic function of the atomic weight and the arrangement of the ions according to the type and intensity of their influence on swelling leads to the Hofmeister series. Salts which are hydrolyzed in water producing an excess of hydroxyl ions, show a general tendency to favor swelling. Acids have no greater action than salts of the same concentration; even in this case the anion determines the direction of the displacement of the gelatinization temperature. However, solvate formation characteristic of acids has its rôle. Bases favor swelling of starch even in very dilute solution, showing relatively the greatest influence in the more dilute solutions.[55]

The nature of gelatinization has not yet been satisfactorily explained. The substances present in the paste may have been preformed in the starch granule: in this case the granule may be represented as mixed crystal of its constituents,[56] and gelatinization could be conceived as the formation of an aqueous solution and a water-containing gel.[57] According to this theory solutions result only at high temperatures because of the high temperature coefficient of solubility of certain granule constituents (amyloses) which hinder gel formation as long as they remain undissolved.[58] The gel constituents may, however, result from combination of the granule constituents with water during the gelatinization.[59] Since the reaction would occur in a two phase system and be the resultant of the cooperation of several unit processes (as for example, electrolytic dissociation of water, convection of the ions formed to the granule surface, sorption (imbibition) of water after use of the previously imbibed water, hydrate formation from the granule constituents), the extraordinarily high temperature coefficient (as high as 83,900,000) would be understandable.[60] In both cases substances which exert an influence on the physico-chemical state of water (as an active constituent) must influence the gelatinization and it is understandable why crystalloids with lyotiopic action change the gelatinization temperature and may even cause gelatinization at ordinary temperatures.[61]

On the other hand any change in the granule material would result in a change in the gelatinization temperature. Since bases react with the H_2PO_4 groups of the amylophosphoric acid as well as with the OH of the polysaccharide to produce changes in the granule material, the influences of bases on the gelatinization temperature is comprehensible.[62]

Stronger acids cause fundamental changes of the granule substance by disaggregation of the starch micelles and partial hydrolysis of the polysaccharides. This becomes evident in changes of the gelatinization temperature and of the entire swelling process.

Starches gelatinized by cold water have recently become of great practical importance in commerce under the name of "Quellstarken." * The technical process of their production depends in part on the treatment of the starch with alkali or salts which favor gelatinization. The starch is partially gelatinized and dried.[63]

STRUCTURE OF STARCH PASTE.[64]

Starch paste prepared by gelatinization of starch granules and not heated further, consists of two constituents: an aqueous *solution* of the granule substances giving a blue iodine color, and a highly swollen *jelly* which originates from the hulls of the starch granules which have been in part broken up and agglutinated. The jelly gives a violet or brown-red color with iodine. A. Meyer believes that the solution and gel are formed from a single substance (β-amylose) and speaks of an aqueous amylose solution and of a solution of water in amylose.[65] L. Maquenne and E. Roux, however, assume that the power of gelatinization is associated with a special substance which they call amylopectin, while they reserve the name amylose for the substance soluble in water at the gelatinization temperature.[66] According to this theory amylocellulose represents the largest micelles of the amyloses and would result from aggregation of the smaller micelles of the amyloses. Along with the organic components the starch paste also contains the electrolytes originating in the starch granule[67] apparently partly dissolved in the water, partly adsorbed by the starch, and partly chemically combined with the starch and the complexes so produced bestow special properties on the starch. Phosphoric acid is esterified with the polysaccharide and it is this colloidal ester (amylophosphoric acid) which is the true gelatinizing substance (amylopectin).[68] The concentration of silicic acid in the molecular aggregates appears to lend them a special resistance. Thus the amylocellulose is found to be especially rich in silicic acid.[69]

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* The best English equivalent is "Cold-water Paste Starch."

Separation of the paste constituents by filtration is not possible. The paste filters through paper very slowly and the filtrate from a paste containing 1 per cent dry matter contains but 0.02 to 0.03 per cent. The fraction passing through the filter increases with the dilution of the paste, the length of time of heating, and the higher the temperature of storage.[70] Starch solutions produced from partially de-ashed starch granules may be filtered through collodion membranes.[71] The filtrate, however, contains both those granule constituents present in the sol and the gel.

With a very dilute paste in which the gel particles are not strongly agglutinated, a separation of sol and gel may be effected by settling.[72] A similar result is obtained by gelatinizing the starch grains with lye, followed by neutralization of the paste. Upon considerable dilution (sometimes after addition of alcohol) the gel portion of the paste settles out.[73] A much more complete separation of the sol and gel portions is obtained by subjecting a paste, preferably heated for a long time, to a somewhat prolonged electrolysis.[74] It must be remembered that the gel fraction obtained by one of the above-described methods is not pure amylopectin but may contain any other granule constituent not soluble under the conditions of preparation, such as retrograded amyloses and amylocellulose. Neither does the solution contain only amyloses, for amylopectin is capable of existing in the sol form. Actually amylocellulose may be isolated from the gel by treatment with 0.5 per cent HCl.[75] This is the cause of the extreme variations in the relative proportions of amyloses to amylopectin.[76]

FORMATION OF STARCH SOLUTIONS AND THEIR COMPOSITION.[77]

On continued heating of the paste at temperatures above 100° C. the amylopectin jelly increases its water content and after ½ hour at 120° C. the paste changes into a highly viscous solution, which can still be considered a two phase structure. G. Malfitano calls this slow solution "deflocculation" and considers the formation of a starch solution in a manner similar to that used by W. Nägeli for the process of solution of a crystal of sugar.[78] In the starch-water system there still remains a gel fraction which gives to the solution a certain stability of form which may be observed through suitably performed viscosity determinations.[79] Accompanying sol formation from the gel are other processes which essentially influence the constitution of the fluid. The amylophosphoric acid is hydrolyzed to the electrolyte-free organic component and dialyzable phosphate.[80] The organic component enters the sol fraction while the amylocellulose increases in concentration in the gel fraction and becomes less and less hydrated. It is still an open question whether the amylocellulose is entirely pre-formed or results from the loss of electrolyte.[81] After the greater part of the amylophosphoric acid has been destroyed, the amylocellulose precipitates in the form of flocks. At this point both the sol and gel fractions contain various components in various colloidal states according to the method of preparation of the solution.[81]

The properties of the starch solution undergo corresponding changes on heating. The viscosity and the influences on it of acids and bases decreases, the electrical conductivity and the quantity of dialyzable electrolytes increase while the substance becomes poorer in phosphorous content. The quantity of electrically transferable substance decreases; the alcohol precipitability decreases; the solution becomes more turbid, the content of dialyzable organic substance increases (though very little); associated with this the mean molate size of the colloid residue increases.[80]

Notable disaggregation or hydrolysis of the starch substances does not occur in neutral solutions within six hours at 135° C.

At 150° C., however, in the first three hours new phenomena appear. The solution becomes clear, the viscosity decreases rapidly, the mean molate size of the colloidal residue decreases and 60 per cent of the soluble substances pass through a collodion membrane. Reducing substances also appear in the solution.[82]

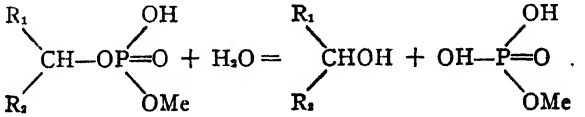
STARCH SOLUTIONS PRODUCED FROM DRIED OR PARTIALLY DE-ASHED STARCH GRANULES.

In drying the starch granules the water contained in the starch micelles is removed and the molecular bonds' adhesiveness is lessened. Starch solutions made from previously dried starch show a finer degree of dispersity than solutions made from the same starch without previous driving out of water. In spite of the fact that the phosphorous content of the starch substance in solutions prepared from dried starch is not different from that of other solutions, the viscosity and the amylopectin content determined under similar conditions are lower than in solutions prepared from untreated starch.[82] Starch dried some days at 105° C. gives solutions which contain reducing substances even if not boiled long.

Starch granules are de-ashed by treatment with dilute HCl followed by quantitative washing out of the acid.[83] Amylophosphate is converted by this treatment into free amylophosphoric acid. The hydrogen ions of this substance have a decisive rôle in the formation of the paste and solution. A starch solution having a mean molecular weight of 75,000 and relatively low viscosity is obtained in ½ hour at 120° C. from starch so de-ashed.[84] Combination of both treatments (washing with dilute acids and drying) gives a form of starch which passes through collodion practically without residue.[85] Solutions prepared either from dried starch granules or acid-treated starch show little resistance to heating under pressure. Their dispersity increases rapidly, reducing substances appear and the blue color with iodine potassium iodide solution changes to a violet.[82, 84]

The presence of H ions is the cause of the rapid and fundamental change of the pre-acid washed starch. The H^- originates from the amylophosphoric acid and in a 2 per cent solution of potato starch reaches a concentration of $8 \times 10^{-5}\ N$[87]. Solutions of native starch if boiled after the addition of acids which raise the H^- undergo like changes which are only quantitatively different.[82]

A measurable but slight quantity of free H^- appears spontaneously on boiling untreated starch granules. These arise from the dissociation of primary phosphate formed in the solution by saponification of the amylopectin according to the equation



$$\begin{matrix} R_1 & & OH \\ & \diagdown & \diagup \\ & CH{-}OP{=}O & \\ & \diagup & \diagdown \\ R_2 & & OMe \end{matrix} + H_2O = \begin{matrix} R_1 & \\ & \diagdown \\ & CHOH \\ & \diagup \\ R_2 & \end{matrix} + \begin{matrix} & & OH \\ & & \diagup \\ OH{-}P{=}O & & \\ & & \diagdown \\ & & OMe \end{matrix}\ .$$

Up to a certain time the processes occurring in boiling starch solution have the character of an autocatalytically accelerated reaction. Accompanying the disaggregation of the micelles carbonyl groups appear and oxygen rings are opened. Molates result from these processes which are not capable of sharp characterization and delimination but which have often been described as amylo, erythro, and achroödextrins.[86]

In view of the great sensitivity of the starch micelles to H^-, it is conceivable that slight OH concentrations will exert a stabilizing action. Alkali concentrations up to 5×10^{-3} initially increase the dispersity of the starch but the process of further colloid-chemical change is similar to that in pure water. In $\frac{N}{100}$ alkali an increasing peptization occurs with increasing time of boiling, the chemical processes producing yellow-colored reducing substances by some little-understood mechanism.[87] Starch solutions are therefore complicated structures which contain according to the manner of production, various quantities of amylo-amyloses, erythroamyloses, amylopectin (amylophosphate) amylocellulose and their disaggregation products, as well as the derivatives resulting from the opening of 0 bridges and carbonyl groups and electrolytes. Partial solution of starch substances occurs after sufficiently fine grinding even in cold water. The explanation that the heat resulting from grinding is responsible is accepted by some,[88] but it is not adequate, for a sufficiently fine grinding is of itself a sufficient condition for the production of colloidal solutions, a fact now well known in colloidal chemistry.

ISOLATION AND CHARACTERISTICS OF STARCH CONSTITUENTS.

The constituents contained in a starch solution may be separated by electrodialysis.[89] The amyloamyloses so produced form a colorless clear solution the essential properties of which agree with the amyloses prepared by O. Bütschli,[90] C. Tanret,[91] and Z. Gruzewska.[92] The mean molate size in 0.3 per cent solution is 80,000, the iodine color is pure blue, and color saturation is reached when the stoichiometric relationship $(C_6H_{10}O_5)_2$ is satisfied. The solution is stable for several days up to concentration of 0.35 per cent, but because opaque on long standing and flocks out partially. At higher concentration the "amyloamyloses" separate after a few hours at room temperature. The coagulum resulting from freezing does not redissolve on thawing at room temperature. A 0.35 per cent solution of amyloamyloses is electrically neutral, electrolyte free and shows a specific conductivity of 0.4×10^{-5} reciprocal ohms. In the electric field the amyloamyloses migrate to the positive pole, although very slowly. The optical activity is $a = 196°$, the viscosity in 1 per cent solution 1.008.[89] Ultramicroscopically this solution consists of numerous moving particles which agglutinate and form large groups in time.[92] Amyloamylose is strongly adsorbed by cotton.[91]

Amylopectin (usually containing amylocellulose) produced from potato starch has an electrical conductivity of 8.3×10^{-5} reciprocal ohms in 2 per cent solution, a hydrogen-ion concentration of 2.4×10^{-4}. The iodine color is violet; the viscosity in 0.2 per cent solution (from potato starch) is 2.79. In the electrical field it migrates rapidly to the positive pole. The dry substance contains 0.175 per cent P_2O_5. On heating with water amyloamyloses and erythroamyloses are formed.

Amylopectin from cereals forms turbid, slightly viscous gels while the amylopectin from subterranean storage organs (potatoes, arrow root, tapioca, meadow saffron) give clear pastes. The P_2O_5 content varies from 0.175 per cent for potato amylopectin to 0.010 per cent for rice amylopectin. The H-ion concentration and the nature of the cations present varies.[93] Amylopectin gels are not resolvable with the ultramicroscope.[92]

The *erythroamyloses* are colored wine red by iodine; color saturation is reached at a stoichiometric ratio $(C_6H_{10}O_5)_8I_2$. Their molate size averages 130 to 140,000. The specific rotation is 182° to 192°. They are electrolyte poor, little sensitive to precipitating agents, show no retrogradation and after precipitation by freezing readily dissolve again on thawing at ordinary temperatures. A 2 per cent solution shows an electrical conductivity of 0.5×10^{-5} reciprocal ohms.[89]

PROPERTIES OF STARCH SOLUTIONS.

The properties of a starch solution are determined by the properties of its constituents. All observations relating to one individual property can be evaluated only when that property is especially characteristic of one of the constituents of the solution.

Dispersity of Starch Solutions.—Starch solutions freed from salts by dialysis show no lowering of the freezing point or raising of the boiling point. Particle size must be determined by another method. The values found vary greatly since the problem is not exactly defined. For instance, the two concepts of molecular and micelle (or molate) weight have not been sufficiently differentiated.[94] The direct measurement of the osmotic pressure of the starch solution with a collodion membrane is the only thoroughly studied method which leads to reproducible results.[95] When the osmotic pressure reaches a constant value the amount of substance which has dialyzed may be determined; thus highly dispersed particles may be separated.

The mean micellular weight in similarly prepared solutions varies from one kind of starch to another. Thus in 2 per cent solution the mean micellular weight is 260,000 for arrow root starch and 120,000 for potato starch. A few per cent of the dissolved substance passes through collodion. The remaining properties of particular species of starch are much less dependent on the mean size of the particles than, for example, on their content of non-dialyzable electrolyte.[74] As previously stated the dispersion of a starch solution is highly dependent on the reaction of the solution. As a secondary factor the degree of dispersion is lower the more intensive the predrying of the granules.[82]

Viscosity.—Amylopectin causes the high viscosity of starch solutions. Transformation of this constituent from the state of "flocks" or spherocrystals to a gel is accompanied by a great increase of viscosity and the reverse process by a corresponding fall.[68] The viscosity of solutions of various species of starch is directly proportional to their content of amylopectin. The transformation of amylopectin to the electrolyte-free carbohydrate, such as occurs on heating starch solutions under pressure, is accompanied by a large decrease in viscosity.

Within certain limits a decrease in the micellular size of the amylopectin without loss of phosphoric acid, is accompanied by a decrease in viscosity.[96] The viscosity rises greatly if phosphoric acid is introduced into the amyloamyloses or erythroamyloses without great changes in dispersity.[97] Amylophosphoric acid and amylophosphates react with acids, bases, and salts, like true electrolytes. The transformation of the free acid to a strongly ionized primary salt is accompanied by a great increase in viscosity. The formation of the secondary salt of the alkali metals as well as the calcium and barium salts is accompanied by a decrease. Reaction of the polysaccharide with alkali—similarly to the reaction with alcohols—causes a great increase in viscosity.[98] The enormous increase of hydration of the submicroscopic particles capable of swelling on alkali addition, is easily understood on the assumption that a Donnan equilibrium is established.[99] The rule of W. Biltz that viscosity and molecular size are proportional [100] holds only with the limitation that all other conditions are unchanged. In general starch solutions deviate from Poiseuille's law. The resistance to flow is greater at low pressures and only in the higher pressure regions does the ordinary Ostwald method measure the resistance to flow due to internal friction. In the lower pressure regions the influence of cohesive force is important and obscures the results.[101] The viscosity was applied by L. W. Harrison [102] to the determination of stiffening power and by Dafert to the determination of adhesive power. Nevertheless according to our experience, the viscosity does not give a correct picture of the technically important properties such as the sizing power, thickening power and strength. For example: corn starch has an essentially greater sizing power than potato starch, although the latter gives pastes which are nearly 6 times as viscous as those of the former. O. Wolff used the viscosity to measure how far a starch will go in use.[103]

The Precipitability by Alcohol.—Like the viscosity, this is dependent on the hydration of the dissolved substance and shows a parallel behavior on addition of acids and alkalis. By the use of the precipitability test the neutralization of free amylophosphoric acid may be followed.[98] The various constituents of a starch solution are precipitated by different concentrations of alcohol and it was through this property that the amylose and amylopectins were separated from alkali-swollen starch granules.[73] The various compounds of starch with metals which were used in the evaluation determination of the elementary molecule of starch, were prepared by alcohol precipitation of the suitable reaction mixture.[104] With increasing disaggregation of the micelles, the precipitability by alcohol decreases so that a fractionation of the starch decomposition products is possible on the basis of their alcohol solubility.[105] By careful alcohol precipitation of starch solutions, H. L. Van de Sande-Bakhuyzen as well as C. L. Alsberg and E. P. Griffing obtained crystalline starch with marked double refraction.[106]

Coagulation by Freezing.—On freezing starch precipitates in the form of flocks which are only incompletely soluble on thawing.[107] Coagulation by freezing has been used for the separation of the starch from electrolytes.[108] The process, however, alters the starch considerably.[109] The constituents of the solutions behave differently on thawing. The amyloses do not redissolve, while amylose-free amylopectin readily redissolves.[73] The erythroamyloses behave like amylopectin.[110] A. R. Ling and O. R. Nanji [111] have constructed on this basis a method of separating amyloses and amylopectin, which has been tested by many authors, especially H. Pringsheim and K. Wolfsohn.[112]

Precipitably by Reagents.—The starch substances are precipitated by tannic acid,[113] * barium hydroxide, lead acetate,[114] colloidal iron,[115] and by I-KI solution in the presence of electrolytes.[115] In consequence of their slight hydrophylic nature amyloses are precipitated in very slight concentrations of precipitating agents; for example, the amylodextrin A. Mayer [116] or the erythroamyloses.[110] Three fractions may be separated from starch solutions by means of colloidal iron. One precipitates on adding the iron solution; another is precipitated by colloidal iron in the presence of electrolytes; while the third remains in solution after this treatment.

Precipitation with iodine solution and salts made it possible to prove that starch contains a fraction which yields no color with iodine, that the bulk gives a blue color and that the end fraction gives a brown color. Starch is also coagulated under the influence of certain enzymes.[116]

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* The ripening of some fruits (e.g. persimmons) involves a lysis and saccharification of tannin-starch complexes. *See*, e.g. the papers of Francis E. Lloyd (McGill University). J. A.

Ultramicroscopic Behavior.—Since starch solutions are a mixture of amyloamyloses and amylopectin, they give a complicated picture in the ultramicroscope, which depends on the concentration of the solution and the duration and intensity of the heating to which it has been subjected. When a separation into a sol and a gel fraction has occurred, there are observed a great number of round or egg-shaped particles in a highly viscous fluid, which contain luminous particles imbedded in a transparent mass. The viscous fraction becomes less prominent on dilution or continued heating, so that under these conditions the ultramicroscope shows particles in very active movement in an amicroscopic field. The amylopectin *may* appear in the same form after addition of precipitating agents such as alcohol.[117]

Ultrafiltration.—Carefully produced solutions of native starch scarcely contain any material which will pass through collodion.[71] The material which does pass through the membrane is very small in quantity and differs with each sample.[74] The fraction which passes the ultrafilter increases with increasing duration of heating, especially if the solution is slightly acid or if the starch granules have been thoroughly predried. This fraction decreases on ageing of the solution.[71] The increase in the ultrafiltrable fraction is not related to the appearance of reducing groups.[118]

Optical Activity.—Starch solutions are dextrorotatory, the rotation being variously reported ($\alpha_D = +196°$ to $+204°$). The cause of variation is on the one hand the difficulty of determining the starch content of the solutions, since different methods give different values. On the other hand the asymmetry of the starch molecule or micelles easily changes. For instance on heating under pressure, the rotatory power is demonstrably increased.[109] A systematic study of the relationship between rotatory power and constitution of the solution is in progress. A decrease of hydration is accompanied by an increase in rotation; and rotation decreases if the hydration is increased, for example by the action of alkali[98] or formaldehyde.[119] Analogously, salts with a pronounced lyotropic action decrease the rotation, although they decrease the color obtained with iodine like alkali and formaldehyde.[120] Peptization of the starch substance to the point where it passes through collodion causes no measurable change in the asymmetry.[118] The initial changes in starch occurring under the influence of diastase are not accompanied by a change in the asymmetry.[121] Under the influence of H ions the rotation of starch increases,[122] but the formation of reducing substances is accompanied by a decrease in optical activity. A satisfactory explanation is not available for the behavior of optical activity based on disaggregation, depolymerization, opening of O rings and formation of CO groups which are known to accompany some of these processes.

Iodine Color.—Starch solutions give with I-KI solution a dark blue, to violet blue color, depending on the relative ratios of amyloamyloses, amylopectin and erythroamyloses which are present. When amyloamyloses and erythroamyloses, or amylopectin are simultaneously present, the iodine first reacts with the amyloamyloses to give a pure blue, and after this is saturated the erythroamyloses react, and the mixed color, violet, appears. A mixture of α and β amyloses behave similarly.[123] Under the influence of lyotropic salts such as KI, $BaCl_2$ and LiCl, the blue changes to violet and on removal of the salt the blue is restored. The iodine color is destroyed by various organic and inorganic substances.[124]

Investigation of the nature of the substances capable of influencing the color given by starch and iodine is not yet complete. The modern conceptions of the structure of colloid solutions more or less consolidates the theories on the constitution of starch iodide. The fact that the taking up of iodine by dissolved starch follows the adsorption law,[125] does not exclude the secondary formation of a compound with certain stoichiometric relations.[126] On the other hand the idea that the starch iodide is formed by a solution of the iodine in the starch[127] is closely like the theory of adsorption in finely dispersed starch solutions.[128] This also applies to the view that the color is due to colloidal iodine protected by the starch[129] and that the coloring substance in the colloid flock consists of starch micelles and colloidal iodine.[130] Why some of the starch constituents give blue colors with iodine and others reddish brown, is not at all explained by any theory, or only partially. It has been established that the color produced by iodine is independent of the dispersion from micellular weights of 200,000 to 2,000, and that it is independent of the haste-making property.[131] Polyamyloses $(C_6H_{10}O_5)_6$ which give both red and blue colors with iodine are known.[132] Therefore the cause of the various colors appears to be in the organic chemical constitution. This is analogous to the deepening of iodine color caused by the substitution of H by halogens in hydrocarbons.[133]

Electrical Conductivity.—Electrolyte free amylo- and erythroamyloses form solutions which are only slightly better conductors than distilled water.[81] The greater conductivity of amylose solutions is caused by the presence of amylophosphoric acid salts, free amylophosphoric acid, or inorganic electrolytes. The conductivity increases under the same conditions as the number of ions; that is, by continued heating[80] or increasing age of the solution,[134] both of which cause phosphoric acid to be liberated by hydrolysis. The change of amylophosphoric acid salts to the free acid[80] and the binding of alkali by the starch constituents can be easily followed.[135]

Cataphoresis.—Starch constituents are transported to the + pole in the electrical field.[135] The speed of migration is greatest for the amylophosphate, and much slower for electrolyte-free carbohydrate, so that a partial separation occurs during cataphoresis. The amount of material transported in a given time interval therefore decreases as the amylophosphate is decomposed.[80] The transport of starch constituents is practically annihilated by the addition of alkali and the charge is reversed in the presence of excess alkali, so that in strongly alkaline solutions there is migration to the — pole. The reversal of charge occurs at the alkali concentration at which combination with the alcoholic hydroxyl groups of the starch begins.[136] A reversal also occurs because of the nitrogen-containing compounds in starch.[137]

Reaction of Starch Solutions.—According to the method of production, starch solutions are weakly acid, neutral, or even alkaline. They show different acidities towards different indicators due to the ionization of the phosphate.[138] The hydrogen-ion concentration in a 1 per cent potato starch solution is of the order of 10^{-4} N and in cereal starches 10^{-6} N.[139] Heating the starch solution increases the hydrogen-ion concentration as does pre-treatment of the granules with acid in consequence of the removal of cations. The colloid chemical as well as the other behavior of starch constituents is highly dependent on the reaction of the solution.[140] Because of the presence of OH groups, starch constituents have a small acid dissociation constant of about 10^{-13}.

Starch Solutions as Protective Colloids.—The protective action of the starch constituents is very slight; the reciprocal gold number for potato starch is 0.04.[141] The protective influence of wheat starch with silver and gold sols has been extensively studied and the influence of other factors on the protected sols established.[142] A gold sol thoroughly purified by dialysis until the conductivity was 1.48 $\times 10^{-5}$ reciprocal ohms precipitates at KCl concentrations between 0.01 and 0.02 *N*, or HCl concentrations between 0.00025 and 0.00035 *N* for HCl to 0.011, the same concentration of amylopectin raises the KCl necessary to 0.08 *N* and the HCl to 0.0015 *N*.[142] The change of amylopectin to the electrolyte-free carbohydrate may therefore be recognized by a decrease in the protective action against KCl.

The Ageing of Starch Solutions.—Starch solutions are the seat of several processes from the instant of their production. Some of the processes represent reversal and some continuation of those taking place in the production of the solution. The phenomena accompanying these processes are different depending on whether one works with a dilute or concentrated solution and how long the solution has been heated. The fraction present as gel loses water and agglutinates on ageing so that with a sufficient concentration there is a great increase of viscosity and the formation of an apparent jelly[143] (spontaneous gelatination). However, if the solution is dilute, this same process leads to precipitation and a decreased viscosity. Since the gel constituent consists mainly of amylopectin and some amylocellulose under these conditions the amylopectin has been precipitated. The material remaining in solution consists of amyloamyloses and if heating has been continued a certain time, of erythroamyloses. The solution therefore produces a blue to blue-violet color with iodine. Amyloamylose shows a greater tendency to agglutinate than erythroamylose, so that solutions precipitate a granular mass gradually after showing increased turbidity and a decrease of the fraction liquefied by malt.[144] These masses collect in a form similar to the acid curd of milk when the concentration is high enough (retrogradation).[145] In this process the relative quantity of amyloamyloses decreases in the solution, and the iodine color changes to violet or red-brown because of the preponderance of the erythroamyloses. It is to be noted that this change in color is not accompanied by any degradation of the starch such as is frequently assumed.[146] The amylopectin slowly loses phosphoric acid and as a consequence loses its adhesive properties, the viscosity of the solution decreases while the quantity of dialyzable electrolyte rises.

The coagulation of amyloamylose is favored by the decomposition of the amylopectin, since this exerts a protective action on amyloamylose. The disaggregation products of starch constituents produced by drying or pretreatment with acids, form solutions which also show a decrease in degree of dispersion on ageing, due to agglutination; but on redissolving, micelles are formed of the size which they had before precipitation, and not that of the original material.[147]

Spontaneous gelatinization occurs more rapidly the lower the temperature of the paste, and is influenced by various reagents.[148] Strong acids in low concentrations favor gelatinization. Their action is due to the liberation of feebly water-soluble amylophosphoric acid from the amylophosphates present in the native starch. If the concentration of acid is sufficient to bring about a disaggregation of the starch micelles, gelatinization is prevented.

In general alkalis greatly favor gelatinization; the intensity of the effect is, however, dependent on the nature of the cation. The structure of the resulting gel also depends on the cation. Potassium and sodium hydroxides produce soluble amylophosphates and amylates and in sufficient concentration produce clear gels. Calcium and particularly barium amylophosphates and amylates are difficultly soluble and produce turbid gels. The action of salts depends in the first instance on whether they produce acid or alkaline reaction in the solution, and in addition on the solubility and degree of hydration of the amylophosphates produced by metathesis. In every case the lyotropic action of the electrolytes is observable (M. Samec).

Retrogradation, defined by Maquenne as the production of starch forms not liquefied by malt, is more rapid and complete the lower the temperature of the solution.[149] The process is favored by acids and amylocoagulose [150] and retarded by alkali [151] and is relatively more complete the more concentrated the starch solution.[152] The coagulum has the form of small starch granules and is called artificial starch. Whether inner anhydride formation in the polysaccharide molecule is an accompaniment of association in the retrogradation of starch, has not been proven.

Retrograded starch contains amyloamyloses in various stages of association.[152] It is completely soluble in water at 155°.[153] This solution produces a blue iodine color and is completely converted to sugars by malt. On standing, it again produces a granular precipitate which, because of its great similarity to fine grained starch, is called artificial starch.[154] The ageing of starch follows regular laws, different for each variety, which may be formulated mathematically.[155] The problem of ageing is closely related to the staling of bread which has been extensively treated by J. R. Katz.[156]

PEPTIZATION OF STARCH CONSTITUENTS TO THE MOLECULARLY DISPERSED STATE.

A. Without Formation of Reducing Groups.

The micelles of the starch constituents found in aqueous solutions can be decreased in size without hydrolytic opening of O rings, simply by overcoming the associative power. The particles may be so small that we may conceive of them being at the upper limit of molecular dispersity (solution parfaite).[157] This disaggregation occurs on dissolving starch previously treated with HCl and dried. It is more complete the longer the solution is heated [158] and the more dilute the solution.[159] It occurs on heating starch with glycerin with the loss of phosphoric acid.[160] A similar process occurs under the influence of *Bacterium maccrans Schardinger.* On the relationship of the polyamylose so produced to the elementary molecule of starch, intensive but variously interpreted work has appeared.[161] The displacement of hydroxyl groups by methoxyl groups leads to the formation of molecularly dispersed soluble methylostarches.[162] Starches are peptized by ultraviolet light.[163] Starch acetates are disaggregated by heating in solvents that have no effect on starch itself. H. Pringsheim and T. Meyerson produced from the acetate of tetra- or hexa-amylose an acetate of diamylose.[164] A. Steingöver depolymerized an acetate of amylose by heating with benzene sulfonic acid or in naphthaline and obtained an amylose with a molecular weight of under 600.[165] A molecular division of the starch acetate has also been observed by M. Bergmann and E. Knehe.[166] On depolymerization by ethylene glycol or monochlorhydrin *see* I. G. Farbenindustrie.[167] J. R. Katz and P. J. P. Samwell determined the maximum water surface covered in by a given amount of starch acetate. From this the dimensions of the molecule were calculated. They arrived at the conclusion that the elementary group of starch was $(C_6H_{10}O_5)$.[168]

B. With Simultaneous Appearance of Carbonyl Groups.

Diastatic ferments and acids also cause disaggregation. This, however, is accompanied by the appearance of CO groups and the products obtained have been designated as *amylo-, erythro-,* and *acroodextrins.*[169] These designations are however merely collective names for many depolymerization and decomposition products of starch which are grossly similar in their solubilities, iodine colors, and reducing power—not for strict chemical or colloidal individuals.[170] During the process of diastatic hydrolysis there is always present a colloidal fraction along with a fraction passing through collodion. The percentage of the former and its mean micellular size always decreases coincidentally with a decrease of the optical activity and the formation of reducing groups. In both fractions amylo-, erythro- and achroödextrins may be found.[171] Similarly direct osmotic observations on dextrins give very variable values for the molecular weights.[172] Phosphoric acid is not hydrolyzed from the colloidal residue by diastase.[173] In view of this poorly defined term "dextrin" and the great confusion in the naming of amyloses (α and β amyloses), it appears worth while to establish a rational nomenclature and grouping of starch constituents and their close derivatives. The following table collected from names already used by individual workers is proposed: [174]

	Blue Color with Iodine	Red Color with Iodine	No Color with Iodine
Non-reducing	amyloamyloses	erythroamyloses	achrooamyloses
Reducing	amylodextrin	erythrodextrin	achroodextrin
Acids	amylodextrinic acid	erythrodextrinic acid	achroodextrinic acid

The French workers [175] do not accept this nomenclature, but designate all starch constituents producing a blue color as starch as "amyloses," even if they contain reducing groups. The term "dextrin" designates substances giving a red color or no color with iodine irrespective of their reducing action. Caution is advisable in reading various papers on the subject.[176]

Properties of "True Starch Solutions." [177]

"True" solutions of starch obtained by filtration through collodion show no Tyndall phenomenon, do not brighten the field of the ultramicroscope and are not coagulated by acids or salts; the dissolved material does not undergo electrophoresis.

These solutions produce a stable deep blue color with iodine and are hydrolyzed in a few minutes by acids. In the course of time the dissolved particles increase in size and the solution becomes colloidal. After several weeks a part of the dissolved material precipitates as granules. These changes occur more rapidly on freezing. During ageing the fraction passing through collodion decreases and the material that passes is of decreasing rotatory power.

The molecular grouping in this solution is very labile. Boiling the solution a short time is sufficient to increase the specific rotation from $\alpha_D = 186°$ to $\alpha_D = 193°$. By filtration through graded membranes the "true" solution may be separated into various fractions which differ in their optical activity.

Action of Alkalis on Starch.

The sphere of reaction of starch constituents with bases includes both chemical and colloidal reactions. In consequence of the presence of amylophosphoric acid, the starch has the character of a true acid and may react with bases or salts to form salts.[178] A 1 per cent solution of amylopectin from potato starch contains $1.51 \times 10^{-4}N$ free H^+ and combines with 2.8×10^{-4} equivalents of NaOH on titration to the electrometrically established neutral point. The total H^+ is twice the free H^+.[179] The nature of the cation is of importance in the properties of the salt, such as taste, appearance, etc.[180] Neutralization of free amylophosphoric acid is accompanied by an increase in viscosity and stability. After titration of the phosphoric acid group, the starch constituents begin to take up alkali. The electrolyte-free amyloamyloses as well as the salts of amylophosphoric acid participates in this step. Complete reaction occurs when the alkali added satisfies the formula $C_6H_{10}O_5.KOH$. The starch solution on addition of alkali becomes clearer, more stable,[181] the viscosity increases,[182] the optical activity is depressed,[183] the dispersity increases [184] and the solution is no longer resolvable in the ultramicroscope.[185] No clear results have been obtained from the investigation of the processes occurring. Whether an adsorption [186] or a chemical combination [187] similar to saccharate formation occurs, is not definitely settled. Both kinds of reaction may participate, as in many such cases.

Disregarding theoretical aspects, experimental observations establish that for many of the changes the fundamental factor is the presence of OH^-, which causes an increase in surface tension bringing about a change in state. Actually the activities of various bases are in many respects similar only when the OH^- concentrations are equal.[188] *

Formaldehyde Starch.[189]

The action of formaldehyde is very similar to the action of alkalis on starch. The viscosity increases and the optical activity decreases. The opaque or nontransparent starch paste is transformed to a transparent but very viscous fluid, which no longer produces a color with iodine. The dispersity is, however, not changed, and retrogradation does not occur. The much-discussed question as to whether formalin produces products similar to diastase [190] must be answered in the negative. However since formalin is very often strongly acid, a gradual degeneration of the starch under its influence is readily comprehensible.

Soluble Starch.[191]

The various products designated as "soluble starch" are chemically quite different. From the foregoing discussion it may be seen that starch is rendered soluble either by disaggregation of the native starch micelles, by hydrolytic splitting of the molecule, by the introduction of acid residues and saturation of the resulting of the esters obtained with cations, by the introduction of carboxyl groups by oxidation and neutralization of the resultant colloidal acid by certain bases, or by the addition of formaldehyde. The expression "soluble starch" is not scientifically desirable because most of the methods used in producing such products involve a combination of several of the above procedures.[192] The different "soluble starches" differ greatly in their chemical and colloidal properties [193] and experiments dealing with the constitution of starch based on "soluble" and not native starch must be evaluated with great caution. If the term "soluble starch" is to be retained then it should be reserved only for disaggregated amyloamyloses and erythroamyloses.

Dextrin.[194]

Like the group of soluble starches the group of dextrins embraces a variety of disaggregation and decomposition products of starch. In view of the wide range between the dispersity of native starch and the elementary molecule, it is easily understood why the members of this group described by various

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* *See also* paper by V. G. Bloede in this volume. J. A.

authors differ radically. Work in progress at this Institute has as its object a rational division of the dextrins and a clarification of the relations of the individual products to a native starch.

At present it seems almost certain that the α series of polyamyloses originates from amyloamyloses and that the β series originates from erythroamylose.[195] The conception that the dextrins from amylopectin are resistant, has been established. The erythro- and achroodextrins produced by diastatic action on starch[196] and the gummy dextrins produced by the action of *Bacterium macerans*[197] contain phosphorus and therefore come from amylopectin. The molecular weights obtained for the different dextrins by the cryoscopic[198] diffusion velocity[199] and osmotic pressure[200] methods agree well. Nevertheless the results obtained by each method were not corrected for dissociation or the presence of dialyzable ions. The protective action of dextrins is generally higher the higher the molecular weight.[201] Particular dextrins have a multiple gold number.*

The viscosity of dextrin solutions decreases with the molecular weight.

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Starch and Some of Its Derivatives.*

By Victor G. Bloede, Ch.E.,

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One of the most interesting as well as most commercially important of the numberless vegetable colloids occurring in nature is starch, which in its various forms is distributed so abundantly throughout the world. This article will treat of the colloidal aspect of starches and some starch compounds and derivatives from the practical and technical viewpoint rather than from the theoretical, particular reference being made to their respective adaptability as adhesives and textile sizings.

As is well known, colloidal dispersion of starch and starch products in water is not obtained until the temperature is raised to the "bursting" point of the grains, at which time suspensions in water of starch, dextrin, British gum and allied starch derivatives pass into colloidal solution. When thus dispersed the starch or starch derivative does not settle out or revert to the suspended form on cooling but remains dispersed, the viscosity increasing as the temperature decreases. Certain special starch products, known commercially as "cold water soluble," are exceptions in that they gelatinize or go into colloidal dispersion without heating, and they will be discussed later. At the outset, let it be stated that for the sake of brevity, reference herein will be occasionally made to colloidal dispersions, hydrosols or colloidal solutions as "solutions," although it is, of course, recognized that they are not true solutions.

The subject will be discussed under the headings:

1. Raw starches.
2. Starch products of reduced viscosity.
   (a) Hydrolysis with acid.
   (b) Oxidation.
   (c) Enzyme action.
   (d) Thin-boiling method (suspension in acidified water below bursting temperature).
3. Cold-water-soluble starch products.
4. Vegetable glue.
5. Precipitation of starch from its dispersions.
6. Some starch compounds and effects of chemicals on starch.

Within the limits of a paper of this length, one of necessity cannot go into great detail, but an effort will be made to describe some of the interesting properties of starch and its compounds, some of which vary greatly in their characteristics depending on the treatment to which the starch has been subjected.

Raw Starches.

The properties of the raw commercial starches vary markedly. Confining ourselves to the most common commercial grades, it is noted that there is

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* *See also* paper by H. Schade on Concretions in Vol. II of this series, and paper by M. Samec on Starch in this volume. J. A.

a great difference in their cohesiveness, viscosity, clearness, color and adhesive properties.

Potato and high-grade tapioca starch, for example, are of high viscosity, quite transparent in hot solution and very cohesive. Cornstarch, on the other hand, when colloidally dispersed, forms solutions which are translucent when hot—in fact practically opaque in concentrated solution—and it has poor cohesiveness compared to that of tapioca and potato starch. Solutions of sago and medium grades of tapioca starch lie between the two above extremes, being more turbid than potato and high-grade tapioca and clearer than cornstarch. When neutral pastes made from potato, tapioca or sago starch are allowed to cool and set, however, they all in time become opaque.

When a very small percentage of soap or fatty matter is added to potato or tapioca starch, their colloidal dispersions in hot water become more opaque and less cohesive and resemble those of corn. This would indicate that the translucency of cornstarch solutions and their comparative lack of cohesiveness may well be due to the presence of a very small amount of natural oily or fatty matter in the cornstarch grain.

STARCH PRODUCTS OF REDUCED VISCOSITY.

As the acid hydrolysis of starch paste is successively continued the colloidal dispersion passes through a wide gamut of modifications until finally the sugar stage is reached and we have crystalloidal dispersion. The fluidity of starch in solution can be increased not only by acid hydrolysis, but also by oxidation, enzyme action and other methods, all of which can be controlled to produce any desired viscosity.

The physical properties of the dispersed modified starches made by one method are quite different, however, from the properties of the same starch treated by one of the other methods—even when the viscosities of the resultant modifications are the same. For example, a colloidal dispersion of one part of tapioca starch in five parts of water when hydrolyzed to a definite viscosity by heating in the presence of one-half of one per cent of HCl (based on the weight of dry starch) yields a product of a different quality and appearance from the starch modification of the same viscosity made by thinning the same amount of the colloidal starch dispersion with one-half of one per cent malt diastase instead of mineral acid. The adhesive made by the malt method forms a better stripping glue for paper boxes than that made by the acid method, and the effect of these two modifications in sizing rayon or finishing cotton goods might be noticeably different. The amount of sugar, dextrin content, color and other properties vary as a result of the two different treatments.

Similarly, when the hot starch paste is thinned by oxidation with chlorine or with sodium peroxide, sodium perborate or other "per" salt, great differences are noted in the resulting products. Some adhesives and sizings made by oxidizing the raw starch dispersions are much more fluid when hot and set more rapidly to rigid gels on cooling than those made by acid hydrolysis.

Again, if the hydrolyzing with acid is carried on in the presence of water below 130° F. without allowing the starch to burst and the action stopped at the desired point by neutralizing (which is one of the chief methods of making so-called "thin-boiling starch" and "soluble starch"), then the resultant product manifests different sizing and adhesive characteristics from the converted starch made by the other above-described methods.

So far we have spoken of wet methods of conversion. When dry starch is heated with one-fourth per cent or less mineral acid in a roasting cylinder or pan by the usual commercial process, it is converted into British gum, and then if the action is carried further viscosity is further decreased and it is hydrolyzed to dextrin. Solutions of any of the dextrins or intermediate products between starch and dextrin made by this dry method differ in their physical working properties from conversions of similar viscosity made by the wet method. Here again sugar and dextrin content, color and adhesive values vary.

If a salt, such as $MgCl_2$, which at high temperature splits up into acid, is employed instead of mineral acid in dry conversion, we again get a dextrin having different properties when colloidally dispersed, particularly in respect to higher body.

By this means one succeeds in not actually introducing the acid into the starch until the starch reaches a high temperature and the sudden intimate contact of the generated acid with the hot starch yields a colloid of greater body and adhesiveness when dispersed in water.

The solutions of conversions made from potato, tapioca, sago and corn differ from one another as markedly as the colloidal dispersions of the raw starches differ.

Starch dispersions can also be thinned by mechanical means, such as stirring. If one part of potato starch is colloidally dispersed in five parts of hot water, the resulting mass is thick and rubbery. By subjecting such a heavy paste to strong agitation in a kettle equipped with paddles revolving in opposite directions which have a whipping action, the body of the starch is considerably reduced without hydrolysis. This is doubtless due to great shattering and puncturing of the starch grains. The addition of a small amount of caustic soda to the paste before agitation gives in the end a still thinner-bodied, smooth-flowing dispersion. This latter will be referred to under the head of "Vegetable Glue."

It is interesting to note the differences in the films made from colloidal dispersions of raw starch, dextrin and the intermediate products. Films made from raw starch are characterized by horny toughness whereas films made from dextrin are quite brittle. Films made from British gums and products lying between the range of starch and dextrin have toughness or brittleness proportional to the degree of conversion If a colloidal dispersion of raw starch is mixed with about 100 per cent glycerin a film can be made which is quite flexible and leathery.

COLD-WATER-SOLUBLE STARCH PRODUCTS.

When starch or hydrolyzed starch dispersions are dried on a hot cylinder and the re-dried material pulverized, we obtain a "crystallized" form which in commerce is known as cold water soluble. This re-dried product when stirred into cold water gradually dissolves. About an hour is usually required to effect complete cold water dispersion.* Such solutions have the same general properties as the original solutions before they were dehydrated. In addition they are usually smoother and more thoroughly dispersed, due perhaps to the fact that in the drying process starch, gum or dextrin is subjected to an extra degree of heating and the grains are more thoroughly broken up.

Another mechanical way of making starch absorb cold water more readily is to subject the dry starch to the action of a pebble mill for a number of hours. The constant pounding of the stones on the starch grains punctures and de-

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* Fineness of grinding is an important factor. J. A.

forms them, so that when cold water is added, it is absorbed into the grains and they swell. Perfect colloidal dispersion, however, is not readily obtainable in this way. In industrial usage pebble milling only yields partial cold water soluble products.

It might be pointed out that although raw starch is not colloidally dispersable in water alone except with heat, nevertheless dextrin is to an appreciable extent. This is indicated when the tapioca dextrin on a United States government postage stamp is moistened with the tongue when a sufficient degree of dispersion takes place to effect satisfactory adhesion. Dextrin, however, is only thoroughly colloidally dispersable with heat.

Suspended starch can be put into colloidal dispersion in cold water also by the addition of (*a*) one-tenth of its weight of NaOH; (*b*) by the addition of an appreciable quantity of $CaCl_2$; (*c*) by adding $ZnCl_2$, also other chemicals. These are probably compounds of starch and some of them will be discussed later.

VEGETABLE GLUE.

Tapioca or potato starch is usually employed in making the colloidal dispersions known in industry as "Vegetable Glue." Their dispersions have much more cohesiveness and show greater adhesion than cornstarch. Numerous modifications and special methods of treating starch have been proposed and employed in making adhesive products for various purposes which might come under this classification, but reference here is made to vegetable glue such as is used in large tonnage at present in gluing veneers and wooden panels.

One hundred parts high-grade tapioca starch are agitated thoroughly with heat for several hours in from 250 to 300 parts water, to which has been added 3 parts NaOH. The caustic soda has a solvent action on the thick, swollen mass of starch grains, and the prolonged whipping action of the paddles on the dispersion serves to produce a final dispersion which has a stringy flow, beautiful smoothness and powerful adhesive strength. Wooden panels glued with such a dispersion when dry give a joint practically equal in strength to that obtainable with animal glue.

PRECIPITATION OF STARCH FROM ITS DISPERSIONS.

Certain hydroxides, notably $Ba(OH)_2$ and $Ca(OH)_2$, precipitate starch from colloidal solution. Unquestionably a compound is formed. The starch settles rapidly to the bottom of the vessel and the supernatant water can be readily decanted. For example, when 16 parts of NaOH dissolved in 32 parts of water are added to a starch paste containing 60 parts starch, 21 parts calcium chloride and 500 parts water, the $Ca(OH)_2$ which is generated precipitates the starch from solution immediately. $Ba(OH)_2$ behaves similarly.

When, in a general way, the above procedure is reversed a very interesting property of raw unburst starch in suspension is noted. In the presence of sufficient $Ba(OH)_2$ solution raw starch will not burst. 100 parts tapioca starch is suspended in 1,300 parts cold water. Then 250 parts of a cool solution made from 50 parts $Ba(OH)_2$ and 200 parts water is added. Then heat is applied. Instead of the starch forming a dispersion, as would be the case in the absence of $Ba(OH)_2$, the starch does not burst. It behaves as if it were so much sand, and as soon as stirring is stopped, settles to the bottom, even though the temperature is above the bursting point of starch.

Starch can be separated from its dispersions in pure form by precipitation with an excess of alcohol. It settles out as a flocculent, fibrous mass. Dextrin and other starch conversions behave similarly in the presence of excess alcohol. Starch can also be partially separated from its hydrosols by freezing and subsequent thawing.

SOME STARCH COMPOUNDS AND EFFECTS OF CHEMICALS ON STARCH.

The more common reagents have been tried out in industry on starch dispersions and many impart properties which have commercial importance. This likewise applies to some of the less common chemicals.

One of the best known and most interesting reactions is the effect of a comparatively small amount of borax on starch dispersions. When a solution of borax is added to a starch hydrosol, the mixture thickens and the starch assumes a rough, somewhat rubbery form. Such a mixture rubbed on the hand does not spread with buttery smoothness as does a normal starch dispersion, but rolls and balls up unevenly. Adding sufficient acetic or other acid to acidify the mixture restores the dispersion to its original thinner body and brings back the normal physical appearance and working properties. Borax when added to fairly thin dispersions of British gum or dextrin (in amount less than 10 per cent of the weight of the dry gum) has an appreciable thickening action which improves the adhesive quality in some cases but does not affect the smooth-spreading properties. More than 15 per cent of borax will, however, impart the uneven, balling-up property.

A solution of calcium chloride imparts to dispersed starch and British gum a smooth buttery feel. From one to two parts of calcium chloride to one part of starch are preferable for this reaction. Heating is not necessary but hastens the formation of the compound. If a comparatively small amount of water is present the final product sets to a semi-solid gel, smooth to the touch, which crumbles easily when cold, but which when warmed goes into smooth fluid form as if it were wax melting. This compound finds extensive use in the textile industry for imparting leathery feel, body and flexibility in finishing cotton piece goods, the calcium chloride acting as a softener.

Raw tapioca or potato starch treated with an excess of glacial acetic acid at a temperature of 140° F. for 48 hours is converted into starch acetate. The diluted pastes made from the finished product do not show the usual turbidity on standing, and the clear, smooth-flowing hydrosols do not set to rigid gels when cold.

Starch paste can be rendered smooth flowing by precipitating $BaSO_4$ into it under suitable conditions. For example, if Na_2SO_4 is stirred into a suspension of burst starch, which, as described previously, has been precipitated by $Ba(OH)_2$, then the precipitated $BaSO_4$ is distributed in finely divided form throughout the resulting colloidal starch dispersion, and even when there is but a comparatively small amount of water present the smooth white dispersion has a very syrupy flow, quite different from that of the usual starch paste of the same concentration, and on standing for some time it does not set to a gel. The intimately mixed $BaSO_4$ particles act somewhat as if they have a "lubricating" effect on the starch paste.

Chemicals such as zinc chloride, sodium thiocyanate and others also have a gelatinizing action on starch, but space prevents more than mentioning these. The effects of those which have been described above, however, indicate the manifold varieties of modifications of starch dispersions and hydrosols of starch derivatives.

In quite a few of the reactions the reagent acts as a solvent on the starch grain. As an example, when three parts NaOH are added to a suspension of 100 parts starch in 1,000 parts cold water, the suspension on standing is converted into a smooth colloidal solution, and a microscopic examination reveals that the original characteristic outlines of the starch grains have vanished. If this alkaline hydrosol is then neutralized and stained with iodine the microscope shows particles and shreds very much smaller than the original starch grains and having no definite shape—just as if the grain had been exploded and shattered to bits.

So much for the action of some of the more common chemicals. Although the effect of many of the more remote and rarer inorganic and organic compounds has also been investigated, the writer feels that there is still a vast unexplored field of experimentation in this direction. The rare chemical of to-day frequently becomes the common compound of to-morrow, and who knows but that some reaction with a starch dispersion, still as yet untried, may prove of great value in medicine or in the arts some day?

I desire to express my appreciation of the assistance given me in the preparation of this paper by Mr. Elmer L. Greensfelder, of Baltimore, Md.

Sizing and Finishing of Textile Materials.

By Louis A. Olney, B.S., M.S., Sc.D.,

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Colloidal chemistry plays an important rôle in the sizing and finishing of textile materials. The processes of sizing and finishing as carried out in the plant involve many purely mechanical principles in conjunction with the application of many different chemicals involving chemical reactions chiefly of a colloidal character. We shall omit all discussion of the mechanical aspect of these processes, other than to note that calenders of different types, various devices for pressing and stretching, specially devised humidifying and drying apparatus, and numerous other pieces of mechanical apparatus are used.

The sizing of textile materials may be of a temporary nature, for the purpose of assisting in some way during the manufacturing process, as, for instance, the sizing of warps preliminary to weaving, whereas the finishing process as a rule produces results of a more or less permanent character and intended to be maintained, at least, until after the merchandise has reached the customer and is put into actual use.

The materials used for sizing and finishing may be classified as follows: adhesives, filling materials, weighting materials, binding materials, softeners, deliquescent materials, fire-proofing materials, and water-proofing materials. Strictly speaking the two latter do not come under the heading of sizing and finishing and need not be considered here.

While sizing and finishing processes vary greatly and are seldom carried out exactly alike in different plants, certain fundamental principles are involved and similar objectives are sought, which briefly stated are as follows: To improve the general appearance of the cloth; to impregnate the material with various substances in order that the feel may be improved and more body imparted to it, thus making it useful for certain purposes for which it would otherwise be unfit. and in general to render it more readily salable.

Another important object of finishing is to increase and improve the quality of the surface luster and appearance of the fabric. In some instances mineral matter may be added in order to increase the weight and in the case of low grade fabrics the cloth may be filled with a considerable quantity of foreign material both mineral and organic.

In the case of warp sizing the object is to render the warp yarns stiffer and smoother so that they will not tangle or break during the weaving operation, but at the same time render them sufficiently flexible so that the individual fibers will not break or be injured during handling. This is accomplished by treating the material in a machine known as a slasher or dresser with a mixture of various adhesive materials such as starch, which will act as a stiffener, together with a certain amount of tallow or some other softening material used in order to maintain the necessary flexibility. Such a treatment still further holds the loose fibers firmly upon the surface, and to a considerable extent protects the surface fibers from injury.

In a few instances the sizing on the warp may be carried along through the entire manufacturing operation and appear in the finished fabric, but in most cases it is completely removed during the early stages of the bleaching and finishing processes. If a uniform sizing of the entire cloth is desired, this must be accomplished after the weaving and usually not until after all of the warp sizing has been removed, it not being practical to reserve the warp sizing as a part of the final finishing materials. Cotton warps and rayon warps are almost always sized, woolen and worsted warps are sized rather less frequently.

In the finishing of cloth, stiffening materials are used for the purpose of adding body and fullness to the fabric and filling the interstices between the threads. The adhesive materials are intended more particularly for the purpose of holding the filling and weighting materials in the fabric. Softening materials in many instances are used in order to give the proper handle and pliability and prevent injury to the fabric upon folding, which might result through the use of stiffening materials alone. Deliquescent substances are sometimes used in order to maintain a somewhat higher condition of hygroscopic moisture in the fabric for one purpose or another.

The most extensively used finishing material is starch in some form or another, which acts in the dual capacity of a stiffening and binding agent. Potato and corn starches * are both used for this purpose. Some finishers prefer one and some the other. These two starches have somewhat different properties, but with proper handling and treatment they will give almost identical results. In case a more adhesive substance is required various converted starches, dextrins and gums are used. In fact, the colloid chemistry of these substances constitutes a considerable portion of the chemical aspect of finishing.

The colloidal nature of sizing and finishing operations is still further emphasized owing to the fact that most of the textile fibers are of a decidedly colloidal character. Our views in this respect may have been modified somewhat during recent years owing to the results of X-ray fiber study but it remains a fact that many finishing processes involve colloid chemical reactions between fiber and finishing material. Such action may proceed even to the point of partly, at least, homogenizing the two, as is the case with certain cellulose nitrate and cellulose acetate finishes.

In the case of mercerizing cotton and in the fulling of wool, there is no question as to the colloidal modification of the fiber substance itself and similar modifications take place in other finishing processes. The process of chlorinating wool used chiefly for preventing subsequent shrinkage also results in a decided modification of the wool fiber substance.

Two important factors entering into sizing and finishing materials are penetration and coagulation. These may be accomplished by applying hot fluid finishing preparations which coagulate upon cooling and also by depending to some extent upon the coagulating effects of electrolytes. Penetration is aided to a considerable extent through the use of various dispersing and emulsifying materials and during recent years there has been much activity in the commercial development of reagents of this type.

The advantage of having the insoluble finishing materials as finely divided particles, and of obtaining emulsion globules and their more complete dispersion in the finishing preparation, has in recent years become better understood.

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* Tapioca and sago starches are also used to obtain certain effects. J. A.

As a result colloidal mills and homogenizers frequently play an important part in their preparation.

While the finisher of textile materials is chiefly concerned with the fixation of the various sizing and finishing materials upon fabrics, there are times when the converse is true and he is confronted with the task of their removal. This is quite regularly the case as far as warp sizing is concerned, because it is the common practice to remove the sizing more or less completely, previous to or during the bleaching process. In many instances also the cotton finisher finds it necessary to refinish cotton cloth. Before this can be properly done, the finishing material already present must be removed. The process of desizing consists chiefly in rendering the stiffening and binding materials soluble, and when they are removed the remaining insoluble ingredients are released and mechanically removed during rinsing. In the earlier days boiling with water containing alkali was largely depended upon to facilitate the removal of starch; later the use of cold or slightly warmed sours (dilute acid treatments) were used. But modern practice depends very largely upon certain malt preparations or other vegetable preparations (bacterial and fungus), containing starch converting enzymes. The principle involved is the more or less complete solubilization of the starch present through conversion into the more soluble dextrin, or if the process goes far enough, into glucose. Enzymes of animal origin prepared from the juice of pancreatic glands are occasionally used as desizing agents. This type of enzyme not only solubilizes the starch, but also aids in the removal of wax-like and oily substances, and in the solubilization of such protein substances as glue.

In the printing of textile material we have a process somewhat allied to the finishing of textiles, although usually considered under a different heading. It involves to a great extent the same starches, gums and thickening agents as the finishing process. The thickener in this instance is used almost entirely as an incidental means to an end, and usually plays no part in the final result. One important exception is the use of albumen in the production of a pigment print, the albumen being the essential medium for holding the pigment on to the cloth. This is accomplished by incorporating a considerable quantity of albumen into a cold printing paste, together with the desired pigment. Upon subsequent steaming the albumen coagulates and fastens the pigment permanently to the fiber.

It is not surprising that the textile manufacturer has always evinced a far greater interest in obtaining certain *results* in sizing and finishing than in any desire to learn the *fundamental chemical principles* * involved in bringing such results about. This fact, together with the rather indeterminate nature of many of the reactions taking place, has delayed to a considerable extent the scientific study of the chemistry of sizing and finishing operations. This subject therefore presents a wide field for further research.

Classification of Sizing and Finishing Materials.†

1. **Stiffening and binding materials.**

Vegetable.

- Starches
  - Potato or farina
  - Corn starch
  - Wheat starch
  - Tapioca starch or cassava
  - Modified and converted starches including dextrin and British gum
  - Irish moss
- Alginated soda
- Gums
  - Gum tragacanth or dragon
  - Gum arabic
  - Gum tragasol

Animal

- Albumen (egg and blood)
- Casein
- Glue
- Gelatin

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* The peculiar effects obtainable with *mixtures* are frequently due to effects which are rather physical than chemical, and are generally not obtainable with any single commercial substance. J. A.

† These are the raw materials mainly employed to make up the multitudinous mixtures actually used in sizing. J. A.

Mineral

- Silicate of soda
- Magnesium sulfate
- Sodium sulfate

2. Filling and weighting materials.
   - China clay
   - Calcium sulfate (Gypsum)
   - Barium carbonate (Witherite)
   - Barium sulfate
   - Lead sulfate
   - Alum
   - Magnesium carbonate
   - Magnesium oxide
   - Powdered soapstone and talc
   - Sodium silicate
3. Softeners and emulsifying agents.
   - Soaps
   - Sulfonated oils (particularly sulfonated castor oil)
   - Pine oil
   - Glycerin
   - Tallow
   - Paraffin wax
   - Stearine
   - Chloride of zinc, calcium and magnesium
   - Diethylene glycol
   - Triethanolamine
4. Bluing and tinting materials.
   - Ultramarine
   - Prussian blue
   - Various coal-tar dyes
5. Antiseptic substances.
   - Zinc sulfate
   - Formaldehyde
   - Salicylic acid
   - Phenol
   - Zinc chloride
6. Fire-proofing materials.
   - Metallic oxides
   - Tin
   - Aluminum
   - Tungsten
   - Phosphate of ammonia
   - Chloride of ammonia
   - Sodium phosphate
   - Borax
   - Sodium silicate
   - Sodium tungstate
   - Ammonium sulfate
7. Waterproofing materials.
   - Gelatin-tannin combinations
   - Gelatin-formaldehyde combinations
   - Coagulated casein
   - Insoluble soaps of calcium, magnesium and barium
   - Zinc and alum
   - Paraffin
   - Collodion
   - Rubber
8. Starch-converting agents.
   - Various enzyme preparations including
     - Diastafor
     - Rapidase
     - Diax
     - Polyzime
     - Degomma
   - Acids
   - Alkalis

The Process of Dyeing.

By Dr. Georg Georgievics,*

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Whenever a dye is produced upon any object, we can speak of having dyed this object. In a narrower sense, however, the term, "Färben," dyeing, is understood to mean only the application of dye upon fibers. And this term must be still more narrowly defined if the dye process is to be considered from a scientific standpoint; in this case, only those dyeings enter into consideration which are produced by the absorption of dyestuffs by fibers from aqueous solutions (substantive dyeing). In all other cases where the dye is produced either by oxidation (for example, aniline black) or by synthesis of its components on the fiber (for example, ice colors and the mineral colors produced upon the fiber, manganese bistre, chrome yellow, etc.), our knowledge is limited to the fact that we must suppose the presence of a physical affinity, which enables the insoluble dyestuff to hold fast within and upon the fiber.

The dyeing process in the narrower sense of the word proceeds in such a way that the dyestuff upon being dissolved in water diffuses itself through the fiber and is precipitated within and upon the fiber as a dye no longer soluble in water, or at least only slightly so. This process, which is so greatly dependent upon the nature of the fiber as well as on the character of the dyestuff used, is carried out in general in the following way: the dyestuff is taken up by the fiber gradually and preferably with the use of heat, and the process is completed within a short time, in most cases in about 1 hour. After this period of time [1] no more of the dyestuff is taken up even if the fiber is left for days in the dye-bath.

The more slowly the dyestuff is taken up, the more proof against fading will the fiber be when washed (that is, the dye will be less soluble in water); this, however, is true only within certain limits. Some of the dyestuff almost always remains unabsorbed in the dye-bath, and the quantity of dye thus remaining is the greater, the more water and dyestuff are used in proportion to the quantity of fiber to be dyed, and the less proof against fading the resulting dye is. The more dyestuff a fiber has taken up, the less its capacity becomes to take up further quantities of the dye. The first portions of the dye are therefore taken up more quickly and with greater energy and adhere most firmly to the fiber. The fiber has a tendency to take up relatively greater amounts of dye from dilute solutions than from concentrated solutions and a light color is always more proof against fading than a dark shade of the same dye. If it is desired to remove from the fiber the dyestuff it has taken up, by treating the fiber with water (in which the dye was originally soluble), then that characteristic property of dyes becomes evident, namely, that the dye—with almost no exceptions—may be only partially removed, even if enormous quantities of water are used. Dyeing is, therefore, not a completely reversible process. If in dyeing a fiber several dyes are used, the last

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* Translated by Elisabeth D. Kruse, Wilmington, Del.

portions of each separate dye to be absorbed are generally independent of the order of their application. It therefore makes no difference in the end, whether we dye a fiber with several dyes at once, or apply first one, then the second, third, etc.

In any case, however, if the process has to be carried out in one and the same dye-bath, the dyes to be used must not have a precipitating action upon each other, and finally the process must be carried out for the full period of time required for the complete absorption of the dyestuff.

The process of substantive dyeing just described is, as already mentioned, dependent to a great extent on the nature of the dyestuff used and on the fiber. Substantive dyeing on cotton can be done only with dyes of the salt group (direct cotton dyes) (benzidine dyes, congo dyes, diamine dyes, etc.); wool and silk can be substantively dyed with salt colors as well as with basic dyes (fuchsin, methylene blue, etc.) and acid dyes (Ponceaux, patent blue, etc.). One complication in this process lies in the fact that, with the exception of the basic dyes, the others are taken up by the fibers only when additional substances are placed in the dye-bath in sufficient quantities. To these groups can also be added the vat dyes, since in the case of these dyes also the fiber to be dyed is treated in a bath which contains the dyestuff. In the latter case, however, it is not the dyestuff itself which is taken up by the fiber but rather its reduction product which is found in soluble form in the bath, and the color is not produced in the bath itself, as in the case of the other dyestuffs discussed, but appears first by means of oxidation upon exposure of the fibers to the air. Dyeing with sulfur colors is carried out in a similar way, although not exactly the same.

The question of the nature of this process of dyeing was investigated quite early and has led to the promulgation of a whole succession of theories, to which the general objection can be raised, not entirely without right, that they are too earnestly concerned with viewing the various phenomena of dyeing from one uniform point of view. In fact, however, one finds even in one and the same dyestuff group[2] quite notable differences in regard to their behavior when used in dyeing; even one and the same dyestuff sometimes behaves quite differently toward the different fibers. On the other hand, however, all the substantive dyes show such similar characteristics, that one may conclude that there is an inner correlation among these single processes in spite of the many differences in detail.

In the *finished state* all dyes, even those which are not substantive, show some common characteristics, namely, in the fact that the essential characteristics of the dyestuffs can again be found in the dyed product. So, for example, the property of being easily sublimed is shown in the product dyed with the proper dyestuffs; dyestuffs which may be diazotized and those which may be used in coupling and are easily oxidized show these properties even when on the fiber, etc. Only in one respect is there a great difference between substantive dyes before and after dyeing, which even today cannot be explained; namely, the property of the dye to become insoluble when absorbed by the fiber.

The innumerable treatises which have been written on the dyeing process concern themselves almost exclusively with only its first phase, that is, with the absorption of the dyestuff from the dye-bath by the fiber, since apparently only this part of the process lends itself to experimental investigation.

The theories proposed in explanation of this process may be divided into two groups: the chemical and physical theories. If we consider the process first from the chemical standpoint, we must admit first of all that a substantive dyestuff must possess either acid or basic characteristics; chemically indifferent substances are not taken up by the fibers. Concerning the chemical reactions which take place in the bath we can say only the following: When dyeing with basic dyes only the dye base is taken up by the fiber, while the acid of the dye salt used, as Ed. Knecht[3] first established, remains in the dye-bath. In the case of acid dyestuffs the dye acid is set free by the acids added to the dye-bath, and only the latter is taken up by the fiber and not the dye salt used. Salt dyes finally are taken up by the fiber in practically unchanged chemical condition.

From the chemical standpoint the processes of substantive dyeing are quite different and hardly comparable. In fact, most of the advocates of the chemical theory of dyeing are of the opinion that dyeing is a process which cannot be conceived as uniform. In dyeing wool and silk with basic and acid dyestuffs it is generally understood that the formation of salt takes place between the fiber and the dye, whereas dyeing with salt dyes should be considered a process of a different kind. The many arguments which are brought up for and against this conception cannot be explained more closely here; let us mention only, that the principal objection which has been raised against the conception of dyeing as a chemical combination is the fact that dyeing does not proceed according to stoichiometrical conditions and this fact still holds good today. The experiments carried out by Walker and Appleyard[4] are said to prove that, under certain conditions—in highly concentrated dye-baths, the dyestuffs are taken up in molecular quantities. This theory cannot withstand the serious criticism of special note aimed against the opinion (already expressed by Chevreuil) that, in dyeing wool and silk with basic and acid dyestuffs, more or less loose salt-like compounds of the dye and fiber are formed. They furnished a solution of diphenylamine in water with varying quantities of picric acid and determined after each addition of the dye the amount of picric acid combined with the diphenylamine. It was found that in thus "dyeing" the diphenylamine an actual formation of salt takes place and the absorption of the dyestuff proceeds quite differently from the usual dyeing process.

In the year 1890 O. N. Witt[5] expressed a very original idea concerning the nature of the dyeing process. Witt compared the taking up of the dyestuff by fibers from an aqueous solution with the shaking out of aqueous solutions with ether and similar solvents not miscible with water, so frequently carried out in chemical laboratories. This conception of dyeing as a solid solution was at first strongly contested, especially because solutions were known to belong to the class of reversible processes, where as the dyeing process, as already mentioned, is non reversible.

Here began the physico-chemical study of the dyeing process, wherein strictly quantitative experiments up to the point of equilibrium were carried out in order to ascertain the distribution of the dyestuff in the bath and in the fiber. The surprising result was obtained that, in dyeing, a uniform distribution of the dyestuff takes place between the dye-bath and the fiber, which, however, did not correspond to the process of solution, or in other words to the simple Henry's law. By the latter law in all dye experiments (comparable to each other) the ratio of the concentrations should remain constant in both phases (the fiber as the solid phase and the bath as the liquid phase) or, $\frac{C \text{ Bath}}{C \text{ Fiber}} = k$. This is, however, not the case, since the fiber has the tendency to take up comparatively more dyestuff from dilute solutions than from more concentrated solutions. The distribution of the dyestuff between the bath and the fiber corresponds more nearly to the formula $\sqrt{\frac{C\text{ Bath}}{C\text{ Fiber}}} = k$, in which $x > 1$, just as in the adsorption phenomena which were known even at that time. Since it was proven by comprehensive investigations that this uniformity held good for all substantive dyes, carried out in this way, the dyeing process could now be considered as belonging to the group of adsorption phenomena.[6] As is well known adsorption processes are mostly not reversible, or only in part, like the dyeing process.

Even though the first mathematically formulated rule for the dyeing process and an analogy to another important phenomenon had now been found, still it was years before this knowledge was utilized for a further penetration into the riddle of the dyeing process. Nothing much could be attained with this knowledge because the adsorption processes themselves were so mysterious and caused as much contention as the dyeing process. A continuation of our study of adsorption processes including dyeing processes led first to the study of the taking up by wool fibers of simple acids free of dyestuffs, the usual inorganic and organic acids.[7] It was first shown that this process was carried out in accordance with the adsorption formula first formulated by Boedecker (1859): $\sqrt[x]{\frac{C\text{ Bath}}{C\text{ Fiber}}} = k$ in which the $x > 1$. Even then, it appeared at first quite impossible to reconcile the quantity of acids taken up, "adsorbed," by the wool fiber—under given conditions—with any other characteristics of the acid. The strongest acids, such as nitric and hydrochloric acid, were taken up in the largest quantities; on the other hand, weak acids such as phosphoric, benzoic and salicylic acids were adsorbed in larger quantities than many of the stronger acids. In addition, there is the difficulty that these differences in adsorption were also dependent to a great degree on the concentrations used.

An explanation for this unexpected phenomenon led to experiments in which only extremely dilute acids were used. It was learned that in this case the adsorption of acids within certain limits progressed according to the simple Henry's law, or in accordance with the formula $\frac{C\text{ Bath}}{C\text{ Fiber}} = k$. *From this fact one can conclude that in the adsorption of acids by wool fibers a true solution at first occurs,* that is, a completely uniform distribution of the acid in the fiber, *and only later occurs that distribution of the acid between bath and fiber which corresponds to the Boedecker's formula for adsorption. The adsorption of acids by wool fibers is, therefore, not a uniform process* and it is also to be understood that no relation could be found between the amount of the adsorption and the properties of the acids taken up. However, if one considers only that part of the process of acid adsorption which progresses according to the adsorption formula, then it is clear that the root exponent "x" of the different acids in the adsorption formula runs parallel with the strength of the acids.

This regularity was the first and until now the only proof that led to the fact that in such processes chemical affinity plays a rôle, a fact which is applicable not only within an acid group but is common to all weak and strong inorganic acids as well as to aromatic and fatty acids of different basicity. If one arranges the acids according to the size of their x-value, then the relations, only mentioned in passing above, show themselves clearly between their adsorption by wool and their other characteristics such as: interior friction (of their aqueous solutions), different physiological actions, etc. There was found, among others, the rule that the absorption of an acid by wool is aided by a greater interior friction, whereas adsorption in the narrower sense of the word, measured by the size of the x-value, becomes less, the greater the interior friction of the acids in question in their aqueous solutions. This uniformity, however, holds only within one and the same acid group, for example, only when the x-value and the internal friction of formic acid, acetic acid, propionic acid and butyric acid, agree.

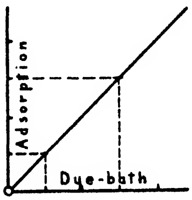
Under the assumption that a process following Henry's law may be described as a solution, and that, on the other hand, the process of adsorption is sufficiently characterized by Boedecker's formula, we can have a very clear picture in mind of the way in which acids are taken up by sheep wool: the acid first penetrates the fiber in a uniform way at the same time forming a solid solution; if the concentration of the acid solution is increased, a regular decrease in acid absorption takes place, which decrease is the greater, the stronger the acid used. Since only this part of the process proceeds according to the law of adsorption, one may no longer say that the wool fiber possesses a strong adsorptive capacity for weak acids such as phosphoric, benzoic, salicylic, etc., because they take up these acids in greater quantity. Adsorption itself is only one part of the process, which is characterized by the size of the "x" of the adsorption formula; and when the "x" of the acids mentioned above is small, we will have to assume that they are present in the wool fiber mainly in a dissolved state. The kinetic investigation of this process[8] confirms this result, and the process may no longer be called by the earlier term adsorption but should be called "sorption" according to a suggestion made by McBain.[9] The study of the rate of the sorptive action of wool on acids resulted first of all in finding out that this process was carried out more quickly when the concentration of the acid solution was increased, a fact which, however, varies in characteristic manner with different acids, since the sorption of the strong acids is much more greatly accelerated by an increased concentration than in the case of weak acids. *The effect of concentration upon the velocity of sorption runs parallel to the x-value of the acids.* This influence is, therefore, least in the case of the monobasic fatty acids of the acetic acid series; if other sorption phenomena are compared, this process may be likened to the transition into gases, wherein charcoal is used as the sorptive medium and equilibrium is attained at an almost invariable rate whatever pressure variations are made.[10] *The closer the "x" of the acids used approaches the value 1 the more nearly their sorption by wool corresponds to a diffusion.* In fact, even in the case of the monobasic fatty acids a complete agreement between the velocity and fusion coefficients was established. With the other acids this agreement is naturally smaller in proportion to the size of their x-value. Since the taking up of acids by wool is considered a chemical process by so many technologists, the temperature coefficient of sorption has also been determined. It is 2 to 3 for a chemical reaction (according to Van't Hoff), and about 1.25 for diffusions. For the sorption of hydrochloric and acetic acid by wool it is 1.5.

Now the question arises whether one is justified in assuming that the above-described sorption of acids by wool and the taking up of dyes by the fiber in substantive dyeing are processes of the same nature. That there is a great analogy between the taking up of acids free from dyes on the one hand, and dye acids on the other, is beyond doubt, and this analogy becomes stronger in view of the fact that also in the case of dye acids for dyeing in very dilute solutions, the distribution of the dye between the fiber and the bath follows

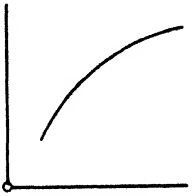
Henry's law $\frac{C\text{ Bath}}{C\text{ Fiber}} = k$. Here, too, the process of absorption by the fiber is a sorption, which very probably conforms to the same rules in all essentials as the sorption of acids free of dyes.

Now, however, the different substantive dye processes show no essential difference in regard to the manner in which the dyes are absorbed by the fibers, so that the conception of dyeing as a sorption phenomenon may be applicable to all substantive dyeing processes.[11] This sorption theory presents to a certain extent a combination of the three main theories of the dyeing process (1. chemical theory, 2. solution theory, 3. adsorption theory), and it gains in probability when one considers that it is not artificially constructed but is derived from experimentation.

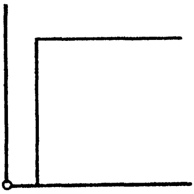
This much appears to be quite certain, namely, that one may not conceive of the dyeing process as either a true solution or chemical compound or as adsorption. The differences between all of these processes are shown most plainly when graphically represented as in the following figures:



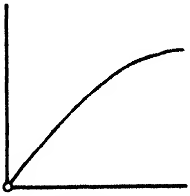
Solution



Adsorption



Chemical Compound



Dyeing

From the above one can also readily see the manner in which the transition from one process to another takes place (solution—adsorption—chemical combination).[12] They are evidently in close relation to each other; in the sorption process there is indeed a transition from solution to adsorption; and adsorption itself presents a process preparatory to chemical reaction, as van Bemmelen has already shown. *We can even question whether it is then permissible to separate the processes described as solution and adsorption,* since, as we know, the distribution of several substances between two liquid solvents often does not obey the simple rule but rather the so-called "higher power," Henry's law $\frac{\sqrt[n]{C_1}}{C_2} = k$. Indeed it was claimed for some time, that sorption by carbon, of iodine by starch, etc., and also substantive dyeing could be considered solid solutions. This standpoint, however, was soon given up. In accordance with the Nernst distribution law, the distribution of a substance between two liquids which do not mix is dependent on the molecular size in this way: if the molecular size of the substance is the same in both liquids then it is distributed according to Henry's law; if this is not the case, then its distribution corresponds to the formula which we learned earlier as the adsorption formula. The use of this law in connection with the solid solutions mentioned above led to molecular weights which could not possibly be correct.

It was then necessary to consider the process which takes place in the distribution of a substance between two phases one of which is solid, as different from that process in which two liquids are used as the distributing agents.

The two processes, however, show such a marked similarity that it is hard to believe in any essential difference. Furthermore, none seems to exist. For, on the one side, a whole series of cases is known in which the distribution of a substance between two immiscible liquids does not follow the theoretical assumptions of Nernst's distribution law; and on the other hand, an experiment[18] especially conducted for the determination of this question, disclosed that the root exponent *"x"* of the distribution formula possessed the same meaning for the distribution of acids in water and benzol, as it had for the sorption of acids by wool—in so far, that is, as the size of this *"x"* is dependent on the chemical affinity of the substance to be distributed for water or for wool. From this the conclusion was drawn that the Nernst distribution law cannot be entirely applicable, and that in aqueous solutions processes can be carried on which are analogous to adsorption—an opinion which has also been expressed by Wo. Ostwald.

As the final result of our studies we have the fact that substantive dye processes can be considered as solid solutions of the dyestuff in the fiber. What relation exists between this substance that accomplishes the dyeing and the dyestuff which was used in dyeing, we unfortunately do not know at present. We can only say that in the case of acid dyestuffs, the dye acid penetrates the fiber, in the case of basic dyestuffs the dye base, and in the case of salt dyes the dyestuff itself. What change brings about its insolubility within and upon the fiber will probably not be learned until we have succeeded in producing this change without using a fiber.

This and other questions touching upon the dye process belong quite evidently to the field of colloid theory. To this latter study we are already indebted for the *knowledge that an important part is played by the particle size of the dyestuff itself in the taking up of dyestuffs by fibers*—a circumstance not considered before. This is important at present only in the dyeing of cotton with salt colors which is not achieved satisfactorily except when salt is added (generally Glauber's salt). Since by this addition the degree of dispersity of the dissolved dyestuff is very easily and quickly decreased to the point of flocculation of the dyestuff, one may conclude that a definite particle size of the dyestuff is one of the conditions which must be fulfilled to admit its being taken up by the fiber (R. Haller). But even the acid dyestuffs are scarcely "sorbed" from an aqueous solution; this occurs in sufficient quantity only when an acid is added to the bath in much larger quantities than would be necessary to free the dye acid. Perhaps the acid added in this case plays a rôle similar to that of the salt added in dyeing with salt dyes.

EDITOR'S NOTE.

Dreaper and Wilson have observed [*J. Soc. Chem. Ind.* **28**, 57 (1908)] that the color-changes produced by immersing in dilute acid fibers dyed with sensitive dyes, vary considerably with the nature of the fiber. Thus with cotton the changes were about the same as those produced in aqueous solutions of the dyestuffs in question, whereas silk and wool showed color-changes of a different nature.

In a paper presented to the Seventh International Congress of Applied Chemistry, J. Alexander pointed out that after the addition of protective colloids (gelatin or gum arabic) to solutions of benzopurpurin, dilute acids produced color-changes analogous to those observed in the dyed animal fibers, silk and wool.

In the case of a pure dilute solution of benzopurpurin, the addition of dilute mineral acids quickly changed the color from bright red to dark blue, reminding one of the change of pure colloidal gold. Stronger acid coagulated the dye, which settled out of solution but which could be re-dissolved with restoration of the original color, by neutralizing the acid with alkali. The same solution of benzopurpurin, to which gelatin or gum arabic had been added, gave with dilute mineral acids a claret-red solution. More concentrated acid changed the shade to chocolate-brown, without, however, causing any precipitate.

As previously planned [see *Trans. Am. Inst. Chem. Eng.*, **2**, 222; *J. Soc. Chem. Ind.* **30**, p. 517 (1911)] J. Alexander examined these color-changes in the ultra-microscope, and results seem to throw some interesting light on the nature of the combination between dyed fiber and dye.

A very dilute solution of benzopurpurin shows in the ultra-microscope a field full of ultramicrons which, from their brilliancy and motion, appear to be about 50 to 60 $\mu\mu$ in size. When a little acid is allowed to diffuse in under the cover glass, the ultramicrons gradually gather together into clumps or groups, whose motion decreases as their size increases, until the whole dye is deposited on the slide in coagulated masses of bright ultramicrons. Stronger acid causes instant coagulation in large masses.

When, however, acid is added to the dye solution containing gelatin or gum arabic, no change is produced unless the acid be strong enough to cause a more or less extensive agglutination of ultramicrons into small groups of two or three, which, however, still have sufficient motion to keep afloat. Gelatin has apparently much greater protective action than gum arabic.

Test-tube tests showed that starch exerts very slight protective action, for the color-changes produced in solutions of benzopurpurin containing large quantities of thin starch paste were very pronounced, resembling those of dyed cotton fibers. It would seem, therefore, as previously stated, that the variation in the color-changes produced by immersing in dilute acid the different fibers dyed with benzopurpurin *is due to their difference in protective action on the "adsorbed" dye.*

REFERENCES.

[1] Dyeing at room temperature which is of no practical importance is a much longer process.

[2] This refers to the dyestuffs which are placed in one group according to their behavior when used in dyeing, for example, the acid dyestuff group, the basic dyestuffs, etc.

[3] *Ber.*, **1888**, 1556.

[4] *J. Chem. Soc.*, **1896**, 1334.

[5] Lenhe's *Färber-Ztg.*, **1890/91**, 1.

[6] Georgievics, *Monatsh.*, **1894**, 705.

[7] Georgievics and Pollak, *Monatsh.*, **1911**, 655. Georgievics, *ibid.*, **1911**, 1075; **1912**, 45; **1913**, 733, 751, 1851; **1915**, 391. Georgievics and Dietl, *ibid.*, **1914**, 643.

[8] A. Dietl, *Monatsh.*, **1914**, 643.

[9] *Z. physik. Chem.*, **68**, 471.

[10] Giesen, *Ann. Phys.*, IV/10, 842 (1903). McBain and F. Bergten, *ibid.*, IV/37, 472 (1912).

[11] Georgievics, "Die Sorptionstheorie," *Chem. Ztg.*, **1914**, No. 42, p. 445.

[12] On account of the class relation between solution and adsorption Boedecker's adsorption formula mentioned in this article is preferred to all other formulæ which might enter into the explanation of this process.

[13] Georgievics, *Monatsh.*, **1913**, 1852; **1915**, 392.

Dyeing.*

By Wm. Harrison, M.Sc Tech. (Manchester), M.Sc. (Leeds), F.I.C.

The phenomena met with in dyeing are numerous and many attempts have been made to explain them. The chemical theory received considerable support from Knecht, but was found to apply only to a limited number of cases. The mechanical theory was strongly supported by Georgievics from experiments with substances regarded as chemically inert. These experiments, however, depended for their results on forces which are not purely mechanical, the substances which are chemically inert are not electrically inert and electrical forces account for their results.

Langmuir, having shown conclusively that the phenomena of surface tension are accounted for by the orientation of molecules by virtue of their electrical polarity, surface tension or adsorption theories become merged in the electrical theory.

The purely chemical theory fails to account for the dyeing of cotton with direct colors merely because it seeks to prove that the cotton forms a compound with the dyestuffs. No one will deny that chemical decomposition and combination occur even during direct dyeing but it is not a direct combination of dye and fiber. However, as chemists nowadays realize that there are no separate chemical forces, as distinguished from more or less complicated distributions of electrical forces, there is no need to attempt chemical interpretations. One can easily translate the electrical explanations into chemical ones when this is desirable.

The electrical theory of dyeing was first put forward by Perrin in 1904 and was based on the following facts.

1. Any two dissimilar bodies placed in contact become oppositely charged with electricity.
2. Bodies charged with opposite kinds of electricity attract one another.
3. Bodies charged with the same kind of electricity repel one another.

It has been shown that dyestuffs are electrically dissociated in water, the color ion carrying a positive charge in the case of basic colors and a negative charge in the case of direct colors.

Materials which need dyeing such as wool, silk, cotton, leather, etc., all acquire a negative charge when placed in water. In an acid bath wool, silk and leather acquire a positive charge.

The parallel relations between the phenomena of contact electricity, colloidal coagulation and dyeing are shown in the following tables.

Laws of Contact Electricity (Perrin)

1. Dissociating liquids electrify fibers strongly by contact.
2. Acids decrease the charge on a fiber already negative, and may reverse its sign.
3. Acids increase the charge on a fiber already positive.

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* For an extensive literature on Dyeing see First British Association Report in King, "Colloid Chemistry," p. 20.

4. Bases increase the charge on a fiber already negative.
5. Action of salts:
   - (a) The ions of reverse sign to that of the fiber diminish its charge.
   - (b) The ions of the same sign to that on fiber may increase its charge.
   - (c) Polyvalent ions have the greatest effect.
   - (d) Acids and bases may act as salts, but in an abnormal manner.
6. Negatively charged fibers have a maximum charge at about 40° C.[1]

Laws of Dyeing Basic and Acid Colors (Pelet-Jolivet)

1. Dissociating liquids, such as water, are best for dyeing purposes.
2. Acids diminish the dyeing of fibers with basic colors and may cause them to dye only with acid colors.
3. Acids increase the dyeing of fibers with acid colors.
4. Bases increase the dyeing of basic colors.
5. Action of salts:
   - (a) Ions of reverse sign to that of the fiber decrease the dyeing with dyes of sign also opposite to that on the fiber.
   - (b) Ions of same sign to that on the fiber increase the dyeing with dyes of opposite sign to that on the fiber.
   - (c) Polyvalent ions have the greatest effect.
   - (d) Acids and bases may act as salts, but in an abnormal manner.
6. The dyeing of a negatively charged fiber with basic color is greatest at about 40° C.

Laws of Colloidal Coagulation

1. Dissociating liquids favor the production of colloidal solutions.
2. Acids coagulate negatively charged colloids.
3. Acids make positively charged colloids more difficult to coagulate.
4. Bases, within limits, increase the stability of negatively charged colloids.
5. Action of salts:
   - (a) The ions of reverse sign to that of colloid diminish its stability.
   - (b) The ions of the same sign as that on colloid increase its stability.
   - (c) Polyvalent ions have the greatest effect.
   - (d) Acids and bases may act as salts, but in an abnormal manner.
6. The mobility of a negatively charged colloid (alizarin used) is greatest at about 40° C.

Laws of Direct Dyeing[2]

1. Dissociating liquids are best for dyeing purposes.
2. Acids within limits assist the dyeing of direct colors.
3. Acids diminish the dyeing of cotton with colloidal solutions of positively charged substances.
4. Bases within limits decrease the dyeing of direct colors.
5. Action of salts:
   - (a) The ions of reverse sign to that on fiber and dye increase the dyeing.
   - (b) The ions of the same sign as that on fiber and dye diminish the dyeing.
   - (c) Polyvalent ions have the greatest effect. (Al, PO_4)
   - (d) Acids and bases may act as salts, but in an abnormal manner.

Schwalbe[3] expressed the opinion that the electrical theory would not explain the dyeing of cotton with direct colors. As the dyeing of cotton with direct colors had always been a stumbling block in the way of theories, the author carried out a series of investigations with a view to explain this important practical process. A comparison was made of the effect of various salts on the electric charge of cotton, the electric charge on the dye particles, and on the dyeing of pure cellulose (filter paper) with direct dyestuffs. The results showed that the negative charge on the cotton was diminished by the action of salts, which acted in the following order of increasing power: NaOH, Na_3PO_4, Na_2SO_4, NaCl, $MgSO_4$, HCl. A few experiments indicated that the negative charge on the dye would be effected in a similar manner.

The absorption of dye (Diamine Blue 2B) by pure cellulose increased in the order: NaOH, Na_3PO_4, Na_2SO_4, NaCl, HCl, $MgSO_4$. Except for the reversed position of $MgSO_4$ and HCl, the results are in agreement with the conclusion that the dyeing increases as the charges on the fiber and dye become less negative, and, as we have seen that bodies charged with the same kind of electricity repel the dyeing increases as the repulsion decreases. This conclusion is qualitatively in agreement with the electrical theory. It pointed to the conclusion that in order to prevent dyeing—i.e. to obtain a resist—the electrical charge on the fiber should be increased as much as possible.

In experiments made with caustic soda it was found that the electrical charge increased as the concentration of the alkali increased, up to $N/1000$, but decreased with the higher concentrations. The absorptions of dye varied in the reverse manner.

The next method of attack was to treat cotton in various ways and compare the electric charges and the dyeing properties of the resulting products. The results were in agreement with the above; the dyeing increased as the electric charge decreased, the order of increasing dyeing being:

1. Nitrated cotton, 2. ordinary cotton, 3. cotton mercerized under tension and dried, 4. cotton mercerized loose and extracted with alcohol, 5. cotton mercerized loose and dried, 6. cotton mercerized and tested while wet, 7. cotton treated with concentrated nitric acid.

Thus, all the experiments were in agreement with the electrical theory as far as the relative actions of different additions to the dyebath were concerned; but the important point was brought out that the dyeing would not be zero when the electrical charge was zero but would have a value somewhere between the values when the charge on dye and fiber were of the same kind and when the charges were opposite.

This point applies not only to cotton but to all cases of dyeing. It is clear, therefore, that the dye can get to the fiber without the aid of electrical attraction, but will be accelerated or retarded according as the charges on the fiber and dye are of opposite kinds or of the same kind.

Now according to the generally accepted kinetic theory, all molecules in a liquid, whether they are from the liquid itself or from dissolved substances, are continually in motion; the speed of this motion is variable but its mean value is so great that the molecules would easily arrive on a fiber unless strong electric charges oppose them. The Brownian motion of colloid particles is direct proof of this kinetic theory.

There is, thus, no need to make any further assumption concerning the manner by which the dye gets to the fiber. The question is: How is the dye held by the fiber? Electrical attraction may be quite sufficient when fiber and dye carry opposite charges but not when they carry the same charge. Another important question is why cotton dyes with direct colors and not with acid colors, both of which have negatively charged ions? There is very little chemical difference between these two classes of dyestuff, but the direct colors are generally precipitated by dilute acids, whereas the acid colors are not.

When carrying out experiments on the determination of the electrical charge of cotton is in contact with solutions of sodium chloride, the observation was made that hydrochloric acid was liberated when the sodium chloride solution was forced through the cotton. This acid was detected electrically; the solution leaving the cotton had a greater electric conductivity than that entering, although all possible sources of soluble impurities in the cotton had been carefully removed.

A similar process occurs with dyestuffs, the free acid being formed; and since the free acids of the direct colors are not soluble in water we have all the essential facts for the explanation of direct dyeing. The cotton takes out the positive ion from the dyestuffs, leaving the color ion to combine with the positively charged water layer immediately in contact with the cotton fiber; and since a positive charge in water would be represented by a hydrogen ion, the free acid would be formed and precipitated on the fiber or within its pores.

It is therefore clear that the direct dyeing also conforms to the electrical theory; the fiber does not directly attract the color ion, but attracts the positively charged ion and so causes precipitation of the dyestuff.

This precipitation, or coagulation, is also a process dependent on electrical forces. The particles in colloidal solution are almost always electrically charged and it has been proved experimentally that coagulation occurs when the electrical charge becomes zero or is reduced to a very low value.

Direct dyeing is then a process of electrical coagulation of the dye on the fiber or within its pores. It is well known to colloid chemists that colloids, such as gelatin, prevent or reduce the coagulation of colloidal solutions, so that, if the above theory is correct, gelatin should reduce the absorption of dye by cotton. Experiment proves this to be the case, thereby substantiating the theory.

The analogy between the laws of contact electricity, coagulation and direct dyeing may be seen on tabulating the facts (vide supra).

It will be observed that limits are evident in the tables showing application of electrical rules to both coagulation of the dyes and dyeing with direct colors.

With caustic soda, for example, dyeing increases up to $N/1000$; the electrical charge on both fiber and dye increases; while the solubility of the dye in $N/1750$ strength increases. Above $N/1000$, the effects all become reversed; the soda then acts like a salt, the positive ion exerting its effects, but to a less extent than in trisodium phosphate.

Effect of Size of Dye Particles and of Pores in Fibers.

It has been found by microscopic examination that during dyeing the dye enters into all portions of the fiber, from which one learns that there are spaces or pores within the fiber which are larger than the molecules of dye. Experiment shows that cotton fibers can also be dyed through with certain colloidal solutions, so that the pores must be considerably larger than molecules of dyestuff.

Examination of cotton fibers in the ultramicroscope also points to the pores being considerably larger than the dye molecules, but of various sizes. The average diameter of the pores is approximately $10^{-5} = 1/100000$ cms.

The condition for dyeing of fibers throughout their mass is that the dye particles shall be smaller than the pores of the fibers; if they are larger, the dyeing will be a surface action, and the result will be a dyeing loose to rubbing. On the other hand, the dye particles having got into the pores must stay there, and in order to do this, must increase in size or coagulate. The action of electric charges in causing this has been discussed. The less the amount by which the particles must increase in order to remain in the pores, the more easily will the fixation proceed.

From these points we arrive at the conclusion that, as the degree of coagulation increases, the rate of dyeing will increase until the size of the dye particle becomes very near to, or greater than, the size of the pores, after which only surface dyeing can proceed. This is actually found by experiment; Glauber's salt increases the dyeing until a great excess is added, when the dye becomes precipitated and remains in the bath or on the surface of the fiber.*

As already mentioned, colloids, such as gelatin, prevent coagulation of colloidal solutions—that is to say, prevent the size of the particles from increasing indefinitely. If we, then, add gelatin to the bath, an amount of Glauber's salt, which in the absence of gelatin, would precipitate the dye and prevent dyeing, will no longer cause precipitation, and dyeing should proceed. This has been found to be the case by actual experiment.

The importance of the size of the pores in the fibers leads us to some further considerations on colloid chemistry, which have been included in the electrical theory of dyeing.

In all these cases already considered, the surface of the fiber including that within the pores, has been taken to be constant, so that the relation between the electric pressure or potentials, as measured, is also the relation between the electric charges or quantities of available electricity. The actual quantity of electricity available is the product of the electrical potential and the area of the surface.

Calculating on the approximate diameter of pores in cotton fiber (10^{-5} cms.) we find that the surfaces inside the pores have an area sixty times as great as the area of the outside surfaces. One gram of cotton has approximately 1,000 square centimeters external surface, and 60,000 square centimeters internal surface.

We have now to consider what effects are produced by changes in surface and in diameter of pores. If the surface diminishes, the available electricity will diminish and the quantity of dye absorbed will also diminish. As an example of this, Weber [4] observed that dinitrocellulose dyed like ordinary cotton, but when made into a film absorbed little or no color.

Conversely, an increase in surface would produce an increase in the amount of dye absorbed. As an example of this, precipitated cellulose is known to absorb more than ordinary cotton.

A change in the diameter of pores would also produce some change in the available surface. If the volume of space occupied by pores remained constant, a decrease in diameter of pore would produce an increase in absorption of dye. The author has shown [5] that mercerization of cotton increases its internal surface, and also diminishes the size of its pores. The great increase in dye absorption consequent upon mercerization is thus explained.

The complete consideration of the possible results of changes in surface and the size of pores would lead to many complicated problems.

CONSIDERATIONS ON FASTNESS OF DYEING.

There are several important points connected with the size of dye particles. In most cases of dyeing the dyes are applied in solution—that is, dispurposed to deal with.

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* See Jerome Alexander, "Colloid Chemistry and Some of its Technical Aspects," *J. Soc. Chem. Ind.*, **28**, 280 (1909); *also* "Degree of Dispersion as an Influence in Tanning," *J. Am. Leather Chemists Assocn.*, Aug., 1923, p. 407 *et seq.* J. A.

tributed in molecules. During direct dyeing, these molecules become clotted together in clots of size varying with the size of the pores in which they are formed.

It will be easily seen that a small clot will be more difficult to break up than a larger one, and that it will be much more difficult to remove a clotted dye from a small pore than from a larger one. We should find, therefore, that any process which accelerates the coagulation of dye, since it would tend to increase the size of the particles in the bath and form the clots in larger pores, should decrease the fastness of a dyeing; and as we have seen that this coagulation follows the laws of contact electricity, the fastness of a dyeing should also be in agreement with the electrical theory. This was found to be true by actual experiment; the fastness toward the sodium soap of oleic acid, of dyeings made with the addition of different salts, decreased in the same order as the dyeing was accelerated—that is: $NaOH$, Na_3PO_4, Na_2SO_4, $NaCl$, HCl, $MgSO_4$.

The dyeing made with the pure dye was the fastest because the coagulation was unassisted, and the clots would be formed in the smallest pores of the fiber.

Usually the fastness of the dyeing is only considered in relation to the soap and water, but it is obvious that other substances may produce or prevent bleeding.

The removal of the dye from the fiber should proceed more rapidly in contact with the materials which assist the least. That is to say, they should act in the reverse order to that given above for the fastness of dyeings against soap. This also was found to be the case.

The size of the dye particles is, then, of very great importance with reference to the fastness of the dyeings. The greatest fastness should be obtained when the particles in the dye bath are the smallest possible, and particularly if they become clotted only when they have entered the pores of the fiber. An ingrain dyeing should therefore, always be faster than the same coloring matter dyed direct. This has been shown to be true by Dreaper[6] for primuline colors, dyed on silk.

Effect of Temperature.

The influence of temperature on the factors considered in the electrical theory is by no means simple.

Rise of temperature increases the molecular movement of dye molecules or particles, so that they get into contact with the fiber more rapidly and with greater velocity. This may assist dyeing or retard it, according to the changes made in the other factors.

The electrical charge on the fiber may alter; negatively charged fibers attain their maximum charge at about 40° C. This causes wool to dye more rapidly with Methylene Blue and certain other dyestuffs, at about 40° C., but does not necessarily produce a similar effect on all dyes on account of other changes which take place.

As a rule, the size of dye particles diminishes with rise of temperature. This may increase the rate of dyeing, when the particles are nearly the same size as the pores in the fiber, or diminish it when the particles are already very small. Generally speaking, increase in temperature should increase the fastness of dyeing.

In practice it is known that the changes in the rate of dyeing caused by changes in temperature are by no means uniform; some dyes are absorbed quickest at the boil, others at various temperatures.[7] Considering the numerous factors involved this is not surprising. The maximum at 40° C. in the dyeing of Methylene Blue on wool gives strong support to the electrical theory and has not been explained by any other theory.

Summarizing, the author's theory takes into account the following factors:

1. The molecular movement of dye molecules and particles.
2. The electrical charge on the dye particles.
3. The electrical charge on the fibers.
4. The size of the dye particles.
5. The surface area of and the size of pores in the fibers.

The further application of the theory to particular cases of dyeing is considered below.

Acid Colors on Cotton

Acid colors, generally, do not dye ordinary cotton to any appreciable extent, although there are one or two which give weak shades, such as Crocein Scarlet 3BX, and a brand of soluble blue, at one time sold by Brooke, Simpson and Spiller, under the name of Non-Mordant Cotton Blue.

In the experiments made with Crocein Scarlet 3BX, the addition of salts increased the absorption of color, acting in the order NaOH, Na_3PO_4, Na_2SO_4, NaCl, HCl, $MgSO_4$, $Al_2(SO_4)_3$—that is to say, essentially in the reverse order, that as these substances act on the contact charge of cotton. HCl again is in the wrong position, just as in the case of direct colors. Knecht showed that treatment of cotton with concentrated nitric acid, 83° Tw., for three hours, caused it to acquire an affinity for acid colors. As mentioned in a previous paragraph, cotton, treated with nitric acid, had the lowest contact charge of any of the treated samples of cotton, and it should therefore have the greatest affinity for acid colors A process [8] has been brought forward for the dyeing of acid colors on cotton, in which a colloidal precipitate of basic (positive) character is used as mordant.

Fort [9] proposed to use benzidine, which also carries a positive charge, as a mordant for acid colors; he found that the absorption of benzidine by cotton was considerably increased by first mordanting with tannic acid, which itself carries a strong negative charge. These points are entirely in agreement with the electrical theory.

Basic Colors on Cotton

Unmordanted cotton under ordinary conditions does not dye with basic colors; if it absorbed the color ion, the acid in combination with the color, usually hydrochloric acid, would be left free in the bath, and this would reduce considerably the negative electric charge of the cotton as well as tending to dissolve the color off it. A small amount of color is actually absorbed, but it is limited by this liberation of free acid. If this free acid is removed as fast as it is formed, cotton will absorb a considerable amount of basic color. This can be affected by forcing a solution of basic color, by pressure, through tightly packed cotton; a colorless solution of the acid originally in combination with the color passes out and the cotton becomes dyed. A similar effect occurs if the acid is neutralized by the addition of alkalis or insoluble magnesium hydroxide.

Biltz and Steiner [10] found that cotton absorbed less color from a strong solution of basic color than from a weaker one. The reason for this is that in the more concentrated solution of dye the fiber has less electrical charge.

Nitrated cotton on account of its greater negative charge is able to absorb more basic color.

All insoluble substances with a strong negative charge should act as mordants for basic colors. The most common mordant is tannate of antimony, which has a strong negative charge. Tanned cotton has the property of absorbing considerable quantities of basic colors leaving in the dye bath the free acid originally in combination with the dye.

The first process in mordanting with tannic acid is to steep the cotton in a solution of tannic acid and since this compound carries a negative charge, its absorption should follow rules similar to those applying to direct colors. This has been found to be the case; the addition of salts and acids produces a slight increase in absorption and the substances act in the same order as for dyeing with direct colors.

The process of fixation of the tannic acid prevents this substance from passing back into the dye bath and causing precipitation of the dye. In addition to this, the increased volume of the antimony compound enables it to take up more dye.

Mordant Colors on Cotton

The mordant colors for cotton are substances carrying a negative charge, and their absorption takes place best when the fiber is positively charged. The processes of mordanting cotton are numerous. In alkaline mordants such as sodium aluminate, and plumbate, the heavy metallic ions are negatively charged, and consequently they are taken up by cotton in a similar manner to direct colors. The absorption of alumina from sodium aluminate is increased by the addition of salts which act in the same order as for direct colors.

In the ordinary salts of the heavy metals the metallic ions are positively charged and hence are taken up by cotton in the same manner as basic colors with liberation of the free acid, which prevents further absorption. The removal or neutralization of this free acid facilitates the process of mordanting, hence it is customary to use basic sulfates and acetates of the heavy metals.

There are also processes of mordanting depending mainly on precipitation, which require no explanation.

The colloidal state of the mordant plays a very important part in the process of dyeing and in the fastness of the resulting shades. For example, an iron mordant applied by soaking the cotton in a solution of a ferric salt, drying and exposing to ammonia gas, gives a very poor result in dyeing, and the shade is loose to rubbing and to washing. If precipitated with caustic soda solution instead of ammonia a better result is obtained, but the best results are obtained by the use of a ferrous salt, because precipitated ferrous hydroxide is more gelatinous than ferric hydroxide and is more easily fixed in the fiber. Subsequent oxidation makes little difference in the physical state of the precipitate.

The dyeing of mordanted cotton with alizarin colors follows from the attraction between the positively charged mordant and the negatively charged dyes. The action of the lime used usually with alizarin is to reduce the size of the dye particles and enable them to enter the pores of the fiber more easily. In addition, the surface of the dye exposed is greater and consequently larger quantities of electricity come into play, as discussed in the previous article.

Dyeing of Cotton with Colloidal Solutions

Feilman[11] found that colloidal solutions of indigo and paranitaniline red prepared by precipitating the dyes in the presence of a protective colloid, casein, had the property of dyeing cotton, although the resulting shades are not very fast. Colloidal solutions of mineral substances, such as Prussian blue and molybdenum blue, also dye cotton.

In all these solutions the particles are very much larger than the particles present in solutions of direct dyestuffs, and consequently their coagulation is limited to the pores of comparatively larger diameter so that the shades are not fast.

Gee and the author [12] found that colloidal solutions of positively charged dyestuff, such as Night Blue, Spirit Blue, and Crystal Violet, were rapidly absorbed by cotton, although more quickly by tanned cotton and wool.

It is well known that basic colors are precipitated by acid- and direct colors. The author prepared compounds of Night Blue, with picric acid and of Crystal Violet with Chrysophenine, washed them thoroughly to remove impurities, such as the salts formed during the reaction, and after drying, dissolved them in alcohol. Colloidal solutions of these were prepared by pouring the alcoholic solutions in water.

Tanned cotton was found to absorb the positively charged Night Blue from the colloidal solution of the negatively charged Night Blue picrate, leaving the whole of the negatively charged picric acid in the bath. This experiment is analogous to the dyeing of basic colors by wool, made by Knecht in support of the chemical theory, but in this case the dye is not in true solution. This result shows that ionization is not limited to substances, termed crystalloids, which form true solutions and show a normal rise in boiling point when dissolved in water. The fact that the Night Blue picrate carries a negative charge illustrates the predominance of the negatively charged (acidic) portion over the positively charged (basic) portion.

The tanned cotton also extracted the Crystal Violet from the compound with Chrysophenine, leaving most of the latter free in the bath.

Acid Colors on Wool and Silk

Acid colors dye wool and silk from a salt bath and from an acid bath.

The dyeing of wool and silk in a salt bath is governed by similar rules to those which apply to the dyeing of cotton with direct colors.

Dreaper and Wilson [13] investigated the dyeing of silk in the presence of sodium carbonate. They found that the first addition of soda produced a marked decrease in the amount of color absorbed, but with further additions the shade gradually increased in depth. They stated that the color is fixed under conditions, which give little support to the electrical theory of dyeing or to a theory which assumes ionization of the dyestuff.

The above experiment is exactly analogous to the dyeing of cellulose with Benzopurpurine and Rosophenine in presence of caustic soda, which has already been explained by the effect of the alkali on the electrical charge of the fiber and dye.

The above authors also found that, of the dyeings made on silk with Acid Anthracene Red, that dyed without addition was the fastest. The explanation of this has been stated in the paragraph relating to fastness.

It is thus clear that the dyeing of silk with acid colors in a bath containing sodium carbonate is entirely in agreement with the electrical theory as put forward in this section.

The dyeing of wool and silk with acid dyestuffs proceeds more rapidly in an acid bath. It is known that when wool is boiled with acid it acquires a positive charge thus enabling it to attract directly the negatively charged color ions of the acid colors. It has also been found that Glauber's salt reduces considerably the positive charge acquired by wool in an acid bath and may change it to negative. For this reason Glauber's salt acts as a restrainer.

Pelet-Jolivet and Anderson [14] found that in the dyeing of wool with Crystal Ponceau, acids acted in the order H_3PO_4, H_2SO_4,HCl—that is, in the same order as these acids increase the positive charge on wool.

Pelet-Jolivet and Siegrist [15] observed that in the dyeing of wool with Crystal Ponceau the gradual addition of sulfuric acid produced first an increase in the absorption of color, and then a decrease after a certain concentration had been reached (about 5 per cent solution). A similar observation has been made by Fort.[16]

It is probable that the positive charge acquired by wool in an acid bath would attain a maximum at a certain concentration of acid in a similar manner to the negative charge of cotton in an alkaline bath. Further additions of acid would then decrease the charge and the amount of dye absorbed would then be reduced. It is difficult to prove this by electrical methods because the acid in the solution interferes with the measurements. Attempts were made to measure the electrical charge on wool boiled with acid and washed thoroughly. The results were variable, because the acid gradually dissolved out of the wool. More recent experiments [17] have shown that all the acid absorbed by wool can be removed by boiling water.

Knecht found that in the dyeing of wool in an acid bath with the magnesium salt of Crystal Scarlet, the magnesium was left quantitatively in the bath. This proves that the wool only absorbs the color ion, and, as is expected from the electrical theory, the strong positive charge on the wool when in acid solutions repels the positively charged magnesium ions and prevent their absorption. In a faintly acid bath, where the charge is less or may be negative, some magnesia is also absorbed.

Basic Colors on Wool and Silk

Basic colors dye wool and silk both from a neutral and acid bath although to a less extent in the latter cases.

In a neutral bath the negatively charged fiber attracts the positively charged color base and leaves free in the bath the acid originally combined with it.

Knecht [18] found that the acid was left quantitatively in the bath.

Pelet-Jolivet and Grand [19] found that the dyeing of basic colors on silk was modified by the addition of salts. The resulting shades increased in intensity in the following order: $Al_2(SO_4)_3$, $MgSO_4$ no addition, NaCl, Na_2SO_4, Na_3PO_4, NaOH. The substances are in the same order as for their effect on the electrical contact charge on cotton.

In an acid bath the shades increased in the order: HCl, H_2SO_4, H_3PO_4.

Dyeing of Mineral Substances

It has long been known that substances of apparently inert character such as sand and powdered quartz have the power of absorbing coloring matters. These facts were quoted by Georgievics in favor of the mechanical theory of dyeing.*

Experiment shows that these so-called inert substances when placed in water acquire an electric charge; sand and quartz become negatively charged. The absorption of color base and liberation of the free acid in combination with basic colors is then due to the action of this electric charge and is not merely a mechanical effect.

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* *See* paper by Georgievics in this volume. J. A.

Animal charcoal is known to have a strong affinity for acid colors in an acid bath and also acquires a positive charge in acid solution. This effect has been shown by Knecht [20] to be due to the action of nitrogenous compounds in the charcoal. Graphite, purified by chemical treatment so that it contains 99.6 per cent of carbon and no nitrogen, was shown to have no affinity for dyestuffs when treated with their solutions in the ordinary way.

Knecht also found that purified quartz even in the form of powder absorbed no Methylene Blue from its solution.

In the paragraph on the dyeing of basic colors on unmordanted cotton it has been shown that the free acid, which must be left when a negatively charged substance absorbs the positively charged color base from a basic color, effectively prevents further absorption.

This explains why no measurable amount of color is taken up by purified quartz, the small surface exposed by quartz as compared with precipitated silica or with cotton fiber, also keeps the absorption very low.

Even purified quartz will absorb appreciable quantities of the color base of basic colors, if the solution is forced through a column of the powdered quartz, because in this case the free acid is removed from the sphere of action as soon as it is formed.

The absorption of dyestuff by mineral substances takes place generally in accordance with the electrical theory, the surface of the substances having a very important bearing on the amount of dye absorbed.

THE DYEING OF ARTIFICIAL SILK.

One of the difficulties met with in the dyeing of cellulose artificial silks, viscose, cuprammonium and denitrated nitro-silk is unlevel dyeing. This problem was put before the writer, who, by application of the theory of dyeing, outlined in this section, put forward suggestions which eventually led to the solution of the problem. Firstly artificial silk is made in such a manner as to leave it porous, but the porosity is irregular and varies with the previous history of the cellulose composing it.

If the particles or molecules of dyestuff are nearly as large as the pores in the cellulose, then variations in porosity will necessarily cause larger variations in dyeing properties; the maximum difference would arise if the dye particles were of a size intermediate between the two sizes of pores in the different silks.

If one arranges things so that the dye particles or molecules are small in comparison with the pores in the cellulose, then these differences in dyeing property will disappear.

There are two ways of effecting this, one to swell the cellulose and thus increase the size of the pores and the other to reduce the size of the dye particles. The latter may be effected by using higher temperatures for dyeing, using pure dyes and soft water (since salts and hard water tend to increase the size of the dye particles) and finally, which is obviously the best way, to use dyestuffs of low molecular weight. This last method was developed by L. P. Wilson and M. Imison from the above-mentioned methods.

Recently cellulose acetate silk has become an article of commerce and its introduction was delayed because of the difficulty in dyeing it. In very few cases have the ordinary direct cotton colors any affinity for acetate silk.

The methods of attack on this problem may be classified into the following:

A. Testing all the known dyes in order to select those having an affinity for the fiber.

B. Modifying the fiber or the dyeing process to enable ordinary dyes to be used.

C. Making new dyes for the direct dyeing of the silk.[21]

Method A led to the selection of some acid colors, many basic colors and particularly the gallocyanines.

Method B. The cellulose acetate was hydrolyzed to permit the use of direct cotton colors.

1. The silk was swollen in ammonium thiocyanate, so as to increase its absorption capacity for certain basic and acid colors.

2. The writer [22] made use of the strong electric charge of cellulose acetate to make it retain direct cotton color, which had been given a strong positive charge by combination with a strongly positive base, dianisidine, benzidine, etc. The dyeings were resistant to water but not to soap or other alkaline solutions which decomposed the compound of base with direct color. When, however, the same process was applied to the leuco compounds of vat dyes the subsequent oxidation fixed the dyestuff.

3. Use of foam dyeing,[23] since by this means one can apply a strong solution of dyestuff thereby increasing the absorption by the silk.

Method C. Clavel [24] states that the dyeing of cellulose acetate is not, as hitherto generally supposed, merely a physical phenomenon, but that dyeing is due to the presence in the dyestuff of chemically active groupings which enable the dye to combine chemically with the cellulose acetate. The following groupings are claimed as active groups; hydroxyl, amino, imido, imide, nitro, nitroso, isonitroso, acidylamino, and azo groups. Carbonyl groups arrest or weaken the power of chemical combination.

As examples of dyestuffs containing active groups, the following are mentioned. Pyramidol Brown, with four hydroxyl groups, Chrome Violet and Alizarin with two, Magenta with three amino groups, Rhodamine with one ethyl amino and one diethyl amino group, Gallocyanine with one hydroxyl and one dimethyl amino group, Indanthrene with two imino groups and Algol Rose with one hydroxyl and one acidylamino group.

If this theory were true the production of dyestuffs suitable for dyeing cellulose acetate would be a comparatively simple matter which it is not.

Within certain limits it is quite possible that the dyeing may be governed to some extent by definite groupings but even then it is by no means certain that the dyeing of cellulose acetate is due to chemical combination between dye and fiber.

If Clavel's theory were correct, the effect of these special groupings would always be the same, and the ordinary chemical activity of these groupings should be inhibited by their chemical combination with the cellulose acetate. Neither of these conditions holds in practice. For example, when comparing aminoazobenzene with its derivatives having hydroxyl or amino groups ***meta*** to the parent amino group, it is found that the aminoazobenzene is almost completely exhausted from the bath by the cellulose acetate silk, the dye containing the hydroxyl group comes next, while the dye with two amino groups is absorbed least. One cannot compare the depth of color on the silk, as the compounds have different coloring powers; the degree of exhaustion is the best test.

The experiment clearly shows that the addition of the so-called active groups, hydroxyl and amino, reduces the affinity of aminoazobenzene for the cellulose acetate. The effect is due to increased solubility of the dye itself in water.

In the case of simple amino compounds dyed on acetate silk the free amino group is easily diazotized, showing that the grouping cannot be chemically combined with the fiber.

There is no doubt that the dyeing of cellulose acetate is governed by electric forces exactly like the dyeing of other materials. Taking a large selection of dyestuffs, those of basic character, which carry a positive charge, have the greatest affinity for the silk which itself carries a large negative charge. Cellulose acetate silk, however, behaves as if it were much less porous, or rather has much finer pores than viscose silks or other silks which swell in water.

The attachment of the amino grouping to the cellulose acetate is not a chemical one in the true sense of the word, it is more analogous to a solution effect. On this account amino compounds on cellulose acetate silk behave in a similar way to a solution of the amino compound in a solvent like ethyl acetate.

The writer observed that amino compounds dissolved in ethyl acetate could be diazotized and coupled with phenolic compounds at high temperatures, up to 80° C., whereas in water, as is well known, diazo compounds are unstable even at ordinary temperatures. This observation led to the development of a method of dyeing which was the first one to give a complete range of colors from yellow to black, giving all the deep shades of blue and brown, which together with black, were the great stumbling blocks in the dyeing of cellulose acetate at the time.

The method is described in the English patent,[25] and consists of applying first the amino compound, in acid solution to the cellulose acetate silk. This treatment is followed by the addition of the phenolic compound, dissolved in a little ammonia. Glue or other protective colloid is added first to prevent precipitation of the phenolic derivative. After a time, the requisite quantity of sodium nitrite is added to the hot bath at 60° to 80° C. and a rapid development of color ensues. Very beautiful shades of red, blue, brown and black have been obtained by this method. Greens are difficult because there are few green azo dyes known which contain no sulfonic acid groupings and these prevent absorption by the cellulose acetate.

The insolubility of many of the useful amino compounds led to the use of colloidal solutions of these compounds by the writer.[26] Since that time the idea has been developed by the British Celanese Co., who prepare the colloidal solutions in different ways. An attempt was made to apply the process of the Society of Chemical Industry, Basle,[27] whereby difficultly soluble dyes were rendered more soluble by treatment with formaldehyde bisulfite. Two compounds were of particular interest to the writer at the time, one was the aminoazo compound, prepared from aminophenol and *alpha*-naphthylamine and the other from *para*-nitro-*ortho*-anisidine and cresidine. In both cases, the formaldehyde bisulfite compounds were absorbed to a very much less extent than the colloidal solutions of the original aminoazo compounds: in the second case mentioned the affinity was practically destroyed. On this account the idea was dropped by the writer. A short time later the same idea was adopted independently by Green & Saunders[28] and dyes of this series were named Ionamines, but not because they formed ions.

The idea has been applied further to amino compounds of the anthraquinine series.

Generally speaking, it may be assumed that a colored compound which dissolves in ethyl acetate and is slightly soluble in water will act as a dye for cellulose acetate. If it is insoluble in water, a colloidal solution will be of some use provided it can be made of high degree of dispersion or associated with a liquid disperse phase which itself is soluble in ethyl acetate. Formaldehyde bisulfite derivatives of amino compounds are hydrolyzed in water to form highly dispersed amino compounds. In a few cases the hydrolysis is slight and then the derivatives are useless.

The numerous examples given will serve to illustrate this fact.

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[20] *J. Soc. Dyers Colourists*, **4**, 72 (1888).
[21] *Cf.* Baddiley, Hill and Anderson, Eng. Pat. 202,157; Burgess, Ledward and Harrison, Eng. Pat. 190,312.
[22] Burgess, Ledward and Harrison, Eng. Pat. 179,384.
[23] Clavel, Eng. Pat. 176,535.
[24] Clavel, Eng. Pat. 182,830.
[25] Burgess, Ledward and Harrison, Eng. Pat. 193,646.
[26] Eng. Pat. 193,646.
[27] Eng. Pats. 172,056, 172,057.
[28] Eng. Pat. 200,873.

Theory of Dyeing.

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Dyeing consists in imparting a moderately fast color to a substance as a result of immersing it in a suitable, true or colloidal, solution. Such a solution is known as a dye-bath and usually contains a colored substance dissolved or peptized; but may contain a substance which can be converted into a colored material. Thus the indigo vat is not blue and does not contain indigo. The vat is yellow and contains reduced indigo (indigo white), the blue color appearing subsequently when the indigo white is oxidized on the cloth. When dyeing with paranitraniline red, the bath contains β-naphthol which is not a dye. The color is developed with diazotized paranitraniline. In most cases the coloring matter is adsorbed by the substance dyed and does not form a definite chemical compound with it, as is shown by the fact that we get a smooth curve when we plot dye concentration in bath against dye concentration in fiber at constant temperature. In 1843 and again in 1863, Crum[1] put forward the view that the dyeing of cloth was precisely similar to the adsorption of gases and other substances by charcoal. This part of his theory was right, though his explanation of the way in which charcoal acts is not accepted nowadays. It is interesting to note that in 1907 the same theory of dyeing was expressed clearly by Hübner,[2] who says that his experiments prove that dyeing is a phenomenon of adsorption and takes place in practically the same manner, regardless whether the coloring matter is taken up by textile fibers or by such substances as charcoal, graphite, etc. The differences are only in matters of detail.

While all sorts of substances are dyed at one time or another, from feathers to marble, the most important technical dyeing has to do with the textile fibers, and chiefly with wool, silk, and cotton, though the total weights of dyes used in the paper and leather industries are larger than in the silk industry. Only the dyeing of these textile fibers will be considered in this article. There are no new principles involved in the dyeing of other materials.

MORDANTS.

Many substances used as dyes will not dye some or all of these fibers satisfactorily. It is often possible, however, to get the fibers to adsorb strongly certain other substances which can themselves be dyed. The name mordant has been given to substances which are adsorbed strongly by the fiber and which adsorb the dye strongly. Mordants are divided into two groups, basic and acid, the chief basic mordants being the hydrous oxides of aluminum, tin, iron, and chromium, while tannin, albumin, and certain fatty acids, such as oleic acid, sulfonated oils, etc., are the most commonly used acid mordants.

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* I am indebted for many helpful criticisms to Messrs. Derick, Rose, and Watkins. This does not mean that these gentlemen endorse the theory as presented.

Williamson[3] has shown that the addition of caustic soda to solutions of potassium aluminum alum and of potassium chrome alum causes first the precipitation of basic aluminum sulfate, $Al_2(SO_4)_3.(Al_2O_3)_4.15H_2O$, and of basic chromic sulfate, $Cr_2(SO_4)_3.Cr_2O(SO_4)_2.25H_2O$, respectively, and then of hydrous oxides. Consequently, it is probable that when wool is heated with either of these solutions, there is precipitation of the basic salt or the hydrous oxide, depending on the conditions of concentration and acidity. Since wool will adsorb sulfuric acid independently of the hydrous oxide, we do not yet know how to determine just how the acid is held. The problem is apparently even more difficult in the case of chrome-tanned leather.[4]

When wool is boiled with a solution of alum or of aluminum sulfate, some of the alumina becomes fixed on the fiber. Mordanting with chromium, which is far and away the most important mordant for wool,[5] is not usually done with chromium sulfate or with chrome alum; but with sodium chromate and the salt of some easily reducible organic acid, tartrate or lactate. This is equivalent in principle to mordanting with chromium tartrate or lactate. Silk does not take up the basic mordants quite as readily as wool, and dyers therefore use a basic alum solution or a basic aluminum sulfate solution. Ferric acetate or a basic ferric sulfate solution is often used with silk which is to be dyed black, while the weighting of silk usually involves mordanting with stannic oxide. The adsorbing power of cotton for alumina is so feeble that it does not cause an effective hydrolysis of alum. Cotton is therefore usually mordanted by being heated with aluminum acetate;[6] but it is possible to mordant cotton with a strongly basic alum solution. Mordanting with iron salts is usually done after a previous mordanting with tannin.

Wool is not often mordanted with tannin; but silk and cotton are, taking up tannin readily from colloidal solution. Silk holds the tannin firmly but cotton does not and it is necessary to fix the tannin by a treatment with potassium antimony tartrate. Hydrous antimony oxide is adsorbed by the tannin and cuts down the peptization of the latter by water practically to zero. When cotton is mordanted for basic dyes with sulfonated castor oil or other substances of that general nature, the oil mordant is usually fixed by a treatment with aluminum acetate. If an excess of alumina is precipitated, we have an alumina mordant fixed by oil. The basic mordants are usually fixed by means of arsenates, silicates, phosphates, stannates, oil acids, and tannin; sodium phosphate being used especially for alumina and sodium arsenate for iron. Tin and tannin are used a great deal in weighting silk. While we cannot say that no definite chemical compounds are formed in any of these cases, we are dealing chiefly with the precipitation and adsorption of oppositely charged colloids, except in the case of sodium phosphate.

CLASSIFICATION.

Dyes are usually classified as basic, acid, substantive (or direct), developed (or diazotized), mordant, vat, sulfur, miscellaneous, and inorganic (or mineral) dyes. The basic and acid dyes are always in true solution under the conditions of use; all the others exist only in colloidal solution with the exception of sodium alizarate. Basic dyes are salts of color bases which dye wool and silk but do not dye cotton satisfactorily without a mordant. Acid dyes are salts of color acids which dye wool and silk but do not dye cotton satisfactorily without a mordant. Substantive dyes are salts of color acids which dye cotton direct (without a mordant); they may also dye wool and silk. Developed or diazotized colors are substantive colors which are formed on the fiber by diazotizing one member and coupling this with another. Mordant dyes do not dye wool, silk, or cotton direct but require a basic mordant. Vat dyes are colors whose reduction products are peptized by alkali and which are then adsorbed strongly by cotton in the absence of a mordant. The true color often does not appear until the adsorbed reduction product is oxidized. Sulfur dyes are reduced and peptized by sodium sulfide; they dye cotton direct. The miscellaneous dyes include aniline black and the natural dyes. The chief inorganic dyes are Prussian blue, chrome yellow, iron buff, and manganese bistre. Ultramarine blue is used a great deal with paper. The developed, vat, sulfur, and inorganic dyes are theoretically substantive dyes in so far as they dye cotton without a mordant; but it is simpler, for the present, to treat them under different heads.

BASIC DYES WITH WOOL AND SILK.

Since the basic dyes are electrolytes in true solution, the relative adsorption by the fibers of the different ions in the bath is of great importance.[7] Consequently the basic dye will normally be taken up most strongly in an alkaline solution and least strongly in an acid solution. A strongly adsorbed cation decreases and a strongly adsorbed anion increases the amount of a basic dye taken up by the fibers. A striking instance of this last is the action of sodium sulfate as an "assistant," the readily adsorbed sulfate ion causing more dye to be taken up.[8] Since hydroxyl ion is adsorbed strongly by wool and silk, there will be a strong tendency for the free color base to be taken up, leaving the acid behind. It was found by von Georgievics [9] that with silk and rosaniline hydrochloride all the magenta goes into the silk and all the hydrochloric acid stays in the bath,[10] while wool adsorbs a portion of the acid. This is remarkable because the free color base is not stable except when adsorbed by the fibers.[11] The tendency to adsorb the color base is so strong in the case of silk that silk can be dyed magenta from a colorless ammoniacal solution [12] of the dye.

The exceptions to the rules are fairly simple. If the color base is instable or insoluble, one cannot use an alkaline solution. The Janus colors, for instance, are insoluble except in acid solution.[13] Mr. Rose tells me that the Janus dyes are now marketed in a soluble form. If the dye is adsorbed too strongly and therefore too rapidly from an alkaline solution, it may be necessary to dye in acid solution. This is apparently the case [14] with Victoria Blue B. In certain cases, as with rhodamine for instance, the effect of hydrogen-ion concentration is practically negligible over quite a range of hydrogen-ion concentration. There is no explanation for this at the present time.

When we say that basic dyes do not dye cotton well without a mordant, we must remember that our views as to what constitutes satisfactory dyeing may change. In 1879 Auerbach [15] speaks of alizarine blue as having been replaced "by a much faster and more splendid colour, the so-called methylene blue, which resists not only sunlight but also alkalis and acids, and dyes cotton without a mordant." Nowadays methylene blue is classed as a dye which does not dye cotton direct. In presence of sodium acetate the water-soluble induline dyes, such as indazine, indazine blue, nigramine, and methylene gray, dye cotton direct; [16] but are much more satisfactory if tannin is used.[17] The Janus dyes will dye cotton direct in acid solution,[18] though one usually uses tannin mordant except in the case of union dyeing.

ACID DYES WITH WOOL AND SILK.

In addition to the regular acid dyes, many of the other dyes can be converted into acid dyes by sulfonation. Thus acid magenta is derived from a basic dye and indigo sulfonic acid from a vat dye.

Like the basic dyes the acid dyes form true solutions. Since the color is in the anion and not in the cation, the behavior of the acid dye is exactly the opposite of that of the basic dye.[19] The acid dye is normally adsorbed most strongly in acid solution and least strongly in alkaline solution. A strongly adsorbed cation increases and a strongly adsorbed anion decreases the amount of an acid dye taken up by the fibers. Sodium sulfate therefore decreases the amount of an acid dye taken up while increasing the amount of a basic dye. Alkali blue is often cited as an exception because it is not used in acid solution; but this is merely because the color acid is insoluble. Less dye is adsorbed the more alkaline the solution, which is as it should be. If enough sodium sulfate is added to make the dye form a colloidal solution, its effect will change. This is also true with basic dyes such, for example, as methylene blue.

Since adsorption is selective, it is easy to predict that some acid dyes will be adsorbed more strongly than others by wool or silk. We may have the extreme cases that one dye may be adsorbed quite strongly by wool and scarcely at all by silk or the reverse. We may also have acid dyes which will dye wool and silk practically equally. Matthews[20] gives lists of dyes meeting these various requirements. Ganswindt[21] states that azofuchsine G, naphthol yellow S, fast yellow, and indigo carmine dye wool strongly and silk very slightly or not at all, while rhodamine and new Victoria blue dye silk very strongly and wool only slightly. Between these two extremes we have azocarmine, fast acid violet A2R, azo yellow, fast acid violet 10B, patent blue A, and fast green, all of which dye wool and silk to about the same extent. Most of the adjustment is done by regulating the temperature and the acidity of the bath, the silk being dyed more strongly relatively to wool at low temperatures and low acidity.

BASIC AND ACID DYES WITH COTTON.

To dye cotton satisfactorily with basic or acid dyes, one must use a mordant, an acid mordant so-called, for the basic dyes and a basic (or metallic) mordant for the acid dyes. The eosines are said to be an exception and to dye cotton direct; but the color is not fast.[22] Tannin is by far the most important of the acid mordants and is precipitated from colloidal solution by basic dyes. This precipitate is peptized however by a slight excess of basic dye or of tannin and one can get satisfactory dyeing only by fixing the tannin with metallic oxides, usually antimony, though tin has been used with mauve[23] and alumina with rhodamine.[24] The adsorption of oxides by tannin decreases the power of the tannin to adsorb basic dyes; but this disadvantage is more than compensated by the increased fastness of the dyeing. As might be expected, acids decrease the amount of basic dye which can be taken up by tannin.

Oils—meaning certain organic acids—may also be used as mordants and they too are fixed by metallic oxides. Albumin is used occasionally as an acid mordant[25] and it has been suggested[26] that the adsorption of basic dyes by silk is due in part to albuminous matter on the silk acting as a mordant. Acid dyes are used on cotton with hydrous metallic oxides as mordants, the oxides of aluminum, chromium, iron, and tin being the most important. The acid dyes are taken up by the basic mordant in acid solutions and the presence of sulfate ions decreases the amount adsorbed just as happens with the same dyes on wool and silk without any mordant and for the same reason. In fact the oxides of aluminum, tin, and titanium will adsorb basic dyes from alkaline solutions.[27]

SUBSTANTIVE DYES.

Until 1884 turmeric, safflower, saffron, and annatto were the only dyes known which would dye cotton direct from an ordinary solution, and none of these were good dyes. Annatto [28] is still used for coloring oils and butter; but is very fugitive to light. Saffron is used in Spain for coloring rice. In 1884 Böttger [29] prepared Congo red, the first synthetic substantive dye. Since then an enormous number have been made. Green [30] classifies them as diazo, trisazo, tetrakisazo, stilbene, and thiazole colors.

None of the substantive dyes form true solutions in water; but most of them are peptized readily by it. They dye wool and silk also, sometimes more strongly, than they do cotton and sometimes less so. Curcumin S and Mikado yellow,[31] for instance, do not dye wool so strongly as they do cotton, while purpuramine dyes wool much more strongly than it does cotton.

Owing to the substantive dyes being in colloidal solution, the important factor in determining the adsorption is the degree of stability of the sol. Anything which tends to precipitate the dye will increase the adsorption until the coagulation becomes so great that the dye begins to settle out even in the absence of the fibers. Addition of a precipitating agent in increasing amounts will therefore first increase and then decrease the amount of adsorption by the fibers. On the other hand, addition of a peptizing agent will decrease the amount of dye taken up by the fiber, or will strip dye from the fiber.[32] This is exactly what happens. The dye is forced on the fiber by acid or alkali, by sodium chloride, sulfate, or phosphate, the amount of adsorption passing through a maximum with increasing concentration of the electrolyte. Soap and gelatin decrease the adsorption because they peptize the dye. Biltz [33] has observed the increased adsorption of benzopurpurine due to sodium sulfate. It is stated by von Georgievics [34] that sodium chloride and sodium sulfate precipitate the substantive dyes, while caustic soda, sodium carbonate, and sodium phosphate peptize them. This is true in more concentrated solutions; but, in dilute solutions, they all decrease the stability of the sols and therefore all act alike. The occurrence of the maximum is due to different reasons, however, with the two sets of salts. Fort [35] says that many of the substantive dyes are insoluble in water but are peptized by sodium carbonate. He finds that molecular quantities of sodium chloride and of sodium sulfate cause the same change in adsorption.

In neutral or alkaline solutions the salts of the substantive dyes are adsorbed as such.[36] That it is a true case of adsorption has been shown by Biltz [37] and by Schaposchnikow.[38] Benzo indigo blue and benzo blue black R require a high concentration for peptization; St. Denis red, rosophenine 4B, etc., require high alkali concentration to force them on the fiber.[39] These are not exceptions; they are merely differences in degree. Substantive dyes may act as mordants for basic dyes,[40] chrysamine being a good mordant [41] for methylene blue, safranine, methyl green, and Victoria blue. Mr. Rose tells me that nowadays no dyer would top chrysamine with methylene blue. Two dyes are taken which are as nearly as possible of the same hue.

DEVELOPED COLORS.

Developed colors are essentially non-peptizable substantive colors produced on the fibers. The colors are obtained by the interaction of a diazotized base with an alkaline phenol or amine solution. The fundamental reaction in the case of β-naphthol, $C_{10}H_7OH$, and a base may be written:

$$RNH_2 + HNO_2 + HCl = RN_2Cl + 2H_2O$$

$$RN_2Cl + C_{10}H_7OH + NaOH = RN_2 \cdot C_{10}H_6OH + NaCl + H_2O.$$

The fibers are impregnated with either the diazotized or the non-diazotized constituents of the final color and are then treated with a solution of the other component. We distinguish three classes of developed dyes, depending upon the order in which we mix the solutions.

1. **Naphthol or Azoic Colors.** Treat the fibers with alkaline phenol solution and Turkey red oil; then develop with a diazotized base. The object of oiling the cotton cloth is to increase the brilliancy of the color by decreasing the amount of diffuse reflection. The most important of these colors is paranitraniline red which is obtained by the interaction of diazotized paranitraniline with β-naphthol, which is made on a very large scale, though benzo fast scarlet and Columbia fast scarlet have cut in on it somewhat because of greater fastness to light.[42] Some of the colors obtained by combining β-naphthol with certain aromatic bases are given in the following list:

Base	Color	Base	Color
Paranitraniline	Red	Xylidine	Red
Phenetidine	Scarlet	Cumidine	Bluish-scarlet
Paranitro-toluidine	Orange	Amino-azo-benzene	Crimson
Paratoluidine	Yellow-orange	α-Naphthylamine	Claret
Aniline	Orange-yellow	β-Naphthylamine	Bluish-red
Tolidine	Reddish-brown	Dianisidine	Blue
Azo-black base	Black	Benzidine	Purplish-brown

With the exception of paranitraniline red most of these colors[43] are used chiefly for calico printing. In 1912 naphthol AS was introduced and bids fair to replace β-naphthol.[44] "The blue obtained by coupling dianisidine in the presence of copper chloride with naphthol AS is claimed to be faster to chlorine than indigo or hydron blue. The red obtained by coupling fast red G base with naphthol AS is claimed to be faster to light than para red. The great advantage of naphthol AS over β-naphthol is that, owing to the substantive dyeing qualities of naphthol AS as compared with β-naphthol, it is not necessary to dry the naphthol-prepared material, but it may be passed straight into the developing bath after well squeezing it out of the naphthol bath. Another difference is the addition of formaldehyde to the naphthol bath, which permits the impregnated cotton to remain wet, so that a large quantity may be prepared, then dyed altogether, instead of two pounds at a time.

2. **Developed Substantive Colors.** Dye with an inferior substantive dye, diazotize, and treat with alkaline phenol or amine solution. Primuline was a rather unsatisfactory substantive dye, which dyed cotton a primrose yellow, whence the name. As a starting-point for a new color, it has been a great success. Some of the colors obtained with primuline and some other dyes are given in the following list:

Base	Phenol	Color	Base	Phenol	Color
Primuline	β-Naphthol	Red	Diazurine	β-Naphthol	Blue
Primuline	Resorcinol	Orange *	Primuline	*m*-Phenylene-diamine	Red-brown †
Primuline	Phenol	Yellow	Diazo-black G	β-Naphthol	Black

* Matthews calls this a brown.
† Rose calls this a brick red.

While nearly all the colors are represented in this list, Reibert[45] says in 1905 that the blues and blacks are the most important, the reds next in importance, and the browns fourth. On the other hand, Whittaker[46] says in 1919 that the reds and blacks are the most important. Mr. Rose accounts for this confusion by saying that the dyer distinguishes between those colors which give full shades before they are developed and those which, like primuline, change entirely. The reds are the most important of the primuline group. If one includes Zambesi black V and diazo black BH under the developed substantive colors, the blacks become easily the most important. Mr. Derick says that new and important reds have been developed since Reibert wrote.

Photography on silk has been done with primuline colors.[47] The sensitive surface is prepared by dyeing a silk fabric with primuline and then diazotizing. On exposure to light the diazo group decomposes with evolution of nitrogen and probably with formation of primuline phenol. The positive thus obtained can be fixed (and changed in color) by treatment with β-naphthol orange or any of the other suitable phenols.

3. **Coupled or Benzo-nitrol Colors.** Dye with a suitable substantive dye and develop with a diazotized base. Actually one practically always uses paranitraniline. Benzo-nitrol brown and paranitraniline give a brown.

MORDANT DYES.

A mordant dye should require a mordant, usually a basic one, when dyed on wool, or silk; but the term is often extended to cover dyes which usually are dyed with a mordant or which are chemically similar to dyes which are used with a mordant. Whittaker[48] classifies mordant dyes under the headings of anthracene (alizarine), monoazo (mordant yellow O), diazo (diamond black F), oxazine (gallocyanine), triphenylmethane (chrome violet), nitroso (gambine), oxyquinone (alizarin black), and xanthene (coerulein) dyes, the names in the parentheses being those of the typical dyes of each class.

According to Matthews[49] and Whittaker[50] the true alizarine dyes will not dye wool at all without a mordant, while the others are said to dye wool deep shades, which, however, are not fast to washing. Mr. Derick tells me that this statement is inaccurate and that alizarine cyanine green, alizarine saphirol, alizarine astirol, alizarine rubinol, etc., behave like acid dyes. Edward Bancroft[51] claims that wool can be dyed with madder alone so that it will bear exposure to the sun and air during two months without any considerable injury. This statement needs confirmation.

All the mordant dyes are said to form colloidal solutions in water; but Paddon at Cornell found that sodium alizarate does form true solutions. It is therefore an acid dye which is practically not adsorbed at all by wool. In 1813 alumina was the most important mordant and was used chiefly for dyeing Turkey red (madder, alizarin) on cotton. Nowadays, the mordant dyes are used a great deal with wool to produce dark shades and chromium oxide is practically the only mordant used with wool. Liebermann [52] has experimented with the hydrous oxides of cerium, thorium, zirconium, yttrium, beryllium, aluminum, cobalt, nickel, uranium, chromium, copper, zinc, cadmium, manganese, antimony, bismuth, lead, tin, and iron; but without finding anything that was better than the oxides of chromium, aluminum, iron, and tin. Barnes [53] believes that titania has a future both as a mordant and as a substitute for tartar emetic in fixing tannin.

Sodium alizarate, being an acid dye in theory, is taken up more strongly in acid solution by alumina and less strongly in presence of sulfates. It is still generally believed that lime is necessary to dyeing with alizarin.[54] The madder from Avignon [55] is said to contain lime, while the madder from Alsace does not, and it was not possible to dye with Alsatian madder in the Vosges Mountains until lime was added to the water. This is a very interesting story, as is also the one that pure alumina will not absorb alizarin from a sodium alizarate solution; [56] but unfortunately it is none of it true and the whole difficulty arises from having sulfate in the alumina. Alumina made from aluminum acetate solution behaves quite differently.

Dreaper and Wilson [57] report that both acid and alkali force acid anthracene red on the fiber, which is what they should do in the case of a colloidal solution. The use of oil when dyeing Turkey red is chiefly to make the color more brilliant by giving a medium with an index of refraction more nearly that of the fiber than air. Spohn [58] states that alizarin dyes the mordant and not the fibers, a conclusion which is confirmed by Minajeff.[59]

VAT DYES.

Vat dyes are substantive dyes which are reduced and then used for dyeing. The dyes themselves are insoluble in water; but the leuco compounds made from them by reduction are peptized by alkali and then dye cotton direct. Indigo was the first of the vat colors and is by far the most famous, though everybody has heard of the Tyrian purple [60] of the ancients, which turns out to be 6.6′-dibromindigo. It has been made synthetically; but nobody considers it good enough nowadays to be worth carrying in stock.

Indigo can be reduced to indigo white during the fermentation of organic matter in alkaline solution, by ferrous sulfate and lime, by zinc and caustic soda, by alkaline sodium hydrosulfite, and by catalytic hydrogenation. The indigo white is peptized readily in alkaline solution and is then adsorbed by the fibers, turning blue later when the substance oxidizes. Since the dyeing is done in a bath containing a high concentration of electrolyte, it is hard to determine just what the effect of any particular electrolyte may be; but Binz and Rung [61] state that the adsorption of indigo white resembles that of substantive dyes. Excess of alkali decreases the amount adsorbed. Sodium chloride, sodium sulfite, and sodium thiosulfate increase the amount adsorbed especially when there is an excess of alkali, because they counteract to some extent the peptizing action of the alkali. Whittaker [62] states that vat dyes will bleed when treated with alkali [63] and Knecht and Nair [64] point out that increasing the alkali in the indigo vat above the amount necessary to form monosodium indigo decreases the amount adsorbed. That the taking up of indigo white by the fibers is a case of reversible adsorption is shown by the statement by Knecht and Nair that indigo white can be washed out of cotton with cold, air-free water.

The other vat dyes behave like indigo so far as the general principles go, though there are differences in detail. Thioindigo red B is more easily reduced than indigo, and, unlike indigo, is not affected by oxidizing agents such as chromic acid, or alkaline ferrocyanide and bleaching powder.[65] Indanthrene blue remains blue when reduced, so that the degree of reduction cannot be told by the eye. The anthracene vat dyes require more alkali for peptization than the others and are therefore not well adapted for dyeing wool, unless the wool is protected in some way.

SULFUR DYES.

The first sulfur dye was prepared in 1873 by the action of sodium sulfide and fused sulfur on sawdust. In 1877 it was given the name of Cachou de Laval. Nowadays sulfur dyes are made by melting mixtures of sodium sulfide and sulfur with definite organic compounds,[66] almost exclusively "compounds of the aromatic series containing nitro-, amino-, or imino-groups, such as dinitrophenol, dinitronaphthalene, *p*-aminophenol, *p*-phenylene diamine, oxydinitrodiphenylamine, dimethyl-*p*-oxidiphenylamine, indophenols, safraninones, etc."

The sulfur dyes are substantive dyes[67] which are reduced and peptized by sodium sulfide solutions. The early sulfur dyes were said to be soluble in water; but they really contained enough sodium sulfide to peptize them. The sulfur dyes can also be reduced and then peptized by alkaline reducing solutions and may therefore be considered as vat-dyes. It is better, however, to make a special group for them because they are usually applied from sodium sulfide solutions. Hydron blue is usually classed with the vat dyes because it is as fast to bleaching as the colors of the vat class. It is dyed after the manner of indigo; but it is made according to the general methods for making sulfur dyes. It is said that it may be used in a sodium sulfide bath;[68] but Mr. Rose disputes this.

All the sulfur dyes form colloidal and not true solutions.[69] They behave like substantive dyes and require large amounts of salts to force them on the fiber.[70] Sodium chloride and sulfate both tend to precipitate sulfur dyes and both force the dye on the fiber. On the other hand, glucose, dextrine, and Turkey red oil promote level dyeing,[71] which means that they act as restrainers, and not, as Matthews[72] thinks, to secure better exhaustion of the bath.

MISCELLANEOUS DYES.

Aniline black is the insoluble black pigment produced by the oxidation of aniline[73] in acid solution. Three important successive products of the oxidation of aniline are recognized: emeraldine, nigraniline, and ungreenable black. Emeraldine is a grayish-green substance, which is supposed to contain four or eight aniline residues linked in a chain or ring. Nigraniline appears to contain eight aniline residues. It is sometimes called aniline black, though improperly. It is violet-black and is turned green by mild reducing agents with formation of emeraldine. Ungreenable black is the final product in the technical formation of aniline black and is produced by the further oxidation of nigraniline in presence of free aniline, which suggests that it is a condensation product. Chlorates or chromates, together with salts of copper, vanadium, cerium, etc., have been used as oxidizers and as oxygen carriers. One part of vanadium chloride is sufficient to convert 40,000 parts of aniline into aniline black in presence of chloric acid. Green has used air with *p*-phenylenediamine as an accelerator and cuprous chloride as an oxygen carrier.

Since the coloring matter is produced on the fiber, aniline black could be classed under the developed dyes by changing the definition a little, and this is where W. M. Gardner [74] puts it; but most people limit the substantive dyes to diazotized products.

Green and Wolff [75] say: "It is interesting to note that whereas emeraldine, nigraniline, and aniline black are all, when produced in substance [mass], easily soluble in eighty per cent acetic acid, they cannot be extracted from the fiber by this solvent, but remain completely undissolved. That this must be attributed to some state of combination existing between the fiber and the dyestuff is proved by the fact that after removal from the fiber they are all obtained in a soluble condition. The removal is effected by dissolving the cotton in cold, concentrated, sulfuric acid and pouring into water. The emeraldine or aniline black is obtained as a voluminous precipitate, which is filtered off, thoroughly washed, and basified by boiling with ammonia. The products thus obtained give the same reactions as the compounds prepared in substance." Green and Wolff attribute the insolubility to a reaction between the cotton and the dye; but it is evident that this is merely a case of strong adsorption with no real change in the aniline black. As soon as the adsorbing agent, the cotton, is removed, the normal properties of aniline black reappear.[76]

Under the heading of miscellaneous dyes, we usually include most of the natural dyes, with the exception of indigo and madder. Logwood, Brazil wood, weld, fustic, Persian berries, quercitron, and cochineal, are mordant dyes, and are used with basic mordants. Catechu or cutch can be classed either as a substantive dye or as a tannin mordant. While the natural dyes have been driven out a good deal by the synthetic dyes, that is not entirely the case,[77] especially for logwood.

INORGANIC DYES.

Like aniline black the inorganic dyes are produced on the fibers. Chrome yellow is made by treating the cloth with lead acetate followed by sodium sulfate or lime, and then potassium bichromate. Iron buff is made from ferrous sulfate and sodium carbonate, oxidized by bleaching powder in air. Ordinary khaki is made from ferrous and chromic acetates, treated with sodium carbonate. To make French khaki,[78] pad with ferrous acetate and chromic formate, and then boil with sodium silicate solution containing chalk in suspension. Prussian blue is obtained by dyeing cotton an iron buff and then treating with acidified potassium ferrocyanide solution. Alizarin blue [79] has pretty well displaced Prussian blue in dyeing uniforms. Wool and silk can be dyed manganese brown by boiling with permanganate and adding magnesium sulfate to prevent excess of alkali. Mohair plush dyed in this way is said to pass as imitation fur. To make it more realistic, the color is discharged from the tips with sodium sulfide. Green tea used to be made by dyeing with indigo and kaolin [80] or with Prussian blue, turmeric, and either gypsum or kaolin.

The inorganic dyes are theoretically substantive dyes produced on the fibers. This view requires that these pigments should be adsorbed by the fibers if obtained in suitable colloidal solutions. This appears to be the case. Spohn [81] states that the mineral colors are adsorbed by cotton. Vignon [82] reports that some of them are adsorbed from suspension by silk, wool, or cotton. At Cornell we have dyed cotton with colloidal solutions of Prussian blue. Ultramarine blue is used on a large scale in the paper industry and is also used in "blueing" in laundry work, and in sugar.

Fastness to Washing.

It is often urged that an insoluble compound, conforming to the laws of definite and multiple proportions, must have formed between the fiber and the dye, because, otherwise, the soluble dye would wash out with great ease. This is one of the inaccurate methods of reasoning which are so painfully frequent in most books on dyeing. So far as we now know, all cases of dyeing are cases of reversible adsorption with one exception. If we treat silk with diazotized paranitraniline, for instance, the silk is dyed a beautiful and fast shade of old gold.[83] This of course means the formation of a definite chemical compound with some constituent of the silk; but the cases in which one treats wool or silk with a diazotized base to produce a dye are so few and far between that they can be ignored completely. That is not what people have in mind when they speak of definite compounds between the dye, the fiber, and the mordant.

Fastness is of course a relative term;[84] but, without quibbling over details, we can say that fastness to washing, milling, etc., means that the dye is not easily dissolved, peptized, or rubbed off under normal conditions. Concentrated acetic acid or absolute alcohol, applied boiling, will remove most organic dyes;[85] but it is not the custom to wash dyed fabrics in these liquids and consequently this is not a fair test for fastness. We shall have fastness to washing: (1) if the dye bath is exhausted in absence of special electrolytes; (2) if the dye can be peptized only in an unusual bath; (3) if the dye undergoes an irreversible coagulation on the fiber; (4) if there is increased adsorption due to a change in the fiber in the hot dye-bath. [Several of these factors may co-exist. J. A.]

If the fabric takes all the dye out of a water solution, it is clear that water will not cause that dyed fabric to bleed, though soap may affect the relation somewhat. The more strongly a dye is adsorbed, the less readily will it bleed and consequently one can say, as a first approximation, that a dye is likely to be fast to washing if the dye-bath is exhausted. This is subject to some limitations, especially with the substantive dyes which are forced on by additions of salts. Fabrics dyed in this way would be expected to bleed readily in pure water and they do, even though the dye-bath may have been exhausted. What makes it possible to wash fabrics dyed with substantive colors is that hard water makes the colors less soluble. The recommendation "to add salt when washing blue goods" probably refers to substantive dyes, though it is not so stated.

There is no general rule about the exhaustion of the dye-baths[86] because one can get all ranges of adsorption with different dyes in each class. If one keeps the other conditions the same and obtains a deeper shade by adding more dye to the bath, the tendency of the bath to exhaust will be decreased and the tendency of the fabric to bleed will be increased. Consequently deep shades with basic, acid, and substantive dyes will, in general, be less fast to washing than paler shades. Mr. Rose says that, from a practical point of view, the reverse of this statement is true; but what he means is that a slight removal of color from a pale shade fades it a great deal more than the same removal of color from a deep shade. It might have been safer to have said that in these cases deep shades tend to bleed more than pale shades with the same dye.

As one might expect from the relative exhaustions of the dye-bath under comparable conditions, basic dyes are fairly fast to washing, acid dyes less so, and substantive dyes still less. The vat dyes and the sulfur dyes are usually quite fast to washing; but that is because they are not peptized by water. Anything which increases the solvent or peptizing action of water on a dye will make that dye less fast to washing. It is known that the introduction of the sulfonic group into the dye molecule decreases fastness to washing.[87] Acid dyes made by sulfonating basic dyes are always less fast to washing than the dyes from which they were made. Indigo is insoluble in water and fairly fast to washing, though it does crock. Indigo carmine is a sulfonated dye and is soluble in water. Knecht says in regard to it [88] that "the shades produced with indigo extract are much brighter than those given by vat indigo, but, unfortunately, they are not fast. By conversion into its sulphonic acid derivatives, the properties of indigo are entirely changed. Washing with soap and weak alkaline solutions more or less readily removes the colouring matter from the fibre, and, on exposure to light, the shade fades, the time varying of course according to its depth of colour, and the conditions under which it is exposed."

That developed dyes are faster to washing than substantive dyes [89] follows from the fact that the former are so insoluble that they cannot be applied as substantive dyes. It is not mysterious in any way.

Matthews [90] says that "the vat dyes have come to be very essential dyes for cotton, as it is only by the use of these dyes that laundry-fast colors in cotton-wash fabrics can be obtained. They are necessary dyes for the production of colors in shirtings, blouse material, cotton shirtings, and hosiery, and such fabrics or garments that require to be frequently laundered. . . . It was on the great fastness of the vat dyes that the reputation of the excellent quality and fastness of the German-made dyes became so strongly fixed in the minds of the public." Mr. Rose says that hosiery is never dyed with vat dyes in practice.

The vat dyes are practically insoluble in water. They are not fast to washing if one uses a sodium hydrosulfite solution. The sulfur dyes are remarkable for their fastness to washing; but that is because they are not peptized by soap solutions. They are not fast if washed in sodium sulfide solutions which peptize these dyes readily. The Janus dyes are basic dyes which are so insoluble in water that they have to be used in sulfuric acid solution.[91] Consequently, when dyed on cotton with or without tannin mordant, they are relatively fast to washing. They would undoubtedly bleed in sulfuric acid solution. [Since they are dyed from such solutions, their strength should govern. J. A.]

We know that, in many cases, a precipitate, such as silver bromide or hydrous chromic oxide, coagulates or sinters on standing, and is then much less readily peptized. There is no reason why something of this same sort should not occur with dyes; but there are no experimental data to show that fabrics, dyed with dyes which form colloidal solutions, become faster to washing on ageing. It is the usual custom in dyeing to introduce the fabric into a relatively cool dye-bath and then to raise the temperature, usually to the boiling-point with wool and cotton, and to a lower point with silk. I have made the statement [92] that the real object of this is to coagulate or agglomerate the dye, thus making the dye much less soluble. This was in line with the experiments of Bayliss [93] on Congo red and paper and was apparently proved by the experiments of Lake [94] on acid violet and wool. It may be wrong, however. Subsequent experiments have thrown doubt on the irreversibility of adsorption in these cases. With several acid dyes it was found that practically the same amount of dye was taken up in a month at room temperature as in an hour or less at 90° C. If this proves to be general, the object of heating the dye-bath will be simply to cut down the time factor. The slowness of dyeing with these dyes at room temperature may of course be due to a slow, irreversible adsorption. There is no way at present of determining to what the slowness of dyeing is due.

It is of course possible that heating wool in a dye-bath might change the wool to some extent and thereby alter its adsorptive powers. This would certainly happen if one heated wool with an acid solution in a sealed tube to a sufficient temperature; but special experiments at Cornell indicated that under normal conditions there is no really appreciable change in the wool. The two factors that actually count, therefore, in determining fastness to washing are sufficient adsorption to exhaust the bath completely or sufficient insolubility in the washing solutions to make the amount of peptization negligible. The amount of dye taken up in a given time will pass through a maximum at some temperature if we have slow dyeing at low temperatures and marked peptization at high ones.

The problem of the fastness of mordants to washing is the same as that of dyes, for the mordants may be considered as colorless or slightly colored dyes. Of course there are some special problems. Sulfuric acid is said to help fix alumina mordant on wool.[95] On the other hand, sulfate cuts down the adsorption of an acid dye by wool and consequently an acid dye will bleed more readily if the alumina mordant contains sulfate than if it does not. We know that presence of hydrous ferric oxide may prevent the peptization of hydrous chromic oxide by alkali. It is quite possible therefore that a mixture of iron and chrome mordants might be faster to washing than the chrome mordant alone. Of course there might be disadvantages as to color which would overbalance the hypothetical advantage. The oriental dyers used a mixture of tannins for mordants. It is possible that these mixtures may have advantages over the single constituents.[96] While the chemist is keen for the use of pure substances, it is quite possible that he sometimes sacrifices artistic effects thereby, because a uniform shade is not necessarily the handsomest. Silk adsorbs tannin more firmly from a hot solution than from a cold solution; but this is probably due to the fact that colloidal tannin has smaller particles hot than cold.

Fastness to Light.

The question of the fastness of dyes to light is in a hopeless state, apparently because nobody has gone at the problem either systematically or intelligently. Only light which is absorbed can produce chemical action and all light which is absorbed tends to produce chemical action.[97] Whether a given substance is changed appreciably by light depends upon the readiness with which the substance reacts or upon the presence of suitable depolarizers. What change takes place in any given dye when exposed to light will depend on the chemical characteristics of the dye and on the chemical conditions prevailing when the dye is exposed to light. Methylene blue, for instance, may fade as a result of reduction[98] or of oxidation. The bleaching of methylene blue is usually an oxidation because of the oxygen of the air; but, in presence of gelatin[99] or of stronger reducing agents, the bleaching of methylene blue by light is due to a reduction. One can therefore make methylene blue more sensitive to light either by soaking the dyed fabric in a dilute solution of hydrogen peroxide or in a dilute solution of sodium hydrosulfite. [Living yeast reduces methylene blue; dead cells are dyed blue. J. A.]

There are a number of problems in regard to the effect of the fiber or the mordant on the fastness to light, for which we can give no satisfactory answer at present. Diazotized primuline[100] is much more fugitive on cotton than in mass. Paranitraniline red[101] is faster on cotton than on wool, and indigo[102] is faster on wool than on cotton. The substantive dyes[103] are faster on wool than on cotton, and methylene blue is faster on cotton than on wool. One would naturally ascribe this last to the tannin mordant; but fuchsin[104] is faster on wool than on cotton. Alizarin black[105] is faster on chrome mordant than on alumina, tin or iron mordant. The eosines[106] are faster on alumina or lead mordant than in mass; but many lakes with inert bases[107] are fugitive to light. Albumin lakes are four times as fast as tannin lakes,[108] presumably because albumin oxidizes more readily than tannin.

It will undoubtedly be a very simple matter to clear up all these points once we have satisfactory data in regard to them; but we are not even certain that the facts are as stated in all these cases. Gros[109] says that a mixture of chrysaniline and fuchsin fades as rapidly as chrysaniline alone, which implies that chrysaniline accelerates the fading of fuchsin. Stobbe[110] states that a mixture of chrysaniline and fuchsin fades more rapidly than either dye alone. Actually Paddon[111] showed that fuchsin protects chrysaniline considerably.

Unpublished experiments by Ackerman in the Cornell Laboratory show that, with two colorless mordants which should have no appreciable reducing or oxidizing action, a dye will be faster to light on the mordant which adsorbs it most strongly and which therefore decreases its chemical potential the most.

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The Colloid Chemistry of Rubber Latex and Its Industrial Applications.

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Rubber latex is a milky white to cream colored fluid, which exudes slowly from incisions in the rubber tree. Though latex is the primary substance for the preparation of raw rubber, it has been a scientific curiosity for more than a century. As far back as 1826 Faraday carried out an analysis of a sample of latex, which he obtained from Thomas Hancock,[1] who intended to use rubber latex as a primary material for the manufacture of rubber articles. As the experiments in this line were not successful, this idea was abandoned.

Since the development of the plantation rubber industry and its scientific management rubber latex has come gradually into the focus of scientific investigation, in the country of its origin as well as in the United States and Europe.

Though the number of botanical species which produce latices containing rubber, usually in small quantities, is large, only a few have aroused the interest as sources of rubber; and among these *Hevea brasiliensis* is the only rubber tree which has proved to be a success from an agricultural standpoint. More than 98% of the raw rubber on the market is nowadays derived from *Hevea brasiliensis.* For this reason this article will only consider the colloid chemistry of Hevea latex i.e. latex derived from *Hevea brasiliensis,* Müller Aug.*

RUBBER LATEX AS A COLLOID SYSTEM.

Rubber latex may be described as a suspension or an emulsion of rubber globules in a watery serum containing various salts, proteins, l-methyl inositol and a multitude of other substances, mostly of insufficiently defined character and present in small amounts.

In the study of a stable colloid system such as latex, four points which are of primary importance must be considered.

a. The electrical charge of the particles;
b. The size and form of the particles;
c. The structure of the particles;
d. The nature and properties of the adsorption layer.

Electrical Charge of the Particles

V. Henri[2] in his important treatise on the coagulation of Hevea latex proved by cataphoresis experiments that under the influence of direct current the rubber particles in latex pass to the anode and therefore possess a negative

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* Where other latices are mentioned these will always be called by their special names.

charge. In 1909 Th. Cockerell[3] proposed to coagulate rubber electrically on to a platinized belt anodically connected, but this process has never been put into practice. However in 1913 P. S. Clignett[4] introduced a new method for the preparation of raw rubber, which was based on the use of direct current, the raw rubber being deposited on the anode. This method of preparation of raw rubber was abandoned after several years of estate practice for economic reasons.

Recently the electro-deposition process once more utilized direct current for the deposition of rubber mixes prepared from latex for the manufacturing of rubber articles.* In studying this process S. E. Sheppard[5] has carried out accurate cataphoretic measurements on rubber latex, which was preserved with ammonia. This investigator came to the following conclusions:

a. The migration velocity of the rubber particles is 2.7×10^{-4} cm. per second per volt per cm. width.

b. The negative charge of the rubber particles corresponds to a contact potential of 0.035 volt.

c. The formula of Laing and McBain for electrophoresis $n = \frac{c\,m\,f}{\mu}$ indicating that the quantity of rubber transported per unit of current will be proportional to the concentration of the rubber in the latex and inversely proportional to the total conductivity, was approximately verified.

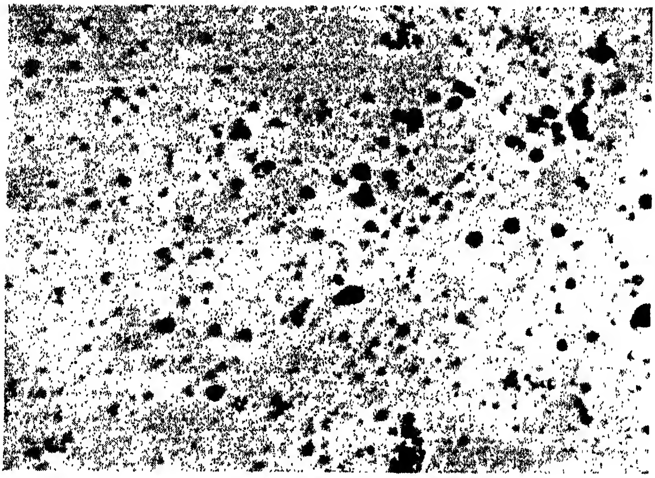

FIG. 1.—Diluted Hevea latex. × 1700.— Courtesy of the Director of the Research Association of the British Rubber Manufacturers, Croydon, England.

Size and Form of Rubber Particles

In 1912 T. Petch[6] had drawn attention to the fact that the rubber particles are not uniform in size and appearance. He described rubber particles which showed a kind of tail.

In 1919 W. Bobilioff[7] carried out microscopic investigations on a great many samples of latex derived from different parts of the rubber tree and

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* *Vide infra.*

from various Hevea trees. Bobilioff discriminated 4 classes of rubber particles according to their shape:

(*a*) Very small round globules, diameter approximately 0.5μ.
(*b*) Round globules up to 2μ.
(*c*) Pear-shaped globules 1.5 to 2μ.
(*d*) Pear-shaped globules showing a tail 1.5 to 3μ in length.

E. A. Hauser[8] came to the same conclusions as Bobilioff, pointing out that the lower limit of size of these particles could not be fixed, as a large number were ultramicroscopic. With the Szegvary-azimuth ultramicroscope he could prove that most of the particles were of non-spherical shape. In Figure 1 a photograph of a diluted Hevea latex is given in which the pear shape of rubber is clearly evident.

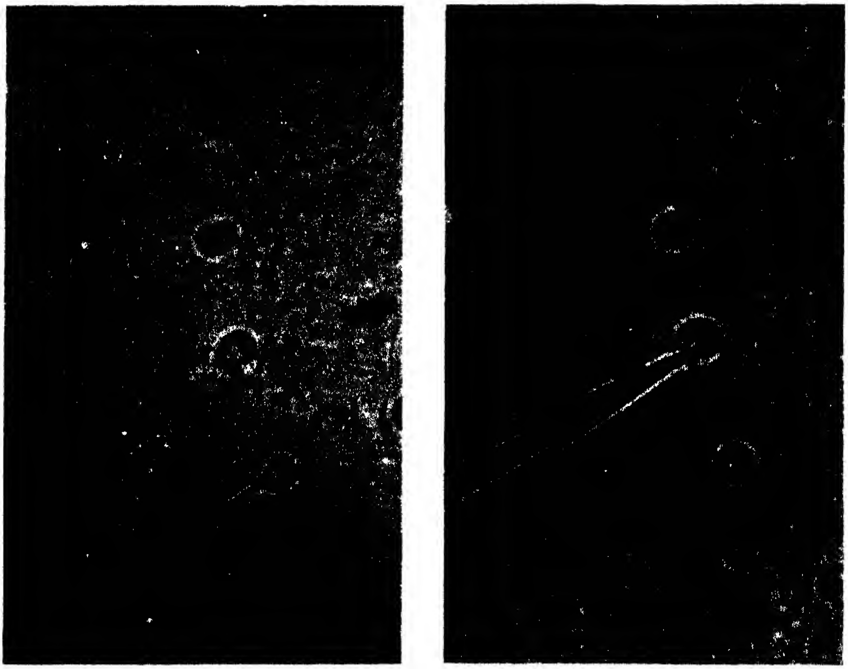

FIG. 2.—Pricking of rubber globules with fine needles of the micro-chirurgical apparatus of Peterfi. Courtesy of E. A. Hauser.

A. Particle just pricked by needle. B. Particle thoroughly pricked by needle.

The view of E. H. Wightman and Trivelli[9] that the rubber particles are in great centripetal motion and are continuously altering their shape, has never been confirmed and cannot be regarded as justified.

Until quite recently it was taken for granted that all visible particles in the latex consisted of rubber. Fatty acids in rubber should either be present in the adsorption layer or dissolved in the rubber. Recently A. Frey-Wijssling[10] after careful microchemical investigation, came to the conclusion that some particles show different physical properties, such as refraction index, cohesion, surface tension after drying, and specific gravity. With microchemical color reactions this investigator proved that these particles are composed of fatty acids. It is however not likely that all the fatty acids of raw rubber are present in the latex in the form of minute globules.

Structure of Rubber Globules

Modern research has led to two conflicting concepts regarding the structure of rubber globules in latex, i.e. those of E. A. Hauser and P. P. von Weimarn.

Many of the older theories of the structure of raw rubber in general contain the unproved suggestion that rubber is built up of two physically different phases.[11]

Special attention should be given the view of E. B. Spear,[12] who clearly pointed out that in case of a two-phase structure, it is probable that the rubber globules in latex consist "of a tough elastic outer layer, and an interior substance which has a greater plasticity or possibly a viscosity resembling a viscous liquid." *

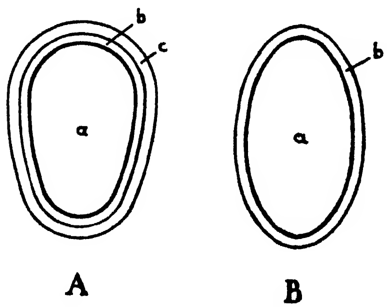

FIG. 3.—Structure of the rubber particle.
A. after E. A. Hauser (a) center of viscous rubber (b) skin of tough difficult soluble rubber (c) adsorption layer.
B. after P. P. von Weimarn (a) center of viscous rubber (b) plastic solid film of proteins and resins.

E. A. Hauser[13] was first to attack the structure of the latex globule experimentally. With the aid of the Zeiss micromanipulator he pricked the rubber globules with exceedingly fine needles prepared after Peterfi, see Figure 2 A and B, and from their behavior came to the conclusion that they consist of a center of viscous rubber, easily soluble in benzene, with a skin of tough more difficultly soluble rubber, the whole being surrounded by an adsorption layer.

P. P. von Weimarn,[14] on the other hand, has suggested that the viscous rubber is surrounded by a transitory layer which in its outer section (turned to serum) is composed chiefly of proteins with an admixture of resins † (in general of substances which are in the serum), while the inner section of this layer is in close contact with the rubber hydrocarbon.

According to von Weimarn this transitory layer is of the nature of a plastic solid film, such as is formed on the surface of oil drops in water in presence of an emulsifier. R. E. Wilson and E. D. Ries[15] ‡ showed that oil drops in water in the presence of an emulsifier surround themselves with a film which can become of considerable thickness and is of a plastic solid nature. They showed that the oil drops of such emulsions are able to assume non-spherical forms. Von Weimarn showed the same phenomenon in an emulsion of immersion oil in a concentrated aqueous solution of NaI, containing pear-like oil drops, oblong drops, and drops with a tail.

Figure 3 gives a diagrammatic sketch of Hauser's and von Weimarn's idea of the structure of the rubber particle. It should be stated that L. B. Sebrell,

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* Quoted from E. B. Spear.[12] It should be stated here that this theory of Spear, which was given prior to the experimental work of Hauser, has not been given sufficient credit in many articles on rubber latex. (*See also* papers by E. B. Spear and P. P. von Weimarn, in this volume. J. A.)

† It seems advisable to abolish the term "resins" in regard to rubber and rubber latex. Since the careful analysis of G. S. Whitby, P. Dekker and others it is now well established, that the acetone extract of raw rubber does not contain "resins" or "resin acids" and therefore these products cannot be present in latex. (*See also* von Weimarn's paper in this volume. J. A.)

‡ *See also* paper by R. E. Wilson in Vol. I of this series. J. A.

C. R. Park and S. M. Martin Jr.[16] in 1926 expressed the opinion that the rubber globules were originally surrounded by a plastic film after Wilson-Ries; they supposed however that this film would gradually polymerize to the permanent solid skin of Freundlich-Hauser.

Adsorption Layer

The composition of the adsorption layer has been the subject of much speculation and conflicting views. It is remarkable that the old controversy between C. O. Weber and Tromp de Haas, in the early years of this century on the film surrounding the particles of *Castilloa* latex, has been carried on in later years in regard to *Hevea* latex.

Various investigators, amongst others Clayton Beadle and H. P. Stevens,[17] and later W. C. N. Belgrave [18] supposed the adsorption layer to consist of proteins. G. Stafford Whitby and J. Dolid,[19] on the other hand, have expressed the opinion that the fatty acids which are present in the acetone extract of raw rubber, would play an important rôle as a protective layer to the globules in latex, and would add considerably to the stability of ammoniated latex by the formation of soaps, which would be able to act as stabilizers.

H. Freundlich and E. A. Hauser [8] and also Wo. Ostwald [20] believe that the adsorption layer consists of proteins and resins (read fatty acids vR.). In 1925, W. C. N. Belgrave [21] modified his original view and supposed that the rubber globules are surrounded by a lipin (lecithin)—protein complex in which the fatty acids of the lipin attached themselves to the caoutchouc while the protein was attracted by the water of the serum. The fatty acids present in the acetone extract of raw rubber are perhaps to be regarded as decomposition products of this complex.[21a]

Recently N. Van Beumée-Nieuwland [22] has extended this hypothesis. She drew attention to the fact, that in latex there are present esters of phytosterin (Whitby) and lecithin (Belgrave), and supposed that the rubber globules have a skin of these sterols and lecithins and are suspended in an emulsoid of protein, which may act as protective colloid.

The opinion of Belgrave and N. Van Beumée-Nieuwland is certainly tempting in view of recent research work of E. Gorter and F. Grendel,[23] who proved by spreading experiments that the chromocytes of blood of man and many animals are surrounded by a layer of lipoid which is 2 molecules thick. It seems quite reasonable that the rubber globules are also surrounded by a lipoid layer of perhaps similar thickness, but in this case it is more difficult to prove experimentally because the globules are very different in size, and their total surface is for that reason much more difficult to estimate than in the case of the blood corpuscles.

Considering the complicated structure of the adsorption layer, we must doubt Hauser's conception of the structure of the latex globules. There seems no sufficient proof that Hauser's tough layer is really a second *rubber* phase. In the opinion of the writer the rubber globules are to be regarded as particles of viscous rubber, which are surrounded by a sterol-lecithin-protein complex, which has a plastic-solid character.

A last point in relation to the structure of the particles is the question whether these particles are to be regarded as hydrophobe or hydrophile. Both de Vries [24] and Belgrave [18] have independently accepted the idea that rubber globules are to be regarded as lyophylic colloid particles having a limited degree of hydration. It is obvious that this solvation is not to be compared in extent with that of emulsoids such as, e.g. rubber in benzene, where it amounts to many thousand per cent. The hydration of the rubber globules will probably for the greater part, be limited to the outer adsorption layer.

OTHER COLLOID CHEMICAL PROPERTIES OF RUBBER LATEX.

The old controversy whether latex is to be regarded as an emulsion or suspension is certainly moot in the light of the researches discussed above.

Brownian Movement

It is well known that the rubber particles are in an active Brownian movement. V. Henri[2] studied the influence of salts and acids on this motion. He drew attention to the fact that on diluting latex with a 20 per cent solution of sodium chloride, the movement of the particles stops before coagulation takes place. Brownian movement can also be diminished by adding glycerin and gelatin to latex, probably owing to the increase of viscosity. Bobilioff[7] found that the addition of various dyestuffs to latex, also caused the Brownian movement of the particles to stop.

The viscosity of rubber latex was studied thoroughly by O. de Vries[25]. In high concentration the viscosity increases rapidly with the concentration. Addition of ammonia decreases the viscosity considerably. A. Van Rossem[26] pointed out that the viscosity of latex is very low in comparison with rubber solutions, which is an important point in the application of latex for impregnation purposes. Recently probably unaware of de Vries's work, C. M. Blow[27] has published viscosity figures of a number of samples of latex at various concentrations, diluted with their own serum.

Surface Tension

Surface tension has been measured by W. C. N. Belgrave[28] by the drop number method. Recently E. A. Hauser and P. Scholtz[29] have measured the surface tension by the wire ring method. They concluded that latex contains a surface active substance. Addition of ammonia diminishes the surface tension.

Hydrogen-ion Concentration of Latex

There has been considerable controversy regarding the reaction of latex immediately after it leaves the tree, because the acidity was formerly determined by titration and was given in cc. normality or in grams of acetic acid.[30] This is obviously of little value, since the serum of latex contains various salts and is a buffer mixture; so that its acidity must be expressed in pH values. Later various investigators determined the pH value of fresh latex, as per Table 1.

TABLE 1. *pH Values of Fresh Latex.*

Investigator	Fresh Latex
W. C. N. Belgrave	6.4 -5.8
W. Bobilioff	7.0 -6.2
E. A. Hauser and P. Scholtz	7.2 -7.0
N. H. van Harpen	7.07-6.73

W. C. N. Belgrave[18] determined the pH of latex with the indicator method by spotting, checking his results with the electropotentiometric method. Results of both methods agreed.

W. Bobilioff[31] determined the pH value in a dialysate of latex preserved with glycerin, having previously established that this method was trustworthy.

E. A. Hauser and P. Scholtz[32] have used the Wulff's plate colorimeter, which is a very simple device for determining the pH value of latex. N. H. Van Harpen[33] determined the pH values of fresh latex and a large number of other latices (flocculated, etc.) with the quinhydrone electrode. In his opinion the results of Belgrave are too low.

All investigators agree that the pH value of fresh latex very soon decreases, owing to the formation of acids by bacteria, spontaneous coagulation resulting. In the next paragraph the rôle of pH value in the coagulation process will be considered *in extenso.*

THE COAGULATION PROCESS.

In plantation practice, latex is coagulated by the addition of acid. A few years ago acetic acid was mainly used, but nowadays formic acid has generally superseded acetic acid because it is cheaper in practice.

In the tropics, latex left to itself coagulates in less than 24 hours. This process is known as *spontaneous coagulation.* G. Vernet [34] and independently B. J. Eaton [35] have given as their opinion based on many experiments, that spontaneous coagulation is in reality acid coagulation, the acid being developed by intensive growth of bacteria in latex. Recently A. S. Corbet [36] found that one organism, called by him *Bacillus pandora* predominates in latex and is able to decompose latex substances under the simultaneous production of acid.

V. Henri [2] considered the coagulation process from a purely electrochemical standpoint: by the addition of acids or salts, positively charged ions are introduced into the latex, the rubber particles are discharged and are flocked out, converting the liquid into a gel.

G. S. Whitby [37] on the other hand developed an enzymatic theory of coagulation. In his opinion a coagulating enzyme is the essential cause of coagulation, the acid added or formed being only an activator for the enzyme. This investigator was the first to draw attention to the remarkable fact, that with increasing amounts of acid there is a range of acidity where ordinary coagulation is prohibited. With increasing amounts of acid we pass successively from the first liquid zone into the first coagulation zone, then to the second liquid zone and the second coagulation zone.

De Vries [38] started his studies on the coagulation phenomena with the system latex-water-acid (HCl, HNO_3, H_2SO_4, acetic acid), and from the standpoint of the phase rule, carefully determined the boundaries between the various zones in acid normalities. He firstly pointed out that these phenomena, which were used by Whitby as an argument for his enzymatic theory were in full accordance with the behavior of irregular series in colloid chemistry.* Therefore he suggested that latex shows irregular coagulation series. By the addition of large amounts of acid the rubber particles are recharged and in the second liquid zone should have a positive charge. Belgrave,[18] independently of de Vries, has proved experimentally by cataphoresis tests that this conception is correct. Belgrave was the first to establish in pH values the boundaries between the various liquid zones and zones of coagulation.

Recently Van Harpen [33] has carefully determined these boundaries with the aid of the quinhydrone-electrode. The results of both investigators are given in Table 2 below.

TABLE 2. *Boundaries of Various Zones of Coagulation of Fresh Latex in pH.*

	Belgrave	van Harpen
Fresh latex	7.0–6.2	7.07–6.83
Boundary first coagulation zone	5.2–4.8	5.0
Boundary second liquid zone	2.5–2.2	3.49
Boundary second coagulation zone	1.50	0.80

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* On these series see paper by A. Lottermoser in Vol. I of this series. J. A.

De Vries as well as Belgrave has carried out very important work in regard to the elucidation of the coagulation process. Independently of each other de Vries [38] and Belgrave [18] both rejected the arguments of Whitby's enzyme theory on the following points:

1. Bactericides such as toluene, thymol and choloroform, which do not prevent spontaneous coagulation, are inactive in latex and do not, as Whitby suggested, preclude bacterial action.
2. Enzyme poisons such as hydrocyanic acid, potassium cyanide, and hydrogen sulfide are not able to prevent spontaneous coagulation.
3. The irregularities in acid coagulation occur also after the enzyme is destroyed by boiling the latex, and for that reason cannot be due to enzymatic action.

In 1924 de Vries [39] advanced his general theory of coagulation, which he tried to prove experimentally in a great number of subsequent publications, in collaboration with N. Beumée-Nieuwland. Following the older work on the coagulation of latex by Clayton Beadle and H. P. Stevens,[17] de Vries differentiates the following various stages in coagulation phenomena:

1. Creaming

Owing to the difference in specific gravity, the rubber particles gradually form a surface layer. They are still in Brownian movement and have not united into flocks. This phenomenon occurs after long standing, e.g. in latex which has been preserved with ammonia. The creaming is reversible; upon shaking the layer disappears and the rubber globules disperse again homogeneously.

2. Flocculation

A number of rubber globules form small flocks, without making a coherent coagulum. Microscopically, these flocks are easily visible; they show no Brownian movement. Flocculation is irreversible.

3. Coagulation

The latex changes into a coherent clot or coagulum. This phenomenon is the ordinary one in plantation practice and is irreversible.

4. Coalescence

Under certain conditions the flocks are able to unite to a coherent coagulum; following C. O. Weber this phenomenon is called *coalescence.*

According to the theory of de Vries, ordinary latex coagulation must be considered as a combination of two processes:

(*a*) Flocculation under the influence of acids, salts, etc. This is caused by the addition of positive ions, which discharge the negative rubber particles to such an extent that upon meeting, they form small flocks.

(*b*) Coalescence of the flocks to coherent coagulum.

De Vries believes that in ordinary latex an enzyme called *coalase* is present, which is able to bring about the coalescence. *The coalase alone is not able to bring about flocculation, but the enzyme may play a rôle in bringing about the coalescence.* The action of the enzyme is rather slow and by no means indispensable. Several agencies, e.g. larger amounts of acid, bring about coalescence much more rapidly, even instantaneously.

In the ordinary coagulation process on the rubber estates, the addition of a small amount of formic or acetic acid causes the flocculation of the rubber globules; but the amount of acid is not large enough to cause direct coalescence. This coalescence gradually follows by the action of the enzyme. Large amounts of acids, however, not only produce flocculation, but also coalescence.

In natural or spontaneous coagulation bacteria produce so much acid that flocculation occurs, after which the coalase brings about the coalescence. When the coalase has been destroyed by heating the latex, infection with bacteria brings about flocculation but no coalescence.

In a large series of publications O. de Vries and N. Beumée-Nieuwland[40] had given the results of experimental work, which have led de Vries to this theory.

The properties of the coalase have been thoroughly studied with the aid of so-called B-liquid, named after Barrowcliff[41] who was the first to experiment with latex which had been boiled with the purpose of destroying the enzymes eventually present. The B-liquid is prepared by adding 100 cc. latex to 900 cc. boiling water, boiling the mixture for 3 minutes and, after cooling, adding to 100 cc. of the mixture 2 cc. of 2½% acetic acid. In the boiled liquid the coalase is destroyed, and the acid causes flocculation but no coalescence. This flocculated B-liquid is an excellent medium to study coalescence. B-liquid gives coalescence on addition of fresh latex in very small quantities; the addition of latex in the proportion of 1 (rubber) : 20,000 (rubber) causes coalescence in 24 hours, in some cases 1 : 256,000 in 48 hours.

The coalescence-action of fresh latex is destroyed by heating the latex at 70° to 75° C., also by addition of a quantity of acid sufficient to reach the second liquid zone, and by the addition of relatively small amounts of NH_4OH and NaOH. Ammoniated latex has not lost the property of coalescence, but the power to produce coalescence in B-liquid. This is a proof that the coalase has been destroyed by the addition of ammonia.

The clear serum resulting from acid coagulation has no power to produce coalescence in B-liquid. From this fact it is concluded that the coalase is precipitated in the coagulum. It was not possible to extract the coalase from the coagulum with acids, but with a diluted Na_2CO_3 solution coalase was extracted from the coagulum; for this extract causes coalescence in B-liquid.

Apart from coalase, coalescence of B-liquid occurs on the addition of larger quantities of acids. There are also certain chemicals which were found to possess a decided coalescing power, such as thymol, and β-naphthol, also alcohol and alum. Table 3 gives an idea of the coalescing power of these chemicals in comparison with coalase. In this table the quantity of the chemicals which causes coalescence of B-liquid in 6 hours is taken as unity. It is shown clearly that the coalase has a much stronger coalescing power than such chemicals as thymol and β-naphthol.

TABLE 3. *Coalescing Power of Various Chemicals in Comparison with Coalase (after De Vries).*

Time of Coalescence	Unit Quantity of Chemicals				
	Alcohol 12.5 cc.	Alum 110 mg.	Thymol 14 mg.	β-Naphthol 15 mg.	Coalase (1 Drop of Fresh Latex 1 :9) 0.1 mg.
In 1–2 hours	1⅕	1 1/10	2	1½	4
In 6 hours	1	1	1	1	1
In 10–20 hours	9/10	9/10	⅞	—	½–⅛
In 2–3 days	¾	⅔	¾	⅔	1/20
No coalescence in three days	11/20	½	½	½	1/30–1/40

Recently O. de Vries and N. Beumée-Nieuwland have also studied the influence of salts of heavy metals such as $NiSO_4$, $CuSO_4$, $MnSO_4$ and $HgCl_2$ on the coagulation and coalescence. These salts all have a coagulating influence on fresh latex; they promote the acetic acid coagulation. $NiSO_4$ does not show any coalescing power on B-liquid, $MnSO_4$ and $CuSO_4$ a small one, and $HgCl_2$ a decided coalescing power on B-liquid. The observed phenomena are of a very complicated nature.

The theory of O. de Vries on the presence of the enzyme coalase in fresh latex, causing the coalescence of the rubber particle with ordinary acid coagulation has various opponents.

J. Groenewegen [42] was of opinion that the coalescence was caused by the proteins, constituting the adsorption layer of the rubber globules. By boiling latex these proteins are precipitated, changing their nature from hydrophylic into hydrophobic. Because of this change, addition of acid to boiled latex only brings about flocculation.

By inoculating with fresh latex, a new layer of hydrophylic protein should be formed on each globule, bringing about coalescence.

P. Scholtz [43] also is of opinion that latex must be regarded as a hydrophobic sol, which is protected by an adsorption layer of protein.

Belgrave [21] agrees with de Vries as far as the first stage of coagulation, i.e. flocculation, being caused under the influence of the addition of H-ions, but rejects de Vries's conception of the second phase, i.e. the coalescence caused by coalase.

In his opinion fresh latex contains a complex, which is at the same time an emulsifier and is also responsible for the coalescing power of fresh latex. This complex is thermolabile, and is destroyed by boiling, also by the addition of large amounts of acid (second liquid area) and small amounts of alkali (ammoniated latex).

Belgrave suggested that this substance is a lecithin-protein complex or a lecithin-glucoprotein complex. In this respect he proved experimentally that oleic acid and oleates possess also a coalescing power on the flocculated B-liquid. N. H. Van Harpen [33] carefully determined the pH where flocculation and coalescence of various latices occurred. His results, given in Table 4, show that under varying conditions, coagulation occurs at pH of 4.77 with the exception of B-liquid of fresh latex, which gives simply flocculation at pH = 4.77, coalescence only occurring in the second coagulation zone.

TABLE 4. *Flocculation and Coalescence of Various Latices, Diluted 1:9.*

Latex	Hydrogen-ion Concentration				
	7.0–5.05	5.05–4.77	4.77–3.51	3.51–0.80	0.80–0
Fresh latex	—	flocculation	coagulation	—	coagulation
Ammoniated latex	—	flocculation	coagulation	—	coagulation
B-liquid of fresh latex	—	flocculation	flocculation	—	coagulation
B-liquid of ammoniated latex	—	flocculation	coagulation	—	coagulation

From these results Van Harpen concludes: In Hevea latex a substance is present which at pH = 4.77 causes coalescence of a flocculate. This substance is deprived of its effect, when the latex is boiled. After the addition of ammonia, heating does not destroy this coalescing action.

He further proved that ammonium resinate shows a coalescing action in flocculated latex at pH = 4.78. This is exactly the pH at which ammonium resinate is flocculated. From these results he concludes that the substance in latex, which causes coalescence is ammonium resinate. Though there is no reason to object to the fact that resinates show a coalescing action, it seems very unlikely that a resinate should be the coalescing substance in latex. As has been pointed out, resins and resinates are not present in the acetone extract of raw rubber, and it seems therefore unacceptable that they are the substance in latex causing coalescence.

Recently N. Beumée-Nieuwland[22] has proved that cholesterin in minor quantities possesses coalescing power in B-liquid. Summarizing, it may be concluded that the coagulation process consists of two subsequent phenomena: *a.* flocculation, which starts at $pH = 5.05$ (de Vries, Van Harpen), caused by discharging the rubber particles; *b.* coalescence, caused either by a coalescing enzyme coalase (de Vries), by a chemical compound such as lecithin-protein complex (Belgrave), or a phytosterin-lecithin complex (Beumée-Nieuwland).

It seems useful to point out that the difference between these conceptions is less than it seems at first sight. Enzymes, even when called coalescing enzymes, will never be able themselves to cause coalescence, but indirectly they may cause coalescence by initiating an enzymatic action leading to formation of a substance of adhesive character, or the elimination of a substance which prevents the adhesive action.

Seen in this light the difference in de Vries's and Belgrave's views simply involves the minor question whether the adhesive substance was already present or is formed under the influence of the enzyme.

Up to the present time only the acid coagulation process of latex has been considered. Among the other processes of preparation of raw rubber the method used in the preparation of Brazilian rubber deserves some attention. In this process a paddle is dipped in latex and quickly turned in the smoke of a fire. Apparently this process seems one of evaporation, but in reality it is also a coagulation process, as is apparent from the analytical figures which agree with those obtained from coagulated plantation rubber. It is not quite clear, exactly what causes this coagulation, but probably some of the smoke constituents together with heat are responsible. A large part of the serum is pressed out by syneresis, dripping from the ball during its manufacture.

The latex spraying process which was introduced by E. Hopkinson[44] should be considered as an evaporation process, leading to a so called "Whole Rubber," i.e. rubber containing the whole of the serum substances. This process is not so interesting from a colloid chemical standpoint.

PROPERTIES OF THE COAGULUM.

In plantation practice two forms of raw rubber are prepared from the coagulum, i.e., First Latex Crêpe and First Latex Sheet.

In preparing crêpe rubber the coagulum is crêped in a set of washing machines with liberal addition of water. When preparing sheet the coagulation is carried out in pans or tanks in such a way that slabs of coagulum are obtained, which are rolled either by hand or by machine and subsequently are printed on a special printing machine. Crêpe rubber is usually dried in dry-rooms, while sheet rubber is smoked in smoke-houses.[45]

It is remarkable that investigations regarding the colloid chemical properties of the coagulum are entirely lacking, and even descriptions of these properties are lacking in most handbooks on the plantation rubber industry.

De Vries[45] has described some of these properties, which deserve careful attention:

1. The coagulum of a diluted latex shows a strong syneresis. It contracts with exudation of a part of the serum. The more diluted the latex before coagulation, the stronger this syneresis.
2. Continuous pressure does not press out much of the serum. If however

the coagulum is rolled by a handroll it readily exudes large amounts of serum, alternating pressure and tension being necessary. Washing of the coagulum is mainly a kneading, with alternating pressure, under which treatment the serum is quickly expelled.

3. The speed of drying of the coagulum, and also of the wet crêpe and sheet, are highly dependent on the treatment of the coagulum. The young porous coagulum and the crêpe from that coagulum are quick-drying, but keeping the coagulum in the air, or under water, gradually leads to a slow-drying rubber, even after crêping. Though as far back as 1920 de Vries drew attention to this phenomenon, experimental investigations in regard to the colloid chemical causes are still lacking.

In 1925 a new process for the preparation of raw rubber from coagulum was patented by A. F. Van der Mark and H. Kremer.[46] This process has not been carried out on a large scale, but it deserves full attention because of the colloidal properties of the coagulum.

According to this invention the wet coagulum in slab form is folded as a sack leaving open a small hole through which the coagulum is gradually blown up with the aid of compressed air into a balloon, which is left to dry. During the formation of this balloon the wet coagulum is considerably extended. It is remarkable that the coagulum does not collapse under this treatment. After drying, the balloon is cut open and the raw rubber is obtained as thin films, so-called Emka films or Emka rubber.

It is a well-known fact that raw rubber which has been stretched in the cold, shrinks on heating and returns practically to its original shape, with small residual deformation. These Emka films, prepared by extensive elongation of the wet coagulum, show practically no shrinking effect when heated at 70° C. It seemed of considerable importance to elucidate this remarkable behavior and to subject the properties of wet rubber films to a closer investigation.

From the results which have been obtained by Raden Soepardi Prawirodipoero and the present writer, to be published in detail elsewhere, the following summary may be communicated here:

The wet rubber films used for these experiments were prepared by pouring out latex on a freshly prepared 10 to 20 per cent gelatin jelly and waiting till the wet rubber film could be taken off, without damage, a method which has been patented for industrial purposes by J. Traube [47]. Wet rubber films were prepared from ammoniated latex of about 30 per cent concentration and also from so-called "Uterex," i.e., ammoniated latex concentrated by a centrifugal process after W. L. Utermark, having a concentration of about 60 per cent.

Careful investigation showed that the formation of these wet rubber films in each case is a really different process. The formation of the wet rubber film from ammoniated latex is caused by a gradual decrease in water content, the water partly evaporating and partly diffusing into the gelatin, leaving a wet rubber film with a moisture content of about 20 per cent. On the other hand it was shown that when using concentrated latex the formation of the wet rubber film is caused by a coagulation process owing to a diffusion of acid substances from the gelatin into the latex. These substances gradually decrease the pH of the latex to such an extent that flocculation and subsequently coalescence occurs. These wet rubber films from concentrated latex possess a moisture content of about 40 per cent and are to be considered as a typical coagulum in film form. With these coagulated rubber films various systematic investigations have been carried out.

Deformation Tests

Pieces of these coagulated rubber films were elongated 100, 200 and 300 per cent and in this elongated state fixed with metal clamps. A number of such elongated films were kept in an apparatus with a fixed 90 per cent humidity to keep the moisture content of the films constant, a fact verified by test. They were kept in the apparatus for one hour.

The clamps were then loosened and the films left to themselves. The sub-permanent deformation was measured directly. Subsequently the films were left in a drying oven at a temperature of 70° C. for 30 minutes, after which treatment the films were dry and the permanent deformation was measured again. The shrinking effect (S. E.) is the percentage of sub-permanent deformation which disappeared on heating the wet films.

$$\text{S. E.} = \frac{a-b}{a} \times 100\%.$$

The figures obtained with films elongated up to 100, 200 and 300 per cent are collected in Table 5.

TABLE 5. *Shrinking Effect of Coagulated Rubber Films after Elongation.*

	Elongation Per Cent		
	100	200	300
Original moisture content	42.8	42.8	42.8
After 1 hour moisture content	40.2	41.5	40.9
Sub-permanent deformation (a)	70	125	170
After heating at 70° C. (b)	15	35	50
Shrinking effect $\frac{a-b}{a} \times 100\%$	78.6	72.0	70.7

From these figures it is obvious that the wet rubber films show a strong shrinking effect. It was also found that when keeping these films at ordinary temperature they show a strong elastic after-effect. These coagulated rubber films in the wet state therefore show properties similar to the raw rubber, strong elastic after-effect, and high shrinking effect.

Another set of elongated films, were now kept under elongation in the air for 48 hours, after which time the moisture had evaporated, leaving a dry film. The figures obtained with these films for sub-permanent deformation directly after releasing and also after heating in the drying oven at 70° C. are collected in Table 6.

TABLE 6. *Shrinking Effect of Coagulated Rubber Films after Drying under Elongation.* (Original Moisture Content of Films 42.1%.)

	Elongation of Films Per Cent		
	100	200	300
Sub-permanent deformation (a)	90	180	230
After heating at 70° C. (b)	77.5	137	160
Shrinking effect (S.E.) $\frac{a-b}{a} \times 100\%$	13.9	23.6	30.4

From these figures it is obvious, that when drying the films under stretching the shrinking effect is considerably smaller, the elongation being permanent for the greater part. These experiments therefore give an explanation of the possibility of the "Emka" process.

During the "Emka" process the wet rubber films are also elongated considerably, and kept in this state until dry, after which they do not show shrinking effect. It will certainly be of much importance to extend these experiments and get an insight into the causes of this behavior; undoubtedly this stands in close relation with the structure of the coagulum and the changes during drying.

It should be mentioned that similar experiments have been carried out with the wet films obtained from ordinary ammoniated latex, i.e. non-coagulated films. After drying under tension these films show similar results, i.e. a very small shrinking effect. However when kept under elongation at constant moisture content they also show a very small shrinking effect, in this respect showing a different behavior from the coagulated films. Obviously these wet rubber films when being elongated undergo a plastic deformation in contra-distinction to the coagulated films, which, when elongated, give a more elastic deformation.

Water-absorption of Coagulated Films

One of the remarkable phenomena of a coagulum, which can easily be demonstrated, is its property to become dry at its surface when being elongated. A drop of water put on the surface, vanishes quickly into the interior upon elongating the coagulum. Obviously an increase in volume occurs which causes the liquid to be sucked up; and if no liquid is available, air is sucked in.

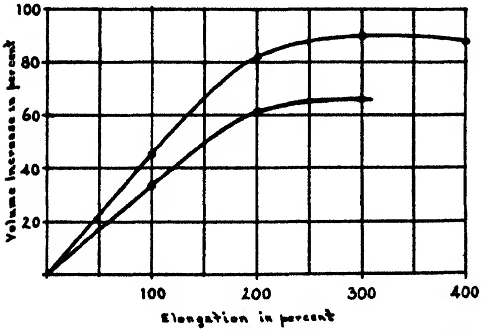

Fig. 4.—The volume increase of a coagulated rubber film when elongated under water.

This phenomenon has been studied more systematically with the wet coagulated films obtained from concentrated latex on gelatin. Pieces of these films were cut exactly 2 cm. wide, the thickness measured and the film stretched under water and fixed at elongations 50, 100, 200, 300 and 400 per cent.

In this state the dimensions were carefully remeasured and from these data the volume increase were calculated. As the variation of the figures was large, the mean value of at least six experiments was taken. These are gathered in Table 7 and graphically reproduced in Figure 4.

Table 7. *Volume Increase of Wet Rubber Films Stretched under Water.*

Elongation Per Cent	Moisture Content Per Cent	
	42.0	32.6
0	—	—
50	28.6	17.0
100	45.7	33.4
200	82.4	61.0
300	90.9	66.8
400	88.1	

These figures bring out the remarkable fact that a coagulated rubber film elongated under water shows an increase of volume of about 90 per cent, in other words its volume is nearly doubled. When the original moisture content is reduced by drying as uniformly as possible, the volume increase is also reduced.

Syneresis

As has been pointed out already, under alternating pressure or tension the coagulum shows a strong syneresis, a large part of the serum being exuded. A few experiments were carried out to get a quantitative insight into this phenomenon.

To verify the opinion that the significance of the washing process of the coagulum is for the greater part a kneading, consisting in alternating the pressure, a washing experiment was made. From concentrated latex a coagulum was made with Na_2SiF_6, this coagulum was cut in two parts which were treated on a washing machine, one without water, the other part with the liberal addition of water. The figures for moisture content after going through the washing machine are given in Table 8.

TABLE 8. *Per Cent Decrease of Moisture Content of Coagulum on Washing Rolls.*

	Without Addition of Water	With Addition of Water
Original moisture content	70.6	70.6
After 5 times through rolls	23.1	23.1
After 10 times through rolls	23.2	22.6
After 15 times through rolls	23.6	21.9
After 20 times through rolls	24.3	21.8
After 30 times through rolls	23.3	20.2

These figures fully confirm the view that under the kneading of the washing rolls, a large part of the serum is very quickly exuded. Additional experiments showed that even after passing through the washing rolls a second time, the exudation is practically finished. At the same time these figures show that the addition of water on the washing rolls, does not have any influence on the amount of moisture left in the washed crêpe. Washing the coagulum leads to great diminution of its moisture content, however paradoxical this conclusion may seem at first sight. Experiments were also carried out to establish the amount of moisture, which is exuded under alternating tension.

Coagulated films from latex concentrated on gelatin, were stretched 100 per cent and released after 15 seconds. After a few seconds syneresis starts, small drops appear at the surface, which rapidly increase in size. This moisture is quickly removed with a piece of filter paper and the film again stretched 15 seconds at 100 per cent. The drops which now appear, after releasing the tension are much smaller and the third time practically no syneresis takes place. These tests were also carried out with elongations of 200 and 300 per cent and from moisture determinations the percentage of the original moisture present which had disappeared by exudation, could be easily calculated. These figures are given in Table 9.

From these figures it is obvious that the moisture exuded increases with the elongation.

There are still other properties of the wet coagulum, which deserve attention, but have not been studied in detail. It would certainly be of considerable importance to study the vapor pressure curve of the wet rubber films when drying. It seems probable that this curve would have a shape like that of other elastic jellies such as gelatin, etc.

TABLE 9. *Percentage of Original Moisture Exuded on Repeated Elongation and Release.*

	Moisture	Original Moisture Exuded
Original moisture	45.2	
After repeated stretching to 100%	33.9	24.8
After repeated stretching to 200%	33.1	26.5
After repeated stretching to 300%	29.7	34.2
After repeated stretching to 400%	28.4	37.1

The rate of drying is another property which demands careful study, owing to its theoretical and practical importance. From a few experiments carried out with the crêpe from various coagula, it is very likely that the rate of drying depends for the greater part on the amount of non-rubber substances. The nitrogen content seems to be the principal factor.*

In this respect the point at which the opaqueness of the drying film changes into transparency deserves attention. It is likely that this point will also be dependent on the properties of the adsorption layer round the rubber globules originally present in the latex.

THE RELATION BETWEEN THE LATEX PARTICLE AND THE PROPERTIES OF RAW RUBBER.

It has been Hauser's special credit to draw attention to the often forgotten truth, that for the elucidation of the structure and properties of raw rubber we must take into account the structure of the latex globule. Soon after the publication of his microscopical studies of the latex particle, there seemed to be a possibility that the properties of raw rubber as such and during the various processes of mastication, calendering, etc., could be explained entirely on the basis of the structure of the latex globule.[48] Nowadays it seems certain that, apart from the structure of the latex globule as revealed by the microscope, however important this is for the understanding of the properties of raw rubber, there are other fundamental considerations which must be taken into account to explain the unique properties of raw rubber.

There have been published in recent years contradictory opinions in regard to the question, as to whether during coagulation and subsequent drying of the coagulum, the original latex globules retain their identity or whether they are fused together into one homogeneous mass of rubber.

As far back as 1909, P. Schidrowitz [49] pointed out that raw rubber must be considered as a close packing of a large number of latex globules, and that it was possible, with the aid of appropriate methods to reveal the original latex particles in raw rubber.

On the other hand C. C. Loomis and H. E. Stumpf [50] were of the opinion, based on microscopical observation, that at the moment of coagulation the latex particles burst and unite fully. It seems very doubtful whether this observation is true, no other investigators having been able to verify this statement.

H. Freundlich and E. A. Hauser [8] have given a description of microchemical observation which lead them to the conclusion that the particles closely pack together on coagulation, in such a way that their single forms persist in raw rubber. These observations have been confirmed and extended by L. B. Sebrell, C. R. Park and S. M. Martin, Jr.[16] They were able to show the

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* *Vide infra.*

original shape of the latex particle in dried films of latex which were treated for a considerable period with water, and gradually became opaque. Figure 5 gives a reproduction of one of their photos clearly showing the original latex particles in raw rubber films.

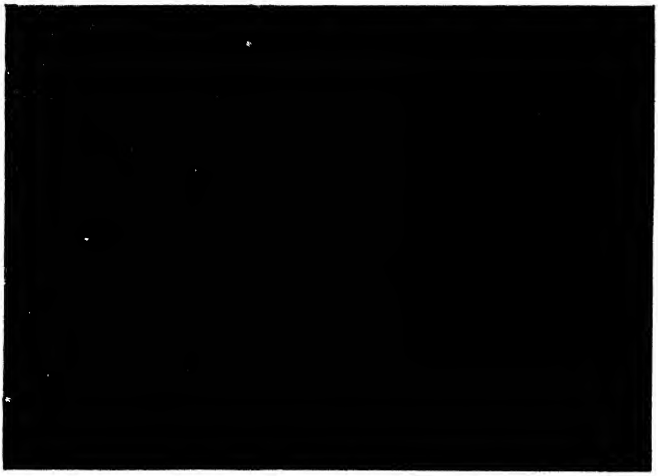

FIG. 5.—The structure of a thin rubber film when treated with water. Courtesy of L. B. Sebrell, C. R. Park and S. M. Martin, Jr.

On the basis of these foregoing investigations it seems justifiable to conclude that raw rubber obtained by evaporation or by coagulation of latex is a closely packed mass of original latex particles. As the original latex particle is surrounded by an adsorption layer, it is obvious that these adsorption layers are the membranes which prevent the rubber hydrocarbon from fusing together into one homogeneous mass. We will now consider to what extent the properties of rubber can be explained on the basis of this structural conception.

Plasticity

O. de Vries and N. Beumée-Nieuwland[51] have carried out extensive investigations on the plasticity of raw rubber in relation to its structure. These investigators differentiate four structure elements in raw rubber:

a. The serum left in the pores of the spongy mass of coagulum, forming irregular deposits of serum substances after the water has evaporated.

b. Substances precipitated from the serum during coagulation, separating in flocks which either remain free in the serum, and finally dry together with the elements of (*a*) or stick to the rubber particles.

c. The adsorption layer of the rubber particle.

d. The rubber particle itself.

De Vries and Beumée-Nieuwland have tried to elucidate the rôle, which *each* of these structural elements plays in the plasticity figure of raw rubber, but they were not able to discriminate clearly between the influence of these elements separately. From their very extensive material one conclusion seems justified, i.e., that by the elimination of the serum substances as far as possible, a rubber is obtained with a greater plasticity (D_{30}, i.e., thickness after 30 min. pressure smaller). When the latex, e.g., was centrifuged and the cream washed repeatedly with water, the rubber obtained from this washed cream showed a larger plasticity, as is obvious from Table 10.

TABLE 10. *Plasticity Figures.*

	Ash	Nitrogen	Plasticity (D_{30} in mm.)
	Per Cent		
Control	0.18	0.38	1.20
Primary cream	0.11	0.13	1.29
Secondary cream	0.10	0.13	0.83
Tertiary cream	0.10	0.12	0.85

Swelling and Solution

When raw rubber is treated with the ordinary rubber solvents such as benzene, petroleum ether, ether, etc. it swells considerably and after some time passes partly into colloidal solution; part remains as a highly swollen mass, which is generally characterized as the insoluble part. W. A. Caspari[52] concluded from this behavior that raw rubber consists of two forms of rubber, one phase of *soluble* rubber and the other phase of "pectous" rubber. In recent years similar experiments have again been carried out by H. Feuchter,[53] who also considers the raw rubber to consist of two phases, i.e. the "Diffusionskautschuk" (DK) and the "Gelrubber."

If, however, raw rubber is considered as a mass of packed rubber globules, each separated from the other by an adsorption layer of serum substances, the experimental proof of the two phase structure of raw rubber on its behavior with solvents seems rather weak, another simple explanation given as far back as 1907 by D. Spence[54] and recently again by H. P. Stevens[55] being more reasonable.

Spence tried to prove by microchemical reactions that the protein is distributed in the raw rubber as a kind of a framework, and drew attention to fact, that the films of protein would hinder the hydrocarbon from going into free solution. The solvent would gradually penetrate through the films, dissolve the hydrocarbon which can only partly go into solution, being partly retained by the firms, until these become penetrated and broken down.

H. P. Stevens[55] clearly pointed out that on swelling a piece of "First Latex Sheet" in benzene, the protein adsorption layer bursts, the rubber hydrocarbon partly enters into solution and gradually escapes through the holes in the adsorption layer, while a part is left between the adsorption layers, which are not entirely destroyed. In this way the separation of the raw rubber by solvent action into a soluble and an insoluble part is far more reasonably explained.* It is also understandable that shaking helps the solution of the rubber considerably as is well known from practical experience. Also G. Stafford Whitby[56] and his co-workers have pointed out in various publications, that the concept that raw rubber is a two-phase system, from which the phases can be separated sharply by solvent action, is open to doubt.

If the adsorption layer plays a rôle in the solution of raw rubber, it is obvious that raw rubbers prepared in different ways must show a behavior which is in agreement with the existence of this film of non-rubber substances. The behavior of a few types of raw rubber, which have been compiled below indicates, that this view is correct.

Hard Fine Para. Coagulation rubber. Adsorption layer of proteins is heated and smoked, which may give a stiff and coherent adsorption layer. Rubber swells strongly in benzene; pieces keep their shape for a long time; rubber solution slowly increases in concentration.

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* It is remarkable that W. A. Caspari also suggested this same explanation in the publication in which he distinguished between the "soluble" and "pectous" rubber.

First Latex Sheet. Coagulation with subsequent pressing and printing; little mechanical treatment. Behaves as Hard Fine Para, but goes into solution more quickly.

First Latex Crêpe. Coagulated and the wet coagulum subsequently washed (milling), during which probably part of the adsorption layers is destroyed. Goes into solution more easily; pieces do not maintain their shape, but soon leave a deformed jellied mass.

In this respect it should be pointed out that it seems likely that part of the rubber hydrocarbon is adsorbed at the adsorption layer, which also accounts for the fact that as a rule not all the rubber hydrocarbon goes into solution, not even after shaking.

Mastication

It is a well known fact that after milling raw rubber quickly goes into solution. This is in accordance with the foregoing. During mastication of raw rubber the adsorption layer is obviously crushed and probably changes its appearance from a tough skin into a dry powder which is mixed homogeneously through the rubber. It is therefore quite comprehensible that the masticated rubber quickly goes into a solution from which, after some time, there separates a white powder consisting chiefly of proteins. This is the adsorption layer, which has gone into suspension into the rubber solution and gradually flocculates, or in any event separates.

The question arises as to why raw rubber after mastication shows such an enormous decrease in viscosity.

According to the researches of H. R. Kruyt [57] and his pupils the viscosity of an emulsoid, such as raw rubber in benzine, is determined by two properties, i.e. the electric charge of the micelle and its solvation, the latter being the more important. There is much evidence that this change in viscosity of rubber after milling is due to a change in solvation.

H. R. Kruyt and W. Eggink [58] showed that the viscosity of a rubber solution is considerably decreased by the addition of such acids as acetic, benzoic and HCl, H_2S, etc. Later G. St. Whitby and Jane [59] showed that this decrease in viscosity is also produced by a number of other organic compounds, including various accelerators.

In the opinion of the present writer there can be traced a relation between these phenomena and the decrease in viscosity after mastication. As stated above, the adsorption layer and in general what is left from the serum substances during mastication is pulverized and mixed as a very fine compounding ingredient in the rubber mass. If we remember that Belgrave considers the adsorption layer to be a lecithin-protein complex, and that raw rubber contains 1.5 per cent of its weight of fatty acids, there is evidence enough to believe that by mastication these localized products are homogeneously dispersed in the rubber and cause a decrease in viscosity (change in solvation). It is obvious that this view needs further experimental proof.

It would be entirely wrong to conclude from the foregoing, that all properties of raw rubber can be explained on the basis of the structure of the latex particle. Unquestionably the elastic properties of raw rubber cannot be explained on this basis. This is obvious when we consider that although in mastication this structure is entirely destroyed, the mastical rubber nevertheless shows considerable elasticity. W. de Visser [60] pointed out furthermore, that the remarkable calendar effect cannot be explained by this latex particle structure, because raw rubber which has been obtained by evaporation from a solution of masticated rubber, also shows calender effect. There are decidedly at least two more important points which have to be taken into consideration for a further elucidation of the remarkable properties of raw rubber:

1. The crystallization phenomenon. In 1925 J. R. Katz [61] was the first

to publish the remarkable observation that raw rubber in the stretched condition, when subjected to x-ray examination shows very distinct interferences, which led to the general conception that raw rubber when stretched is partly "crystallized." Later investigations have emphasized the importance of this phenomenon for the elucidation of the structure of raw rubber. Wo. Ostwald [62] has advanced a theory, according to which the x-ray interferences of stretched raw rubber could be explained by the structure of the latex particle. He suggests that the center of the latex particle gelatinized during coagulation possesses a fibrillar, or rather a net structure, the meshes of the net being too large to show x-ray interferences. On stretching the rubber the net is elongated, the openings gradually become longer and narrower, until their width becomes such that they show x-ray interference. He tried to explain many observations of x-ray analyses and various properties of raw rubber along this line, always keeping strictly to the latex particle as the principal unit structure of raw rubber. Without discussing it in detail, the present writer believes that this theory is not in accordance with the various properties of raw rubber. The phenomena of swelling and mastication especially cannot be explained sufficiently by this theory, "crystallization" of rubber being more in accord with the facts.

2. G. Stafford Whitby [56] and his pupils have pointed out in various publications that raw rubber is not composed of two distinct phases, but consists of a great number of polymers, in accordance with a number of synthetic organic substances such as a meta-styrol, synthetic rubber etc. which under certain conditions all show elasticity and other properties similar to those of raw rubber.

As however this paragraph aims only to consider how far the latex particle is responsible for the properties of raw rubber, the further analysis of these two views is beyond the scope of this article.

COLLOID CHEMICAL PROBLEMS IN RELATION TO THE INDUSTRIAL APPLICATION OF RUBBER LATEX.

The first patent for the industrial use of rubber latex in Europe was taken out by S. Peel,[63] who in 1791 claimed the use of rubber in its native fluid state for waterproofing cotton, paper, etc. Various patents on the application of latex were granted to Thomas Hancock,[1] but after many experiments this great experimentator gave up the use of latex.

In the last decade a sudden revival of interest in the technical application of latex occurred, which led to various industrial uses of latex in the rubber and other industries.[64] In this paragraph various colloid chemical problems, which may be considered of fundamental importance for these applications are briefly reviewed.

Preservation of Latex

For application to industrial use rubber latex must be transported from East Asia to the United States and Europe, which is only possible if spontaneous coagulation during transport is prevented by adding a preservative as soon as possible after collecting the latex. The function of the preservative is to neutralize the acid already present and to prevent further formation of acids by the bacterial processes. To this aim concentrated ammonia has been in use since its introduction by Fourcroy and is still in general use. It neutralizes the acid already formed and in the strong alkaline medium bacterial action is practically inhibited. O. de Vries [65] and his co-operators have carried out extensive investigations on the preservation of latex with ammonia and also other chemicals, such as caustic soda. For a proper preservation 20 cc. 28% ammonia per liter of latex are necessary, "fool-proof" preservation being obtained by the addition of even 30 cc. of 28% ammonia.

By the addition of ammonia the properties of the latex are changed to a considerable degree. The viscosity of the latex is reduced, and coagulation phenomena are also considerably changed. While the addition of acids to fresh latex gradually leads to flocculation and subsequent coalescence, the addition of acids to the ammoniated latex gives coagulation in bulk. As has already been pointed out J. Groenewegen suggested that the hydrophyllic nature of the protein adsorption layer changed into a hydrophobic one and later W. C. N. Belgrave advanced a similar opinion.

By addition of ammonia to the latex, the rate of cure of the rubber obtained by coagulation changes in a complicated way as was distinctly shown by de Vries, these changes being probably caused by the decomposition of non-rubber substances, with the formation of an accelerator of vulcanization.

O. de Vries and N. Beumée-Nieuwland [66] have also carried out experiments on the preservation of rubber latex with caustic soda. It is possible to preserve latex by the use of 0.5 to 1 per cent caustic soda (0.5 to 1 gram per liter latex) but larger quantities quickly cause a creaming of the latex, the rubber obtained from this cream showing a disagreeable tendency to get tacky.

Borax as a preservative has been investigated by N. Beumée-Nieuwland.[67] The amount of borax, necessary for a proper preservation amounts to 30 grams per liter of latex. This large quantity is a considerable drawback to the general use of this chemical.

Apart from the preservatives mentioned above, patents have been taken on various other chemicals and combinations of chemicals to preserve latex.[68] It is difficult to judge the efficiency and practicability of these preservatives, as such investigations must be carried out with fresh latex. The combination of formaldehyde and sodium triphosphate seems to have been in practical use.[69] The use of amines and their derivates [70] deserve some practical attention.

Concentration of Latex

As ordinary latex contains about 33 to 40 per cent of rubber, it is obvious that about two-thirds of the weight transported to Europe and the United States is serum. Various concentration processes have been patented to avoid this expense.

Concentration by Evaporation. Latex may be concentrated by evaporation, the liquid being kept in motion by intensive stirring to avoid skin formation; the process may also be carried out under reduced pressure. In this way it is possible to obtain a concentration of about 60 per cent. It is advisable to add ammonia to replace the ammonia lost by evaporation. The only evaporation process in practical use is the Revertex-process.[71] An alkaline protective colloid is added to the latex to avoid coagulation during concentration. In the patent [72] on which this process is based, gelatin, glue, saponin, albumates, sodium lysalbinate and protalbinate are given as examples of protective colloids; in practice, apart from these, soaps are used. The process is carried out in a cylindrical apparatus of special construction to avoid skin formation. In this way a latex of 80 per cent concentration of a pasty nature may be obtained, which is packed in cases and shipped under the trade name "Revertex." By addition of water, the "Revertex" can be diluted to any desirable concentration.

Concentration by Ultra-filtration. Concentration on a small scale has been carried out after E. A. Hauser [73] with the aid of ceramic filters, such as Pukall cells and Bechhold-König filters.* By this process it is possible to

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* *See* paper by H. Bechhold in Vol. I of this series. J. A.

separate the serum from the rubber globules of the latex, forming a pasty layer. The stability of this paste may also be increased by the addition of protective colloids. As the filter cells are easily blocked and the process is slow, it has not found practical application.

Concentration by Mechanical Centrifugation. Concentration by centrifugal force in an ordinary milk centrifuge was first described by C. C. Loomis and H. E. Stumpf[50] and independently patented by W. L. Utermark[74] and later by W. B. Westcott.[75] When centrifuging latex in an ordinary milk centrifuge (the α-Laval-type) one obtains a creamed latex of a concentration up to 60 per cent and a skimmed latex, which contains a few per cent of rubber, with the major portion of serum substances. Cream and skimmed latex exhibit remarkably different properties, as was found by the writer[76] with ammoniated latex; these may be summarized as follows:

(1) The microscopical appearance of the rubber globules is different, the latex cream containing the majority of the larger particles, the skimmed latex the smaller globules.

(2) The cream latex dries very slowly the skimmed latex much more quickly than the original latex.

(3) The rubbers show considerable difference in appearance, the cream rubber being white and dry, while the skimmed latex rubber has a dark yellow-brown color and is hygroscopic in character.

(4) The rubbers obtained from cream and skimmed latex by coagulation as well as by evaporation, show considerable differences in chemical composition, which accounts for the difference in rate of drying.

(5) Vulcanization experiments show that the rate of cure of the cream rubber is slower, that of the skimmed latex rubber much more rapid than that from original latex rubber. The difference in the amount of serum substances is responsible for this difference in vulcanization properties.

Further investigations of cream latex and skimmed latex and the properties of rubbers obtained from these latices have been carried out by O. de Vries, R. Riebl and N. Beumeé-Nieuwland[77] and W. Spoon.[78]

The industrial value of centrifuging latex nowadays does not lie in the possibility of concentrating the latex, but in the fact that it is thus possible to prepare a latex and a rubber from this latex, which contains a very small amount of serum substances.

By diluting the creamed latex with water and repeating the centrifuging process a creamed latex may be obtained which contains only a very small amount of non-rubber substances, as is obvoius from Table 11 in which figures are given which were determined by the writer[*] in 1924.

Table 11. *Chemical Composition of Rubbers Obtained by Coagulation from Latex Repeatedly Centrifuged.*

	Original Latex	Centrifuged		
		Once	Twice	3 Times
	Per Cent			
Acetone extract	3.3	3.1	2.5	2.3
Proteins (N 6.25)	3.1	2.3	1.4	1.1
Ash	0.1	0.05	0.07	0.03
Water extract	0.05	0.08	0.03	0.03

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[*] Unpublished results.

The direct use of creamed latex is of great importance to the anode process as the amount of rubber deposited is dependent upon the amount of electrolytes present.

The rubber obtained from creamed and washed latex may be of special importance for the cable industry. This rubber shows in the unvulcanized, and also vulcanized state, a much lower water adsorption than ordinary crêpe and sheet-rubber, for the presence of non-rubber substances is principally responsible for water absorption. The electrical properties, such as specific resistance and capacity, are largely determined by water absorption.

Concentration by Creaming with Chemicals. J. Traube[79] found that latex will cream at a temperature of 50° C. after the addition of mucilaginous substances such as a 2 per cent sol of Irish moss. It has long been known that creaming of ordinary cow's milk is considerably accelerated by the addition of such substances, but in the milk industry this process is carried out at a low temperature (about 10° C.). Some experiments carried out at the Netherlands Government Rubber Institute with ammoniated latex showed that the creaming of rubber latex is successful only at higher temperatures, e.g. 50° C. Preliminary experiments proved albumin, casein and gelatin to be ineffective, but besides carragheen (Irish moss), tragacanth, saleb, agar-agar, and pectinous substances gave positive results. The cause of the creaming by mucilaginous substances has not been investigated, but from a colloid chemical standpoint it deserves full attention. It should be mentioned that in the milk industry the increase in the rate of creaming by addition of mucilaginous substances is caused by the fact that they act as adhesives, causing the fat globules to stick to each other temporarily like bunches of grapes which, according to Stokes' law, cream more quickly. It is however unlikely that this is also the case with rubber globules.

O. de Vries and N. Beumée-Nieuwland[80] have observed that ammoniated latex creams upon standing quietly for a long time. This cream contains 72 to 78 volume per cents of rubber. The creaming is not quantitative and therefore has no industrial importance. The same investigators[81] proved the creaming became quantitative upon adding 5 per cent NaOH to the latex. By creaming with 6 per cent NaOH and subsequently washing, they obtained a rubber with only 0.03 to 0.05 per cent nitrogen. This rubber showed a marked tendency to become tacky and for that reason creaming with NaOH has no industrial value. R. Pummerer[82] has effected the creaming of ammoniated latex by addition of NaOH and heating. By washing the cream with water and repeatedly creaming, he obtained a cream of considerable purity, the amount of nitrogen in the rubber being only 0.07 per cent. His purpose was not the concentration of latex, but its purification and the preparation along this line of a pure rubber which did not contain any non-rubber substances.

As has been mentioned before, the original purpose of the concentration process was an endeavor to decrease freight expense. In 1926 J. G. Fol[83] expressed the opinion that the freight of concentrated latex must be compared with that of transportation of latex in bulk, and he pointed out that, seen from this angle, the latex concentration processes had still to prove their pecuniary value. From the description of the properties of the various concentrated latices, it is obvious that the concentration of latex is no longer carried out with the purpose of freight decrease, but rather to prepare latices of special properties.

The ideal concentration process of latex would undoubtedly be a process for the preparation of a reversible rubber, i.e. a rubber which after transport could be reconverted into latex. Hauser[84] stated that by spraying latex, to which stabilization agents have been added, a reversible rubber powder could be obtained, but it seems rather doubtful if this process has had any success on a technical scale.

Related with the concentration of latex there is still another problem, i.e. the increase of viscosity of the latex. For various purposes it is often necessary to use a latex of a normal rubber content, but with a high viscosity. For this purpose organic substances such as glycerin, gelatin, pectinous substances, starch, are advocated. Colloidal inorganic substances such as colloidal clays, various brands of which are nowadays on the market, will also serve.

Mixing the Latex with Sulfur, Compounding Ingredients, etc.

For the direct technical use of latex it is necessary to prepare latex mixtures and pastes with sulfur and a great variety of compounding ingredients.

The addition of sulfur to latex does not offer difficulties. The sulfur may be added as colloidal sulfur, various brands of which are on the market, and also in the form of an ammonium, sodium, or a calcium polysulfide. Of these ammonium polysulfide has many advantages, as it does not cause any trouble in mixing, nor does it cause coagulation and, on evaporation of the latex mix, it leaves only sulfur in minute drops, which soon crystallize.*

Mineral and Other Inert Powders. The principal other compounding ingredients which must be mixed with latex are the inert and mineral powders such as whiting, barytes, zinc oxide, carbon black, etc. If these are added in dry form, without previous treatment, they cause coagulation of the latex. C. C. Loomis and H. E. Stumpf [50] were the first to discuss the causes of coagulation and the method of preventing it, while later on the present writer [64] and also H. P. Stevens [64] treated the problem at some length. Further various ways of overcoming the difficulties are found in the patent literature, but in the last few years very little substantial literature has been added to this fascinating subject.

The possible causes of coagulation and their prevention may be summarized as follows:

Effect of wetting compounding ingredients. When finely divided fillers in dry condition are added to ammoniated latex these powders absorb a considerable amount of water and cause local coagulation of the rubber particles. This difficulty can easily be overcome first by wetting the compounding ingredients with water, ammonia or even caustic soda and adding them to the latex in paste form. In this way it is possible to mix a large number of compounding ingredients with latex as is obvious from the table below, which summarizes some of the results of H. P. Stevens.

TABLE 12. *Mixing of Compounding Ingredients in Latex of 33% Concentration.*

Compounding Ingredients	Added in Dry Form	Added after Moistening with Ammonia
Barytes	Coagulated	Paste
French chalk	Coagulated	Paste
Whiting	Coagulated	Paste
Zinc oxide	Coagulated	Coagulated
Magnesium carbonate	Coagulated	Coagulated
Magnesium oxide	Coagulated	Coagulated
Carbon black	Coagulated	Coagulated

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* It should be pointed out, that a latex-ammonium polysulfide mix on evaporation is an especially suitable preparation for studying the crystallization of sulfur from globules into crystals; *see* C. O. Weber, "The Chemistry of India Rubber," 1902. Front page.

Insufficient wetting power. It appears that in various cases the wetting power of the latex is insufficient to allow the addition of fillers. In such cases advantageous use can be made of soaps and other wetting agents, which are added to the latex or to the paste of compounding ingredients. Thus carbon black is not sufficiently wetted by water or ammonia to add to latex, and causes quick coagulation. This can be overcome by dispersing the carbon black in soap solution and adding this to the latex.[85]

Apart from soap solution, other wetting agents have been patented;[86] β-propyl naphthalene sulfonic acid deserves special attention in this respect. According to the patent specification, it can be used as a preservative and at the same time acts as a powerful wetting agent.

Insufficient stability. In a number of cases the latex shows insufficient stability towards the addition of mineral fillers e.g. zinc oxide, which also causes coagulation.

The difficulty can be overcome by the addition of various stabilizers, emulsifying agents and protective colloids. For this purpose a large number of organic protective colloids have been patented,[87] such as proteins, casein, glue, gelatin, blood and hemoglobin, etc.

There is still another method of mixing compounding ingredients with latex. Loomis and Stumpf noticed that on the addition of aluminum salts, latex is considerably thickened, the mass becoming a thick porridge which flows but slowly. This is probably due to the action of $Al(OH)_3$ or of Al soap, formed from the ammonia or the ammonia soaps present in the latex. It is remarkable that freshly ammoniated latex gives a normal coagulation to a coalescing mass; but on standing the ammoniated latex gradually gives this flocculation on addition of $AlCl_3$ or $Al_2(SO_4)_3$ which leads to a porridge-like mass. To this mass mineral fillers and carbon blacks can be added by stirring, without coagulation. Stevens has remarked that the dispersion of the compounding ingredients in this flocculated mass will not be as great as in the latex itself, owing to the fact that a number of latex particles have already united in small flocks.

This principle of mixing latex with compounding ingredients has also been patented.[88]

Opposite Charge. When positively charged fillers are added to the latex, the particles of rubber and latex may discharge each other and lead to coagulation. This will not occur often, as most suspensions of mineral powders have a negative charge; it may however occur with oxides which have a positive charge. In this case there is probably only one way of overcoming the difficulty, namely changing the charge of the filler with a protective colloid. The positive particles of the compounding ingredient are coated in that way with a negatively charged protective layer and behave in that way as though negatively charged. The better dispersion of mineral fillers in latex flocculated with aluminum salts has also been attributed to a change in charge, but it seems rather doubtful if this is really the cause.

Apart from mineral and other inert powders there are still two other classes of substances which may be of interest in latex mixtures.

Water-soluble materials. It is possible to add to latex water soluble organic substances such as glue, gelatin, casein, agar-agar, sugar, starch paste, etc. Some of these additions have also been the subject of patent applications such as glue and gelatin[89] and cellulose xanthate.[90] Some of these such as agar-agar, tragacanth, etc., will cause a creaming of the latex. Others such as glue and gelatin will separate when the mixed latex is evaporated, resulting in an upper layer of rubber and a lower layer of glue or gelatin. There is also a possibility of adding soluble metal salts, if the rubber globules are sufficiently protected against coagulation.

The third class of compounding ingredients are such substances as oils, resins, waxes, bitumen, substitutes and organic liquids. There is a general possibility of adding these substances to latex if they are properly emulsified beforehand, for this purpose protective colloids are generally used. Even rubber substitutes and reclaimed rubber have recently been emulsified in water and added to latex.

For homogenizing latex mixtures a colloid mill may be used with success. It is obvious that heavy compounding ingredients such as barytes or lead oxide will gradually settle out, while oils and waxes will rise to the surface causing partial separation. This can be overcome by stirring. A patent of the Anode Company in this field deserves attention.[91]

Vulcanization of Latex

In 1921 Schidrowitz [92] discovered that it was possible to vulcanize rubber as latex by heating the latex at vulcanization temperature in the presence of sulfur. The sulfur may be added in the form of precipitated sulfur, colloidal sulfur or ammonium polysulfide. Vulcanization is accelerated by the addition of suitable accelerators, preferably water-soluble ones which may be activated by the addition of zinc oxide or soluble zinc salts.

According to E. A. Hauser [93] the rubber globules in vulcanized latex are more spherical in shape than in ordinary latex; they show increased Brownian movement and a higher electric charge. H. Green [94] tried to study the vulcanization of the rubber globules with ultra-violet light of a wave-length of 2750 Å., which is transmitted by raw rubber and absorbed by vulcanized rubber, but in respect to Hevea latex his conclusions are somewhat vague. W. C. Davey [95] studied the vulcanization of latex in respect to the kinetics of the reaction, i.e. the influence of time of cure, the nature and the amount of sulfur, the effect of ammonia, mineral oxides and organic accelerators.

On evaporation of vulcanized latex a sheet of vulcanized rubber is obtained. Vulcanized latex shows similar coagulation phenomena to ordinary ammoniated latex, even the pH of flocculation and coalescence being the same. On acid coagulation vulcanized latex with a low percentage of combined sulfur gives a coalescing coagulum, but with a higher percentage of combined sulfur only a flocculate. According to P. P. von Weimarn [96] * ultramicroscopic observations give evidence to the supposition that upon pressure the caoutchouc content of the rubber particles flows together and that the caoutchouc acquires "fibrillar structure" which becomes even microscopically visible when the coagulum is pressed and should account for the elastic properties of vulcanized rubber. In the opinion of the writer the elastic properties cannot be explained by a fibrillar structure visible under the microscope. P. Schidrowitz [97] on several occasions published results of the industrial applications of vulcanized latex, called "vultex" and laid stress on the high mechanical and aging properties of rubbers derived from vultex. It appeared also that concentrated latex, such as Revertex, could be vulcanized by the same process, the vulcanized product being called "Revultex." [98] This concentrated vulcanized latex may be used for the preparation of vulcanized latex pastes and mixes.

Artificial Latex

The adhesive power of raw rubber to itself is so high that the coagulation and subsequent drying of the coagulum have long been considered as absolutely irreversible; in other words it seemed highly improbable that it would be possible to re-disperse raw rubber in water and thus obtain an artificial latex. In-

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* *See* paper by P. P. von Weimarn in this volume. J. A.

directly, various processes have been described and patented, amongst others those of Davies and Pratt.[99]

These processes all involve the same idea: the raw rubber is dissolved in solvents such as benzene, gasoline, etc. the rubber solution is converted into an emulsion in water with the aid of emulsifiers, and the solvent is eliminated as far as possible by heating and evaporation. These processes do not promise much from an industrial standpoint, the procedure being too long and expensive because of the loss of volatile solvent. Therefore it seems of considerable importance that W. B. Pratt[100] succeeded in working out a *direct* process for the preparation of an artificial latex from raw rubber without the use of solvents. Raw rubber is intensively masticated and mixed continuously with small quantities of water in a closed masticator at a temperature of about 70° C. with addition of the proper quantity of colloidal clays such as bentonite or gelacol and eventually also casein, glue, gelatin, etc., until the mass gradually changes into a white paste, which may be dispersed by the addition of more water into a latex. Since W. B. Pratt's original patent various processes of similar principle have been patented.[101] It is certainly remarkable that inventors have succeeded in obtaining artificial latices from mixes of raw rubber with compounding ingredients and even from reclaimed rubber. In this way one can obtain latex pastes, which are more difficult to obtain by the ordinary process, i.e. by adding compounding ingredients to latex.[102]

W. B. Pratt originally claimed that in artificial latex the original latex globules were found, but a microscopic study of the artificial latex soon reveals the fact that the globules are not identical with the original latex globules, being larger and perfectly spherical in shape.

Application of Latex and Latex Pastes in the Rubber Industry.

Impregnation of fabric and cord. The impregnation of fabric and cord with latex has many advantages over the older and generally adopted method of impregnating with rubber solutions. The economic and hygienic advantages may be summarized as follows:

1. No loss of solvent, or necessity of apparatus for solvent recovery.
2. No fire risks.
3. No solvent vapors with danger to the health of workers.

However the technical side of the process is not so easy as at first sight appears. Ammoniated latex has a lower viscosity than the rubber solutions used for the same purpose, which gives an advantage in the technique of impregnation. On the other hand the wetting power of latex on ordinary fabric and cord is considerably less than that of rubber solutions as was scientifically established by the investigations of F. W. Staveley and N. A. Shepard.[103] This problem resembles the wetting of compounding ingredients by latex, and its solution has been found in similar lines.

J. J. Schilthuis[104] found that by pre-treatment of the fabric and cord with a diluted caustic soda solution, soaps and sulfonated soaps, processes which are in general use in the cotton dyeing industry, the fibers are more active in regard to the impregnation of latex. On the other hand the wetting power of latex can be considerably increased by adding various soaps and wetting agents to the latex itself.[86] In regard to impregnation, attention from a scientific standpoint should also be paid to the so-called Fichtner-Sahlbom phenomenon. When strips of filter paper, which normally have a negative charge, are hung in various sols, the negative sols rise in the filter paper, whilst the positive ones flocculate just above the surface of the sol. The explanation of this phenomenon is complex, but there appears to be a flocculation of the positive particles by the negative fibers. As the cotton fiber has a negative charge and the rubber particles in latex are small in relation to the capillaries, a proper impregnation of the fabric and cord may be expected, unless wetting is unsufficient.

The impregnation of fabric and cord has for years been established in various rubber factories.[105] If vulcanization of the rubber impregnated in the cord is desired, it is possible to incorporate the sulfur in the latex as ammonium polysulfide.

Spreading Processes. For spreading purposes it is obvious that the latex must be mixed with sulfur and the desired compounding ingredients, softeners, coloring matters, etc. In this respect the low viscosity of the latex is a disadvantage, as in most cases no dough sufficiently pasty is obtained for the ordinary spreading machines. Various ways of overcoming this difficulty deserve attention:

(*a*) Latex doughs can be thickened by the incorporation of organic substances such as gelatin, pectin, agar-agar and starch. Colloidal clays of the bentonite class deserve special attention.

(*b*) To get a sufficiently pasty dough it seems advantageous to start from Revertex and to incorporate in this pasty material the necessary compounding ingredients, after which the dough is spread with the ordinary spreading machines.

(*c*) C. C. Loomis and C. E. Stumpf[50] have suggested that the porridge-like flocculate which is obtained when adding $Al_2(SO_4)_3$ or $AlCl_3$ to ammoniated latex is a suitable material to add the compounding ingredients and they prepare along this line a dough for spreading. These authors state that the porridge-like flocculate shows much better adhesion to the fabric than ordinary latex. It is possible that this is caused by an inversion of the charge, ordinary latex particles having the same negative electric charge as the fabric, whilst the flocculate has a positive charge and therefore adheres better to the fabric. It is certainly astonishing that no scientific investigation in this line has been carried out, where the direct use of latex pastes for the manufacturing of single textures is dependent upon the possibility of their proper spreading.

There is also a possibility of spreading with vulcanized latex pastes. In that case it seems advisable to start from "Revultex," the vulcanized concentrated Revertex, though recently it was stated that a dried Revertex film takes up a considerable amount of water.[106]

Dipping Processes. The use of latex for dipping processes has been patented in various countries.[107] The low viscosity of the latex in comparison to rubber solutions has caused difficulties, for the number of times of dipping has to be increased considerably. The use of organic and inorganic compounding ingredients which cause thickening of the latex, is undesirable in the mixes which are used for the manufacture of dipped articles.

The use of concentrated latices such as a cream obtained by centrifuging, Revertex or Revultex, can only partly overcome the difficulty. R. Ditmar[108] has tried to evade this difficulty by the use of molds which are made of porous materials. Patents have also been taken on molds which could be heated internally.[109]

The most promising way to reduce the number of dippings seems to lie in the combination of dipping and coagulation. This process has been patented by the Dunlop Rubber Company[110] The mold is covered with a thin layer of gelatin or agar-agar containing the acid which causes the coagulation of the layer of latex coming in contact with the mold. In this way it is possible to obtain, in one dipping, a layer of rubber of the required thickness.

Electrophoresis of Latex. The manufacturing of rubber articles by electrophoresis of rubber latex and latex mixes has caused great interest. This process was invented by S. E. Sheppard and L. W. Eberlin of the Eastman Kodak Company and simultaneously by P. Klein and A. Szegvari in Budapest.

It is obvious that in the manufacturing of articles along this line latex must be mixed with sulfur and all kinds of compounding ingredients, which mixtures have been considered above. As the efficiency of the process depends for a large part on the absence of electrolytes, the use of centrifugal latex is of considerable advantage. From the literature of this process [111] is obvious that the co-operation of a large number of chemists has succeeded in overcoming the inherent difficulties. The proper material for the anodes has been found, porosity of the rubber layers has been overcome, compounding ingredients are homogeneously dispersed in the rubber layers. A large number of patents relating to this process, has been taken out in all countries.[112]

Other Applications of Latex in the Rubber Industry. Some years ago there seemed to be a possibility that the ordinary rubber manufacturing process would be revolutionized by the use of latex mixes. Latex was mixed with sulfur and all necessary compounding ingredients and was sprayed, yielding a dry, homogeneous mass which had only to be vulcanized in molds; but in practice this process was not successful.

In E. A. Hauser's process [113] Revertex was mixed with sulfur and compounding ingredients, the paste dried on heated rolls and subsequently vulcanized. Two advantages were claimed, i.e. by this direct latex process the high power cost of mastication was decreased and, on the other hand, the physical properties of the vulcanized rubber were superior to masticated rubber.

This process has not come up to expectations; various objections have been raised.[114] The power cost of drying on mixing rolls appears at least equal to if not more than the ordinary mixing process, and the superiority in mechanical properties is also questionable.

Many patents have been taken out for methods of applying latex for the manufacture of various rubber articles. It seems beyond the scope of this article to review them all, but a few may be mentioned to give a general idea of the directions to which latex has been applied.

The United States Rubber Co. has patented a method for manufacture rubber threads directly from latex mixes by forcing them through an orifice or nozzle into a coagulating bath, washing, drying and subsequently vulcanizing. In the same way it is possible to manufacture tubes.[115]

H. Beckmann [116] has taken out various patents for the manufacturing of porous rubber materials directly from latex. The latex is mixed with sulfur and other compounding ingredients and coagulated. The wet coagulum is vulcanized directly under water, highly porous ebonite resulting.

In Johore (Malaya) coagulating pans and other articles consisting of ebonite, are directly manufactured from latex according to the so-called Laub-process.[117] The latex is mixed with the necessary sulfur and compounding ingredients and subsequently coagulated, the coagulum crêped to thin crêpes, and these after drying are pressed into molds and vulcanized by heat.

The Wilkinson process [118] involves manufacturing crêpe rubber with compounding ingredients directly from latex. The latex is mixed with the compounding ingredients (among others litharge), coagulated, crêped and dried. From this dried crêpe various articles are manufactured, e.g. linings for dredges of ore transports.

Apart from these applications, which are in actual manufacturing practice, there are a great many patents for manufacturing rubber mixes directly from latex,[119] but it is difficult to judge their practical value, with only patent information.

Applications of Latex in Other Industries

A few words may be said about the application of latex in other industries. Some years ago it seemed that latex had a great future in the paper industry by the application of Kaye's process.[120] In this invention latex is added to the paper pulp in the beater before or simultaneously with rosin. Though the mechanical properties of the latex paper were in some respects superior to those of the paper without latex, it soon appeared that this advantage was quickly lost and even became a serious disadvantage because of the oxidation of the rubber present in the paper.[121] There is evidence that this deterioration of the rubber in the paper is caused by the presence of minute quantities of copper in the paper. The presence of rosin was suggested by M. Levin [122] as another cause of deterioration. In the United States the manufacturing of latex papers and book covers is continued, but probably on other lines. It may also be that with the addition of antioxidants success has been obtained.

An industry in which latex has really been applied with success is the shoe industry. Latex and latex preparations have come in general use for fixing crêpe-rubber to leather. The leather is buffed, and the latex applied with a brush. After drying, a rubber solution is applied and the rubber sole affixed. The adhesion thus obtained is superior to that with rubber solution alone. The latex appears to penetrate better than rubber solution. The application of latex in the shoe industry [123] is not limited to this procedure, various parts of the shoe being fixed with the aid of latex. In recent years soling material has been manufactured consisting of fibrous products, such as felts, etc. impregnated with latex.[124]

Latex mixes have been used with considerable success in the sealing of food tins. This process was developed by the Dewey & Almy Co. as far back as 1919.[125] The properties of the latex paste must be adapted to the apparatus used for this purpose. A small amount of the latex paste is squirted on the turning lid of the food can, thus distributing the latex paste homogeneously in the gutter of the lid. The covers are dried in the machine as quickly as possible. It is obvious that the preparation of a reliable latex paste for this use involves various difficulties of a colloid chemical nature, e.g. the latex paste must have the proper consistency, and must adhere sufficiently to the tinned cover so as not to cause any void which would cause leakage. The latex paste must dry quickly at a high temperature, without causing blisters. These difficulties all have been sufficiently overcome; the use of latex pastes for this purpose in the United States has gradually increased to enormous proportions.

In various industries latex has been used for impregnating fibrous materials, such as asbestos,[126] wood [127] and textiles.

Experiments were carried out by J. Olie [128] of the Netherland Fishery Station to impregnate fishing nets with latex, to increase the resistance against deterioration during use. These experiments proved that latex promises considerable advantages; but the use of latex for this purpose has not been adopted, owing to conservatism in the fishing industry.

Experiments have been carried out to use rubber latex in the rayon industry, and various patents have been taken out,[129] but as far as the writer knows these applications have never advanced beyond the experimental stage.

A patent has been taken out by A. P. Cramer-van Deventer [130] for the preservation of fruits, eggs and other food material with rubber latex.

Extensive experiments have been carried out along this line by J. G. Fol[131] with Dutch fruit; by the Netherlands Government Rubber Institute with eggs;[132] Netherlands-Indian fruit preserved with latex has been studied by W. Spoon;[133] but in all experiments the results have proved to be unfavorable.

There are, in addition, a large number of minor applications of rubber latex for which patents have been taken, but their practical use is limited or the patents have even been abandoned.

Many failures have occurred in the past, owing to lack of knowledge of the properties of latex by the experimenters. There is certainly room for other applications of latex, but only a thorough study of the colloid chemical properties will lead to success.

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The Structure of Rubber.

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Caoutchouc, usually referred to as raw or crude rubber in technical practice, presents many interesting problems for investigation in the study and utilization of plastic materials. With the admixture of finely divided compounding ingredients, such as carbon black, the case is further complicated by the introduction of such concepts as adsorption, and the mass indisputably assumes the rôle of a multi-component system.

Any comprehensive theory of the structure of raw or cured rubber should embrace considerations relative to the ultimate rubber particle, the so-called rubber molecule or aggregate, and the relation of these particles to one another in the plastic mass. The former has been the subject of much excellent experimental work and frequent discussion, whereas the latter has not received all the attention it deserves.

It is proposed in what follows to give a brief résumé of the theories that have been advanced from time to time relating to the structure of the rubber molecule and to that of the rubber mass itself, both in raw and cured state. Before proceeding to this end, however, let us examine briefly some of the chemical and physical properties for which these theories account.

COMPOSITION OF CAOUTCHOUC.

High-grade plantation rubber is composed of 95 to 98 per cent caoutchouc, the remainder consisting, chiefly, of resins and proteins. The amount of the last two mentioned depends upon several factors such as the kind and age of the trees, the climate, the season of the year when the latex is collected, and even upon the methods employed to obtain the caoutchouc from the latex. For instance, the most recent procedure, namely, that of spraying,[1] leaves considerably more of the resins and proteins in the coagulum than does the method usually followed on the plantations where the latex is coagulated by means of acids.

The resin content while indirectly affecting the rate cure [2] plays an important rôle as a softener and its effect on the structure may, therefore, be dealt with under that heading. The proteins in the mass are very important to the rubber chemist because of the effect their decomposition products may have on the rate with which the caoutchouc will combine with sulfur, but it is doubtful if they are a paramount factor in the question of structure.

PHYSICAL PROPERTIES.

It would indeed be difficult to account for some of the remarkable properties of raw or cured rubber on the assumption that the physical constitution is constant throughout the mass except, of course, for the presence of the extraneous substances such as resins and proteins.

If the coagulum, caoutchouc, is a one-component system, one might expect it to react much like a cake of paraffin or perhaps a strip of taffy before crystallization sets in. Caoutchouc differs from paraffin or taffy in that it exhibits an extraordinary persistency to regain the shape from which it has been distorted by stress. This is only true, however, if the latter has not been applied for too long a period of time.

In explanation of the last statement, it may be stated that unmasticated raw rubber does not possess plasticity in the strict sense of the term. If the stress is applied for a short time and is then removed, the mass will again assume almost completely its former dimensions. This does not occur, however, should the distorting forces remain in operation sufficiently long. In the latter case raw rubber will flow as a plastic solid and may be made to assume and retain any desired shape.

EFFECT OF MASTICATION.

The story is quite different if the rubber has been subjected to prolonged mastication such as milling, especially if the latter is carried out so that the temperature is not allowed to rise too high, i.e., over 50° to 60° C.[3] More damage results to the rubber in a given time as a result of mastication at the lower temperature because the plasticity is not so great and the rubber struggles more against the applied force. The plasticity is greatly increased but the tendency to regain the original shape may be almost entirely lost if the mass is over-milled. It is very interesting in this connection that over-milled raw rubber has lost much of its quality and by no combination with sulfur and compounding materials can it be cured to give as valuable a stock as could have been attained by more moderate mastication.[4]

For practical purposes, the rubber manufacturer would prefer to have a material in the raw state that would possess a high degree of plasticity and very little elasticity. After curing, however, these two conditions must be reversed. Cured rubber is highly prized largely because it is capable of being stretched to an extraordinary degree. It must not possess appreciable plasticity else rubber bands, tire treads, etc., would lose their shape rapidly. The bands would stretch until they were useless for the purpose for which they were intended, while the stress would squeeze the tread sidewise from underneath the load, the tread would become thin in the center and finally wear through to the carcass of the tire in a relatively short time.

The tendency of raw rubber to regain its shape is often the source of much difficulty in the factory. When a mass of material is pressed between the rolls of the mill or calender, the thickness is, of course, greatly lessened, whereas the length of the mass circumferentially around the roll is very greatly increased. There is also a considerable increase in the width of the mass lengthwise of the rolls.

As soon as the sheet of rubber is released from stress by cutting it off the roll, the rubber begins to "crawl" in such a manner that the length becomes less, the width often slightly greater, and the thickness is much increased. This phenomenon is so pronounced at times that cord tire friction, where the "gum" has been pressed into the spaces between the parallel cords, has often been found to be shorter than the fabric was before it went into the calenders, in spite of the fact that the cords are stretched by tension during the operation. This decrease in length is due to the tendency of the rubber to become shorter and, of course, to carry the fabric with it as soon as the tension is released.

As a consequence of the milling, rubber becomes anisotropic. The tensile, elongation, and the resistance to tear have different values if determined on the mass in the three different directions. Moreover, Ames[5] has shown recently that calendered rubber will polarize light as long as the sheet remains in a strained condition. In practice, this phenomenon is spoken of as "grain" and has been investigated by several experimenters.[6] This grain persists in the cured sheet, unless the rubber is given the opportunity of recovering either before or during the cure.

We must distinguish clearly, however, between two fundamentally different kinds of grain. One is due doubtless to a readjustment in the orientation of the rubber aggregates during the milling, whereas the other has its probable cause in the relative positions taken by the particles of the compounding ingredients. According to Vogt and Evans[7] the shape of the particles of the added material also plays an important rôle.

STRESS-STRAIN CURVES.

When we come to a consideration of cured rubber, we encounter another striking phenomenon, namely, the shape of the stress-strain curve. Metals require a comparatively great load in order to produce an appreciable stretch. Moreover, the Curve A, Figure 1, which expresses these relationships, approximates a straight line until the elastic limit is reached. Not so in the case of rubber. Curve B, Figure 1, shows that rubber is very easily stretched at first but it becomes more and more obstinate as the process is continued. Furthermore, there is no elastic limit before the point of rupture is reached.

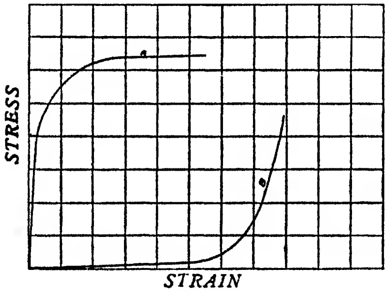

FIG. 1.—Curve A shows the shape of the stress-strain curve of metals; Curve B that of rubber.

Another striking feature of rubber is its remarkable capacity for elongation before it breaks. A well-cured piece may often be stretched eight to ten times its original length before rupture ensues. Moreover, even after it is broken, the portions will snap back until the total length of the two is only a few per cent greater than the original test piece.

In this connection, another property of rubber becomes prominent; viz., the process of stretching is not quite reversible. That is to say, energy of hysteresis is lost, at least during the first thousand or so cycles.[8]

JOULE EFFECT.

At temperatures in the neighborhood of the freezing point of water, cured rubber, when stretched, behaves normally; that is to say, it becomes colder. This, of course, is quite in accordance with the behavior of other substances under similar circumstances. On the other hand, if the temperature is about that of the normal surroundings, rubber when stretched gives out heat, or contracts as the temperature is raised. This behavior would not be anticipated from a knowledge of the action of metals for instance. Should the stretching operation be carried out at temperatures around boiling point of water, or even lower, rubber no longer becomes warmer when it is stretched and, therefore, behaves once more in a manner similar to other substances.[9]

CHEMICAL PROPERTIES.

It is not within the scope of the present article to deal exhaustively with the chemistry of rubber. For such information, the reader is referred to the many excellent publications on the subject, a masterly bibliography of which has been compiled by Bedford and Winkelman.[10] A few salient features pertinent to the subject at hand will be enumerated.

High grade rubber is sufficiently stable to be kept for years in a state of excellent preservation if the temperature is moderate, e.g., around 20° C. It becomes very hard and brittle in cold weather and soft and sticky in hot. It may be reduced by hydrogen[15, 16] or oxidized by many reagents such as air, O_2, O_3, the halogens, S, Te, Se, nitrous anhydride, etc.[11]

Raw rubber will swell in certain organic solvents, such as benzol or gasoline, and finally become dispersed in them. If the rubber is milled before the treatment with the solvent, the dispersion takes place in a much shorter time. Should the milling be continued sufficiently long, the rubber no longer swells perceptibly, but disperses rapidly and easily. Moreover, the milling has a pronounced effect on the properties of the resulting cement. For instance, the viscosity of the liquid is lowered markedly as a result of the premastication of the rubber.

Sulfur, in amounts varying from 0.5 per cent to 32 per cent of the weight of the mass will unite with caoutchouc to form soft or hard rubber respectively. The rate at which sulfur and caoutchouc combine may be greatly altered by the presence of certain substances called accelerators. Soft rubber usually contains 0.5 to 3 per cent of sulfur that cannot be extracted by solvents. The product exhibits greater tensile, greater stretch before breaking and is much more resistant to chemical action than the raw caoutchouc. It is not very susceptible to changes of temperature and is quite soft and elastic at the freezing point of water.

Well-cured soft rubber is fairly stable at ordinary temperature where it is protected from strong light, but will decompose comparatively rapidly if it is subjected to mechanical work continuously. Depending upon the state of cure, which is by no means synonymous with the percentage of combined sulfur, it may become hard and brittle in some cases, or soft and sticky in others if treated with heated air,[12] or heated oxygen[13] under pressure. This phenomenon is made use of in technical practice in order to predetermine the aging qualities of rubber stocks.

Soft-cured rubber may be reclaimed by mastication coupled with chemical treatment at higher temperatures. This treatment does not, however, take out any of the combined sulfur but apparently, merely breaks down the caoutchouc which has not united with the sulfur. The resulting product is not so good as the original rubber, nevertheless, in many instances, it may be vulcanized with sulfur to give a fairly satisfactory stock. Usually the so-called "reclaim" is mixed with a portion of new rubber in technical practice.

Hard rubber is quite stable toward air or even chemicals unless the temperature is high during the treatment. It is comparable to wood in strength but is unfortunately rather brittle and has a very low elongation before break.

The highest percentage of sulfur that can be chemically united with caoutchouc is thirty-two on the resulting mass. This means that one atomic weight of sulfur and no more can be chemically associated with each C_5H_8 caoutchouc group. While this is quite satisfactory from the standpoint of the chemist, how can one account for the extraordinary change in properties that occurs by additions under suitable methods of curing of less than one-half per cent of sulfur? This whole subject has been ably treated recently by Kelly.[14]

The outstanding chemical and physical properties of raw and cured rubber may be summarized as follows:

Caoutchouc unites with sulfur to form a new material having greater strength and stretch but lessened plasticity and chemical reactivity. The upper limit of the amount of sulfur that will add on is 32 per cent of the total mass or 47 per cent of the weight of the caoutchouc.

The change in these properties is not a direct function of the amount of sulfur which enters into chemical combination with the caoutchouc.

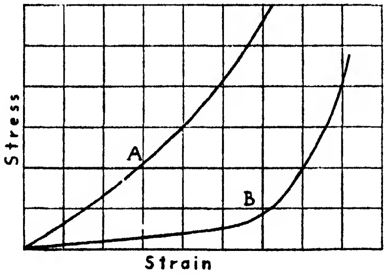

FIG. 2.

Caoutchouc is degraded by mastication, the degradation being less rapid as the temperature is raised while the mastication is being carried out. Mastication on a mill, calender, or in a tubing machine imparts a grain to the rubber mass.

Rubber may be degraded by long curing periods even when sulfur is entering into chemical combination all the while.

Soft-cured rubber will age (perish) as a result of the action of sunlight, heated air, oxygen, or mechanical manipulation at higher temperatures.

The raw mass may be rendered stiffer by the admixture of certain substances in a finely divided state called reinforcing agents, such as carbon black; or may be rendered softer and more plastic by the addition of certain others, usually termed softeners; e.g., mineral rubber, pine tar, oils, resins, and many others.

In the cured mass, reinforcing agents will increase the tensile but decrease the stretch whereas the softeners have the opposite effect.

The stress-strain curve shows rubber to be easily stretched at the beginning and with more and more difficulty as the point of rupture is approached.

Reinforcing substances cause the stress-strain curve to approach more nearly a straight line, Curve A, Figure 2.

At ordinary temperatures, rubber exhibits the Joule Effect, that is, it gives out heat when stretched or contracts when heated.

The Rubber Molecule.

Practically all chemists are now agreed that the ratio of carbon to hydrogen atoms in caoutchouc is 5 to 8. The simplest formula would consequently be C_5H_8. With the evidence at hand, we must conclude that the individual particles, or molecules, are much more complicated than this formula would indicate. Harries,[15] in one of his famous researches in this connection, was forced to the decision that the molecule of caoutchouc contained at least 40 carbon atoms, 32 of which formed a ring. The formula for caoutchouc would therefore be $(C_5H_8)_8$.

C. Harries and Fritz Evers have published an important contribution to the chemistry of rubber in a somewhat inaccessible journal.[15] These authors reduced the dihydrochloride of rubber in $C_2H_4Cl_2$ solution by means of zinc dust. Thereby, they obtained a yellow elastic body which has been called *alpha*-hydro-caoutchouc. The molecular weight of the latter when determined in $CHBr_3$ indicates the formula $(C_{10}H_{18})x$. This body can be oxidized to give a substance which closely resembles natural rubber.

The authors believe that the hydrogen has been added on to the double bonds of the caoutchouc during the formation of the *alpha*-hydro-caoutchouc, as it is improbable that the hydrogen during the hydrogenation would build up larger aggregates. They finally concluded that a molecule of caoutchouc must contain 40 carbon atoms, 32 of which form a ring compound.

Pummerer and Burkard[16] succeeded in hydrogenating caoutchouc in either hexane or hexahydrotoluene by means of platinum black which had been activated by oxygen according to the method of Willstätter and Waldschmidt Leitz.[17] The hydro-rubber thus obtained was analyzed by combustion. This substance is similar to rubber itself in that it is highly elastic. Oxygen transforms it into a substance with the same empirical formula as natural rubber but the properties are not identical. It has, therefore, been called iso-rubber H. The last mentioned may be hydrogenated also where two atoms of hydrogen are added for each C_5H_8 nucleus. H. L. Fisher[18] has drawn attention to the fact that the same sort of reaction will occur during the mild oxidation of 1,2-dihydrobenzene whereby benzene is obtained. That is, of course, a rather stable but, in some respects, a more highly unsaturated system.

Pummerer and Burkard conclude from their investigation that rubber must have the formula $(C_5H_8)x$ and that the molecule must contain a ring system or an extremely long open chain.

Recent work on the structure of the rubber molecule has been ably reviewed by H. L. Fisher.[18] The reader is referred to this article for further details.

The Relation of the Molecules to One Another. The Aggregates.

The coagulation process and the structure of the resulting coagulum, caoutchouc, are so closely related that it seems well to pause a few moments in our discussion of structure and ask, what occurs when the elastic mass is separating from the serum?

Victor Henri[19] states that the caoutchouc particles in the latex are ovoid or nearly spherical in shape. According to Schidrowitz[20] they are globular. Bobilioff[21] recorded the observation that the larger particles were somewhat pear-shaped. This has been corroborated recently by Loomis and Stumpf[22] during their work on the centrifuging of the latex.

Henri[23] believes that the first stage in the coagulation is the formation of small aggregates each consisting of a few particles lying close together.

As the process continues, other particles join these nuclei and form in straight lines running in all directions. The result is a network or mesh of filaments. If the latter is fine, the strength and elasticity of the resulting mass is greater than if the mesh is coarse and more or less open. The particles, however, are the same although somewhat distorted perhaps, as those originally present in the latex. Beadle and Stevens [24] are of a similar opinion. It has been suggested by Pratt [25] also that a large portion at least of the particles in the coagulum are identical with those in the latex.

Quite different from the picture presented alone is that of Loomis and Stumpf. According to this account, the particles retain their identity only up to a certain stage in the coagulation process, after which they burst and flux together. Even when a very much diluted sample of latex was allowed to dry on a microscopic slide, the individual particles disappeared and became minute shapeless patches of rubber.

Lewis [26] has pointed out that the properties of plastic substances change in the direction of greater chemical and physical stability as the individual aggregates become larger.

Spear [27] has elaborated this idea in the case of rubber and believes that the individual aggregates do not, in all probability, have the same size. The formula for caoutchouc should therefore be written $[C_5H_8)\underline{\hat{N}}]$. $\underline{\hat{N}}$ is probably 8, whereas *X* is a variable, the value of which depends upon a number of factors brought into play with different degrees of potency during the previous history of the sample. According to this conception $\underline{\hat{N}}$ and *X* differ in that the former indicates solely a chemical union between the various carbon atoms involved to form an ultimate unit, whereas *X* implies that a varying number of the ultimate units may unite together, due to some physical forces, and form a larger aggregate. This means that the value of *X* may be lowered, for instance, by long continued manipulation, without changing fundamentally at least the chemical nature of the compound. On the other hand, if the value of $\underline{\hat{N}}$ were lowered by any means, we should no longer have caoutchouc but rather its decomposition products. This conception depicts rubber as a mass consisting of aggregates, more or less orientated and differing in size, floating in a matrix of a more finely divided substance having the same analytical composition.

Wolfgang Ostwald [28] has suggested that rubber belongs to the class of substances known as iso-colloids. That is to say, the structural elements consist of large aggregates in a mass of smaller ones having the same analytical composition. Stated in more technical language, polymeric particles are dispersed in a matrix of nomeric particles if the word "polymerizing" is used in a loose sense to denote physical as well as chemical union. This postulates that rubber, physically, is a two or possibly a polycomponent system.

Jean Duclaux [29] views rubber as a reversible gel containing a multitude of small discrete cells which are filled with fluid that is soluble in certain solvents. The swelling of rubber would, therefore, be due on this hypothesis to the osmotic pressure set up in these cells because of the solubility of the interior liquid in the solvents in question. This view is substantiated by the fact that over-milled rubber disperses in solvents, benzol for instance, without appreciable swelling. If, as it is generally believed, milling breaks down the larger particles, or cells in this case, the solvent would find no semi-permeable membranes to penetrate in the mass, could not therefore set up any osmotic pressure and the rubber consequently could not swell.

H. P. Stevens [30] concludes that cured rubber may consist of two phases, i.e., particles of C_5H_8S or some polymer dispersed in caoutchouc.

These ideas are not fundamentally new for we find several authors [31] who have taken the point of view that the mass is composed of more than one physical substance. Mallock drew attention to the similarity of behavior between vulcanized rubber and a mass of putty, chalk and linseed oil. If the latter is subjected to a stress that tends to stretch it, only comparatively light loads are required at first. As the process is continued, however, the ratio $\frac{\Delta \text{ load}}{\Delta \text{ stretch}}$ becomes rapidly greater. The stress strain curve will, therefore, have a form similar to that shown for rubber in Figure 2, Curve B.

Mallock explains this unique behavior on the grounds that the more resistant particles are floating in a liquid, or at least a plastic medium. The stretching causes the particles to approach one another in a direction at right-angles to the application of the load. As long as there is plastic material between the hard particles, the extension takes place easily, but as soon as the hard particles begin to touch one another, further stretching must either deform them or the mass must increase in volume due to the formation of voids.

Fessenden [31] has suggested and more recently Lunn [31] has elucidated the spheroidal theory of the structure of rubber. According to this, the mass consists of, or contains at least, spheres which have a liquid or semi-liquid interior surrounded by an elastic skin. Any attempt to stretch the rubber would necessitate a deformation of the spheres, which, in turn, would subject the interior liquid to pressure because the sphere has the largest volume for a given amount of surface.

The explanation offered by Lunn [31] for the Joule Effect is that the larger aggregates are surrounded by an elastic film or skin which latter contains either a liquid or at least a much more plastic substance. These larger aggregates are suspended or float in a matrix which has the same analytical composition but which exists in a much lower state of aggregation. As the rubber is stretched, the matrix and also the larger aggregates suspended therein are not very plastic at low temperatures. Therefore, rubber behaves very similarly to any other mass such as one composed of a pure metal or of alloys. When the temperature is very high, on the contrary, both the matrix and the suspended aggregates are very plastic, once more they flow readily and there is very little difference between the plasticity of the matrix and the suspended particles. On the other hand, at room temperature, the matrix is much more plastic than the suspended aggregates. If the mass is now stretched, the matrix will tend to thin out between the particles in a direction normal to the stretching force. The more resistant aggregates approach closer and closer together until they begin to exert a pronounced resistance to further stretching, because as soon as they touch their contour must be distorted from the more or less spherical shape. This distortion, of course, involves an increase of surface for a given volume or, in other words, the interior of the large aggregates will be under compression. This compression should, of course, generate heat and the temperature must necessarily rise so that heat will be given off from the rubber to the surroundings. It goes without saying, that this heat must be taken up again by the rubber as the mass returns to its original shape.

X-RAY INVESTIGATIONS ON RUBBER.

X-ray analysis has thrown considerable light on the structure of rubber. This work was first reported by Katz in 1925 [32] and has been ably pursued by several authors [33] since that time. Clark [34] has given an excellent summary of the experimental facts established by this method of attack. Briefly they are as follows:

1. Under normal conditions of temperature raw (unvulcanized) rubber gives an ill-defined halo characteristic of "amorphous" substances.
2. At low temperatures frozen rubber after standing for a long time becomes opaque and reveals an X-ray pattern similar to that obtained from crystalline matter.
3. If raw rubber is stretched rapidly at normal temperature to about a 75 per cent increase in length a well-defined X-ray crystal pattern appears. Vulcanized rubber requires stretching to approximately 250 per cent in order to induce the same phenomenon.
4. The X-ray diffraction pattern disappears in stretched raw rubber if the temperature is raised above 60° C.
5. Isothermal (very slow) stretching produces only a very faint interference pattern and frequently none at all.
6. The intensity of the diffraction spots increases with the elongation, whereas the intensity of the broad amorphous ring decreases.
7. The position of the interferences does not change with increasing elongation.
8. The breadths of the interferences are constant with increasing elongation, at least up to 800 per cent.
9. On releasing the strain the pattern disappears, but a time lag is quite noticeable. This time lag is longer if the temperature is lowered.
10. Solvent vapors cause the pattern of stretched specimens to disappear.
11. Racked rubber, that is rubber subjected to repeated rapid stretching and heating, which may be carried out to 10,000 per cent elongation and over, gives a sharp pattern. The rubber becomes insoluble and nearly nonswelling in the ordinary organic solvents.
12. Calendered rubber gives the diffraction pattern without stretching. On the other hand, excessive mastication, such as long milling operations, tends to prevent the appearance of the interference spots.

Investigations on latex have brought out certain facts pertinent to a theory of the structure of rubber.[34] According to this work the hydrocarbon, comprising the chief constituent of raw rubber, exists in at least two forms, α and β. These have the same analytical composition, but β is a higher state of aggregation than α. The latter is readily soluble in the usual organic solvents, whereas the β form is comparatively insoluble.

One form may be transformed into the other depending upon circumstances. For example, racked rubber becomes largely β as attested by the decreased solubility. On the contrary, β changes into the α form on gentle heating above 70° C.

From a consideration of the above-enumerated and other well-known facts pertaining to the subject,[34] Bary and Hauser [35] have ascribed a more or less definite structure to rubber. A similar picture, but differing in certain minor details, has been presented by Clark.[33] * He suggests that the ultimate architectural unit in rubber may be represented by the formula $(C_5H_8)_8$. 10,000 to 20,000 of these groups are united to form micelles. A single micelle would therefore contain 80,000 to 160,000 isoprene groups. When rubber is stretched long chains of isoprene groups are arranged in parallel orientation. This orientation disappears in unstretched rubber, although the long chains are not necessarily resolved into short single chains. From this it follows that rubber has a fibrous structure and the similarity between the X-ray patterns of rubber and cellulose is accounted for.

Bary and Hauser also assume the existence of chains, but in unstretched rubber the isoprene groups are arranged like a coiled spring. When the rubber is stretched a parallel orientation is superimposed upon the original structure. The further assumption is made that β rubber is swollen by the α modification and that during stretching α rubber is squeezed out of β. The last assumption is supported by the experimental facts enumerated above that

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* *See also* Clark's paper in this volume, and von Weimarn's paper in Vol. III. J. A.

swollen rubber does not give an X-ray crystal pattern, and that a similar phenomenon is observed when other fibrous substances, such for instance as cellulose, are swollen by suitable agents.

VULCANIZATION.

The theory of vulcanization is of paramount importance both scientifically and practicably. Although this has been the subject of a great deal of experimental work and strenuous controversy, we are obliged to admit that all theories proposed to date are inadequate. Of course, this statement does not intimate that our present theories are necessarily wrong, but they are not sufficiently comprehensive to account for the extraordinary changes that take place in rubber during vulcanization.

The large majority of rubber chemists are convinced that the addition of sulfur to rubber during the vulcanization is a chemical process. While this is doubtless true, it is difficult to conceive of the true relations between the atoms of sulfur and the rubber group.

As already stated, the maximum ratio of atoms of sulfur to the C_5H_8 group is 1 to 1. The formula would therefore be C_5H_8S. But this is hard rubber and in soft-cured rubber the ratio of sulfur to the C_5H_8 group must be very much less than this.

We are now confronted with the two horns of a dilemma. Uncured rubber will swell in such solvents as benzol. Soft rubber, even where combined sulfur is less than 1 per cent, does not swell appreciably in benzol, nor can rubber be dispersed in it. If we assume that sulfur has combined with very few of the C_5H_8 groups we should expect the remainder to swell or disperse in the solvent.

On the other hand, if we assume that one atom of sulfur unites with many C_5H_8 groups to form very large aggregates, we are forced to conclude that these groups are broken down again during subsequent vulcanization where more sulfur has been added to the mass. Thus we tacitly assume that there are a very large number of caoutchouc-sulfur compounds and that the law of definite proportions has no place in our considerations.

Recently Boggs and Blake [35a] have proposed a theory of vulcanization that is in harmony with a large number of experimental facts. According to this theory vulcanization consists of two distinct processes, and two kinds of unsaturation in raw rubber are postulated. The rubber aggregate has double bonds at the ends of long chains, and other internal double bonds situated, probably symmetrically, along the chain. The end double bonds are much more reactive than those farther from the ends. If sulfur is added at the ends only, soft rubber is produced, whereas the addition of sulfur at the internal bonds causes the formation of hard rubber.

Because of the greater reactivity of the end bonds, soft rubber is formed first. This reaction can be hastened by the presence of accelerators, whereas the formation of hard rubber is unaffected by them. In other words, hard rubber is produced from sulfur and soft rubber, but not from sulfur and raw rubber directly. In practice it is impossible to eliminate entirely the hard rubber reaction during hot vulcanization where sulfur is used. This has been accomplished in the case of some other reagents, such as selenium and dinitrobenzene.[35b]

The formation of hard rubber during the vulcanization of tires, shoes, etc., causes a progressive lowering of desirable qualities. Suitable accelerators increase the rate of the soft rubber reaction to such a degree that the proportion of hard rubber is greatly reduced. On this basis the superior quality of accelerated stock is accounted for.

This and other arguments in support of the theory have been ably presented in the original article, to which the reader is referred.

It seems probable however that some sort of caoutchouc-sulfur complexes are brought into being during vulcanization. It may be these complexes exert such an influence on the surrounding caoutchouc that the entire mass becomes appreciably less sensitive to the action of solvents. The reader is referred to recent articles by Kelly[14] for a more comprehensive treatment of this interesting problem.

Plastic Film Theory.

Although fairly satisfactory from many points of view none of the above-mentioned theories offer any explanation for the fact that under suitable conditions high grade compounding materials, such as first class carbon black, will stiffen rubber, increase the tensile and decrease the total stretch before rupture ensues. Spear[36] has attempted to fill up this gap by applying Wilson's[37] Plastic Film Theory to rubber.* From experimental evidence obtained by himself and his collaborators and also from that previously recorded in the literature, Wilson concluded that the formation of foam, soap bubbles for instance, cannot be explained on the basis of surface tension effects alone, although these are usually involved. He has proposed the theory that when liquids are drawn out into thin films, the latter take on the properties of plastic solids. That is to say, they are much stronger than the original liquid and may be stretched sometimes to a very considerable extent. In other words, they have elastic properties.

This theory applied to rubber both in the raw and the cured state, offers an explanation for many of the extraordinary properties which rubber exhibits. Granted that there exist relatively resistant aggregates suspended in a more plastic matrix, it will be readily seen that the mass should stretch very easily during the application of light loads. This means that the matrix may be displaced relatively to the aggregates without the application of great forces. As the stretching operation is continued, the matrix will become thinner between the particles, and the thin films which are formed will now assume properties very different indeed from those of the thicker mass from which they are formed. It will be expected, therefore, that the resistance to further stretching would increase more rapidly toward the end of the process. As a consequence, the stress-strain curve of rubber should turn upward quite rapidly as the elongation becomes comparatively great. See Curve B, Figure 2.

From the above, it will be easily seen that the theory of Lunn is by no means precluded if we are to accept the plastic film theory. It is obvious that as soon as the films begin to exert a resistance, there will be a tendency to deform the larger aggregates, whether or not these aggregates have a liquid or semi-liquid interior. In fact, the plastic film theory makes the spheroid theory supported by Lunn even more plausible.

The plastic film theory makes a strong bid for acceptance if we consider what occurs when rubber is compounded with various ingredients. Let us take, for instance, the case of carbon black which stiffens or reinforces both the raw and the cured rubber mass, increases the tensile and decreases the total elongation before break. In addition to this, carbon black also improves aging qualities of rubber, a property which the former holds in common with

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* See Wilson's paper in Vol. I of this series. J. A.

many other finely divided substances, zinc oxide for instance. Before the plastic film theory will account for the effect of carbon black on the rubber, one more assumption, a very probable one, is necessary; namely, that the rubber and the surface of the carbon should form a relatively strong adhesive union. This phenomenon is undoubtedly closely allied to adsorption, but as it is difficult to conceive of a change in the relative concentrations at the surface, it would seem that adhesion will be in this case a less controversial term. This assumption has received a fairly conclusive experimental basis as a result of the work of Endres.[39] * In this work, it has been shown that rubber clings tenaciously to the surface of the compounding materials that reinforce rubber but it may be separated relatively easily from the surface of large particles of such substances as barium sulfate, which latter has very little reinforcing effect until the particles have been reduced to colloidal dimensions.

As the carbon black is being mixed with rubber, we should expect the matrix to adhere to the surface of the carbon particles. But it is the matrix which is responsible for the ease with which rubber may be distorted by light loads. If the carbon is taking up this matrix, it follows at once that the mass should become stiffer. Moreover, the stress-strain curve of the cured stock should much more nearly approach that of a straight line; or stated otherwise, the curve should not turn upward so readily as the extension is continued, but it should be much steeper at the outset than the stress-strain curve of the pure rubber. (Curves A and B, Fig. 2.)

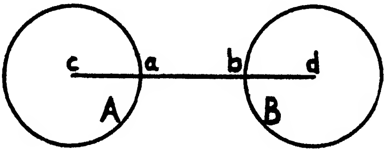

FIG. 3.

It is clear from what has been stated that if the plastic film theory obtains for compounded rubber, the mass should require a greater load to produce rupture for the reason that the very large surface of carbon black will necessitate the formation of an enormous number of very thin plastic films. The thinner these films and the more numerous they are for a given mass of rubber, the greater should be the resistance to distortion; hence, the greater will be the recorded tensile at break.

It will be evident that the properties of rubber constituting these thin films are materially different from those of the rubber which does not contain reinforcing agents. From this alone, we should not expect that the mass would be capable of the same extensibility. There is another factor, however, that enters into the consideration of this phase of the subject. If a large portion of the mass is occupied by particles of carbon, there will be a correspondingly smaller amount of rubber in the given volume. Assuming for the instant, that the original rubber and that in the compounded mass, have the same extensibility before break, an assumption rather improbable if we accept the plastic film theory, it is clear that the total extensibility of the given test piece could not be so great in the case of the compounded mass as it would be if the entire volume were occupied by rubber alone. It is interesting to note that the decrease in extensibility runs parallel with the

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* *See also* Endres' paper in Vol. I of this series. J. A.

decrease in the relative amount of rubber in the given volume. For instance, a tread stock which may contain approximately 60 per cent of rubber has roughly 60 per cent of the stretch that the same rubber would have if it occupied the entire volume, or, in other words, if no compounding ingredients were present. This can be easily illustrated by Figure 3. If *A* and *B* are two particles of compounding material which are separated by a comparatively pure rubber, *a-b,* then the total stretch from center to center of the particles must be less than if the entire distance *c* to *d* were occupied by nothing but pure rubber.

SOFTENERS.

Certain substances, such as mineral rubber, pitches, resins, oils, have the property of softening the mass whether the latter consists of relatively pure rubber, or of a mixture of compounding materials and rubber. The device of adding these so-called softeners is made use of extensively in technical practice to facilitate the molding of the raw stock and in many cases also, to render the cured mass somewhat more pliable. The question may be justifiably raised at this point as to how the incorporation of these substances affects the structure of the rubber. Some authors[38] have shown that most of these softeners will degrade rubber at higher temperatures. While this is doubtless true, it seems difficult on this basis to account for the pronounced softening effect where the temperatures have been kept relatively low. A plausible explanation occurs at once on the assumption that both in raw and cured rubber, there exist aggregates which are suspended in a more plastic matrix. These softeners ought, in the natural course of events, to increase the relative amount of matrix between the particles and thus increase the plasticity of the entire mass. If the vulcanizing process does not change radically the nature of the softener, then the cured mass should also be softer than if none of these substances were present. If, on the other hand, the softener takes up a considerable portion of the sulfur and assumes other properties, it is quite conceivable that the cured mass containing the softener should not show so great a modification as the uncured mass itself. This seems to be the state of affairs in the case of mineral rubber. The action on the raw rubber is very pronounced, but in the cured mass the effect is much less noticeable. It is also clear that softeners should make a mass heavily compounded with carbon black more plastic, because the amount of matrix between the particles is increased. Moreover, we should expect that the percentage elongation before rupture would be considerably greater in the cured stock. This prediction is borne out in practice where the device of adding softeners to a rubber mix is often resorted to in order to increase the amount of stretch that the cured rubber is capable of withstanding without breaking.

PARTICLE SIZE AND STRUCTURE.

It has been generally accepted by rubber chemists and physicists in recent years that the reinforcing power of compounding ingredients becomes greater as the average particle size decreases. The evidence upon which this opinion is based is largely circumstantial but nevertheless convincing. We are indebted to Endres,[39] however, for a clear case in support of this view. Barium sulfate was prepared with a wide variation in particle size between the different lots. The coarse samples had very little effect on the rubber except to dilute it, whereas, those with very fine particles showed a pronounced stiffening action. As might be expected from the theory colloidal barium sulfate was much superior in this respect.

Spear[86] has drawn attention to the improbability that this law holds if the particle size is decreased indefinitely, because the kinetic activity of each particle becomes too great. In fact, we know of no substance having a particle size comparable to the molecules of ordinary inorganic salts which will reinforce rubber.

With these facts in mind, a compounding curve for $BaSO_4$, that is reinforcing power plotted against particle size, should resemble that drawn in Figure 4. The solid line represents the field investigated by Endres whereas the dotted line gives a suppositional path that the compounding value would follow if the particle size were decreased still farther. To date, we have no recorded observations covering this region.

It will be noted that Alexander's "Optimum Colloidality" curve is very similar to that given for $BaSO_4$. This author[40] has pointed out that there is a fundamental relation between optimum colloidality, the size of particle, and, therefore, the amount of surface for a unit weight of substance, and the kinetic activity of the particles. The kinetic activity increases more rapidly with decreasing diameter than the surface increases. These features are lucidly brought out by curves C and B in Figure 4.

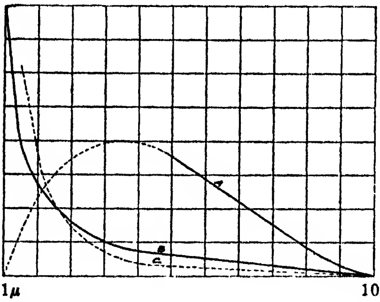

FIG. 4.—Curve A represents the reinforcing value of a given pigment; curve B the surface for a unit weight of substance; and curve C the kinetic activity of the particles, plotted against the diameter.

The shape of the particles seems to have a marked effect on the structure of compounded stocks.[7] Vogt and Evans have shown that if materials with flake-like particles or acicular crystals are milled into rubber, the modulus in a direction perpendicular to the rolls is less than that for either of the other directions. This is easily explained by the plastic film theory. The crystals take up a position with the flat side toward the roll during the milling. Assuming they are very thin as compared to the dimensions of the other two diameters, there will necessarily be much larger spaces between the particles filled with pure rubber perpendicular to the rolls than in the other directions. Consequently, when the rubber is stretched, these spaces empty of compounding particles, cannot so easily become the scene of thin films and the elongation will therefore be greater in a direction which was perpendicular to the rolls.

SUMMARY.

The theories outlined above account in some degree at least for most of the important properties of rubber but it would be too much to say, of course, that they satisfactorily settle the question at issue.

To recapitulate, raw rubber appears to consist of aggregates in a surrounding matrix. These aggregates may be partially broken down by mechanical manipulation, and possibly by chemical action with sulfur, oxygen, etc., under the influence of heat. Other aggregates are built up as sulfur unites with the caoutchouc.

The existence of aggregates regardless of their nature explains the behavior of rubber in relation to the stress strain curve.

The spheroidal theory makes the strongest bid for acceptance when we consider the unusual behavior of rubber as it is stretched. This theory also has offered an explanation for the Joule Effect.

The plastic film theory explains in a fairly satisfactory manner the stiffening effect, increase of tensile and the decrease of elongation due to the incorporation of certain compounding ingredients. In conjunction with the chemical effect demonstrated by North and Aultman [38] it also accounts for the action of softeners.

Doubtless further light will be thrown upon the structure of rubber by future experimentation. When this is at hand, we may be able to discard the erroneous and retain the useful portion of our present theories.

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Physico-Chemical Aspects of Hevea Rubber.

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Rubber, which is one of the most remarkable raw materials known to mankind, has, in the past twenty years, assumed a commercial position of commanding importance. It is only necessary to reflect that rubber is an essential constituent of automobile tires, water and steam hose, a large variety of surgical goods, rubber transmission belts, rubber heels, rubber boots and shoes, and many other daily essentials, to realize its tremendous practical importance.

It may be said in passing that the crude rubber of commerce is chiefly plantation-grown *Hevea brasiliensis*. This is from the same seed as Fine Para, first produced by the natives of Brazil over a century ago, and is the best quality known. Therefore, unless otherwise stated, when rubber is mentioned, plantation Hevea is indicated.

In 1910 the world's production of crude rubber was 80,000 tons. In 1920 the production was 341,000 tons, and in 1928 actual consumption reached the imposing total of 679,000 tons.

It is significant that, over a period of several decades, during which the price has fluctuated over a wide range, no substitute or laboratory synthetic has received any general commercial application. This is *prima facie* evidence, first, that the properties of natural rubber are unique, and second, that they are extremely difficult to duplicate.

This, too, is the almost unanimous verdict of physicists and chemists who have investigated the field. They find that the more fundamental structural phenomena of rubber are difficult to study, both because of the variety of materials which the rubber contains and because the properties of the hydrocarbon make difficult the application of ordinary methods of measurement.

Nevertheless, we have gradually accumulated a store of information about the chemical and physico-chemical properties of rubber which is enabling us to approach more closely to the core of the whole matter.

This chapter will be devoted chiefly to a presentation of the most important and best-authenticated physico-chemical data on rubber, with secondary consideration given to theory. Latex will be touched upon only as found necessary to supply clarifying details.

PREPARATION.

Rubber is prepared from latex, which is a milky fluid consisting of minute rubber globules suspended in a watery liquid. The rubber particles are in constant Brownian motion.

Various investigators[1] have found that the rubber particles vary in size from 4μ in diameter down to particles below the limit of visibility. The particle shape varies from slightly ovoid to pear-shaped.

The composition of Hevea latex varies considerably, but de Vries[2] gives the following composition for latex coagulated with acetic acid:

		Amount after Coagulation			
	In Latex	In Rubber	In Serum	In Rubber	In Serum
	Per Cent				
Rubber hydrocarbon	28	100	—	92–94	—
Commercial rubber	30	100	—	100	—
Total solids	33–34	90	10	98.8–99.7	5
Ash (mineral substance)	.3–.7	16	84	.15–.45	.5–.9
N-containing compounds (protein)	1–2	66	34	2.5–3.5	.3–.9
Acetone-soluble compounds (resin)	2 est. ?	?	?	2.5–3.2	?
Quebrachite	1–2	?	?	?	1.5–2.5
Reducing sugars	.15–.35	—	100	—	.25–.5

The quality and quantity of the latex is affected by the age of the tree, the soil, the surface cultivation, method of tapping, time of year, and duration of the tapping period. Ordinarily, the tree is not tapped until it is about seven years old. The yield of mature trees varies from 300 to 1,000 pounds per acre per year. The average yield[3] is about 400 pounds per year per acre in Malaya.

Although, for some time, there was diversity of opinion amongst investigators as to whether latex is an emulsion or a suspension, it is now reasonably well established that it is a suspension. Sebrell, Park and Martin[4] have shown that the behavior of the particles in respect to fluidity-concentration is in accordance with the laws governing suspensions of solid particles. They also show that most of the rubber particles are ovoid or pear-shaped. This is in agreement with the observations of Hauser and Freundlich[5] and Loomis and Stump.[6] These particles are in colloidal suspension and have a negative charge.

Latex is obtained from the rubber tree by excising a thin strip of bark .04″ wide on an angle of about 15 degrees. The trees are tapped for a six-weeks' period and then given a six-weeks' rest-period. The latex is collected in cups and is periodically transferred to central reservoirs. The usual plantation practice is to collect the latex from the cups in milk cans, from which it is transferred to a local receiving station tank with about a thousand gallons capacity. These tanks are emptied, as soon as filled, into tank trucks by means of which the latex is transported to the factory storage tanks, which are generally lined with tile. At various stages during handling, the latex is strained, usually through copper screens, in order to remove any clots or lumps of rubber. The central storage tanks have a useful function, in that they permit the blending and bulking of rather large quantities of latex. On some plantations, this amounts to as much as 50,000 gallons.

Various anti-coagulants are used to prevent the premature coagulation of latex during the handling period. According to de Vries[7] the following materials are used: (1) Ammonia—relatively expensive; (2) formalin—has an undesirable effect on rubber; (3) sodium sulfite—generally used—retards drying of the sheet, and exerts bleaching action; (4) sodium carbonate (soda ash).

Anti-coagulants may be added to the cups at the tree, or to the buckets into which the latex is transferred from the cups.

In latex for use in pale crêpe, sodium bisulfite is commonly used to assure a clear, light color.

Rubber may be prepared from latex in several ways, e.g., heating, freezing, electrolysis and evaporation. However, the two methods generally employed in commercial practice are acid coagulation and evaporation.

The only feasible means of mechanical separation is by the use of the centrifuge.[8] Loomis and Stump, however, were only able to obtain a concentration of 76 per cent rubber in this manner.

Utermark[9] obtained very high grade material, by centrifuging latex, with a rubber concentration of 60 to 65 per cent.

Electrolytic methods are used, commercially, in the Anode Process to form commercial articles directly from latex. The process is not used, however, for the manufacture of crude rubber.

The preparation of crude rubber by evaporation has its most extensive use in the sprayed-latex process, described by E. Hopkinson[10] and by G. H. Gotz.[11] In this method, the latex drops on a rapidly revolving horizontal disc which throws it, as a spray, into an atmosphere of heated air or inert gas. The evaporated rubber is collected at the bottom of the chamber as a dry, cream-colored, spongy mass, which is compressed and baled for shipping. This rubber contains most of the solid constituents of the original latex. A comparative analysis of sprayed latex, smoked sheet, and pale crêpe is as follows:

	Ash	Acetone Extract	Water Extract	Sugars	Proteins
Pale crêpe	.30	3.20	.40	.30	2.94
Smoked sheet	.31	3.10	.85	.30	2.40
Latex-sprayed rubber	1.10	4.25	6.50	1.40	4.20

The practice most commonly used, commercially, in the separation of crude rubber is by acid coagulation. Latex will coagulate naturally, by fermentation, if allowed to stand, without the addition of preservatives, but the most common practice is to use preservatives and bring about coagulation by the addition of definite amounts of acid to latex containing a standard concentration of rubber. A common concentration is 22 per cent coagulable material.

During the handling of latex, various stages of incipient coagulation may be obtained. A certain layer-separation takes place on standing which is called creaming. This is merely a concentration of rubber particles at the surface of the liquid, and is probably completely reversible. Sometimes curds and small clots of particles appear on the surface, which do not have much tendency to unite to a coherent clot. This is a common occurrence on rainy days in plantation work. Certain handling conditions produce large clots which must be strained out of the latex before acid coagulation.

Various observers[12] have studied the course of coagulation by microscopic and cinematographic methods. Loomis and Stumpf observed the following four stages in the coagulation of dilute latex: (1) A progressive tendency to form small groups; (2) the drawing together of from two to ten particles without complete loss of vibration; (3) the collection of larger groups of particles closer together and becoming distorted; (4) coagulation in which the particles appear to burst and flux together.

The bursting of the particles is not confirmed by Hauser and Freundlich, or Sebrell, Park and Martin, who contend that latex particles exist as such after coagulation.

Since the protein exists as a layer of protective colloid around the latex particle, the theory has been advanced[13] that the precipitation and coagulation of the protein as a protective colloid accounts for coagulation. This does not seem to be definitely established.

Twiss[14] observes that, while acids of a sufficient concentration can unquestionably coagulate latex by their own action, the influence of the very small proportion of acetic acid used on the plantations is not a simple acidic effect. Raw latex which has been sterilized by heat does not behave normally with the customary proportion of acetic acid unless treated with a small amount of fresh latex. This effect is attributed to enzymes.

In commercial practice, acetic acid and formic acid are in common use. Alum is used on certain native plantations, but produces a slow-vulcanizing rubber. Sulfuric acid has been used to some extent, but an excess has a marked effect in retarding the vulcanization of the resultant rubber.

After the addition of acid, coagulation usually takes place in from one to two hours, at the end of which time the rubber has separated into a coherent, spongy, white mass, and the serum remains as a clear liquid. Coagulation is carried out in many kinds of receptacles. If the rubber is to be made into smoked sheets, the coagulum is sheeted through smooth rolls and then passed through a marking mill, after which the sheets are soaked in fresh water for about thirty minutes. The sheets are then hung on poles and allowed to drain for an hour, after which the poles are placed in a smoke-house where the rubber is dried in an atmosphere of smoke. The drying usually takes one and one-half days at 45° C. and one day at 48° C. The drying is finished at 50° C. for about five and one-half days more.

The effective constituents of the wood-smoke are the phenolic bodies which prevent putrefaction of that part of the serum which is not removed by soaking. The smoking gives a characteristic odor and color to the resultant sheet.

In the preparation of pale crêpe, sodium bisulfite is used as a bleaching agent in the proportion of about one gram to a liter of standard latex. The latex is coagulated, as in the case of smoked sheets, after which the wet coagulum is washed on a regular roll-type rubber washer, and finally crêped out by running through tightly set differential-speed crêping rolls. The resultant crêpe is dried at atmospheric temperatures in from four to ten days' time, depending on weather conditions.

Many crude modifications of the foregoing processes are used on small native estates. Extreme irregularity of treatment is the rule. The rubber is quite likely to be contaminated with considerable foreign material, and it may go undried for long periods of time without any particular washing treatment, which, of course, permits various degrees of putrefaction to take place.

The foregoing pages have given an outline of the essential features which affect the preparation of the more common grades of crude rubber. This detail has been supplied in an effort to show the background of the crude rubber of commerce—the background which is too often not thoroughly appreciated by the investigators of the properties of rubber as it is received and used at the factory. With this preparation history in mind, we may now turn to a consideration of the chemical and physico-chemical behavior of rubber itself.

COMPOSITION.

Protein.

The occurrence of protein in raw rubber was noted in 1826 by Faraday.[15] Later, Weber expressed the opinion that the protein surrounded the rubber globule in the form of an envelope or sheath.[16] Also Spence [17] investigated the insoluble constituent of Para rubber and found it to contain protein, which he said was distributed throughout the rubber mass in the form of delicate fibers or films. Beadle and Stevens [18] have shown that when the insoluble material in a rubber solution is removed by filtration, all but 10 per cent of the total nitrogen is removed in the case of smoked sheets, whereas, 90 per cent remains in the case of pale crêpe.

Various methods have been used to remove and isolate the insoluble constituents of rubber. Harries attempted to do this by extraction with acetone which always gave an incomplete separation. Tschirch and Schmitz[19] tried heating with pentachloroethane at 80° C. and were able to separate out a material which contained 11 to 12.6 per cent nitrogen from raw Para. This was about 97 per cent of the nitrogen contained in the original rubber. The use of trichloroacetic acid for reducing viscosity prior to filtering was tried by Spence and Kratz[20] and this method furnished an insoluble constituent containing 10.3 per cent nitrogen and giving reactions for both protein and carbohydrate. Dekker[21] made a separation by heating in petroleum at 230° to 260° C. and diluting with benzol and filtering. He obtained an insoluble constituent containing 8.5 to 11 per cent nitrogen.

The most effective method for obtaining nitrogen-free rubber was introduced by Pummerer and Pahl,[22] who treated ammonia preserved latex with 2 per cent caustic soda at 50° C. in an atmosphere of nitrogen. A cream separated out upon which the treatment was repeated three times, followed by washing, dialyzing, coagulating and vacuum-drying. Later observations by Pummerer, Andriessen and Gundel[23] indicated that, although the rubber was protein-free, it was not entirely nitrogen-free unless subsequently extracted with acetone. This was confirmed by Cummings and Sebrell.[24] They further made the observation that the nitrogen-free rubber cures slowly to give a lower quality vulcanizate than the rubber before the last acetone extraction. Their work indicates that protein is not essential in producing the physical properties of vulcanized rubber, although it may have some indirect effect on the quality. Frank[25] investigated the chemical nature of rubber proteins and obtained positive biuret, xanthoproteic and lead sulfide reactions. Millon's reagent showed the presence of tyrosine. Hydrolysis with sulfuric acid showed the following classes of materials: Monoamino carboxylic acids, aromatic amino acids (phenyl-alanine, tyrosine), heterocyclic amino acids (tryptophane), diamino monocarboxylic acids, monoamino dicarboxylic acids and cystine.

Belgrave[26] reports that in Hevea latex the total nitrogen is distributed as follows:

	Per Cent
Protein	—50
Albumoses	5
Amino acids	7
Unidentified	10

Bruson, Sebrell and Vogt, and Whitby, Dolid and Yorston have found valine (α-aminoisovaleric acid) in raw rubber.

Resins.

The so-called resins in raw rubber usually include all the acetone-extractable portion consisting of fatty acids, esters, high-molecular-weight alcohols and nitrogenous substances. Although various kinds and grades of rubber vary between 2 per cent and 90 per cent resin, high-grade plantation Hevea rubber usually runs between 2 and 3 per cent.

There is some dispute as to the state of resin in crude rubber. Adsorption, molecular addition and separate globule formation have been postulated.[27] Whitby and his co-workers[28] have summarized the constituents of the extract of Hevea rubber as follows: A sterol ester (m.p. 83° C.; free sterol, m.p. 133°-4° C.), 0.075 per cent; quebrachitol, trace; d-valine, 0.015 per cent; an insoluble sterolin, 0.175 per cent; a free phytosterol, 0.225 per cent; oleic and linoleic acids, 1.25 per cent; stearic acid, 0.15 per cent.

Bruson, Sebrell and Vogt[29] have isolated the antioxidant constituents of the unsaponifiable part of the acetone extract. In addition to the materials isolated by Whitby, they have found the following: (1) n-octa-decyl alcohol, a non-inhibitor; (2) $C_{27}H_{42}O_3$ (probably a phytosterol derivative), a powerful antioxidant; (3) $C_{20}H_{30}O$, a sterol which is an antioxidant; (4) $C_{15}H_{24}$, a non-inhibitor; (5) $C_{15}H_{24}O$, an inert ketone.

Acids.

The acid number of plantation rubber is rather variable. Lower grades have lower acid numbers. There appears to be no relation between the water-soluble acids and the rate of cure. A large amount of free fatty acid in Hevea rubber resin distinguishes it from other rubber resins. This acid content seems to play an important part in vulcanization with the use of catalysts. Whitby[30] gives the following figures for the acid content, expressed in milligrams, of KOH to neutralize the extractable acids from 100 grams of rubber:

Rubber	Acid Number
Smoked sheets	234–289
Fine hard Pará	100–384
Pale crêpe	272–296
Brown crêpe	92–223

Sebrell and Vogt[31] have shown the effect of the resin and resin acids on the rate of cure and physical properties of the cured rubber. In all cases where the presence of zinc oxide improved the physical properties, it was converted into the soluble form. Although this usually requires the action of the resin acids, certain accelerators, namely, the thiurams and dithiocarbamates, probably combine directly with the zinc oxide. Further data on the effects of stearic and oleic acids in vulcanization with organic accelerators are to be found in a brief paper by the author on "Stearic and Oleic Acids as Rubber Compounding Ingredients."[32] It was pointed out that stearic acid by itself is a retarder of chemical and physical cure, while with zinc oxide it accelerates chemical cure and with mercaptobenzothiazole and zinc oxide it definitely accelerates physical cure.

Mineral Constituents.

The ash in plantation rubber is relatively low; extreme values ranging from 0.15 to 0.87 per cent. The average percentage ash[33] for Hevea sheet is 0.38 per cent, and for crêpe, 0.30 per cent. Bruce[34] gives the composition of ash from Hevea latex as follows:

	Latex	Crêpe	Sheet
		Per Cent	
CaO	8.7	16.4	11.4
MgO	5.8	6.2	7.6
K_2O	43.	23.4	24.4
Na_2O	12.4	8.9	6.8
P_2O_5	24.	43.	42.2
SO_3	2.8	1.4	1.8
SiO_2	2.6	—	—
Cl, CO_2, Fe, etc.	0.7	0.7	3.6

Hydrocarbon phases.

Among the first to recognize the fact that there are at least two hydrocarbon phases present in Hevea rubber were Caspari[35] and Beadle and Stevens.[36] The former separated various rubbers into soluble and insoluble phases and claimed both phases to be hydrocarbons of the same percentage composition. Beadle and Stevens made a phase-separation and found the insoluble phase to give a better vulcanizate than the soluble phase. In 1925, Feuchter[37] published the results of an investigation on the hydrocarbon phase of rubber. He separated unmilled rubber into a dissolved fraction and a gel skeleton. Pummerer and Koch,[38] the following year, published the results of a similar investigation in which they report that the soluble fraction was in the proportion 65 to 75 per cent, and the insoluble fraction, 25 to 35 per cent; both fractions analyzed $(C_5H_8)_x$. Since that time, Pummerer[39] and his associates have made extensive investigations on this subject.

Gel rubber dissolved in benzol and precipitated with ethyl alcohol becomes partly or completely soluble in ether but, after standing for some time, it again becomes insoluble. The solubility of the gel rubber is greatly increased by small amounts of basic or acidic substances, such as piperidine, ethylamine or acetic acid. Mastication also renders gel rubber soluble in ether, indicating that the molecular chain may be ruptured by mechanical means; though this is probably a colloidal disaggregation rather than an intermolecular breakdown. Both gel and sol rubber give X-ray interference diagrams when stretched, and probably have the same structural formula. By the Rast-camphor method, molecular weights of 1,100 to 1,600 were found. In menthol the values were 1,200 to 1,600 for 2 per cent solutions and only 600 for 0.5 of 1 per cent solution. Osmotic pressure and diffusion experiments indicated molecular weights of 30,000 to 50,000. Pummerer points out that rubber probably has a parent molecule which, by aggregation and disaggregation, accounts for the various phenomena. Gel rubber combines with tetranitromethane in the ratio of 1 mol of the latter to 5 isoprene groups. Sol rubber combines in the ratio of 1 to 6. Pummerer has also shown that the ether extract of crêpe, heated six days at 60° C., increases from the original figure of 40 per cent to 82 per cent. He later shows that the ether-soluble constituent, after heating, becomes similar to gel rubber. These facts would indicate an unstable equilibrium which slight changes in the conditions might disturb in either direction.

Pummerer has stated the opinion that the insoluble component is identical with the shell of the latex globule. However, Hauser[40] points out that the two-phase structure of rubber as revealed by chemical experiments and X-ray studies should not be confused with the structure of the latex particle, as indicated by his experiments with the micromanipulator.

Bruson, Sebrell and Calvert[41] furnished additional evidence in favor of the two-phase theory by treating unmilled rubber with tin tetrachloride in benzene solution and splitting the resulting addition product with alcohol. They obtained a mixture of two isomers in approximately the same ratio as that of the figures previously obtained for the two hydrocarbon phases of the original rubber. Ether-soluble rubber gives only a soluble isomer, whereas the gel rubber produces an insoluble isomer. Heat causes a depolymerization of rubber so that only one isomer is obtained. This, however, differs from the soluble and insoluble isomers obtained from ordinary rubber.

CEMENTS.

There are many so-called crude-rubber solvents. The coal-tar and petroleum hydrocarbons, and chlorinated compounds such as carbon tetrachloride, chloroform and C_2HCl_5 and ether are the most common ones. Treatment of rubber with these solvents produces a combined effect of partial solution and dispersion. Such rubber "solutions" are commonly termed cements.

Mastication by crêping or heating increases its rate of solution.[42] Oxidation renders rubber insoluble and [43] rubber in an atmosphere of N_2 or CO_2 exposed to ultra-violet rays becomes less soluble (in toluol), although ultra-violet treatment in air gives soluble rubber.

Ether treatment causes a certain portion of the rubber to diffuse out into solution, leaving a gel skeleton behind.[44]

If rubber is agitated in solvent giving a thin cement or if it is rendered thin by heating,[45] by exposure to light, or acidification [46] a truly insoluble precipitate will settle out. This is chiefly protein. Beadle and Stevens [47] found the amount of protein to be less in the residue of worked rubber.

Cements have a strong tendency to vary in viscosity. This was mentioned by Woudstra.[48] Gorter reported thinning of cement when exposed to sunlight.[49] Sometimes an increase in viscosity is observed, as when cement is exposed to daylight away from air, jelling occurs, but air liquefies the gel rapidly.[50] Besides the effect of light, air, and heat, impurities and added chemicals affect viscosity of cements. Van Rossem [51] found that, although extracted rubber gave a lower viscosity than the original, this was probably due to the heat of extraction, because the return of the resins produced a still thinner cement. Munro [52] also showed that there is a tendency for the viscosity to decrease with the resin content. The work of Fol [53] confirms this and he points out the effect of milling and drying.

Acidic materials lower viscosity. de Vries [54] has done considerable work with acidified benzene in which he finds the viscosities reduced to about one-half the original.

Kruyt and Eggink [55] investigated the effect of HCl, SO_2, H_2S, CH_3COOH, C_6H_5COOH, HgCl and NH_3. Of these HCl had the greatest effect.

van Rossem [56] found that sulfur, litharge and magnesium oxide in vulcanization proportions had no effect on cement viscosities.

de Vries finds [57] that Na_2SO_3, $NaHSO_3$ and AcONa used in latex coagulation increase the viscosity of subsequent cements. He also shows [58] that varying the amount of acid used in coagulation has no effect on viscosity in the case of acetic acid, a distinct effect with formic and a pronounced effect with oxalic acid. An excess of H_2SO_4 decreases subsequent cement viscosity.[59]

Rubber in the cement form may be vulcanized by sulfur and heat.[60] It can also be vulcanized by sulfur chloride [61] and by the Peachey process with SO_2 and H_2S. Upon evaporation these vulcanized products are similar to those which have been formed in the absence of solvent.

In vulcanization with sulfur, the proportion of sulfur used seems to be important, as well as the previous treatment of the rubber.[62]

In vulcanization with sulfur chloride, the rate of vulcanization decreases as the quality or grade of rubber decreases.

THE INFLUENCE ON RUBBER OF HEAT, OXYGEN AND LIGHT.

As may be anticipated from its constitutional peculiarities, rubber is greatly influenced by heat. It is likewise in accord with expectation that the nature and extent of the effects of heating depend not only upon the temperature and duration of heating but also upon the nature of the rubber and the presence of impurities.

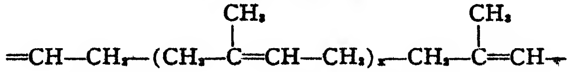
Thus it has been noted by de Vries and Hellendorn [63] that heating latex results in an increased rate of cure, lower viscosity and no change in tensile; the influence of heat on a wet coagulum (soaking in water 60° to 70° C.) was very injurious to rate of cure and tensile strength, while the effect of heat on dry rubber was a lower viscosity and tensile, but no change in rate of cure.

Fry and Porritt[64] heated rubber at temperatures from 100° to 150° C. in an inert atmosphere and found no change in the solution viscosity as was the case when the heat treatment took place in air. Thus it appears that heat treatment of rubber is greatly influenced by the presence of oxygen. This observation has been made by many investigators and studied in considerable detail by van Rossem,[65] who found that rubber undergoes depolymerization when heated as a solid or as a solution, the change being more pronounced in the presence of oxygen and at higher temperatures. Using solubility in benzol as a test for depolymerization, van Rossem found that heating at 130° C. in CO_2 for 4 hours increased the benzol-insoluble portion and lowered the viscosity of the soluble portion. On the other hand, when crêpe was heated in the air at 80° C. for 3 hours, it became slightly transparent and easily and completely soluble in benzol. It appears that little further evidence is needed to emphasize the importance of excluding oxygen in studying the effect of heat on rubber, for according to van Rossem[66] oxygen exerts a catalytic effect on the softening or "melting" of rubber.

It is stated by Staudinger and Bondy[67] that rubber undergoes a disintegration when heated even at fairly low temperatures. Boiling solutions of raw and purified rubber results in viscosity changes the greater, the higher the boiling point of the solvent. The authors look upon the changes taking place by heating at the lower temperatures as a breaking down of the macro molecule that constitutes the colloidal particle. This giant molecule is an isoprene structure having a molecular weight of 100,000, and is readily broken down by heat. Low-temperature heating in the presence of steam and absence of oxygen is said by Park, Carson & Sebrell[68] to result in an increase in plasticity, acetone extract, acid number and rate of cure, and a decrease in total N. Evidently the hydrolysis of protein matter is in this case added to the previously observed effect of heat. Low temperature heating as observed by Staudinger and Geiger[69] does not alter the number of unsaturated bonds, at least through the point of fusion. Low-temperature heating of masticated and unmasticated rubber of different kinds is said by the same authors to reveal large differences in softening point. Thus Para rubber before and after mastication softened at 130° to 140° C. and 100° to 110° C., respectively, in air, and at 210° to 220° C. and 120° to 130° C., respectively, *in vacuo*. Plantation sheets before and after mastication softened at 130° to 140° C. and 100° to 110° C., respectively, in air, and at 170° to 180° C. and 120° to 130° C., respectively, *in vacuo*.

Staudinger and Geiger found that when heated in a vacuum, rubber begins to decompose at about 250° C., the change being accompanied by disappearance of double bonds and the formation of cyclo rubber:

Normal Rubber

I 

$$=CH-CH_2-(CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2)_x-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-$$

II 

Monocyclo-rubber

Continuing the heating *in vacuo* and raising the temperature to 300° to 320°, a 50 per cent yield of poly-cyclo-rubber is obtained, lower molecular weight products also distilling. A similar poly-cyclo-rubber may be obtained by heating rubber in ether under pressure at 250° C., the substance being somewhat more nearly saturated. Staudinger and Geiger further describe the destructive distillation of rubber in a stream of CO_2 at atmospheric pressure to result in a recovery of 92.8 per cent as distillate, 4 per cent remaining as residue. The products obtained, consisting of dipentene, isoprene and cyclohexadiene, dipentene being most abundant, are decomposition products not only of rubber but also of the poly-cyclo-rubber first formed. The process evidently involves a breakdown of the large rubber hydrocarbon molecules into units of from 20 to 50 isoprenes, some of which unite to form poly-cyclo-rubber, others breaking down still further to form isoprene, dipentene and sesquiterpenes. Geiger [70] heated rubber to 250° C. with ether in an autoclave and noted a disappearance of the double-bond, the product being a poly-cyclo-rubber containing only one double bond to five isoprene residues, the analysis being carried out with bromine titrations. An increase in density from 0.92 to 0.992 was noted as having occurred during the treatment. Geiger is of the opinion that the decomposition of rubber by heat takes place in two stages: the first at 290° to 300° C. (*in vacuo*) involves the formation of isoprene, dipentene and about 20 per cent of a higher-boiling oil; the second at 335° to 345° C. yields a distillate containing a small amount of isoprene, no dipentene and about 60 per cent of the high-boiling oil. Ni, NiO, Co and CoO were found to be catalysts for thermal decomposition of rubber, but the products were found to contain hydrorubber and hydro-cyclo-rubber. The effect of catalysts has also been studied by Midgley & Henne,[71] who report that addition of Mg, Zn, Fe and Al greatly increases the yield of substances other than isoprene and dipentene. Copper is without effect. Among the products obtained by destructively distilling rubber at 700° C. and atmospheric pressure were: methyl butanes, methyl pentanes, methyl hexanes, methyl heptanes, tetrahydro toluene, dihydrometaxylene, tetrahydroethyltoluene, dimethyloctadiene, dipentene and isoprene. Because of its chemical unsaturation, rubber in any form, including latex, is subject to the influence of oxygen.

It was shown by Spence [72] that latex contains an oxidase, and by Whitby [73] a peroxidase the activity of which could be accelerated by phenol, picric acid, amidol, pyrogallol and pyroligneous acid, thus offering an explanation of the dark color of fine hard Para and smoked sheet. On account, however, of the relatively slow absorption of oxygen by latex, most of the attention has been directed toward the effects of oxygen on dry rubber, the oxidizability of which under certain conditions may become very great and of the utmost technical importance.

Spiller [74] reported an oxidized product from rubber containing 27.5 per cent of oxygen and conforming to the formula $(C_{10}H_{16})_8 + 5O_2$.

Peachey [75] by oxidizing thin films of rubber formed reaction products corresponding to $C_{16}H_{26}O_8$, $C_6H_9O_2$, $C_{11}H_{16}O_4$ and $C_{11}H_{16}O_4$, while Geiger [76] states that oxidizing rubber with 5 atoms of oxygen gives AcOH, $(CH_2CO_2H)_2$, $Ac(CH_2)_2CO_2H$ and an acid, $C_{18}H_{18}O_7$.

Herbst [77] had earlier reported finding fractions of varying solubility from oxidized rubber, having the formulae $C_{10}H_{16}O$ and $C_{10}H_{16}O_8$.

Whitby [78] by studying changes in quantity of acetone-soluble material, found that two atoms of oxygen enter into combination for each $C_{10}H_{16}$ present. There appears thus to be difficulty in the attempt to determine a chemical formula for oxidized rubber, the course and extent of the action being governed by many factors such as type of rubber, temperature, impurities, illumination, mastication, etc.

Leon and Lister[79] found that 90 per cent of the available oxygen would be absorbed by brown crêpe more readily than by pale crêpe which in turn showed a faster absorption than fine hard Para; soft Para and smoked sheet showing the slowest reaction of all. An ordinary amount of mastication was found to cause a slight increase in resistance to oxidation, although excessive mastication left the rubber in an easily oxidizable condition. The natural resins and protein matter were found to protect against oxidation. Latex evaporated, with all its constituents present, was observed to oxidize less rapidly than pale crêpe, but after extraction with water it oxidized more rapidly. In general, it may be said that each step in the purification of rubber, washing with water, removal of components insoluble in benzol and removal of resins, decreases the resistance to oxidation. Kerbosch[80] has shown that there is a difference in oxidizability of rubber according to the method of coagulation, whether by acid, alcohol, smoke, evaporation or desiccation. Fisher and Gray[81] found a lowering of the degree of chemical unsaturation when rubber was masticated in air, the change being due to absorption of O_2.

The mechanism of the oxidation reaction has been of unusual interest in connection with rubber. It was noted by Thomas and Lewis[82] many years ago that salts of copper, arsenic, silver, iron and manganese appear greatly to hasten the deterioration of rubber, and by Bernstein[83] that oxidation is favored by light as well as by heat. Ostwald[84] pointed out the similarity of rubber oxidation-time curves and the S-shaped curves characteristic of the auto-oxidation of linseed oil. Gorter[85] reported a six-day period of induction before a steady process of oxidation took place in a rubber film, and van Rossem[86] concluded that oxidation, upon heating, was a secondary process, following a depolymerizing action which was catalytically accelerated by oxygen. In a later report, van Rossem[87] noted that the oxidation of rubber takes place only after the viscosity of its solution falls below a certain critical point, this condition being attained when depolymerization has progressed considerably under the influence of mastication, heat, light or chemical influence.

The foregoing experimental results suggest a rather complicated mechanism for the oxidation of rubber, the catalytic nature of which is outstanding. Kirchhof[88] studied the oxidation characteristics of Para in air and light over a period of a year in order to test the theory of auto-oxidation. Kirchhof noted that the oxidation products would liberate I_2 from a KI solution in benzol. Using this analytical method, the presence of peroxide-like compounds was demonstrated, these bodies being unstable and intermediate in the reaction. Kirchhof also found these same peroxides after oxidizing rubber with H_2O_2 and concluded the process to be autocatalytic in nature. Kohman[89] is of the opinion that the absorption of O_2 by rubber is autocatalytic in nature, consisting of two reactions; a decomposition and an addition reaction. The absorption of O_2 by rubber appears to induce changes in the latter comparable and similar to those caused during cure with sulfur, surface checking being regarded as a preferential surface oxidation. The mechanism of O_2 absorption seems to differ for raw rubber as compared to cured rubber. Curing increases both rate and amount of O_2 absorption over that of crude rubber, and changes the character of the absorption curves. The rate of absorption is greater the higher the degree of cure. Kohman states that the absorption of ozonized oxygen differs from that of pure oxygen, the former being taken up much more rapidly at first, but the rate decreases and less oxygen is finally consumed than in the case of pure oxygen. Kohman does not consider the reaction between rubber and ozone to be auto-catalytic. The extremely detrimental effect of oxidation may be noted in the observation by Kohman that the deterioration is directly proportional to the amount of O_2 absorbed, 0.5 per cent being sufficient to diminish the tensile strength by nearly 50 per cent.

Vogt and Sebrell [89a] have shown that the oxygen absorption of a series of cures increases with the time of cure and that extraction of the rubber (either before or after cure) brings the oxygen absorption rates substantially together and at a much higher point than any of the cures before extraction.

Rubber may be chemically oxidized by such a reagent as $KMnO_4$, the oxidation products in this case, according to Robertson & Mair,[90] being different from those obtained by oxidizing rubber in air in that they are insoluble in alcohol and acetone. The complex nature of these products, which contain 24 to 40 carbon atoms, leads to the opinion that the rubber molecule contains a much larger number of isoprene units than has been generally assumed, and is much larger than $C_{40}H_{64}$.

It is stated by Bernstein (*loc cit.*) that depolymerized rubber is more easily oxidized than it is in a normal condition, but this point will be considered more at length as a corollary of the influence of light on rubber.

In addition to heat and oxygen, light may be looked upon as of importance in its effect upon rubber. The ultra-violet portion of the spectrum appears to have the most pronounced influence on rubber. Henri [91] noted that the action of ultra-violet light rays caused oxidation, while Bernstein [92] considered the first effect of ultra-violet light on rubber to be depolymerization, this being followed by oxidation. The effect of ultra-violet light on rubber solutions was observed by Bernstein,[93] who found that exposure of a solution of rubber and sulfur to the action of ultra-violet light resulted in a vulcanization. Garner [94] exposed solutions of rubber to ultra-violet light and found a lowered viscosity to result. Upon evaporation of the solution a residue of depolymerized rubber was obtained which readily absorbed oxygen. Garner [95] also noticed that a decrease in viscosity could be produced by ultra-violet light even when the exposure was made without oxygen being in contact with the rubber solution.

A report of the Netherlands Government [96] states that solutions of rubber in benzol exposed to ultra-violet light from a quartz lamp rapidly undergo depolymerization regardless of whether O_2 or CO_2 is present during the experiment. It is claimed by Bruni [97] that dry rubber exposed to ultra-violet light in CO_2 becomes tacky through oxidation, the light decomposing CO_2 into CO and O. Kroeger and Shade [98] measured the absorption of ultra-violet light by isoprene, isoprene rubber, stretched and unstretched, and raw and vulcanized rubber. They found that the absorption of ultra-violet light depends upon the state of tension. The transparency of the stretched rubber samples was greater than that of isoprene under comparable conditions. Vulcanized rubber transmits very little ultra-violet light. Vulcanized rubber is said by Kirchhof to oxidize more rapidly in O_2 or air when exposed to ultra-violet radiation, the increase in rate being parallel to the time of vulcanization. Kirchhof found that ultra-violet light causes an immediate oxidation, whereas exposure of the rubber to oxygen alone did not result in oxidation until an induction period had lapsed. Scheibe & Pummerer [99] made absorption measurements on rubber dissolved in hexahydrotoluene, the latter being transparent to the extreme ultra-violet. Absorption curves of rubber of different purity including rubber from latex treated with NaOH, rubber from dried latex, and the soluble phase of rubber, were the same from $\log k = 4$ to $\log k = 2$, but below $\log k = 2$ the curves displayed differences; that of the soluble phase rubber deviating least below log $k = 2$ from its course between log $k = 4$ and log $k = 2$.

Note: $k = \frac{E}{cd}$ where $E = \log \frac{I_0}{I}$, c = concentration, and d = thickness of layer in cm.

In the visible portion of the spectrum, light is active toward rubber. Whitby[100] noted that the effect of sunlight is first to produce a disintegration followed by an oxidation causing tackiness and finally a dry, shiny surface is produced on the sample. The influence of ultra-violet light was not excluded in Whitby's experiment but the action of sunlight appears to differ from that which occurs in ultra-violet only. It is stated by Asano[101] that in protecting rubber from light, radiations below 5,000 Ångström units must be avoided. Asano[102] exposed rubber to sunlight and noted a tackiness followed by a brittleness, indicating depolymerization followed by accelerated oxidation. He observed that in all cases the rate of change caused by light was governed by the intensity of the light and was thus in accord with the general laws of photochemical action.

It will be observed that the action of light is generally considered in connection with oxidation. The action appears to depend, however, upon the wave-length of light employed. In the ultra-violet region Asano (*loc. cit.*) states that between wave-lengths of 3,100 and 2,250 Ångstroms there is a strong fluorescence and that below 2,250 Ångströms there is complete absorption where the effect of light is most pronounced. Asano found no absorption in the visible region, although Jecusco,[103] working with vulcanized mixes at 90° C., found that infra red and green radiations have a detrimental effect. According to Asano, the longer wave-lengths cause depolymerization, while wave-lengths below 5,000 Ångströms cause oxidation.

STRUCTURAL PHENOMENA.

X-ray Structure.

Modern use of X-ray enables physicists to determine, quantitatively, atomic spacing and configuration in crystalline materials. This is based on the fact that regularly spaced atoms in a crystal pattern form a diffraction grating for X-rays similar to the coarser diffraction gratings which have been used for years in connection with visible light. Obviously, any structure which affords a regularly repeated atomic pattern will produce an X-ray diagram of the crystalline type, although the material may not be crystalline in the old accepted sense of the word.

Using rubber in the ordinary, unstretched condition, the X-ray diagram consisted simply of two diffuse concentric rings such as are obtained with amorphous material. This diagram does not give any important insight into rubber structure. In 1925, Katz[104] X-rayed stretched rubber and obtained a Laue diagram, characteristic of a structure with the fibers oriented in the direction of the extension. Numerous investigators confirmed this result and attempted to deduce a structure for stretched rubber from their data. Early results, however, were not concordant.[105]

In a recent article by Clark[106] the essential facts with regard to X-ray work on rubber have been tabulated. The following facts are of interest:

Natural rubber, prepared by practically all common methods, produces the fiber-crystal diffraction pattern upon stretching. So far, no synthetic rubber specimens investigated have given more than the faintest evidence of this phenomenon. The pattern first appears at 75 per cent elongation for raw rubber, and 250 per cent for vulcanized rubber. Increasing the elongation above the critical value increases the intensity of the diffraction spots without changing their positions, while the intensity of the broad amorphous ring is correspondingly decreased. In crude rubber, the breadths of the interferences are constant with increasing elongation. These dimensions permit the calculation of the size of the colloidal micelle. The pattern appears instantaneously upon stretching to the critical elongation.

When stretched isothermally, the interferences, if apparent at all, are very faint. When stretched adiabatically, maximum intensity is obtained. The interference pattern disappears at about 60° C. The interference pattern disappears when the tension is released, although it sometimes persists for a period, particularly if the specimen is cooled after stretching.

Stretched specimens placed in solvent vapors lose their interference pattern. Racked rubber gives a sharp X-ray pattern which is as detailed as that from a pure organic compound. The purest hydro-carbon obtainable from natural rubber gives an X-ray diffraction pattern, proving that the phenomenon is not associated with the impurities of rubber. Rubber which has stood for some time at low temperature and has become hard and opaque gives a pattern of sharp concentric rings, indicative of small crystal grains in random orientation. These rings are so spaced that the interference spots of stretched rubber fall exactly upon them. Warming or repeated stretching of the frozen rubber brings its X-ray behavior back to normal.

The X-ray patterns of the fillers incorporated in rubber appear superimposed upon the rubber pattern. Upon stretching, the filler particles, with a few exceptions, remain in random arrangement. Calendering produces a grain effect, which is indicated by the X-ray pattern for a fiber structure even without stretching. Mastication tends to destroy the ability to produce an X-ray diffraction pattern even when the rubber is strongly stretched.

Early X-ray work on rubber determined the identity period, that is, periodic recurrence of structure with certainty only in one direction, namely, that of extension. By turning a stretched rubber film about an angle with reference to the X-ray beam Mark and Susich[107] succeeded in definitely determining the other dimensions of the crystal unit. Clark[108] confirms these results. (*See* papers by G. L. Clark and P. P. von Weimarn in this volume.)

Mark and Susich conclude that the structure in stretched rubber is rhombic. They give as dimensions for the unit crystal, $a = 12.3$ A. U., $b = 8.3$ A. U., and $c = 8.1$ A. U.; "c" is the length of the unit in the direction of the fiber axis. From these dimensions, it follows that there are 8 isoprene groups in the unit crystal. This is derived from the formula $N = \frac{\rho \times 1.008 \times V}{Mm}$. $\rho =$ density of stretched rubber; $V =$ volume of unit cell; $M =$ molecular weight of the isoprene group; $m =$ absolute mass of the hydrogen atom; $N =$ number of isoprene groups in the unit cell. Experimental evidence in other fields makes it clear that there are many of these unit cells in a rubber molecule.

The unit cells are considered as being oriented in colloidal micelles, which are the largest units of continuous crystal structure in the rubber. Meyer and Mark[109] calculated the dimension of the micelle as 300 to 600 Å along the fiber axis, 100 to 200 Å in the other dimensions. This gives 10,000 to 20,000 crystal units, or 80,000 to 150,000 isoprene units per micelle. From these and other facts resulting from their experiments, Meyer and Mark proposed a structure in which the primary valence chains lie parallel to the fiber axis and extend the length of the micelle. In the unit cell itself, each chain consists of two isoprene groups, turned at 180° to each other. There are four of such pairs in each unit cell and the chains are so arranged as to give two-fold screw axes in all three dimensions throughout the micelle. The length of the micelle determines the length of the valence chains as between 75 and 150 isoprene groups.

Hengstenberg[110] shows, in his study of the polymerization products of formaldehyde, that, beyond a certain degree of polymerization, X-ray methods do not permit estimations of the length of the polymer. In other words, they indicate merely a periodicity along the valence chain. Analogous reasoning may be applied to rubber with considerable certainty.

Meyer and Mark estimated, from the intensity of the X-ray patterns, that 80 per cent of the rubber is effectively oriented by stretching. Since merely the intensity, but not the position, of the X-ray spots changes with the elongation, it is concluded that stretching merely orients more units.

One theory which has been advanced to explain the appearance of the X-ray pattern upon stretching rubber is that the isoprene molecules exist in a coiled-up condition, which is straightened out and oriented when the rubber is stretched. Meyer and Mark (*loc. cit.*) have applied this idea to explain some of the vulcanization processes.

Bary and Hauser[111] have formulated a theory based on the fact that at least two polymers exist in natural rubber in the normal state. The lower polymer is called *Alpha* rubber, and the higher polymer, *Beta* rubber. According to their theory, under ordinary conditions, the thermal vibrations of the *Beta* rubber lattice points are so large that no X-ray interference diagram is produced. Stretching forces out the *Alpha* rubber, allowing the *Beta* rubber to crystallize, fixing its lattice points and giving rise to an X-ray diagram.

Although the above theories may not survive future experimental examination, they represent helpful attempts to crystallize our present X-ray information and may serve as a useful basis for further work.

Effect of Temperature on Density of Crude Rubber.

Very little work has been done on the coefficient of cubical expansion for rubber in its normal state. Kroeger[112] states that when raw rubber is warmed and subsequently cooled to its original temperature, its density is decreased by about 2 per cent. He called this irreversible density change and correlated it with density increases upon polymerization, extension and vulcanization. He refers to a research on the change of density with temperature by J. Russner[113] for the region from 0° C. to 53° C. The formula for the expansion of rubber is given as $V_t = V_0\ (1\ at + bt^2 + ct^3)$, where $a = 0.000636$, $b = 0.00000150$, $c = -0.0000001$. Kroeger gives some further figures from his own work as follows:

	Temperature °C.	Specific Gravity
Aggregated Specimen	18	0.935
	3	0.945
Disaggregated by Warming..............	18	0.917
	3	0.928

Figures on vulcanized rubber by Joule and Lundal are to be found in the "International Critical Tables," Vol. 2, p. 269.

One of the most interesting studies of density change has been in connection with the heating of frozen rubber. This was first reported by

Bunschoten,[114] who showed that the specific gravity of rubber which had been lying in cold-storage for a long period, measured at 15° C., was 0.930; whereas, after heating for one hour at 100° C., the specific gravity at 15° C. was 0.912. He gave figures for density after heating frozen rubber to various temperatures for one, two and three and one-half hours. These figures showed that a marked change in density occurs at 30° C.

van Rossem [115] repeated this work and showed that the sharp break in the density curve comes during warming and not during gradual cooling. The following figure shows this effect.

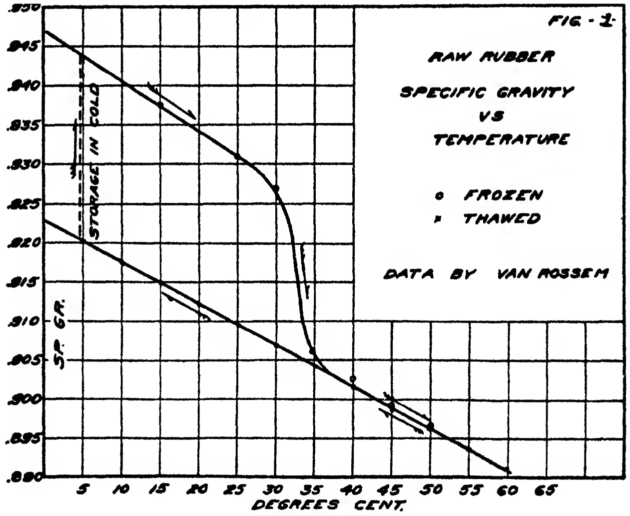


FIG. 1.

These curves indicate a difference in coefficient of thermal expansion between rubber which has been rapidly cooled and rubber which has stood in cold storage. Cold-storage rubber is at least partly crystalline, as shown by X-ray diagrams, yet, all the way up to the transition temperature the coefficient of expansion as shown by the slope of the curve is greater than that for the rapidly cooled, non-crystalline rubber. W. W. Vogt points out that this behavior appears to be peculiar to rubber.

van Rossem and J. Lotichius [116] have recently shown that between 36° and 38° C., as the temperature of frozen rubber is raised, there are sharp breaks in the curves for such constants as specific gravity, hardness and light-absorption.

Joule Effect.

When rubber is stretched it gives up heat. This phenomenon was first investigated by Joule,[117] who showed that the effect is negative at low temperatures and low elongations but increases rapidly, passing through a maximum at about 335 per cent elongation.

Lord Kelvin made a prediction, which Joule verified, that stretched rubber would contract when heated.

The following data are from Joule's work:

Length Inches	Temperature Rise °C.	Length Inches	Temperature Rise °C.
4 (original length)	0	5.2	.014
4.06	—.003	5.87	.053
4.12	—.004	6.6	.095
4.3	—.004	7.75	.187
4.8	—.001		

Also the following on a specimen 3.3 inches long:

Increment of Weight Lbs.	Length Inches	Temperature Rise °C.	Increment of Weight Lbs.	Length Inches	Temperature Rise °C.
2.5	6.8	.110	2	20.1	.004
2	10.9	.242	4	20.1	.001
2	14.6	.330	2	21.3	.009
2	17.6	.132	4	22.0	.004
2	18.5	.088	4	broke	—
2	19.4	.068			

It may be added that the heat effect of stretching is not completely reversible due to hysteresis losses.

These results are in harmony with X-ray and optical evidence regarding the changes which occur when rubber is stretched and afford further indication of the complicated nature of rubber structure. Hock[118] has shown that the work done in stretching rubber is only a small fraction of the heat evolved and hence the frictional factor is negligible in considering Joule effect, which must be looked upon as the result of a marked structural change in the rubber. The density of the rubber changes 2 per cent for 600 per cent stretch,[119] which is further evidence of a structural change such as occurs when a material crystallizes, or when a vapor condenses. The heat of swelling of stretched rubber by solvents,[120] the shape of the stress-strain curve and the X-ray patterns, all indicate a progressive structural change upon stretching.

It is interesting to note that rubber has a remarkable capacity for storing mechanical energy. The following table shows a comparison of the resilient energy of various materials stretched to the elastic limit.[121]

Material	Resil. Energy Ft. lbs./cu. in.	Material	Resil. Energy Ft. lbs./cu. in.
Gray cast iron	0.373	Phosphor bronze	4.08
Extra soft steel	3.07	Hickory wood	122.5
Tempered spring steel	95.3	Vulcanized rubber	14,600
Rolled aluminum	7.56	*Rubber D, racked, 1,100%	49,700

Racked Rubber.

If crude rubber is warmed, stretched and held under tension until it cools it will retain a large part of its deformation when the tension is released. This process is called "racking." Warming restores the rubber very nearly to its original length. The degree of elongation which can be produced by successive rackings is remarkable. Feuchter[122] gives the following data from samples taken from the same sheet of crude rubber:

Racking in %	500	600	700	1,000	2,000	4,000	10,000
Original cross-section (mm.)	2 x 2	2 x 2	2 x 2	2 x 2	2 x 2	2 x 4	2½ x 5
Original length (cm.)	12	13	13	10	5	2½	1
Racked length (cm.)	72	91	110.5	110	105	103	101
No. of rackings	1	1	1	1	4	12	50
Preheating in H_2O (°C.)		30	50	80	80	90	90

* Feuchter, *Kautschuk*, 5, 245 (1929).

Highly racked rubber resembles a catgut violin string.

In the same paper, Feuchter gives some examples of the tensile strength of racked rubber. A strip of unracked rubber, cross-section 2 × 2 mm., torn under slow and normal conditions had a breaking stress of 45 kg. per sq. cm. The extension at breaking was 600 per cent. A specimen of the same material, racked 750 per cent, had a breaking stress of 1,000 kg. per sq. cm. and a breaking elongation of 35 per cent. If the breaking stress is reckoned on one sq. cm. of the original cross section, it comes out to be 125 kg. Higher values of racking give a decrease in the breaking elongation but no more increase in the breaking stress. With racked diffusion rubber, Feuchter got a strength of as high as 2,000 kg. per sq. cm. This is seven times larger than normal values for vulcanized rubber; it is larger than the values for tin, leather, beechwood and is comparable to those for copper, silver, zinc, aluminum and cast iron.

The density of rubber is increased by racking. Feuchter[123] gives the following figures:

Racking Per Cent	Density	Volume Decrease Per Cent
0	0.937	0.0
500	0.946	1.0
1,000	0.950	1.4
2,000	0.953	1.8
4,000	0.953	1.8

Racked rubber has a distinctly fibrous structure. This can be seen by microscopic examination[124] or can be deduced from X-ray diagrams.[125] Racked rubber shows X-ray interferences which are quite sharp compared to those obtained with ordinary stretched rubber. Hauser[126] has taken series of X-ray photographs for various degrees of racking and has also followed with X-ray photographs the process of retraction of racked rubber upon warming.

Feuchter has studied in detail what he terms the melting point of racked rubber. Individual pieces from the same specimen of racked rubber were immersed in water at various temperatures for a given time. The retraction was measured so that the percentage of residual elongation could be plotted against temperature. S-shaped curves were obtained below with a more or less sharp break at the "melting point." By aging rubber or taking other special precautions, Feuchter got exceedingly distinct melting points.

Pigmentation.

Just as gold is seldom used without alloy, so rubber rarely finds a useful place without admixtures of fillers. These may be classed as re-enforcing agents which stiffen the rubber, and diluents which merely cheapen the rubber. Blake[127] considers the first to be those which have a bond with the rubber stronger than the rubber phase itself, while the second have weaker bonds than the rubber phase.

Rubber itself is inert to the fillers dispersed in it, although they may absorb and otherwise influence the curing agents during vulcanization.

The maximum amount of any pigment that can be dispersed in rubber depends upon its particle size, aggregation and ability to be wet by rubber. Carbon black, for example, disperses in rubber from 41 to 154 volumes per 100 volumes of rubber, according to increasing particle size of the black.

The stiffness of carbon black mixtures depends upon the fineness. Depew [128] states that pigments which stiffen raw rubber are poorly wet and flocculated.

The incorporation of fine pigment reduces the rate of solution of rubber in solvents such as benzene. Goodwin and Park [129] have studied this in the case of carbon blacks and found that there is a limiting volume loading beyond which the stock will not disperse in the solvent. Depew [130] has investigated this phenomenon with various grades of zinc oxide and other pigments and arrived at the conclusion that it is due to flocculation of the pigment caused by poor wetting. The flocculated pigment forms a structure which acts as a semi-permeable membrane which prevents the rubber aggregates from passing through. Goodwin and Park do not consider it as retarded solution but as complete inhibition of dispersion, and advance the theory that only the diffusion rubber is extracted by the solvent and the "gel skeleton" material is retained by the pigment.

The effect of pigments on vulcanized rubber is usually determined from the modulus and ultimate tensile of the stress-strain curve.[131] The re-enforcing effect goes through a maximum as the volume loading is increased.

Greider [132] and Cranor [133] give information on the effect of fillers on the rubber stress-strain curve and on abrasion resistance and hardness.

Goodwin and Park [134] give the same information for carbon blacks.

Various theories as to the mechanism of re-enforcement are in the literature.[135] Blake [136] also evolves a theory of fatty acid orientation on the pigment surface.

Hoch [137] treats pigmentation on a thermodynamic basis and states that the free surface energy between the rubber and pigment accounts for the increased work of breaking the rubber.

Depew [138] attributes stiffness to agglomeration and tear resistance to fineness.

The best reënforcing pigments are below 0.5 micron in size, and carbon blacks are about 50 to 80 milli-microns in particle size.[139] There is good evidence that the reënforcing effect depends upon the size of the particle.[140] Endres [141] has pointed out that the effective particle size is the size as dispersed in rubber.

Some interesting work showing the relation of the pigment bond with rubber as compared to the particle size has been done by Shippel,[142] who showed that the volume increase of compounded rubber under strain paralleled the particle size of the filler in most cases. Green [143] confirmed microscopically the fact that rubber pulls away from coarse pigments. [Fine grinding increases specific surface and surface specificity. J. A.]

The principle of close piling of pigments has been advocated by Blake,[144] Spear,[145] Dawson,[146] Esch,[147] and Greider,[148] but has found little or no practical acceptance to date.

Lithopone has been a source of controversy because it does not give the reënforcement one might expect from its particle size. However, Green [149] has shown that it contains agglomerates, and Endres [150] has proved that proper dispersion improves its reënforcing effect 50 per cent.

That there are other factors affecting pigment behavior is indicated by Twiss and Murphy [151] and Goodwin and Park.[152]

The ability of rubber to wet the pigment determines to a large degree its dispersion and effectiveness as a reënforcing agent. Zinc oxide is peculiar in its dispersing power and gives a much lower volume increase in stretched rubber than carbon black, which is much finer.[153] Endres showed that pigments which are chemically active during vulcanization adhere more firmly to rubber. Much has been said about dispersing agents, but very little conclusive evidence has been adduced.

Vogt and Evans[154] have discussed the properties of compounded rubber due to anisotropy of the pigment. In such cases there seems to be a definite pigment orientation which affects the tear and the stress-strain characteristics. These effects persist even when the pigment is made very fine.[155]

VULCANIZATION.

Although crude rubber was known to the civilized world for many years before the discovery of vulcanization, there was no commercial application of any importance until vulcanization made it possible to produce a material which resisted the softening action of heat and the hardening effect of cold. The first vulcanization was produced by Charles Goodyear, who used an admixture with sulfur and subsequent heat treatment, and this was shortly followed by vulcanization with sulfur chloride in the cold. Sulfur vulcanization was soon supplemented by the use of inorganic catalysts such as lime and magnesium oxide, and eventually, about twenty-five years ago, the use of organic catalysts was instituted and still persists in general rubber manufacturing practice.

In general, it may be said that vulcanization has its most profound effect upon the physical properties of rubber. Plasticity is decreased;[155a] elastic recovery is greatly increased; solubility in common rubber solvents, such as gasoline and benzol, is greatly decreased and, in general, the desirable physical properties, such as tensile strength, stiffness, resistance to tear and abrasion, are greatly enhanced.

It is perhaps not surprising, in connection with a material having so complicated a structure, that the mechanism of vulcanization has been a source of considerable controversy. Although it was originally supposed that the addition of sulfur to rubber was a chemical phenomenon, Ostwald, in 1910,[156] produced data in support of the claim that sulfur was adsorbed by rubber and not combined with it. He made the following claims: (1) In all vulcanized rubber a certain proportion of free sulfur (acetone extractable) is present. (2) Vulcanized rubber can be freed entirely from sulfur on prolonged extraction. (3) The rubber always takes up sulfur in an additive way and does not suffer replacement of H_2 with evolution of H_2S. (4) A continuous series of addition products is formed and that no definite compounds have been isolated. (5) The amount of S adsorbed by the rubber increases with mechanical treatment. This could be explained by the assumption of two phases. The degree of dispersion of the disperse phase being increased would lead to an increase in adsorption. (6) The temperature coefficient of S adsorption is more in accord with an adsorption process. (7) The adsorption of sulfur does not proceed uniformly, there being irregular breaks in the combined sulfur time curve. (Data of C. O. Weber.) (8) Adsorption follows the exponential equation $x/a = KC^n$ (a form of the Freundlich equation) where x equals the weight of adsorbed S, a equals the quantity of rubber, C, initial concentration, and K and n, constants. Data of E. Stern[157] were cited in this connection. A number of these claims were based upon wholly faulty data and may be criticized as follows:

Claim 1.—Has been refuted by the work of: (a) Spence and Young,[158] who showed that all of the S present may be made to combine with the rubber in the case of extracted rubber; (b) W. J. Kelly[159] has shown that a portion of the sulfur is combined with substances other than rubber hydrocarbon which are soluble in acetone, thus explaining the small amount of extractable sulfur usually found.

Claim 2.—Has been refuted by the work of H. P. Stevens,[160] who showed that after 9 weeks' extraction the sulfur content of a sample of vulcanized rubber was the same as at the end of one week.

Claim 4.—The work of Spence[161] and his coworkers has shown that the saturation point is reached sharply at 32 per cent S corresponding to C_5H_8S. There is also some evidence of a compound at $(C_5H_8)_2S$. Glancy Wright and Orr[162] have shown that the properties of hard rubber develop rather sharply at a sulfur coefficient of 23.5 per cent, which corresponds exactly to the above compound. Further work by McPherson and collaborators at the Bureau of Standards, Scientific Paper No. 560, has shown that certain properties such as volume shrinkage during vulcanization, the cubical coefficient of expansion and certain electrical properties when examined over a range of rubber-sulfur combinations show sharp discontinuities at an S coefficient of 23.5 approximately. Other intermediate compounds are at present very doubtful.

Claim 5.—This was based upon work by Axlerod,[163] who milled two samples of the same rubber, having previously heated one sample *B* for ½ hr. at 120° C. Upon vulcanization, sample *B* gave uniformly higher sulfur coefficients. Repetition of the work of Axlerod by Spence and Ward[164] gave the opposite result. However, the methods of treatment of Spence and Ward were somewhat different and in my opinion more to the point. Samples were milled for various periods of time previous to vulcanization with the result that while milling has a deleterious effect upon the properties of the vulcanizate, the rate of sulfur combination was identical for all cases. This result has been further verified by van Rossem,[165] and in our own laboratory on several occasions.

Claim 6.—The temperature coefficient of vulcanization is 2.65.[166]

Claim 7.—Data of Weber were obtained under adverse conditions and repetition of the work produced smooth curves.[167]

Claim 8.—Is also the result of faulty data which were corrected by the work of Spence and Young above. See also the article by Kelly, who points out that equilibrium should exist according to the Freundlich equation, whereas this is manifestly impossible, since the combined sulfur time curves approach 32 per cent as a limit regardless of temperature.

In brief, we may conclude that the action of S on rubber has been shown beyond reasonable doubt to be essentially a chemical addition of S to rubber, doubtless at the unsaturated point in the isoprene unit. Practically the only behavior that does not fit the known facts of typical chemical behavior is the reaction rate where $\frac{dx}{dt} = K$ rather than being dependent on the concentration of reactants. W. J. Kelly[168] offers three explanations of this behavior.

(1) Due to Skellon[169] who suggests that the formation of $C_{10}H_{16}S_2$ in the first place and subsequently of polysulfides may cause the reaction to behave as autocatalytic.

(2) The second explanation is that accelerators may be formed from the non-rubber constituents as vulcanization proceeds.

(3) The third explanation is that rubber being depolymerized or disaggregated by heat becomes progressively more reactive.

Another explanation which has been rather frequently made is that, since the sulfur becomes more and more soluble as the vulcanization proceeds that the increased concentration of sulfur may offset the decreased concentration of rubber. Finally, it is well known that few chemical reactions follow the theoretical laws exactly and the deviation in such a complicated material as rubber need not occasion great surprise.

The Effect of Sulfur Combination on the Physical Properties.

The following effects have been observed: (1) The stiffness usually increases to a maximum and then decreases the maximum varying in various cases. (2) The tensile strength increases to a maximum and then decreases.* (3) The solubility of the rubber in ordinary solvents decreases as the cure advances. (4) Swelling in solvents decreases as cure advances[170] ($QuKE = k$ where Qu = per cent volume increase, K = coefficient of vulcanization, E = constant depending on solvent, K = constant). (5) The points of temperature transition are greatly changed by cure; e.g., the *Beta* transition or change on racking is lowered markedly. I believe the *Gamma* transition is absent in proper technical cures. The *Delta* transition is raised very greatly. (No detailed data on this subject.)[171] (6) The plastic properties are reduced. (7) It loses its adhesive qualities. (8) It becomes more liable to deterioration. (9) If amounts of S over 18 per cent are added, vulcanite-like products are produced. These changes take place gradually and raw rubber passes imperceptibly into vulcanized rubber.

Variables Affecting the Rate of Vulcanization or the Properties of the Vulcanizate.

The temperature of vulcanization affects the rate of cure according to the van't Hoff law but the physical properties at mathematically equivalent cures are exactly the same regardless of the temperature at which curing was accomplished. This holds quite well for rubber-sulfur mixes. In case accelerators are introduced, better results are obtained at higher or lower temperatures, depending on the accelerator. In other words, each accelerator has a preferred temperature.

The state of division of the sulfur as used in the mix and the allotropic form used, exerts little or no effect upon the rate of vulcanization.[172] This is probably due to the fact that the sulfur in solution in the rubber exists in a definite state or a definite equilibrium between two states which is very quickly obtained at vulcanizing temperatures.

The use of certain active pigments produces a pronounced difference in the physical properties of the stock while having very little effect upon the rate of sulfur combination. ZnO is the most remarkable example of this type. Used in the amount of 1 volume, the resulting effect on physical properties is beyond anything we might expect from simple pigment reinforcement. Carbon black effects a decrease in the rate of sulfur combination. Certain other materials such as clay, stearic and oleic acids, etc., have a definite effect upon rate of S combination.

Accelerators.

In a general way, accelerators of vulcanization may be said to increase both the rate of sulfur combination and the improvement in physical properties. Usually the physical cure is accelerated more than the chemical cure; in other words, the same or corresponding properties are obtained with lower combined sulfur. The reasons for this are obscure and will be discussed a little later under theories.

Organic accelerators are comparatively new in the industry; the first re-

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* This may possibly indicate a zone of maximum colloidality. *See* Vol. I of this series. J. A.

corded use for the specific purpose of increasing the rate of vulcanization was in 1906 by George Oenslager. He recognized the effect of aniline oil in hastening vulcanization and in improving the product. From that time until now the development of the use of organic accelerators and the production or application of new compounds has been one of the most brilliant chapters in the history of the industry. The number of materials tried has been immense and by a process of elimination, a few very effective agents of vulcanization have come to be used almost universally.

Among the most commonly used accelerators are the guanidine derivatives, mercaptobenzothiazole and certain aldehyde amine condensation products. Most accelerators require ZnO or PbO to function properly and produce given physical results at a much lower vulcanization coefficient than would obtain without their use.[173] Most of the common accelerators are nitrogenous bodies although there are some exceptions such as the xanthates. The mode of action of accelerators has been the subject of much speculation.[174] A mechanism of the action of the inorganic oxides through combination with the natural resin acids in the rubber and subsequent formation of metallic polysulfides of the soaps has been suggested by Bedford and Winkleman.[175] Although the experimental evidence concerning details is, at best, quite indirect, it seems to be the consensus of opinion that accelerators are carrier type catalysts which may or may not be destroyed during the course of the reaction, depending upon the structure and mode of action.

Mechanical Treatment.

The effect of mechanical treatment prior to vulcanization may have a marked effect upon the quality of the product. Milling may be carried to such a point that it is practically impossible to obtain a satisfactory product upon vulcanization.

Sulfur monochloride when used as a vulcanizing agent, either in the form of a vapor or a solution, acts by the addition of both sulfur and chlorine to the rubber molecule. Rubber, so vulcanized, is much more subject to the deteriorating effect of light and oxygen.

It is also possible to vulcanize rubber by subjecting it, alternately, to gaseous sulfur dioxide and hydrogen sulfide—a process which releases sulfur in a very active form.[176] Vulcanization has been produced by a number of other materials such as antimony iodide, certain organic nitro derivatives, benzoyl peroxide, and selenium.

Aside from the question of sulfur combination, there has been considerable speculation regarding the connection between the chemical action of vulcanization and the physical result. Many hold the theory that during vulcanization, rubber is simultaneously polymerized or aggregated by combination with sulfur, and depolymerized or disaggregated by the action of the heat. Since the resultant physical properties go through a maximum, with respect to time of cure, it is assumed that the polymerization effect predominates initially, and the depolymerization, during the later stage of the cure. However, if rubber, untreated with vulcanizing agents, is given a preliminary heat treatment in excess of any received during vulcanization, it frequently gives a faster vulcanizing and better quality product than did the original rubber.

Twiss [177] has evolved an interesting theory in which he assumes the formation of a rubber sulfide in a very fine state of division. He assumes that this rubber sulfide is dispersed in unvulcanized rubber, exerting a reënforcing action similar to that of a fine pigment. Boiry [178] has attempted, without success, to separate the several components postulated by Twiss.

In general, it may be said that a satisfactory explanation of the structural changes involved in vulcanization, which can be substantiated by conclusive data, is yet to be evolved.

This chapter was begun by the statement that rubber is a remarkable material. It may be of interest, in closing, to enumerate some of its most unique features.

Perhaps the most outstanding is the Joule effect, the ability to give up heat during extension. This means that rubber should get stiffer, when heated, a fact which is readily observable provided the deformation is carried out rapidly, in order to prevent obscuring the effect by the tendency for increased plastic flow. It should be observed that the literature is full of references giving figures to prove that rubber is softer at elevated temperatures. This is because it is customary to carry out deformation (usually extension) at slow speeds.

Another unique property of rubber is its enormous extensibility, with no elastic limit. This gives it a very high proof resilience and a very great capacity for absorbing energy. A practical demonstration of this was furnished in our plant by an enterprising workman who attempted to dynamite a pile of massed rubber scrap, without noticeable results.

The temperature transitions of rubber are interesting. In liquid air it is transparent and brittle like glass. It reverts quickly below 0° C. When racked at 10° to 15° C. it becomes hard, inelastic, opaque, anisotropic and of higher specific gravity. It reverts quickly at 18° C. On long storage at 0° to 10° C. it becomes opaque and hard. It reverts slowly at 25° C. and quickly at 30° C. It cannot be extruded with telescopic flow, below 50° to 60° C. Calender grain disappears at 45° to 47° C. Rubber plasticized on a mill tends to reaggregate at 50° to 60° C.

We find also that rubber is one of the very few materials which has a Poisson's ratio of 0.5, which means that it stretches without change in volume.

Few of nature's raw materials are more unique or more useful. As time goes on we will doubtless become better acquainted with the reasons for rubber's idiosyncrasies, and perhaps better able to adapt them to human needs.

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[176] Peachey, *India Rubber World*, **62**, 729 (1920).

[177] *J. Soc. Chem. Ind.*, **44**, 106 (1925).

[178] *Rev. gen. caoutchouc*, **1926**, **23**, 11; **24**, 9-12; **25**, 9-10.

Carbon Black in the Rubber Industry.

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There is perhaps no more interesting or important commercial application of colloidal materials than in the rubber industry. Rubber itself—a substance exhibiting colloidal properties to an extreme degree—attains its most valuable properties only after being blended with another material, carbon black—also of pronounced colloidal characteristics. It is through the joint use of these two colloids in tire treads that the ever-increasing demands of modern transportation are adequately met.

Historical.

When vulcanization was discovered in 1839, it appeared that the key to the application of rubber for industrial purposes had been found. The action of sulfur removed those characteristics—of softening under heat and becoming brittle in the cold—which had made the application of rubber, prior to that time, so limited. This was only the beginning. To obtain proper stiffness and hardness for many commercial purposes, it was necessary to blend other materials with the sulfur and rubber, for a "pure gum" mix is of restricted applicability, owing to its limited capacity for withstanding abrasive wear. Among these added materials may be enumerated various metallic oxides such as lime, magnesia and litharge which not only affected the physical result, but also influenced it chemically, causing a marked increase in the rate at which vulcanization took place. Other materials such as whiting, clays, ground barytes and blanc fixe, were used to stiffen vulcanized rubber and also in order to make products of lower cost, for rubber in the early days was a very costly raw material. Various colorants, such as zinc oxide and lithopone for white products, antimony sulfides, vermilion and iron oxide for red products and lampblack for black products, found application, and it was gradually learned that some of these substances produced unusual properties, aside from color.

In those early days, prior to the advent of the automobile or even the bicycle, the uses to which rubber was applied demanded little in abrasion resistance. These new uses changed the situation and it was probably at quite an early date that zinc oxide was recognized as being extremely valuable for "reinforcing" rubber. It was, however, a long time before the true value of carbon pigments was discovered, though apparently their use in the rubber industry is as old as the art itself. T. Hancock[1] is reported by Twiss[2] to have taken out a patent in 1830, in which lampblack is mentioned as a coloring matter for a rubber-fiber composition. From 1830 onwards, according to Dawson and Hartshorne,[3] the British Patent files contain many references to the use of black—as for example in packing and oil-resisting rubbers.[4] Though it has been repeatedly stated that the purpose for which it was applied in the early days was exclusively as a true pigment, or coloring agent,[5, 6, 7] this is not strictly so. Goodyear[8] in his classical autobiography and work on rubber, published in 1855, stated that: "Lampblack is often used to cause the gum to endure the effects of sun and weather." It is certain that the percentage of black used in those early days was comparatively small and of the lamp or oil black variety.

However, Goodyear would lead us to believe that for certain purposes considerable additions of black to rubber were made, for he states that for tarpaulins, as well as for all other uses where rubberized fabrics are exposed to the sun and weather, "a large proportion of carbon black or lampblack is required to be compounded with the gum. At the time of the first manufacture of vulcanized fabrics for such purposes this was not known, and the articles did not prove as good as was expected." Also Dawson, through D. F. Twiss,[2] has brought to light an early British patent (1868) covering a mixture for rubber soles and heels containing 12 per cent of lampblack. In general, however, according to a review of the boot and shoe industry published in Germany in 1900,[9] the lampblack additions did not ordinarily exceed 0.75 per cent.

Just when gas black, which was first prepared in America in about 1872,[5] was first used in rubber is not known. The fact that its price had dropped from $.35 per lb. in 1881 to an average of $.06 during the years 1891 to 1901[10] would indicate that at least for coloring purposes it would have replaced lampblack, owing to its much greater covering power. According to Perrott and Thiessen[11] carbon black and lampblack were, prior to 1914, used indiscriminately in the coloring of rubber.

Certainly many years elapsed before the value of gas black for reinforcing rubber was discovered. As late as 1914, practically all tire treads were white, the rubber being reinforced with zinc oxide.[12] A few black tires had appeared, but these contained only a small percentage of black used to give color to the tread.

There is a difference of opinion concerning the discovery of the remarkable value of gas black for reinforcing rubber. According to Twiss,[2] the discovery was made in England in 1910.[13] Records in this country,[14] forwarded from England in 1912, indicate, however, that the black British tires contained only a comparatively small percentage of gas black, apparently used to produce a distinguishing black color and it is very doubtful that the reinforcing value was appreciated. Just how much black these tires contained the writer has not been able to ascertain. They were of the new cord construction, which in itself added many miles to the tire life, and when manufacture was begun in this country, under British patent, it was obvious that these tires warranted better wearing treads. The old zinc oxide tread of previous years had lasted as long, if not longer than the carcass made of square woven fabric, but it now proved inadequate. This, coupled with the fact that the increased demand for tires had led to a shortage of zinc oxide with consequent rise in price[7] and that there was no known substitute, made American rubber chemists very active in searching for a better reinforcing agent. It is certain that to Oenslager, as has been stated in a very recent publication,[15] and J. D. Tew[14] goes the credit of developing this tougher tread through the use of higher percentages of gas black. To be sure they had the British formulas in their possession, but the product they developed was outstanding in its superiority. It would thus appear that the credit for developing the modern gas black tread, which has had such a phenomenal effect upon tire mileage, may be claimed for America. It was a matter of several years before a similar practice in tread reinforcing was adopted in Europe.

CLASSIFICATION OF CARBON BLACKS.

In general, the classification by Parkinson,[16] which is quite widely employed, will be used. It is *not* sufficient simply to distinguish between "gas" blacks and "oil" blacks, for in recent years distinct types of gas black have been developed, blacks which are widely different in their effect upon rubber. Again, it is true that "oil" blacks differ considerably in properties, the original lampblack having been improved remarkably chiefly through the efforts of investigators in Europe, where the use of natural gas for the production of "gas" blacks has not been developed. The nomenclature to be used is as follows:

(1) *Rubber Channel Black.*—This black, sometimes specifically designated as "carbon black," was the original black produced from natural gas. It is obtained by the incomplete combustion of natural gas, the flames from small burners being impinged upon metal surfaces or "channels," * on which the black is deposited. This black remains today the most valuable for rubber compounding, and the volume production (in 1929, 327,552,000 pounds of channel blacks for all purposes, or 89.4 per cent of the total carbon black produced in 1929 in the U. S.[17]) exceeds that of all other blacks by an enormous margin. It stands in a class by itself, rightly designated by Wiegand[18] as the "King of Pigments" for rubber compounding.

(2) *Acetylene Black.*—Produced by the explosive combustion of purified acetylene with a shortage of air in closed chambers, this carbon most closely approaches rubber channel black in properties. It is classified[2, 16] as intermediate between channel black and lampblack in particle size. It cannot compete in cost with channel black, with the prevailing price of natural gas, but in the event of the latter source of supply failing in future years, it is the most promising substitute so far developed.

(3) *Lampblack.*—This black is obtained by the incomplete combustion of carbonaceous materials such as oils, tars ("dead oil" from coal tar), resins and natural gas.[19] There are many different lampblacks produced depending upon the conditions of manufacture, which result in a more or less complete conversion of the resins, tar, etc., into carbon.† In general they contain larger amounts of extractable material than the other blacks.[20, 21] These blacks have specific uses where channel blacks fail to give the desired properties.

(4) *Thermal Decomposition Blacks.*—These blacks are made by the thermal decomposition of natural gas out of contact with air. The gas is passed into a decomposition chamber, heated to a temperature sufficient to dissociate the hydrocarbons into carbon and hydrogen. The effluent gas, consisting chiefly of hydrogen, may be employed for heating the gas and the decomposition chambers, or, in some cases, for diluting the natural gas. This latter procedure produces a different quality of carbon. Spear ‡ ascribes this to the dilution and not to the sweeping of the carbon out of the highly heated chamber at a more rapid rate, since he has trebled the rate in the absence of a diluent, without perceptibly changing the particle size. Thermal decomposition carbons are produced in much higher yield per 1,000 cu. ft. of gas than channel blacks; according to the patent literature[22] the yield is increased from less than two pounds by the channel process to as much as ten pounds. The theoretical yield of carbon from a thousand cubic feet of pure methane at

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* It was originally produced on cast iron plates or rolls.[5]

† Certain blacks (U. S. Pat. 1,758,152; U. S. Pat. 1,738,716), prepared from natural gas and developed within the last ten years, show such marked improvement over ordinary lampblack for use in rubber, that they might well be classified separately. They are, however, like lampblack, free-flame (not impingement) blacks.

‡ Private Communication (1931).

20° C. (68° F.) is approximately 31 lbs.; in mixtures of methane and ethane, this figure may run as high as 44 lbs.[28]

A recent modification of the channel process, evolved by Lewis,[24] involves a thermal decomposition of natural gas *prior* to burning by the regular channel method. The temperature maintained is such that no carbon is deposited during the preheating process, so the black produced is not a thermal decomposition black in a restricted sense. The process produces black of the quality of ordinary rubber channel black, according to the inventor, but the yield is very much greater. Such a process appears to have great significance from an economic standpoint.

Owing to the fact that channel black, as has already been pointed out, far surpasses all other blacks in importance in the rubber industry, this black will first be discussed. Of the available pigments, it represents the ultimate in state of subdivision and may well be classified as "ultra-colloidal" [25] in nature. When its influence on rubber—both cured and uncured—is understood, the properties imparted by the other blacks can be readily shown by comparison.

Physical Properties Imparted to Vulcanized Rubber by Rubber Channel Black.

Stress-Strain Relations.—Mention has already been made of the remarkable toughening and reinforcing action of channel black on rubber. This needs considerable elaboration before the extent of the effect is understood. Just what is meant by reinforcement? The dictionary definition, "to strengthen," fits the case. It was Wiegand [18] who first published data (in 1920) showing the effect of increasing volumes of channel black on rubber. The stress-strain curves (Fig. 1) which he presented showed the reinforcing effect; the breaking strength increased up to an addition of 30 volumes of black to 100 volumes of rubber and there was a steady progression of the curves towards the load axis, indicating increased toughness. This behavior was unapproached by any other pigment in the series which included practically all the fillers in common use in the rubber industry at that time—zinc oxide, lampblack, whiting, barytes, red oxide and clay.

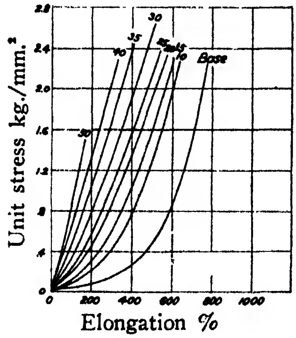

FIG. 1.—Stress-strain curves illustrating the effect of increasing the volumes of channel black on rubber.
Note.—The numbers on the curves refer to the volume loading.

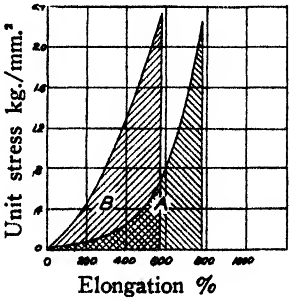

FIG. 2.—Resilient energy areas illustrating the effect of channel black on rubber.
A—Base mix.
B—20 volume loading with channel black.

Resilient Energy.—Expressing his results in terms of the energy of resilience, or work capacity, of the base mix (containing 5 per cent of sulfur and accelerated with litharge) as compared with the corresponding mix containing twenty volumes of black (by measuring the areas between the stress-strain curve and the elongation axis, Fig. 2) he showed that there was an increase in capacity for storing work of nearly 200 ft. lbs. per cu. in., a value nearly 150 per cent that of the base mix. These stress-strain curves for mixes containing large volumes of black approach the linear; thus these mixtures nearly obey Hooke's law (constant proportionality of stress to strain within the elastic limits), which rubber in itself does not do. This is indicative of the increase in rigidity (decrease in flabbiness) of such mixtures and taken together wth the high tensile and high work capacity explain the high wear resistance of such compounds.

Tensile Product.—Work published by North[26] later in the same year, corroborated Wiegand's findings. He expressed his results in terms of "tensile product," which is the product of the tensile strength, and the final length (at break), which closely approaches the strength based on actual cross-section at break. The writer believes this figure is now commonly accepted as of more value than the tensile figured on the original cross-section. Correcting his figures to the volume of rubber in each compound, North showed an increase in tensile product up to 20 volumes of channel black, beyond which loading there was a definite drop.

The resilient energy figures presented by Wiegand have been attacked by Blake[27] as giving an exaggerated picture of the reinforcement of rubber by channel black. It is his belief that channel black does not actually *increase* the strength of rubber, but that it only apparently does this, differing from most other pigments, in that it does not *decrease* the strength. In other words, the bond between channel black and rubber is stronger than that between rubber and rubber, so that the break occurs in the rubber matrix, and the strength of the mixture is that of the rubber, whereas with a pigment such as whiting, the bond between pigment and rubber is weaker than the cohesion of the rubber, and the rupture comes at the pigment-rubber interface and not in the matrix. Taking Wiegand's own figures (Fig. 1) and expressing them as tensile product in lbs. per sq. in., which Blake calls "molecular tensile strength," he concludes that, though the figures show a slight continuous falling off with increase in volume of black, this strength is constant within experimental error, with increase in black up to thirty volumes. (Table 1 and Fig. 3, Curve A.) While these data appear to substantiate Blake's claim, they are contrary to the basic concepts of the influence of materials of colloidal dimensions in a system such as the carbon-rubber system. To accept them

TABLE 1.

Volumes of Black	Elongation at Break (+ 1) (inches)	Tensile	Molecular Tensile
		lbs./sq. in.	
0	8.6	3,000	25,800
10	7.5	3,250	24,400
15	7.25	3,400	24,600
20	6.8	3,400	23,100
25	6.45	3,400	21,900
30	6.30	3,800	24,000
35	5.20	3,500	18,200
40	4.35	3,300	14,400

would require disregarding the fundamental theories concerning interfacial adsorption. However, in the face of such experimental data, the writer has felt it important in rebuttal to collect all the published data bearing on this subject.

Recent data obtained by Street in this laboratory[28] negatives Blake's contention (Table 2 and Fig. 3, Curve B). The mix in this case contained 2.8 parts of sulfur, 0.75 part of mercaptobenzothiazole, 7.5 parts of zinc oxide and 3.5 parts of stearic acid to 100 parts of rubber. The tensile figures were the maxima obtained over a range of cures at 280° F. It is clear from these results that there is a definite reinforcement in the presence of this organic accelerator. How far the accelerator influenced the results, the writer does not know.* It is certain that practically all commercial recipes to-day contain an organic accelerator, hence these results are highly significant from a commercial standpoint.

TABLE 2.

Black Weight (per cent)	Black Volume (per cent)	Elongation at Break (+1) (inches)	Tensile (lbs./sq. in.)	Tensile Product (lbs./sq. in.)	Increase (per cent)
0	0	7.60	2,850	21,600	—
25	13	7.15	4,000	28,600	32
35	18.1	6.75	4,000	27,000	25
45	23.3	6.40	3,850	24,600	14
55	28.5	6.00	3,900	23,400	8

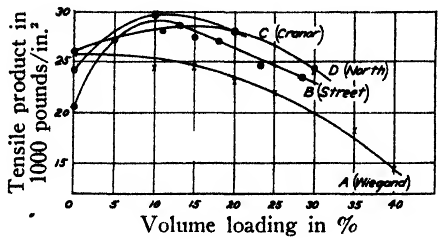

FIG. 3.—Effect of increasing volumes of channel black on tensile products.

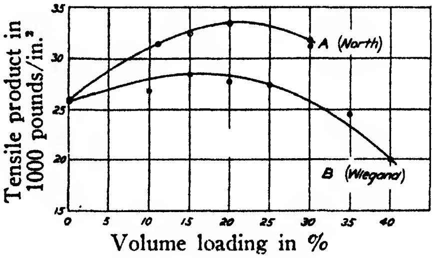

FIG. 4.—Effect of increasing volumes of channel black on tensile product (corrected to vols. of rubber).

The data of Cranor,[29] who also studied the effect of increasing volumes of channel black in a base mix containing an organic accelerator, are in agreement with those of Street. Recalculating Cranor's data as Blake did Wiegand's, the figures shown in Table 3 and plotted in Figure 3, Curve C, were obtained:

TABLE 3.

Volume of Black (per cent)	Elongation (+1) (inches)	Tensile (kgs./sq. cm.)	Tensile Product (kgs./sq. cm.)	Tensile Product (lbs./sq. in.)	Increase (per cent)
0	8.5	200	1,700	24,200	—
5	8.3	230	1,900	27,100	12
10	8.0	260	2,080	29,600	22
20	7.3	270	1,970	28,100	16

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* According to Park (Private Communication), a litharge mix, such as that used by Wiegand, does not bring out the real reinforcing value of a black in the absence of stearic acid.

The organic accelerator used in this case was an ethylidene-aniline and the sulfur ratio to the rubber 4 per cent.

To shed further light on this controversy, the data of North[26] were recalculated according to Blake's method (Table 4, and Fig. 3, Curve D).

TABLE 4.

Volumes of Black (per cent)	Elongation at Break (+ 1) (inches)	Tensile (lbs./sq. in.)	Tensile Product (lbs./sq. in.)
0	10.	2,600	26,000
11	8.6	3,260	28,000
15	8.	3,420	27,400
20	7.4	3,770	27,900
30	6.5	3,800	24,500

These data were obtained on a base mix containing no curing agent other than sulfur, and while the figures indicate only slight reinforcement, the trend is definite.

North has pointed out that in making such comparisons, the actual percentage of rubber in each mix should be taken into consideration, for as the pigment volume is increased the percentage of rubber decreases. For example, the mixture containing 25 volumes of black to 100 volumes of rubber actually contains only 80 per cent of rubber (100 ÷ 125). Correcting the figures in Table 4 in this manner, the data in Table 5 are obtained:

TABLE 5.

			Corrected to 100 Vols. Rubber		
Volumes of Black (per cent)	Rubber (per cent)	Elongation (+) (inches)	Tensile (lbs./sq. in.)	Tensile Product (lbs./sq. in.)	Increase (per cent)
0	100	10	2,600	26,000	—
11	90.1	8.6	3,620	31,500	21
15	87.	8.0	3,940	32,500	25
20	83.4	7.4	4,530	33,500	29
30	76.9	6.5	4,940	31,800	22

Here there can be little argument but that the carbon black has definitely reinforced the rubber (Fig. 4, Curve A). The same holds true, though to a lesser degree, if Blake's calculation of Wiegand's figures is corrected for volume of rubber (Table 6 and Fig. 4, Curve B).

TABLE 6.

		Corrected to 100 Vols. of Rubber	
Volumes of Black (per cent)	Molecular Tensile (lbs./sq. in.)	Tensile Product (lbs./sq. in.)	Increase (per cent)
0	25,800	25,800	—
10	24,400	26,800	3.9
15	24,600	29,400	10.
20	23,100	27,700	7.9
25	21,900	27,400	6.2
30	24,000	31,100	20.
35	18,200	24,500	—
40	14,400	20,000	—

This question of reinforcement has been covered in great detail, since it appears to the writer that it is of vital importance in the discussion of carbon blacks and rubber. It must be obvious from the data presented that channel blacks have a most unusual effect on the tensile properties as judged by either work capacity or tensile strength at rupture based on cross-section at break. If further data in this connection are desired, the work of Wiegand in which data are plotted and expressed as the ΔA function[80] or concavity factor,[81] should in addition be consulted. The former (*ΔA Function*) expresses the added proof resilience due to pigmentation over the entire range of concentrations in which the physical properties of the base mix are enhanced; the latter (*Concavity Factor*) expresses the concavity of the stress-strain curve with respect to the linear or Hooke's law behavior.

Reinforcing Volumes.

Most of the published data[18, 26, 29, 32] places the optimum loading of rubber channel black for maximum reinforcement at 20 to 25 volumes of black to 100 volumes of rubber, which corresponds to a 38.5 to 48 per cent loading by weight. Up to 40 volumes the resilient energy still exceeds that of the base mix, and Wiegand[33] considers this concentration the upper limit, in the present state of the art of dispersing black in rubber. Present practice in compounding tire treads is to hold the black in the neighborhood of 45 to 50 parts by weight to the rubber.[34] It is a surprising fact, that though channel black was in common use in tire treads by 1915, rubber technologists held the concentration down to comparatively low limits for nearly ten years, though costs, if not quality, should have stimulated them to the use of much higher concentrations. During the period from 1920 to 1925, the majority of the quality treads carried only 17 to 18 volumes, the remaining reinforcing pigment consisting of the expensive zinc oxide. [Here is a case where better quality was had at lower cost. J. A.]

It is, in the writer's opinion, a very safe prediction that the volume of channel black in tire treads will not long remain at the present levels. Further research on methods of improving the dispersion of black in rubber will undoubtedly lead to the use of higher concentrations in mill-mixed stocks. Already[2] work on latex dispersions has shown the possibility of incorporating 100 volume per cent or more, if the black be dispersed in the latex with the aid of protective colloids prior to coagulation.[35] Wiegand[33] calculates that even cubical or loose piling of the carbon particles in rubber would permit the incorporation of 100 per cent by volume on the rubber before the particles actually touched each other, while if tetrahedral or pyramidal piling obtained, upwards of 300 per cent by volume should be possible of incorporation. Blake's[27] calculations agree closely with those of Wiegand; in addition he estimates the possible loading with triangular piling at 179 volumes and with rhomboidal piling at 153 volumes, before the individual particles actually come in contact, provided there was perfect dispersion. Such volume loadings at ideal dispersion, the ultimate in compounding, are improbable of practical attainment and, as Blake points out, such close packing of the particles would lead to a product more like steel than rubber. To obtain the desirable properties of resilience and elasticity the film of rubber separating the particles must be considerably thicker, i.e. the volume loading must be considerably less than that theoretically possible. These figures illustrate, however, how far present practice, with a maximum loading of approximately 25 volumes, comes from the theoretically possible loadings, and should stimulate rubber technologists to increased effort in raising this figure, in the interest of greater reinforcement and higher abrasion resistance.

Stiffness.

The displacement of the stress-strain curves toward the stress axis, with increasing loading of rubber with channel black (Fig. 1), defines the stiffening effect of a black. With each increment of black, a greater load is required to elongate a sample of the vulcanized mixture a given percentage, or in other words, a higher so-called "modulus of elasticity" is obtained. Clearly such a stiffening if accompanied by no loss in tensile is an indication of reinforcement, and hence a desirable property. Spear and Moore[36] have found that the wetting equivalent as determined by the capacity of a black to take up neutral raw linseed oil, is a fairly reliable index of the stiffening power of a rubber channel black. They have also stated[36, 37] that there is no consistent inter-relationship between stiffness and tensile strength. A black of high stiffening power may produce a comparatively low tensile. According to Carson and Sebrell[38] an indication of the stiffening action of a black may be secured by measuring the amount of carbon, dispersed in a thin rubber cement, which cannot be centrifuged out in a given time. In practically all cases a high-modulus black showed a high carbon-in-suspension figure. There was, however, one bad discrepancy in their figures; two blacks producing identical modulus figures differed by 100 per cent in the amount remaining in suspension in a cement after a given period.

Hardness.

Hardness, measured by the distance a penetrating element under fixed load will sink into a block of rubber, is among the very important characteristics enhanced by blacks. It is closely related to stiffness measured at very low elongations, and may be defined as resistance to low deformation, while stiffness or modulus is the resistance to high deformation. Per volume of loading, channel black produces greater hardness than any other filler in use at the present time, according to Greider's figures.[39] This is true, with only one exception, as far as the writer is aware. Zimmerman's[40] figures on light magnesium carbonate at low volume loadings do not agree with Greider's. He has shown that up to 4 volume per cent loading, light magnesium carbonate produces greater hardness than channel black; beyond that percentage loading, channel black surpasses magnesium carbonate.

As Goodwin and Park[32] have pointed out, hardness is not necessarily related to modulus. One black may produce greater stiffness or modulus at say 400 per cent than the other, yet impart lower modulus at 50 per cent elongation ("hardness"). The value of hardness in rubber products, for example pneumatic treads and solid tires, needs little emphasis. "Wiping" or "Cupping Out" so prevalent in non-skid treads is obviously worse with a soft compound, than with one that resists deformation and flattening under load.

Hysteresis.

As Twiss[41] has stated, channel black causes more marked hysteresis than any of the other blacks. In rubber mixtures containing high volumes of channel black, the area between the extension stress-strain curve and the corresponding retraction curve is large, and this constitutes one, if not the chief, fault of this black. This characteristic, with which permanent-set is closely allied, limits the use of channel black for many purposes, as for example in solid tires, both for speed service and for use on electrically driven vehicles. The mechanical energy loss, as measured by the area of the hysteresis loop, appears as heat energy; and in a heavy block of rubber, from which the accumulated heat is not rapidly dissipated, owing to the low heat conductivity of both rubber and channel black, there is a rapid temperature rise. So great is this rise that, on vehicles operated at high speed and under heavy load in the summer time, the rubber in the center of the tire may actually reach the decomposition point, i.e. the rubber melts and becomes so hot that it actually undergoes destructive distillation with the formation of sufficient gas to "blow out." It is for this reason that the percentage of channel black in solid tires is held at a comparatively low figure, seldom exceeding 10 to 12 volumes to 100 volumes of rubber; for special high speed work its use is practically barred, only sufficient being added to give the compound the desired "blackness." Likewise in tires for electrically propelled vehicles, the channel black content must be kept low if minimum power loss is to be obtained. Here high efficiency in power transmission is demanded and hence a low hysteresis loss in the rubber. This efficiency, or resilience as Healy [42] describes it, is measured by various rebound tests, such as the rebound of a steel ball or of a pendulum striking a rigidly fixed block of rubber. Measured in this way, the addition of channel black to rubber causes a fall off in resilience from the very start.[42] Dawson [43] has demonstrated an interesting fact in connection with the hysteresis loss of rubber compounds containing channel black. Though a channel black compound (20 volume loading) showed the highest hysteresis loss, compared with a similar loading of zinc oxide, clay, barytes, magnesium carbonate and lampblack, the volume increase after repeated stressing (1,300 cycles to 200 per cent) was extremely small (0.2 per cent) and lower than that for any of the other pigments except lampblack, with which it was equal. This work is in close agreement with that of Schippel,[44] who compared the volume increases of rubber mixtures containing different pigments including rubber channel black, zinc oxide and barytes. In the case of the first two, the increases at 200 per cent elongation were in the neighborhood of 1 per cent, while the ground barytes compound increased under similar conditions approximately 13 per cent. These results are indicative of the strength of the bond between rubber and channel black particles.

Work of Retraction.

It is interesting to note at this point, after discussing the *extension* stress-strain curve, that some work has been done on the work of *retraction* as measured by the area between the retraction curve and the strain axis. Conover,[45] who has done this work, claims that this is practically constant regardless of the volume of black present. Though data were presented which indicated equivalent work of retraction whether the pigment loading was 5 volumes of channel black, 30 volumes of zinc oxide or 20 volumes of a clay, it is difficult to accept Conover's conclusion that the work of retraction is in general quite independent of either the kind or amount of the pigment used. Especially is this true with respect to different loadings with channel black, where the area under the extension curve increases so markedly with increase in volume of black up to 20 volumes. Nor do the figures substantiate this claim, for as closely as the writer can calculate from the curves presented, the work of retraction at 10-volume loading (600 per cent elongation) was approximately 20 per cent greater than at 5-volume loading of black. Conover himself points out differences in the mixes containing barytes (approximately 35 per cent at 600 per cent elongation and 20-volume loading), but fails to note the discrepancy in the channel black series. Certainly further data are necessary before his conclusions can be accepted.

Tear-Resistance.

There is no reinforcing pigment, volume for volume, which has such a remarkable enhancing effect on the resistance-to-tear of rubber, as rubber channel black. When such a black-rubber compound is subjected to a shearing stress, it does not tear uniformly nor smoothly, but irregularly as though it were full of knots.[7, 41] A well compounded and properly cured black tread stock is extremely difficult to tear at all by ordinary hand pulling methods, even though a cut has been made at which to start the tear. It is not unusual for such a compound to require 500 in. lbs. to tear a slit 1 inch in length in a sheet of rubber 1 inch thick (method of Zimmerman[46]). Such a figure is approximately twice as high as that obtained on the corresponding "pure gum" mix.

Abrasion.

It is obvious from the effects already discussed, that remarkable abrasion resistance must accompany the superior reinforcing effect of channel black. Davies[7] estimates that with a ratio of channel black to rubber of 1 to 4 (i.e. 13-volume loading) there may be expected an increase in wear-resistance of approximately 30 to 40 per cent as compared with zinc oxide. Spear, in 1923, stated that the wearing quality of rubber containing channel black is unsurpassed by any other known combination, and in the opinion of the writer, this statement still holds good.

Unfortunately the methods available for measuring the wear-resistance of rubber products have not been developed to the point where they give results which are comparable with road service. Perhaps they will never be developed to this point, for the factors influencing abrasive wear are so involved that it is doubtful whether any one machine can incorporate them all. As a result of this, the many estimates[25] of the extent to which channel black increases wear resistance in tire service (based on abrasion machine results) must be accepted with reservation. Such figures as those presented by Greider,[39] which indicate an 88 per cent increase (loose abrasive method of Sproull and Evans[47]) on adding 20 volume per cent of black to a base mix, accelerated with hexamethylenetetramine, are of interest in comparing the behavior of different substances, but must not be considered as more than indicative of direction, or relative merit. Tire manufacturers still must rely on road testing for the ultimate answer. Suffice it to say that the direction is unmistakable when substituting channel black for other pigments.

The writer believes that still to-day the rubber technologist places more reliance on resilient energy and ultimate tensile (tensile-product) criteria, together with hardness,[47] than on any abrasion machine data. It is necessary, of course, to keep in mind that those criteria based on breaking strength may be misleading if this is adversely affected, or erratic, due to coarse particles or grit in the compound. Gallie[48] has published figures showing the effect on tensile strength; he found that the addition of 5 per cent of grit (collected on an 80 mesh screen) was sufficient to reduce the tensile of a 95.5 per cent rubber: sulfur mix, 25 per cent. Twiss[41] has also presented figures on compounds containing a small proportion of grit. These indicate that the impaired tensile and hence resilient energy, are not reflected in abrasion resistance (Table 7).

TABLE 7. *Effect of Grit on Tensile Strength and Abrasion.*

Grit (per cent)	Tensile Strength (kgs./sq. mm.)	Abrasion Resistance
Essentially none	2.03	1.03
.09 *	1.84	1.06

Goodwin and Park[32] have obtained abrasion machine (Akron Standard Mold) data on stocks accelerated with mercaptobenzothiazole which are in complete disagreement with the optimum loading as found by Wiegand,[18] the resistance to abrasion continuing to increase with volume loading beyond the point of maximum tensile or resilient energy † but they hasten to state that "it must not be assumed that these data are indicative of road wear. Undoubtedly they are in some cases; in others it is quite certain that they are not." The anomalous nature of abrasion machine results is still further illustrated by their results in a series of tests with a base mix accelerated with litharge; the abrasion figures were in approximately *inverse* proportion to the tensile product, which is certainly contrary to road test experience. On the other hand, Grenquist,[49] working with another type of abrasion machine,[50] presented abrasion figures showing good correlation with tensile.

Resistance to Flex Cracking.

The literature is very meager concerning the influence of pigments on this important characteristic of compounded rubber. It has become a matter of increasing significance in these days when treads must be reinforced to the optimum loading to meet the requirements in wear demanded by the present day high-powered motor car. Owing to the high modulus and hardness produced by channel black, it is obvious that this pigment would present difficulties, and it is not at all uncommon to find tires deeply cracked at the base of the tread design on the tire shoulders, where flexing tends to be localized. Fortunately channel black, of all the reinforcing pigments, gives maximum resistance to flex checking per unit of wear resistance. It is clear that dispersion plays an important part in the tendency for compounded rubber to crack.[51]

Ageing.

Obviously all the value of a pigment may be lost if the compounded product fails to maintain its properties during its useful life. It may be said, in general, however, that the ageing of rubber compounds is more dependent upon the chemical state of cure and the heat conditions to which the rubber is subjected both during vulcanization and in service, than upon the reinforcing pigment employed. Furthermore, antioxidants or "anti-agers" and accelerators with antioxidant properties are now known, which make it possible to make almost any rubber mix age satisfactorily.

Reference to the use of blacks in the very early days for improving the weathering of rubber, has already been made.[8] In conjunction with ceresin wax, lampblack was later patented for protecting rubber thread from the influence of light, heat and atmospheric oxygen.[52]

The first aspersion to channel black from the standpoint of ageing was made by Ruby and Depew.[53] Using a high sulfur concentration (6 per cent to the rubber), with extremely high organic accelerator (1.5 per cent of hexa-

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* Removable by a "90" sieve.

† Probably attributable to increased hardness.—N.A.S.

methylenetetramine) they obtained surface hardening and cracking together with inferior tensiles with channel black as compared with zinc oxide, under artificial heat ageing. The recipe used accentuated the difference and the results were unquestionably largely due to a seriously "over-cured" or over-vulcanized condition and were not truly indicative of the different effects of the black and zinc oxide. With respect to such hardening or chipping of a channel black tread, due to poor ageing, Wiegand [54] immediately countered with the statement that "it just doesn't" and shortly thereafter C. Harold Smith [55] emphasized the protective influence of black towards light, due to its opacity, and against atmospheric oxygen, due to the closer knit structure of channel black rubber mixings.

This opinion was concurred in by Neal and Perrott.[10] Davies was not so emphatic,[7] but ascribed the sometimes observed tendency of a channel black tread in cutting service to "chunk out," as being due to the toughness of such stocks. This toughness will not permit smooth rapid wear, but rather, when cuts occur, will cause a somewhat ragged appearance, just because the torn pieces are so strong that they will not loosen and pull out—an entirely logical explanation in the writer's opinion. At any rate, the net result is longer wear, if with a less smooth appearance.

Greider,[56] Vogt,[57] and Somerville, Ball and Cope,[58] have all published data unfavorable to rubber channel black from the standpoint of ageing, based on accelerated ageing tests. The first investigator used a litharge accelerated formula with 5 per cent of sulfur to the rubber and heat aged at 71°C.; the second used a diphenylguanidine mix (0.75 per cent) with 4 per cent of sulfur and aged the samples both at 70° C. in air and at 60° C. in oxygen under pressure; Somerville, Ball and Cope worked with the same sulfur ratio and still higher diphenylguanidine (1.25 per cent) and conducted their ageing tests on stretched samples exposed to sunlight and to ozone. In all these data the sulfur or accelerator ratios were, in the writer's opinion, too high for obtaining the best ageing qualities but the direction is unquestionable. In Greider's work, channel black was inferior to zinc oxide, china clay and blanc fixe (9-volume loading). Vogt's figures showed outstanding decrease in tensile product for the channel black stock as compared with either the base mix or corresponding zinc oxide mix. The percentage of oxygen adsorbed, estimated by the increase in weight of the samples, also placed the channel black mix at the bottom of the list.

Somerville, Ball and Cope's work involved an entirely different type of ageing—weathering and ozone exposure—which has been shown to produce quite different results. The percentage deterioration as judged by tensile strength at the critical elongation for cracking (10 per cent) was greater in both types of exposure than in the corresponding compound containing an equal volume of whiting. Beyond the critical elongation, however, the channel black stock showed appreciation in the sunlight (17 days' exposure), while the whiting stock had definitely depreciated. Shepard, Krall and Morris [59] had previously shown that even so small a percentage as 0.1 per cent by weight of channel black added to a white stock to make it gray increased the tendency to sun-cracking when exposed in a stretched condition; this observation was confirmed by B. B. Evans,[60] who ran a similar experiment adding 1 per cent of channel black to 20 per cent (by volume) of zinc oxide, clay, and magnesium carbonate stocks respectively. Shepard, Krall and Morris also ran a direct comparison of channel black with zinc oxide and several other pigments at higher volume loading. Next to the base mix (pure gum stock) the channel black stock was the worst from the standpoint of checking.

When exposed in an *unstretched* condition, different results are obtained. Tener, Smith and Holt [61] report that the addition of two parts of channel black to a stock containing 50 parts of whiting, reduced the deterioration, when exposed to the weather for six months, to about one-fifth. A stock more highly compounded with black (a tread stock) showed practically no tendency to surface cracking in the *unstretched* condition, while lighter colored ones checked considerably.

The most recent work on this subject is that of Davey [62] whose results are significant, if one accepts the view that the ageing of rubber is entirely the result of chemical changes. He followed the increase in acetone extract and in the weight of rubber samples (10-volume per cent loading) heated in air at 100°C. The change in acetone extract as well as in weight was *least* in the case of the black stock as compared both with the base mix (3 per cent sulfur and 0.8 per cent mercaptobenzothiazole) and the zinc oxide stock (Table 8).

TABLE 8. *Effect of Heat at 100° C. on Acetone Extract and Weight.*

	Unheated			7 Days at 100° C.			14 Days at 100° C.		
	Control	Gas Black	Zinc Oxide	Control	Gas Black	Zinc Oxide	Control	Gas Black	Zinc Oxide
40 min. cure at 20 lbs. steam pressure.									
Acetone Extract* (per cent on rubber)	5.21	5.29	5.65	19.20	22.30	29.60	16.10	13.85	26.80
Increase in weight (per cent on rubber)	—	—	—	5.13	2.83	5.53	14.50	11.56	16.80
75 min. cure at 20 lbs. steam pressure.									
Acetone Extract* (per cent on rubber)	4.50	4.87	4.90	19.90	21.82	28.90			
Increase in weight (per cent on rubber)	—	—	—	9.05	6.73	7.68			

Davey states that he does not conclude from these results that zinc oxide is poorer than channel black from a heat ageing standpoint, pointing out that retardation of cure by the black undoubtedly influenced the results favorably. However, if the results on the 75 minute cure of the black mix be compared with the 40 minute cure of the zinc oxide stock after seven days at 100°C., it is seen that the gas black stock is still superior from the standpoint of acetone extract increase, and only slightly out of line on weight increase.

The work of Cox and Park [63] should also be cited, especially as their data cover natural ageing in the dark at approximately 65°F. for a period of 18 months. Their samples contained different blacks in loadings up to 40 volumes and with four distinctly different organic accelerators. Regardless of the accelerator used, the channel black stocks in general showed the maximum depreciation in tensile properties with the thermal decomposition black distinctly superior. Weight increases after ageing were in close agreement with loss in tensile properties, and Cox and Park concluded that the adsorbed oxygen was probably the cause of the greater deterioration of the channel black mixes. This opinion is in agreement with that of Beaver and Keller,[64] who found that the higher the amount of oxygen carried into their stocks, the more rapid was the deterioration under heat ageing. The amount of deteriora-

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* Corrected for free sulfur.

tion was, however, only approximately proportional to the amount of oxygen present in the black.

The writer's conclusion from the published data and his own experience, is that rubber channel black does have a detrimental effect on the ageing of vulcanized rubber, from the standpoint of tensile properties. On exposure to the weather *in a stretched condition,* there is an increase in the tendency for cracking; *in the unstretched condition,* however, the black reduces the tendency to form a hard brittle surface crust or skin that will eventually become rough and eroded on continued exposure, and the net result is a superior stock for most purposes.

Furthermore, if properly compounded as regards sulfur ratio and organic accelerator and protected with a suitable antioxidant, the detrimental effect of black on the tensile properties can be completely offset, and the result is that the present day black treads leave little to be desired from the standpoint of ageing. As Schidrowitz [65] has put it, such a thing as the perishing of a properly compounded and vulcanized black tire is substantially unknown.

PROPERTIES IMPARTED TO UNCURED RUBBER BY RUBBER CHANNEL BLACK.

Mixing.

While the properties conferred upon vulcanized rubber by channel black are of the greater importance, and for that reason were covered first, those conferred upon the unvulcanized, or raw rubber, are not less interesting and striking. It was immediately learned that this finely divided pigment was a difficult one to handle and incorporate in rubber. Owing to its fineness and relatively low specific gravity, there is a dust nuisance and technologists early attempted to eliminate or reduce this. Through treatment with water [66] and other substances such as kerosene [67] or rosin oil,[68] with or without evaporating the liquid before incorporation with the rubber, much of the dustiness was avoided. This, however, was a costly and inconvenient method of solving the problem, and it is now common practice to single or double press channel black hydraulically after bagging, in this way compacting it. Some technologists [2] question this procedure, as its effect is diametrically opposed to what it is attempted to accomplish in milling black into rubber, i.e. to completely disperse it, but inasmuch as the black becomes packed and pressed anyway in going through the "bite" of the mill rolls, it is doubtful that any damage is done through pre-pressing.[7] It appears to the writer that with the present practice of using enclosed mixers in place of mill rolls for incorporating powders into rubber, the advisability of pressing merits further investigation, for it seems improbable that in these mixers the unpressed black would become compacted so badly as on mixing rolls. Of course, another thing to be taken into consideration in this connection is that it takes longer to incorporate *un*pressed black than pressed black.[69]

Though macroscopic observations, such as those based on the appearance and color of rubber which has been mixed with a very small proportion—0.1 per cent or less—of black,[2] might indicate that channel black is easily dispersed in and wetted by rubber, one does not get this impression on observing tread stock with a high volume of black during mixing. The batch may become very hot (above the temperature of boiling water) and the black disappears slowly. Nor does microscopic examination support a theory of easy wetting, as both Green [70] and Grenquist [71] have pointed out. In fact, it is very difficult to get the black properly incorporated and the heat developed is at times so high that a lumpy, "scorched" mix is obtained, even when no curing ingredients are present, as in the preparation of a master batch of black with rubber. Davies[7] has ascribed this to oxygen vulcanization, the oxygen of the air, at the high temperatures developed, chemically uniting with the rubber hydrocarbon just as sulfur does. Johnson[72] has found at least in two cases where this lumpy condition was encountered, that the blacks were abnormally low in volatile matter; and he theorizes that the gas contained in channel black perhaps acts as a lubricant, assisting dispersion into the rubber. Endres[73] takes quite the opposite view, postulating that the reason for difficulty in milling carbon black into rubber is due to the adsorbed gases, these forming a surface film which prevents contact between the black and the rubber. He believes, however, that it is just this situation that prevents agglomeration and eventually gives complete dispersion. Goodwin and Park[69] suggest that excessive flocculation made possible by the increased mobility of the rubber at the high temperature may be the cause of this trouble.

The high heat developed in mixing channel black with rubber is attributed by Kirchhof[74] to three things: the long mixing time required, hence the accumulation of frictional heat due to working the rubber; the heat of wetting: and the increased stiffness of the batch as the black becomes dispersed, which increases the friction. This explanation appears to fit the case.

It is certain that this heating effect is concomitant with quality in a black. The more difficult it is to get it incorporated, the more pronounced its reinforcing effect. Wiegand[25] has dwelt on this at length, vigorously objecting to the claim made for some of the soft oil and thermal decomposition blacks that they are superior because of the ease of mixing with rubber. He points out that ease of incorporation "is a striking ocular demonstration of the inferiority of a black," for it is an indication of larger particle size, i.e. lower specific surface. The large amount of work expended in dispersing channel black is not lost but reappears in the work capacity of the product, according to Wiegand. Esch[75] judges the quality of a black by the amount that can be incorporated before reaching the point where the mill cannot be operated owing to the stiffness of the batch; the lesser the quantity, the better the black.

Wiegand[25] has always maintained that channel black should be added to a rubber batch, before the rubber has been "broken down" or masticated too much, i.e. that the plasticity should not be decreased too much before adding the black, as the grinding action on the powder is impaired. It is for this reason that he recommends[34, 76] adding only the minimum quantity of softener, such for example as pine tar or stearic acid, prior to the addition of the black, adding the remainder, necessary for subsequent processing reasons, after the black has all been ground in. The writer believes this procedure is rather generally practiced in the industry, though experience has proven that having the rubber too stiff when the black is added, results in serious aggregation of the pigment and in a lumpy poorly dispersed stock. Wiegand's procedure appears to be more practical in the internal mixer, than on the ordinary mixing rolls.

Spear[77] contends that the milling required to incorporate a pigment, which is so difficult to disperse as channel black, tends to degrade the rubber. For that reason he[78] has always favored hot milling (somewhat above 100°C.) for a shorter period, in this way cutting down on the mechanical break-down, since the heat increases the plasticity. To this method he, and his co-worker Moore, ascribe their success in obtaining excellent dispersion of carbon blacks, as judged by photomicrographs. The reader will note that this procedure is exactly opposite to that of Wiegand, who recommends having the rubber as tough as possible in order to obtain the maximum grinding effect. From the standpoint of degradation of the rubber, Spear and Moore's method may have merit. Though it is difficult to prove any serious loss in properties of the rubber with the ordinary periods of milling, it probably occurs to some extent. The ordinary period for factory mixing, which seldom exceeds 30 to 40 minutes with 250-300 lb. batches, is the minimum that can be employed. Heating a mill prior to starting a batch, i.e. working on hot mills, has serious limitations, in these days when extremely active accelerators are employed, for hot milling may result in premature vulcanization or "scorching" on the mills. Stevens[79] also believes that the rubber is likely to be somewhat degraded during the incorporation of channel black owing to the advanced stage to which the mixing must be carried in order to disperse the black. Nor does Wiegand[34] ignore the effect of such grinding on the rubber itself. He designates the dry mixing of channel black into rubber as "terrible" and urges development work to find out how to incorporate carbon black without "tearing the rubber substance to pieces and degrading it." The answer would appear to be the incorporation of black with latex prior to coagulation.[2, 33, 35, 79, 80, 81]

Before leaving the subject of mixing, it is interesting and rather surprising to note that Goodwin and Park[69] have found it possible to identify different blacks by their characteristic odors during milling, due to the different non-carbon materials adsorbed on the blacks.

Plasticity.

The stiffening effect of channel black on vulcanized rubber has already been discussed. It is obvious that there would be a similar effect on introducing this material into raw rubber. As more and more black is introduced, the mixture becomes stiffer and stiffer. Master batches, on cooling, become so hard and stiff that great care has to be exercised in warming them up for subsequent operations, or the mill rolls or housings may be broken. High concentration master batches must first be run through a cracker before the warming-up operation. Spear[77] and Twiss[41] have both made mention of this stiffening action and Grenquist[49] has recently brought out the interesting fact, using a modified Williams plastometer,[82] that even after the black has all disappeared into the batch, the latter continues to stiffen for a considerable period. This would not be predicted as the plasticizing influence of further milling would be expected to offset any further stiffening influence of the black. This effect continued for more than 6 minutes additional milling on a laboratory mill, where breakdown occurs at a rapid rate. In other words, channel black has a definite and powerful reinforcing effect on raw rubber prior to vulcanization. Twiss[83] considers the action comparable with that which occurs when a pure gum stock is vulcanized, becoming stiffer and stiffer with increase in curing period. He uses this fact in support of his theory that many of the effects of vulcanization may be explained by the formation of a colloidal dispersion of a rubber-sulfide in a matrix of chemically unchanged rubber.

A most interesting indication of this reinforcing effect has been shown by Kröger and Yao[84] in an investigation of the behavior of raw rubber and channel black mixtures at low temperatures (—20° to —65° C.). The optimum absorption of energy (resilient energy) was obtained at —25° C.

Present practice in pneumatic tread compounding is to use a minimum of zinc oxide—only enough for the complete activation of the accelerator employed. This has resulted in making the stocks handle less smoothly in the factory. This is perhaps entirely due to replacing the zinc oxide by an equivalent volume of channel black, but Hurlston[85] believes that zinc oxide, owing to its softening effect during mixing, produces a better distribution of the black. Since no data were presented, this point will bear further investigation. Grenquist [49] feels that just the reverse is true, having reached the conclusion through his microscopic studies that there is an antagonistic reaction of zinc oxide on the dispersion of channel black. He assumes this to be due to the depletion of the natural fatty acids of the rubber through the formation of zinc salts.

Viscosity of Carbon Black Rubber Sols.

The effect of carbon black on the viscosity of rubber sols is, to the writer, a most interesting one from a theoretical standpoint. Most uncured rubber mixes disperse readily in such a solvent as benzol or gasoline. In fact it is a common procedure for determining whether "set-up" or premature vulcanization has occurred in a mixing, to test its "solubility" in these solvents; for vulcanized rubber swells, but will not form a sol. To all appearances, channel black mixes containing 25 or more volume per cent [69] of black, behave exactly like vulcanized rubber in this respect. There is, however, a marked difference, in that a sol is really formed, but the sol contains rubber *only*. Though much swollen in size, the piece of black stock retains its shape, but part of the rubber has passed into the solvent, giving a perfectly clear sol. LeBlanc, Kröger and Kloz [86] state that they are able to arrange a series of blacks in the order of their reinforcing quality by estimating the dispersibility of the rubber-black mixture in benzol, or better, by determining the viscosities of the sols formed from the complete dispersion of lower volume loadings. Pavlenko and Nazarov [87] rely on a similar test conducted in a somewhat different manner. They stir the black to be tested into a 5 per cent rubber sol in xylene and measure the relative viscosities when equilibrium, or the peak viscosity, is obtained. The higher the viscosity and the longer it takes to disperse the black in the rubber sol, the higher the tensile strength of the corresponding vulcanizates. These investigators consider the viscosity test a very reliable guide to the quality of a black.

Stamberger's [88] work is interesting in this connection. By measuring the amount of sediment formed when a filler-rubber mix (12 volume per cent) was dispersed in benzol, he was able to determine how much of the pigment diffused with the rubber. With this volume loading, channel black diffused 100 per cent; zinc oxide 98 per cent; magnesium carbonate 87.5 per cent and barytes hardly at all (less than 0.5 per cent). In other words the three most powerful reinforcing agents for rubber gave little or no sediment, while the inert barytes settled out almost completely. Note how little specific gravity influenced the results—channel black 1.77, zinc oxide 5.65, barytes 4.35. In this connection it is interesting to note that Carson and Sebrell [88] were unable, even on high dilution, to completely centrifuge channel black from a rubber cement, the black was held so tenaciously.

Stamberger attributes these results to adsorption; they indicate certainly a very strong union between rubber and channel black. With a higher volume loading of black (20 per cent), a result similar to that of Goodwin and Park [69] was obtained—swelling without diffusion of the black. This behavior, similar to that of unmilled rubber, is ascribed by Stamberger to the formation of a new gel structure. In Depew's [89] opinion, it is flocculation of the channel black that is responsible for it, resulting in the formation of a barrier of almost continuous pigment phase, which acts somewhat like a semi-permeable membrane and does not allow the rubber aggregates to pass through.

Rate of Cure.

One becomes accustomed to the use of superlatives in the literature of channel black; the claims of excellence mount higher and higher, but only one over-enthusiastic author [90] has had the temerity to include among its virtues, that "it reduces the time of cure." It would be fortunate if this were true; but the contrary is the case. The writer knows of no case where channel black does not retard cure and, in some cases, as in the presence of certain of the aldehyde amine accelerators the retardation is so great that the use of the particular accelerator has to be abandoned, for such quantities must be added that the cost is prohibitive.

This undesirable effect of channel black is now known to be connected with the volatile matter,[72] oxygen content [64, 91] and accelerator adsorption.[87, 41, 91, 92] Davies [7] pointed out that in replacing zinc oxide by carbon black the appreciably lower thermal conductivity of the latter would result in an apparent retardation of cure. This undoubtedly is a factor but, of course, does not enter into the case when comparing a pure gum base mix with and without channel black, for the heat conductivity of rubber is lower than that of carbon black. This retarding effect of blacks has an interesting analogy in their effect on the drying time of linseed oil.[93]

THEORIES OF REINFORCEMENT.

The reader has perhaps wondered why, in dealing with rubber and carbon blacks from a colloidal standpoint, the theories underlying their application were not treated, at the beginning. The writer has deliberately chosen to delay this discussion until an extensive presentation of the facts of reinforcement had been completed. The hypotheses and underlying theories should now be more easily understood and applied.

Particle Size and Surface Energy.

In the early papers dealing with reinforcement, the effect was attributed almost entirely to the state of subdivision or particle size. Wiegand [18] interpreted his data in the light of particle size and specific surface, calculating from the average diameter of the particles of channel black (microscopically determined) that one cubic inch would develop a surface in the neighborhood of 2,000,000 sq. in., or 50,000,000 sq. in. to the lb. The pigments studied in this series lined up in reinforcing effect in the order of the calculated surface, with the exception of zinc oxide, and Wiegand attributed its exceptional behavior to some difference in the surface tension.

The average particle size of channel black has been variously estimated through ultramicroscopic studies. The figure of 150 millimicrons [70] has been selected by Whitby [94] for use in the International Critical Tables. Grenquist [95] and Parkinson [16] agree in placing the upper limit at 200 mμ, with the lower limit problematical. Wiegand [25] used a figure of 50 mμ, while Parkinson [16] and Twiss [41] believe that a considerable proportion of quality channel black consists of particles smaller than that. Grenquist [95] places the lower limit at 15 mμ, but Spear,[77] while agreeing with Endres [78] on an average size between 100 and 200 mμ, believes there is a very great variety in the diameter of the various particles—some being beyond the resolving power of the microscope, some showing marked Brownian movement, while still other particles are easily seen at comparatively low magnifications. The colloidal portion not detectable in the microscope diffracts light and the resulting color is yellow or reddish yellow. From the yellow undertone of dispersions of channel black in rubber as compared with various colloidal suspensions in liquids, which are ordinarily dark gray, Spear concludes that channel black disperses as well, if not better, in rubber than in other media.

It is interesting to compare the size of the latex particle with that of rubber channel black. The majority of the latex particles vary in size, from 500 mμ up to 3,000 mμ according to Hauser,[96] though there are always some particles still smaller. In other words, channel black is much smaller in average particle size. This is simply pointed out as an interesting fact; that it has any significance in the reinforcing of rubber by black is hardly likely, for the milling process breaks up the original latex particle to a very large extent.[95] It is, however, of interest, in connection with the dispersion of channel black in latex, as is also the fact that carbon blacks ordinarily carry a negative charge when in contact with water, as is the case with the latex particle. Kruyt and de Kadt[97] in their study of sugar black have shown that this charge may be reversed by heating to 1,000° C. in the absence of air, and then may again be made negative by heating at lower temperature (400° C.) in oxygen. Perhaps the most interesting thing to the rubber chemist about this reversal of charge, is that the capacity to be wetted changes according to these authors. As far as the writer is aware, the literature contains no direct reference to the charge carried by channel black manufactued for use in rubber.

Zone of Maximum Colloidality.*

Whether there is a limit to the particle size beyond which further subdivision will fail to give added reinforcement has been the subject of much discussion. Alexander[98] has presented the theory that there is a zone of maximum colloidality, at a particle size in the neighborhood of 5 mμ, beyond which the reinforcing power of colloidal particles should fall off. For each system in which there is a dispersed phase there is an optimum fineness, and when this is exceeded, the properties, such as viscosity, are reduced. The lowest estimate of the size of the finest particles in channel black has been placed at about 15 mμ[95] with the majority of the particles many times this size.

Spear,[77] Endres[78] and Twiss[2] have discussed this theory in connection with rubber reinforcement, pointing out that sulfur and other substances which dissolve in rubber and hence are in a molecular state of subdivision, show no reinforcing effect. This is attributed by Alexander[99] to the kinetic activity or strain towards activity of the particle, this latter being so great that the particle tends to become detached. In a colloidal dispersion in a fluid where the particle has a size of say 5 mμ or less, the Brownian motion is extremely rapid and the kinetic motion increases more rapidly, with decreasing diameter, than the total surface increases. As a result in rubber, the kinetic strain of the particle becomes so great that the matrix will become more plastic instead of being reinforced. Inasmuch as Spear[100] has covered this point in great detail in the chapter on "The Structure of Rubber" in this volume, further comment on this interesting theory will not be made.

Just what the limit of particle size in rubber reinforcement is, is not known. The finest material with which the rubber technologist has worked up to the present is channel black. There is no concrete evidence[16] to indicate that this is the low limit of subdivision, although at least one investigator[101] feels that the value of still finer state of subdivision is doubtful. Still better reinforcing agents must, according to Spear, be irregular in shape, i.e. have still greater total surface and surface energy, without increasing the kinetic activity through decrease in particle diameter.

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* *See also* paper by J. Alexander in Vol. I of this series. J. A.

Particle Shape.

This brings us to a discussion of the particle shape of channel black. Most rubber technologists doubt that the shape of the ultimate particle has ever been seen. Green,[70] in his extensive study of the particle size of rubber compounding ingredients, makes no mention of the shape of the channel black particle.

There has been considerable discussion even as to whether it is amorphous or crystalline. Clark, Aborn and Brugmann [102] have studied various carbons by means of X-rays and conclude that they range from amorphous active charcoal through a para-crystalline state, where the crystal planes are still too few and distorted to produce measureable X-ray crystal interferences, then to colloidal graphite and finally to the definitely crystalline graphite. Clark's [103] work certainly leads to the conclusion that channel black is crystalline or para-crystalline in nature, for the diffraction interference lines are quite definite. While adsorption tests on channel black show that it is not in a high state of "activation," it is interesting to note the recent X-ray work of Barker,[104] which indicates that the heat activation of carbons is accompanied by a partial conversion into graphite crystals of colloidal dimensions. Pickles [105] concludes from an X-ray examination of various carbon blacks made at the Woolwich Arsenal (England) that the various blacks, including acetylene and oil blacks, probably *all* consist of mixtures of the crystalline and amorphous varieties of carbon. Grenquist [95] from his study of channel black under the ultramicroscope records the same opinion.*

There is certainly distinct evidence of anisotropy in channel black stocks. It is, to be sure, less marked than with any other powder used in rubber compounding, but nevertheless it does occur. Goodwin and Park [69] first called attention to this, pointing out that the stress-strain curves of a rubber sample containing channel black, cut with and across the calender grain, were appreciably different. Grenquist [95] has reached the same conclusion from his ultramicroscopic study of channel black suspensions, confirming the observations of Lachs,[106] and has made the statement that, in his opinion, a sample of channel black contains both isotropic and anisotropic particles, the latter showing a much greater tendency to aggregation. It is instructive at this point to refer to the work of Pohle,[51] in which he describes experiments involving the alternate application of heat and pressure to micro-sections of a vulcanized channel black-rubber mixture. He succeeded, thereby, in splitting it into minute lamellae, much as a stock containing a highly anisotropic clay can be readily split along parallel planes into smooth layers.

To what extent the channel black particle deviates from the spherical is not known. It is certainly highly speculative to ascribe a burr or star-like shape as does Spear.[77] As far as the writer is aware, there is no experimental evidence to support such an hypothesis and as Parkinson [16] has stated, it is unlikely that any known method for determining particle shape would be capable of detecting it. To Grenquist's [95] eye, the individual particles appeared practically spherical. Schidrowitz, however, had apparently accepted the burr hypothesis,[107] while Thiessen has stated in the discussion of Spear's paper [77] that, as far as he was able to judge, the particle was oblong, or oval in shape.†

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* *See also* paper by G. L. Clark in this volume. J. A.

† The facts stated indicate that the primary particles (protones) are various in size and may be variously aggregated into secondary particle groups (polyones). Microscopic and ultramicroscopic images are often illusory. The azimuth ultramicroscope might give evidence as to the existence of rod-shaped aggregates.—J. A.

Plastic Solid Film Hypothesis.

It was Spear[77] who applied the theory of elastic films, propounded by Wilson and Ries[108] and based on the rigid properties of thin films, to the reinforcement of rubber. The writer will not discuss this in detail as Spear has gone into this at considerable length in this volume.[100] With the strong force of adhesion which undoubtedly exists between rubber and channel black, as is obvious from the work of Schippel,[44] Green,[109] and Endres,[78] it is clear that when a rubber-carbon black mix is stretched with resultant lateral contraction, the presence of the black with its very large surface will cause the formation of an enormous number of minute films. The stiffness of rubber-gas black mixes, as well as the enhanced tensile strength, would be logical sequences of the formation of such films, according to the Wilson theory. The writer finds this conception very logical; Wiegand[33] pronounced it the "most stimulating hypothesis so far advanced," though he found it difficult to explain through its application the anomalous behavior of certain pigments such for example as lithopone which exhibits little or no reinforcement of rubber.

Anchorage; Continuity of Stress; Uniformity of Stress.

Elaborating on his earlier surface energy theory, Wiegand[33] ascribes the reinforcement of rubber by channel black to the three factors—anchorage, continuity of stress and uniformity of stress. The first—firm anchorage of the extremely fine colloidal particles—is an accepted fact. There is no weakening through separation from the matrix during extension, hence there is continuity of stress throughout the system. The homogeneity of structure means that a stress will not become localized, that is, each part of the mass will carry its portion of the load and the stress will thus be uniformly distributed.

Extension of the Monomolecular Film Hypothesis.

McBain and Davies,[110] extending the Langmuir-Harkins monomolecular film theory to the layers immediately beneath the surface of a solution, have introduced the conception that there are chains of oriented molecules of solute extending far below the actual air-water interface (Fig. 5). They apply this to explain the viscosity of liquids in which solid particles are suspended and

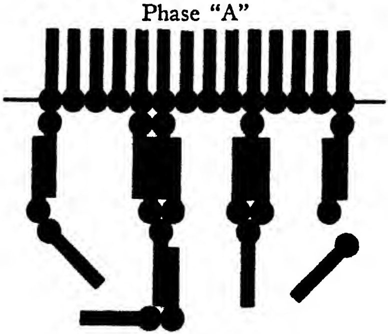

Fig. 5.—Orientation of rubber molecules at rubber-carbon black interface (McBain and Davies).
Phase "A"—Carbon black.
Phase "B"—Rubber.

include the reinforcement of rubber in the examples cited. According to this theory, as the writer interprets it, the surface effect of the oriented molecules of rubber at the interface of the carbon (Phase A) and rubber (Phase B) would be enhanced by chains of oriented rubber molecules below the surface and extending into the surrounding rubber. The finer the particles, i.e. the more carbon surface presented, the greater, of course, would be the reinforcing effect; and with high volume loading of well-dispersed particles the zones of influence would be contiguous or even over-lapping. Such over-lapping of the zones should contribute greatly to the strength of the matrix.

An assumption that rubber must have a marked degree of polarity in order to become adsorbed and oriented at the carbon black surface is unnecessary. Hydrocarbons, such as normal hexane or benzene (essentially non-polar) are, for example, adsorbed to a greater extent by carbon black than is water (polar), according to Bartell and Osterhof.[111]

In the writer's opinion, this is a most stimulating conception, offering an explanation, for example, for the astonishing abrasion resistance of a channel black tread stock. With such a conception there is no need of assuming an irregular or burr-like surface of the particle to explain the reinforcement.

Depew[112] has expressed a somewhat similar view, though he does not refer to these authors. He assumes that surrounding each carbon particle there is a zone of influence within which the strength of the rubber is augmented by the particle and that when the particles are sufficiently closely packed, the zones meet, and the matrix as a whole becomes stronger and stiffer.

Wetting.

It is obvious that any finely divided material which reinforces rubber or any other vehicle, must be wetted to a high degree by the vehicle. Methods of measuring this property in a rubber-channel black system are not well developed, and it is readily seen why this is the case. Owing to the viscous nature of this plastic, methods such as that developed by Bartell and Osterhof[111] are difficult to apply.

There have been many experiments made on pigment wetting in vehicles other than rubber. Besides the very ingenious experiments of Bartell and Osterhof mentioned above, there are the simple experiments first described by Green[113] and attributed to F. P. Ingalls by Depew.[114] The original experiments were made with zinc oxide, which was made up into a thick paste with kerosene. When the consistency was such that the mass was sufficiently plastic to retain its form without flowing or crumbling, a single drop of blown poppy seed oil was added. On stirring this in, the mass immediately lost its form and was sufficiently fluid to pour. Photomicrographs made before and after the addition of the oil showed that in the first instance the pigment was in a highly flocculated condition, while in the second instance the flocculated pigment was completely deflocculated and dispersed. It was obvious that the poppy seed oil had diminished the surface energy in the solid-liquid interface and thereby produced deflocculation. Bierer and Davis[115] repeated this test and showed that the same effect could be produced by stearic acid, oleic acid, rosin and various other acidic materials, including the acetone extract of raw rubber. They also used other vehicles such as turpentine and xylene.

Similar pastes with carbon black behaved quite differently. In the first place the amounts of vehicle required with a given weight of powder to produce a paste of approximately the same consistency varied considerably; ten grams of zinc oxide required 10 cc. of kerosene, while the same weight of carbon black required 25 cc. This was of course to be expected, for the volume of the gas black was more than three times as great, and the number of particles even greater. Furthermore, only a few materials would bring about the deflocculation of carbon black. Stearic acid was not listed among these, though degras and a certain non-acidic organic accelerator (triethyl-trimethylene-triamine stearate) did cause the "thinning." These authors also pointed out that sodium oleate produced deflocculation of a carbon black-water paste. Bancroft [116] has mentioned the difficulty in wetting carbon black with water, pointing out that this difficulty can be removed if the oily material in the black is removed by a preliminary treatment with superheated steam. After such a treatment, according to Bancroft, the black is rapidly dispersed by water and the liquid bubbles like soda water due to the escape of the adsorbed gases.

Depew [114] also studied the carbon black-kerosene paste and found that he did not get wetting or dispersion on adding either stearic acid or blown poppy seed oil. He carried his experiments over into unvulcanized rubber compounds [89] and found that the addition of stearic acid to zinc oxide (an especially finely divided grade) and carbon black mixes, which would not disperse in benzene, resulted in greatly increased dispersion in the case of the zinc oxide, without any noticeable change in the case of the carbon black mix.

It is Blake's [27, 117] contention that there is already sufficient acidic material in high grade plantation sheet to form a monomolecular film around each particle of black up to 30 volume per cent loading, and he presents calculations to prove it. He believes that these acidic materials, with polar molecules consisting of carboxyl groups attached to long hydrocarbon chains, become oriented at the surface of the carbon black particles, the carboxyl groups being adsorbed by the carbon particle and the hydrocarbon chain adsorbed in, or dissolved by, the rubber hydrocarbon; in other words, that the carbon black is wetted by the acid and not by the rubber. The figures presented by Blake are, however, far from convincing. As Parkinson [16] has commented, Blake's calculations are based on the assumption that the average size of the channel black particle is 200 mμ; this is undoubtedly much too large, so that his conclusion, that there is normally sufficient natural acid in rubber to form a monomolecular film of fatty acid around each particle, is quite certainly inaccurate. According to Parkinson, three to four times as much fatty acid as calculated by Blake would be necessary.

Cotton [118] has also attacked Blake's theory concerning the function of stearic acid, on the ground that it is founded upon inadequate experimental data and contrary to the results of others, which indicate that stearic acid has little or no effect on the dispersion of carbon black. If Blake's hypothesis is correct, it should be difficult, or at least more difficult, to disperse carbon black in rubber from which the rubber resins and acidic materials had been removed by extraction with acetone. Grenquist [95] has reported that this is the case. Parkinson [16] on the other hand has reported no difficulty in mixing channel black in acetone extracted rubber and has stated that microscopic examination of the mixes indicated that the black was quite as well dispersed in the extracted rubber as in the unextracted.

Goodwin and Park [82] give it as their experience that stearic acid is actually detrimental to cured properties in a pure gum mix in the absence of zinc oxide. It is their belief that free fatty acid is not responsible for the improvement in channel black stocks when stearic acid is added. If better dispersion of the blacks resulted, the cured stocks should be softer, which is not the case; nor do they believe that the zinc soaps formed from the zinc oxide and stearic acid act as dispersing agents for the black. It is their conclusion that the effect of stearic acid is that of the zinc or other soap-forming materials on the rubber gel itself, and they cite the fact that zinc stearate improves the quality of a pure gum stock.

Though stearic acid may have no value from the standpoint of improving the dispersion of channel black in rubber, there are other and sufficient reasons why its use in high percentage in channel black mixes has become so prevalent. In the first place, as Depew [114] has pointed out, stearic acid has a marked softening action on rubber, surpassing in this respect most of the common softeners used in rubber compounding, as has been shown by Zimmerman and Cooper.[119] Again certain organic accelerators, notably mercaptobenzothiazole, require the presence of a considerable quantity of an acidic material, such as stearic acid, to bring out their full activity.

Opinions differ as to the ease of wetting channel black. As already mentioned, Spear [77] believes that carbon black disperses as well, if not better, in rubber than in other media. Endres [73] feels that zinc oxide and carbon black are the only common rubber fillers that are completely wetted by rubber on the mill. Grenquist [71] agrees that zinc oxide is well wetted by rubber, but concludes that carbon black is wetted less readily. It is the writer's view, that carbon black leaves much to be desired in this respect, and that when it is learned how to wet carbon black better or more completely, much higher concentrations will be used in tire treads and other articles where abrasion resistance is vital. Wiegand [38] has also expressed the view that at the present time a large percentage of the reinforcing power of carbon black is being wasted because of imperfect wetting.

Heat of Wetting.

Hock [120] pointed out the fact that when a rubber-reinforcing pigment system is dispersed or swollen in benzene, there is an evolution of heat, which can be measured calorimetrically. According to Hock, this is not the sum of the negative heat of swelling of the same quantity of rubber and the heat of wetting of the same quantity of pigment, measured separately, but shows a distinctly higher value. The difference represents the heat of adhesion or heat of wetting of the filler by rubber. From his measurements, he concludes that only about one-half of the total surface energy (calorimetrically measured) plays a part in the reinforcement of rubber. In other words, only about half of the reinforcing value of black is being utilized. The data to which Hock referred were obtained by Boström [121] and Hartner [122] on channel black-rubber mixtures containing various concentrations of black. By measuring the absorption of heat when the rubber alone was swelled in benzene (1.18 cal./gram of mix)—28 parts of black to 72 parts of rubber by weight—the heat of wetting of the black by itself in benzene (—0.84 cal./gram of mix), and then the heat effect when the rubber-black mix was swelled in benzene (1.28 cal./gram of mix), he was able to calculate the heat of wetting of the rubber-black mixture per gram of mix [$1.28 - (1.18 - 0.84) = 0.94$ cal./0.28 gram of black or 3.35 cal./gram of black]. It is very interesting to note that he ran similar experiments with a lampblack and a thermal decomposition black and obtained figures of 1.50 for the former and 1.32 for the latter. These figures, according to Boström are in "quantitative agreement with Wiegand's resilient energy results."

Hartner's [122] figures obtained in naphtha differ from Boström's somewhat but in general check them quite satisfactorily. He calculates the force of adhesion in a 8.5 volume per cent loading as 7.96 cal./cc. of black (4.53 cal./gram; this figure was reduced to 4.97 cal./cc. (2.9 cal./gram) when the loading was increased to 34 volume per cent. This decrease in the heat effect is of special interest as it indicates that with the higher loading only approximately 60 per cent of the total surface energy (assuming that the wetting was complete with the 8.5-volume loading) came into play. Hartner goes so far as to state that it is his opinion that present mixing practice results in the utilization of only one-half to one-quarter of the surface energy, depending upon the concentration of black employed. Hock[123] made an interesting observation in his work on heat of wetting—that the figure was perceptibly increased if the unvulcanized rubber-carbon black mix were aged before testing. This indicates that on standing the bond between the rubber and filler increased. Just what the length of the ageing period was, he did not state.

To support his hypothesis that, in the reinforcing of rubber by channel black, the black is wetted by the natural fatty acids of the rubber, and not by the rubber itself, Blake first cites the work of Gaudechon,[124] who ascribes to carbon black, when wetted by fatty acid—acetic or butyric—a heat of wetting of 6 cal./gram. He then quotes Hock[120] as giving a figure of 5.1 calories for 30 volume per cent. loading of rubber with carbon black, which he considers a close check. Hock is incorrectly quoted by Blake, for this figure of 5.1 was in terms of calories per cubic centimeter, not per gram. The corresponding figure per gram is close to 3.0, which is certainly a very poor check. His own figure of 4.7 calories/gram, calculated by his method of "cohering voltages," is neither a good check for Hock's figures nor for Gaudechon's.

In a very recent article, Harkins and Dahlstrom[125] have measured the heat of wetting, or "heat of immersion" as they prefer to express it, of several powders in various liquids. Their explanation of what occurs when a solid is immersed in a liquid is lucid. A certain definite amount of energy is stored up in the surface of each particle. When the particle is immersed in a liquid, the surface disappears, and in its place there is an interface (solid-liquid) of the *same* area, but possessing a *smaller* amount of surface energy. In general the excess energy appears as heat, which may be expressed as the "energy of immersion."

Dispersion and Flocculation.

The question is often asked as to what effect dispersion has on the hardness of a rubber-black mix. On first thought the answer is that the harder the vulcanized stock, the better the dispersion. Further thought casts doubt on this. If by dispersion is meant the wetting by, and surrounding of, each particle with rubber, as compared with aggregated unwetted pigment, then obviously increase in pigment dispersion should increase the hardness. If, on the other hand, the influence of well-wetted, dispersed (deflocculated) pigment is compared with flocculated pigment, it becomes another question, and the writer is inclined to the opinion that flocculation increases hardness.

Going back, for a moment, to the kerosene paste experiments described above, it has been conclusively proven, in the case of zinc oxide at least, that the stiffness of the pastes is associated with flocculation of the pigments. The addition of dispersing or wetting agents causes the pastes to lose their stiffness and flow. The microscope shows a high degree of dispersion when this occurs. Green[70] pronounced channel black a material which has a very strong tendency to flocculate in all media; to this tendency of pigments he ascribed the plastic nature of paints and the stiffness of compounded rubber. In rubber, of course, owing to its plastic nature, the tendency of dispersed pigments to flocculate will be lower than in mobile liquids and will depend upon the relationship between the energy at the interface or the force of wetting, and the force of flocculation of the filler. In other words, if the degree of wetting is high, the force holding the individual particles apart will be high and the tendency for the particles to draw together into groups will be low. When the reverse is true, the dispersed phase ceases to be uniformly dispersed in the continuous phase, and draws together into groups or clusters. Such a structure brought about by flocculation should resist deformation owing to the frictional forces developed when the pigment particles are forced to rub over one another during stressing, according to Depew.[114] Grenquist[95] has concluded from his ultramicroscopic studies that it is the anisotropic carbon black particles that exhibit the greater tendency to flocculate.

Evidence seems to point to better dispersion prior to vulcanization than afterwards, for during that period when the rubber is being heated up to the vulcanization temperature, and before the reaction actually sets in, the plasticity of the rubber increases, a condition which should promote flocculation. Pohle,[126] however, has failed to observe any displacement of the light absorption of a rubber-channel black mix, after vulcanization as compared with the uncured stock, and from these data he concludes that the hypothesis of coagulation or flocculation during cure, such as has been propounded by Greider[127] and accepted by Depew,[114] Green,[70] Grenquist[71] and others, is untenable. Also Hünemörder,[128] in making a comparison of two different carbon blacks, reports no change in dispersion during vulcanization in the case of one of them, with a noticeable improvement in the dispersion of the other. From the writer's review of the literature, however, he is led to the conclusion that flocculation does enter into the changes produced in a channel black stock during vulcanization.

That such flocculation is desirable is emphasized by several investigators. Green has already been quoted. Spear and Moore[36] believe that while high tensile is associated with the colloidal dispersion of at least a part of the carbon black (not resolvable microscopically, but detectable through the brown discoloration of the rubber), the stiffening effect is associated with other particles, larger in size, while a third portion of the black still larger in particle size may be practically inert, both as regards influence on tensile and stiffness, thus acting merely as a filler. They point out that the colored matrix is always concomitant with high tensile but quite fortuitous as regards stiffening of the rubber. In other words, the stiffening is associated with some other characteristic of the black, and it appears to the writer that flocculation offers the best explanation. Certain it is, that zinc oxide particles, which do not show the same tendency for flocculation, do not produce so great a stiffening effect as carbon black, and the same is true of the coarser thermal decomposition, or soft blacks, which are notably low modulus blacks. Goodwin and Park[82] ascribe the hardness of carbon black-rubber vulcanizates to flocculation of the black and also attribute at least part of the beneficial effect of stearic acid (as zinc stearate) to decreased wetting and hence increased flocculation of the black by the zinc stearate formed. Depew[114] also believes that flocculation is advantageous in that it hardens a stock, while dispersed pigment is responsible for enhancing the tear resistance. Since hardness and modulus are factors in reinforcement, flocculation is logically an important feature in the action of channel black on rubber. Both Depew[112] and Greider[39] impute resistance to cutting to flocculation. The former attributes resistance-to-tear, on the other hand, to the dispersed pigment particles, since these should act as obstacles in the path of a tear and change the direction.

The effect on dispersion and flocculation of increasing the milling time has been recently reported by Grenquist.[49] Starting with a mix, which at the end of thirty minutes of laboratory mill mixing, showed poor dispersion even to the naked eye, he found a steady improvement in dispersion, both macro- and microscopically observed, up to 45 minutes of milling, after which the dispersion appeared to grow worse. Whether premature vulcanization entered into this result, the writer does not know; Grenquist suggests that flocculation, brought about by the increase in plasticity, may have been the cause, and he hypothesizes an optimum value for dispersion at which maximum physical properties result. His figures place this at approximately 42 minutes milling, in the case cited, for with 45 minutes of milling there was a decided drop in physical properties, both in tensile strength and modulus. In this case, where the improvement in dispersion was accomplished through milling, two opposing effects probably played parts, flocculation and the breakdown of the matrix through mastication.*

Adsorption.

It is clear from the discussion up to this point, that adsorption effects must play a large part, if not the major part,[67] in the behavior of channel black in rubber. Commercial mixtures are so heterogeneous—containing in addition to the insoluble powders, sulfur, organic accelerator, antioxidant and softeners or plasticizers—that many adsorptions are possible. Unquestionably the rubber molecules are adsorbed at the surface of the carbon particles.[16] Accelerators are adsorbed also,[36, 38, 41, 129] and the result is clearly shown in the retardation of cure effected by carbon black. Experiments, outside of rubber, in benzol or gasoline solutions, confirm this and also indicate that sulfur adsorption by black is not a large factor in the retardation of cure.† To what extent the other ingredients are adsorbed will, of course, depend upon their nature. Little has been published with respect to the adsorption of constituents, other than sulfur and accelerator.

Certain blacks show such marked adsorptive action that their use in rubber compounding is barred,[37] and high adsorptive power has come to be looked upon as a detrimental property. However, it is the writer's opinion that low adsorptive power, as measured by the adsorption for oils, dyes or accelerators,[36] while advantageous from the standpoint of curing rate, is of questionable value, as it appears to be connected with low reinforcing power.

Comparison of Channel Black with Other Types of Blacks Used in the Rubber Industry.

Acetylene Black.

Although acetylene black, as has previously been pointed out, is not used to any large extent at the present time owing to its cost of manufacture, its

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* The orientation of carbon particles to make a gel-like *structure* of reinforcing power must here be considered. This is something apart from the *flocculation* discussed, but may follow it. A *preliminary dispersion* may be a necessary precursor to the production of a gel-like *structure*, as is the case, *e.g.*, with white dextrins.—J. A.

† Ditmar and Preusse[180] emphatically state that it is the adsorption of sulfur, and sulfur only, that is responsible for the retardation of cure by channel black. This conclusion, based on the fact that an increase in the sulfur content of a mix containing a highly adsorptive black and accelerated with tetramethyl thiuram-monosulfide brought up the rate of cure, is entirely unwarranted by the data presented. Obviously an increase in sulfur concentration would increase the curing rate, even if the accelerator were partially adsorbed.

position with reference to reinforcing rubber merits mention. Pickles[105] points out that it differs markedly in tinctorial power from rubber channel black made from natural gas, some samples possessing only one-half the tinctorial power of channel black, though as far as he could determine the particle size and physical effects on rubber were very similar. Judging from X-ray spectra characteristics, he concluded that both blacks consisted of a mixture of crystalline and amorphous carbon, with the percentage of the crystalline variety higher in the case of the acetylene black.

Twiss and Murphy,[92] on the other hand, note differences in the behavior of these two blacks in rubber. In the first place, the time of heating the rubber mix (100 parts of rubber, 10 parts of sulfur and 10 × specific gravity parts of black) to obtain the maxima in tensile properties differed considerably. With channel black approximately 155 minutes were required as against 125 minutes at the same temperature for acetylene black; also the optimum tensile was lower with the acetylene black in spite of the shorter heating period. The modulus curves of the two blacks showed almost identical stiffness at optimum cure.

Similar differences with respect to curing rate have been given by Carson and Sebrell,[38] who placed the best technical cure with acetylene black at 40 minutes at 125° C., while channel black required 60 minutes at the same temperature in a mix accelerated with mercaptobenzothiazole. Figures for the iodine adsorption of the two blacks were identical, and the modulus figures were within experimental error.

Kirchhof's[131] opinion of acetylene black differs somewhat from the above. Referring to the work of Beaver and Keller,[64] he concludes that acetylene black is the best of all the active blacks, owing to the lower oxygen content (2.6 per cent as against 5.3 per cent for channel black in the case cited) and better retention of physical properties on artificial ageing at 70° C. Beaver and Keller's figures on the unaged stocks were distinctly higher for channel black than acetylene black, both in modulus and tensile. This was probably largely due to the fact that these investigators used only one-third as much organic accelerator (a butaldehyde-aniline condensation product) with the acetylene black as with the carbon black in order to obtain approximately the same curing rate. Abrasion figures (Williams' machine)[60] on 70° C. aged samples also indicated superior ageing for the acetylene black. Permanent-set figures on a series of different blacks were published by Dawson and Hartshorne showing the following results:[132] the highest set with acetylene black, the lowest with lampblack, with channel black intermediate.

Parkinson[16] concludes from his study of the particle size of acetylene black, that this black is intermediate between lampblack and rubber channel black, the larger particles resembling lampblack in size, with a fair proportion of the particles coming within the range of channel black. Dilute suspensions of these blacks showed different color tones in transmitted light, a blue in the case of acetylene black and a bright amber in the case of channel black. On centrifuging such a suspension of acetylene black, the color of the remaining suspension was similar to that of channel black, i.e. amber. Twiss[2] is in agreement with Parkinson concerning the intermediate position of acetylene black with respect to lampblack and channel black, pronouncing it superior to lampblack in reinforcing and abrasion-resisting properties, and superior to channel black for certain purposes in that it has a less adverse effect on power loss. His views also coincide with those of Parkinson with respect to relative particle size.

Lampblack.

Lampblack is inferior to both carbon black and acetylene black as a reinforcing agent for rubber.[2] Wiegand,[18] Schidrowitz[65] and Esch[21] have all presented figures on the relative resilient energy of various samples of channel and lampblacks in rubber and their closely agreeing data place the value of lampblack in the neighborhood of 70 to 75 per cent of that of channel black. Abrasion machine results, according to Wiegand,[25] are in close agreement with the resilient energy findings.

The particle size of lampblack has been estimated by Wiegand[18] as 250 to 500 mμ. Green[70] places the particles between 300 and 400 mμ, and while distribution curves referred to by Parkinson[16] support Green's conclusions, they indicate that a fair proportion of the particles are of the order of 600 to 1,000 mμ. Wiegand[18] calculates the apparent surface per cu. in. as 80 per cent that of channel black; volume increase measurements at 200 per cent elongation were approximately 20 per cent greater, indicating lower adhesion to the rubber matrix, than is obtained with channel black.

The superiority of lampblack over carbon black as regards permanent-set and hysteresis loss[131] has been made use of to a considerable extent in the compounding of solid tires.[2] Another advantage lies in the fact that, in general, lampblacks retard cure to a much less extent than channel black.[92]

Thermal Decomposition Blacks.

While these blacks in general have only a comparatively small reinforcing effect on rubber, they play an important part in the economy of rubber compounding. Produced in much higher yield per unit volume of gas, they can in addition be employed in much higher volume in the rubber compound. As Esch[75] has shown, their stiffening effect, as compared with rubber channel black, is so much less, that certain grades may be used up to 300 parts to 100 parts of rubber without the product becoming unmanageable on the mixing mill, while 50 parts of channel black make a stock which is difficult to handle. The marked difference in these blacks is also seen in the behavior of mixtures in rubber when treated with dispersing solvents; the thermal blacks disperse readily, giving sols of relatively low viscosity, which flow easily, while channel black mixes disperse with difficulty, if at all, producing gelatinous cements. The low stiffening effect follows through into the vulcanizate, giving products of moderate stiffness, "rubbery" feel and comparatively low permanent-set. Hence the use of these blacks, especially some of the recently improved types, in tire carcass stocks for insulating the plies of fabric, in inner tubes and in solid tires. Owing to their low reinforcing effect they find little or no application in pneumatic tire treads or in rubber articles which must be highly resistive to abrasion.

This generalization concerning the stiffening effect of thermal decomposition blacks must not be taken as holding in all cases. Certain carbons so obtained may even surpass channel black in stiffening effect, as Goodwin and Park[82] have demonstrated in connection with certain blacks produced by the former.[133] Carson and Sebrell[88] connect this with the high temperature at which the black is formed, though there is a glaring contradiction to this hypothesis in certain of the low stiffening blacks of Spear and Moore,[134] which are formed, according to their patent, at temperatures in the neighborhood of 1,200° to 1,400° C.

These so-called "soft blacks" usually have a grayish cast and, in general, are probably relatively large in particle size, though Spear and Moore[134] estimate that the average, in the case of their special black, is the same as that of channel black. Pohle,[51] referring to one of the earlier "soft blacks," states that, at high magnification (2000 ×), coarse well-defined particles are apparent, and that dark field illumination indicates that no colloidal particles are present. Parkinson[16] places the average particle size in the neighborhood of 1,000 mμ. Wiegand[25] ascribes these characteristics to the high temperature at which they are formed, aggregation reducing the superficial area and hence reinforcing power. [Possibly the aggregates seen in the microscope are deflocculated in the rubber batch. J.A.]

The effect of thermal decomposition blacks upon the rate of cure of rubber is interesting and important. In some cases acceleration[134] of cure, as judged by the physical result,* occurs, which is in marked contrast with the effect of channel black. Spear and Moore[37] suggest that this may be due to the presence in thermal decomposition blacks of an accelerating substance or activator of the natural or added accelerator, since blacks which accelerate cure invariably give an appreciable extract with solvents, according to Spear and Moore. Recent additions to the number of thermal decomposition blacks have shown remarkably improved properties—tensile strength enhancement and increased tear-resistance approaching channel black—and it appears probable that the use of these blacks will show a large increase, as rubber technologists learn how to apply them more intelligently to the solution of specific compounding problems.

Heat-treated Channel Blacks.

Commercially, a heat-treated channel black is of very recent origin, though in the early days it was common practice to repeatedly heat-treat[135] lampblacks to remove the empyreumatic content formed through incomplete combustion of the tar-oil or hydrocarbon used in their manufacture. This practice has now been largely avoided by arranging the process so that calcination follows at the time of deposition.[136] And although Rose[137] in 1922 patented a process of heating channel black at 1,000° C. in air or steam for 90 minutes, and claimed a black for rubber compounding which increased the tensile approximately 10 per cent, reduced the curing time 25 per cent and increased both the abrasion resistance and toughness, no commercial product resulted (as far as the writer is aware) until very recently, when two products appeared on the market as a result of the work of Wiegand and his coworkers, and of Johnson. The investigations of Wiegand, reported in 1929,[138] were directed upon the problem of reducing the adsorption of organic accelerators by channel black. Wiegand found it possible to practically eliminate the adsorptive capacity for accelerators (diphenylguanidine and mercaptobenzothiazole) and thereby cut the accelerator requirement in two. The resulting black was a definitely purer carbon, with the volatile matter content reduced 75 per cent. While the actual black placed on the market has not been carried to so low an adsorptive capacity, the author states that this characteristic can be controlled at will through regulation of the amount of oxygen present during the heating operation. It is also interesting to note that a procedure has been worked out, according to Wiegand, whereby the inactive black is produced in one step, without resorting to a secondary heat treatment. Both Wiegand's figures and those presented by Carson and Sebrell[38] on heat-treated blacks

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* Goodwin and Park[31] assert, without presenting their experimental data, that the rate of sulfur combination is *retarded* rather than accelerated.

indicate somewhat higher stiffening power for these blacks, hence higher work capacity.*

Such blacks have great interest for the rubber industry owing to the economy effected in accelerator costs as well as the possibility of obtaining enhanced properties and superior ageing. General adoption of these blacks by the rubber industry has not as yet occurred, though large quantities have been manufactured and used.

Mineral Black.

As is the case with all ground pigments, mineral black or ground coal has essentially no reinforcing effect on rubber and has found no application in rubber compounding. Far cheaper fillers of similar influence, such as whiting, are used for diluent purposes. Recently, however, Schidrowitz and Philpott[139] have reported a mineral black, found in Devonshire, England, which can be concentrated to give a product containing 80 per cent of carbon with the remainder silica and clay. Though having only about 12 per cent of the coloring power of channel black, these authors place the reinforcing effect on rubber at 42 per cent that of channel black, and close to twice that of lampblack, using Wiegand's ΔA function as their criterion. Such a mineral black appears to have considerable interest, especially in countries where natural gas for the manufacture of channel black is not available.

BLENDING OF BLACKS IN RUBBER MIXES.

That there may be increased reinforcement produced by blending reinforcing pigments, was pointed out by Greider[56] in his work on channel black and light magnesium carbonate. Working with a 9-volume pigment addition to a litharge accelerated stock, he obtained a resilient energy figure with 3 volumes of magnesium carbonate and 6 volumes of channel black, which was some 12 per cent higher than with 9 volumes of channel black. As a matter of fact the blending of various pigments in rubber compounding was in the early days common practice, many times without "rhyme or reason," the number of pigments blended running into ridiculous figures. That the effects may be more than additive was not and is not today generally accepted.

The writer is of the opinion that the blending of different blacks has received far too little consideration, if one may judge from the scarcity of published data. It is clear from the behavior of the different blacks discussed, that they impart widely different properties to rubber, and an intelligent blending should lead, and has led in certain cases, to properties of decided merit for specific purposes. Solid tire compounds are a specific illustration.[88, 140] The writer believes that it is now common practice to blend channel black with the various soft blacks or lampblack in order to obtain through additive effects maximum wear-resistance with efficiency and blow-out resistance sufficient to meet the specific service demands.

Though Greider has presented this case of blending pigments which resulted in properties in excess of what was to be expected on the basis of a purely additive effect, the literature affords little evidence that enhanced properties can be obtained in this way. Beaver and MacKay[140] have shown conclusively that the effect of mixing channel or a soft black respectively with

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* The question naturally arises as to what part is played by the various substances adsorbed by the different blacks at the time of their production. Even though these may be later removed, they may influence particle size, structure, and aggregation, and also behavior in the batch.—J. A.

a clay, whiting or lithopone were purely additive. With zinc oxide and channel black appreciably enhanced figures for ultimate tensile and modulus were obtained with slightly inferior results for abrasion (Williams' machine[60]). The soft black, on the other hand, showed purely additive properties with zinc oxide, with the result that within the range from 60 parts of black with 40 parts of zinc oxide to 0 parts of black with 100 parts of zinc oxide (20-volume loading) the abrasion-resistance (Williams' machine) with the soft black was equal, if not slightly superior, to that obtained with channel black, according to the authors. With equivalent volumes of black, the blow-out resistance with the soft black was markedly superior to that obtained with channel black, so Beaver and MacKay maintain that for solid tires the former should be used as it gave superior blow-out resistance without loss in abrasion-resistance.

These investigators made no study of mixtures of channel black with soft black, but Esch[75] has published results which indicate that the blending of these blacks is not only economical but feasible for certain purposes.

EVALUATION OF BLACKS FOR USE IN RUBBER.

In the early days of the use of blacks in rubber compounding the quality of a black was judged by a few simple empirical tests, such as specific gravity, moisture content, grit content, covering power, acetone extract and ash. Occasionally a vulcanization test would be run, as a check on quality, but this was not common practice.

Obviously specifications which included only the above characteristics, had limited value in assuring uniform quality for rubber reinforcement. Absence of grit and meeting a standard in coloring or covering power, were some indication of particle size and suitability for rubber usage. Low moisture and extractable matter content were indications of purity and uniformity, but again quite inadequate to assure satisfactory quality.

Many attempts to correlate quality with some simple laboratory test outside of rubber were made and it is interesting to note some of the characteristics studied. *Apparent volume* received consideration. Owing to varying adsorptive power for gases, this varies widely; Bancroft[116] quotes one case where as little as 5 per cent of the apparent volume was due to carbon, and another case where a liter of carbon black contained as much as 2.5 liters of air.* The relation between the volume occupied per unit weight of black, and the properties imparted to rubber, was studied by LeBlanc, Kröger and Kloz,[86] by van Rossem and van der Meyden,[141] and by Fromandi.[142] The conclusion reached from the work of these various investigators is that this characteristic has no bearing on the quality in rubber. As LeBlanc, Kröger and Kloz put it, the blacks may show marked differences in "Schuttelvolumen" and yet behave quite analogously in rubber. Van Rossem notes that the more voluminous blacks take longer to incorporate in rubber, and that in a general way the best properties on vulcanization are obtained with blacks showing the smallest volume. This test, however, does not merit inclusion as a control test for blacks.

Volatile matter has recently received much investigation at the hands of Johnson,[72] who finds this a valuable test in gauging the uniformity of black produced at a given plant, but warns against indiscriminately applying it to the evaluation of blacks from different sources. In general, however, it may be said that a black of very high volatile at 950° C. (above 6.0 per cent)

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* **More correctly designated as "gas."—N. A. S.**

should be subject to suspicion and volatile matter limits are finding their way into the black specifications of some rubber companies.

Oxygen content is claimed by both Johnson[91] and Beaver and Keller[64] to have a relationship to quality. The former made an exhaustive study of this and concluded that it is the oxygen of the volatile matter content, which makes a high volatile detrimental. The latter investigators attribute poor ageing to high oxygen content, but not in direct proportion to the percentage present. The oxygen content of a black is not often utilized in evaluating a black, but rather the total volatile matter, which is more easily determined.

Color appears to be of only limited value, unless microscopic studies in rubber are made, or the color difference is very marked. Johnson,[143] who used an intensimeter which he designated a "Nigrometer" for studying the color of blacks, was led to the conclusion that blacks differing appreciably in color gave results in rubber within the limits of experimental error in testing; he deprecated the use of this instrument in testing blacks for rubber. Hock,[144] on the other hand, finds that in general there is a quite definite relationship between the tinctorial power of a sample of black (as judged by the color of mixtures with lithopone, or zinc oxide) and the specific surface estimated calorimetrically, i.e. by determining the heat of wetting. He used a polarization photometer in measuring the reflecting power of such mixtures and also applied it to the measurement of the color of carbon black-rubber mixtures. He concluded from his experiments that the method was of value in determining not only the color but also the degree of dispersion of carbon black in rubber mixes. The method is described as simpler, and more generally applicable, than that of Johnson using the Nigrometer.

Microscopic Examination.

The microscope is of distinct value in determining the suitability of a black for rubber reinforcement. Owing to the difficulty in preparing rubber sections for observation with transmitted light, the color tones have found little application in controlling the quality of blacks. Surface examination by reflected light is, however, a simple matter, and in the writer's laboratory has been found of distinct value in estimating the dispersability of a black and in evaluating various mixing procedures. In Figure 6 are shown photomicrographs * of two vulcanized channel black samples identical except in degree of dispersion. In one aggregation it is very pronounced, while in the other, much improved dispersion is apparent. The results of subjecting these two dispersions to a flex-cracking test are shown in Figure 7. The improved flex-cracking-resistance of the sample exhibiting better dispersion is clearly shown.

Adsorption Tests.

The value of adsorption tests has been, and still is, a moot subject. Spear and Moore[36] have advocated an oil-adsorption test, using neutral raw linseed oil, as a measure of the stiffening power of a black; they point out, however, that this is not always reliable, as exceptions are encountered. Adsorption tests by the same authors using malachite green in aqueous solution, Victoria blue in benzol, and hexamethylenetetramine in benzol, led them to the conclusion that there is no certain relationship between the amount of these substances adsorbed and the stiffening power of a black. Certain carbons of

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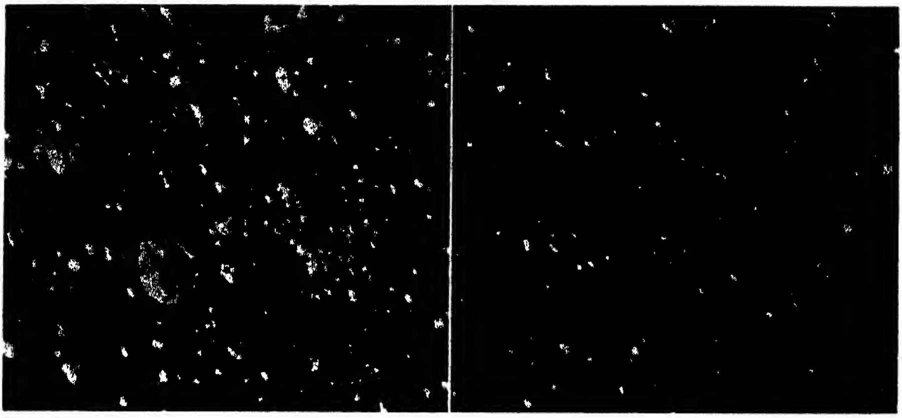
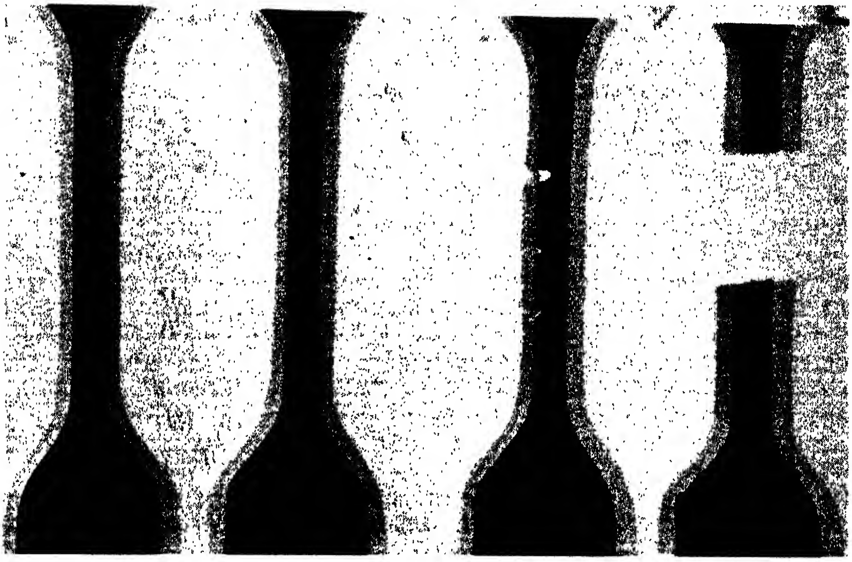
* Taken by H. P. Coats.



A
Poor dispersion.

B
A improved by additional milling.

Fig. 6.—Photomicrographs of channel black dispersion in rubber.
Note: Inclined oblique illumination—100 ×.



A
Poor dispersion.

B
Improved dispersion.

Fig. 7.—Flex-cracking tests on channel black dispersions.

high stiffening power for rubber adsorbed the smallest amounts of these substances.

Goodwin and Park[82] and Twiss and Murphy[92] express the opinion that adsorption of accelerator, either that occurring naturally in the rubber or added to the mix, has a marked effect on the rate of cure of the mix. Though they do not present their adsorption figures, they conclude that both the oil and water adsorption power of a black are indicative in general of the effect of a black on cure, although here again there is an exception noted. Beaver and Keller,[64] on the other hand, are quite positive that the adsorptive characteristics of a black for iodine or oil are not indicative of differences in rate of cure. In the first place, the adsorption of iodine bears no relationship to the adsorption of oil. A case is cited where one black adsorbed 38 per cent more iodine than another, but only 4 per cent more, or practically the same amount, of oil; the former required one-third more organic accelerator in a rubber stock containing 25 parts of black by weight to produce approximately the same rate of cure. The oil adsorption thus proved valueless in bringing out this difference, while the iodine adsorption indicated it quite clearly. In another case cited, a lampblack adsorbed only 21.5 per cent as much iodine and 40 per cent as much linseed oil as a sample of acetylene black, yet required about three times as much accelerator to give approximately the same rate of cure. In other words, there is a definite specificity in the adsorption phenomena and adsorption tests are likely to be very misleading in evaluating a black for use in rubber.

Recently Carson and Sebrell[38] have published results on the relationship between adsorptive capacity and quality of a black for rubber compounding. They reached the conclusion that adsorptive capacity is a most important characteristic. Studying iodine adsorption they conclude that it is a *measure* of the rate of cure; their figures in general bear this out, but with so glaring an exception as two blacks with identical iodine adsorption, with the best technical cures set at 40 and 60 minutes at 125° C. respectively (a 50 per cent difference), these figures are far from convincing that iodine adsorption is a *measure* of curing rate. Johnson,[91] from his work on iodine adsorption, states that "there is no correlation between iodine adsorption and the amount of volatile matter in a black or in the rate of cure of the black when used in rubber," unless the samples are from the same factory, in which case "the iodine adsorption varies directly with changes in volatile content."

Carson and Sebrell also compared the adsorption of mercaptobenzothiazole and diphenylguanidine respectively with curing rate and concluded that the differences were at least partly due to adsorption of accelerator. The writer questions this conclusion, for with two of the blacks, on which the time of best cure was set at the same duration as judged by the behavior of the mercaptobenzothiazole accelerated stocks, the one adsorbed twice as much of this accelerator from alcohol solution as the other. Peculiarly enough the adsorption of diphenylguanidine was identical in both cases and did check with the curing time.

Fromandi[142] is studying the acetic acid adsorption of blacks in relation to the physical properties produced in rubber, but no conclusions can be arrived at as only part of his work has as yet been published.

The writer can only conclude from these data that the adsorptive power of a black is a very uncertain measure of the behavior of that black in rubber, even when the adsorption test is made with the same accelerator as is used in vulcanizing the rubber mix.

Rate of Settling.

Carson and Sebrell[38] investigated this characteristic of blacks, mixing them with two and a half parts of linseed oil and then diluting with benzol, shaking to form a uniform dispersion. No relation between the rate of settling and any physical property of the corresponding rubber-black mixes could be formulated.*

Working with black-rubber mixtures in benzol much more interesting results were obtained. In these experiments, also conducted by Carson and Sebrell,[88] 1 gram of black was ground to a paste in toluene or xylene and then thoroughly mixed, by stirring, with a few cc. of 4 per cent rubber cement. To the resulting paste, 50 cc. more of 4 per cent rubber cement was added and the mixture then diluted with benzene to a total volume of 400 cc. After vigorous shaking for 8 hours, the black was allowed to settle, or was centrifuged out. Under these conditions, the rate of settling showed marked correlation with modulus, i e. stiffening power. There were some discrepancies between blacks of different types, but in the case of a series of rubber channel blacks, there was a progressive reduction in modulus with reduction in the carbon remaining in suspension in the carbon-rubber cement, though the other physical properties of the cured mix did not show this correlation. It would appear that this method of evaluation has considerable merit and is worthy of further investigation.

This method of evaluating blacks ties in closely with those of LeBlanc, Kröger and Kloz [86] and Pavlenko and Nazarov,[87] which have already been referred to. These investigators rely on the viscosities of black-rubber cements as a measure of tensile strength and reinforcing power.

Acetone Extract.

The acetone extract continues to be an item in most carbon-black specifications. It is a valuable indication of uniformity, though Goodwin and Park [69] failed to find any appreciable effect on the curing rate and concluded that the extractable material simply acted as a softener. However, they failed to note any difference in mixing qualities between the original black and the extracted black, from which 4.5 per cent of acetone-extractable material had been removed. As a diluent, however, the high extract did affect the tensile and modulus detrimentally.

Beaver and Keller [64] investigated the influence of the acetone extract of two blacks which influenced the ageing of rubber to a markedly different extent. They could find no relationship. On the other hand, Spear and Moore [87] concluded that all blacks which decrease time of cure of a rubber mix, give appreciable extracts with solvents such as benzene or acetone; they found, however, no relationship between the amount of the extract and the accelerating influence.

In spite of all the work which has been done to devise simple tests outside of rubber, which would evaluate a black for rubber usage, most technologists [18, 86, 145] still rely in the last analysis on a vulcanization test, subjecting the vulcanizate to such physical tests as tensile, modulus, set, tear-resistance, flex-cracking-resistance, etc., depending upon the purpose for which the stock is to be applied. Many rubber technologists, connected both with the laboratories of the producing and consuming companies, are now coöperating in their efforts to avoid the necessity of a vulcanization test and undoubtedly the near future will see much light thrown on the subject. Perhaps too much effort is being expended along this line, for after all the vulcanization test is comparatively simple, the main objections being the length of time required for the test, the expensive nature of the equipment required and the cost per

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* The question is raised as to whether there are not favorable mixtures of particle sizes, as e.g., in concrete mixes, rather than any one optimum size.—J. A.

test. Furthermore, such laboratory physical tests approach closely those to which the product is subjected in service, or have been correlated with them, and it is unlikely that so reliable a chemical test on the black itself will be developed that the vulcanization test will be discarded.

SPECIAL USES.

In the preceding pages reference has repeatedly been made to the uses for which rubber-black mixtures are especially adaptable. Blacks find their greatest and most indispensable application in rubber goods which must be highly resistive to abrasion. While it is undesirable and quite unnecessary to enumerate the many obvious applications of black pigments in the rubber industry, there are certain applications, which are quite non-obvious and surprising.

Perhaps most unexpectedly is the recently suggested application of channel black in rubber compounds for electrical insulation. It would appear that the addition of carbon, which is a conductor of electricity, to rubber, which is a non-conductor, would result in a combination that would be less desirable for insulating purposes. The recent work of Wiegand and Boggs[146] has shown that this is not the case if the black is used in moderate quantities, previous publications on the subject notwithstanding. In fact it has been shown that if the channel black is thoroughly dried by heating for two hours at 325° F. just prior to incorporation with the rubber, there may occur an increase of 40 per cent in breakdown voltage, at a volume loading of black of 5.2 per cent (10.0 per cent by weight). It is suggested by the authors that previous conclusions with reference to the detrimental effect of carbon black have been due to a moisture content or to the adding of excessive or poorly dispersed quantities. The beneficial effect of thoroughly dried black is thought to be due to its high adsorptive power functioning in removing the ultimate traces of moisture and electrolytic impurities from the rubber. With the enhanced toughness and wear-resistance which channel black imparts, the use of carbon black in electric insulation should make rapid strides.*

Another use of blacks in the rubber industry, which has apparently expanded more rapidly in Europe than in America, is that of applying activated carbons for the adsorption of volatile inflammable solvents used in spreading fabrics with rubber cements. Such solvents allowed to escape into the atmosphere constitute not only an economic loss but also a serious health and fire hazard and their removal by one method or another is a necessity. With proper hooding arrangements it is claimed that 85 to 92 per cent of the evaporated solvent can be recovered by adsorption in activated carbon.[147] Price[148] claims a recovery of 90 to 95 per cent of the vapors (benzol) that enter the adsorbers, and an over-all recovery of 75 to 85 per cent of the solvent applied in the water-proofing process.

Additional uses for rubber are constantly being sought and found, especially with the low price of crude at present prevailing. That carbon blacks will play a large part in adapting rubber for new purposes is a foregone conclusion.

In conclusion, the writer wishes to express his appreciation of the constructive criticism of Messrs. Jerome Alexander, George C. Lewis, Charles R. Park, Ellwood B. Spear, and William B. Wiegand; also to the various

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* In a private communication, W. B. Wiegand has advised the writer that a paper is to appear shortly in *Ind. Eng. Chem.* by Wiegand, Boggs and Kitchin, in which the effect of certain blacks on insulating oils is discussed. New transformer oil, e.g., has been improved 40 per cent in breakdown by treatment with properly dried black, according to Wiegand.

members of his own laboratory, especially to Messrs. John N. Street and Vlon N. Morris, for their helpful suggestions, and to Mr. Nathan G. Schwarting, who assisted in the drawing of curves.

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Synthetic Resins.*

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The products commonly known as *synthetic resins* are solid, or semi-solid, organic substances generally amorphous resulting from the chemical union of (usually) non-resinous materials. A substance is considered as resinous by virtue of its physical properties and physical structure rather than its chemical composition. These products have some properties resembling natural resins and are classed as resins because of this resemblance, that is, because of their amorphous structure, conchoidal fracture, resinous luster, etc.

From time to time during the past fifty years [1] organic chemists have been reporting certain reactions as giving "resinous bodies" rather than the crystallizable or distillable products they expected to obtain. For the first twenty-five years these complex and difficult mixtures received but scant attention from their discoverers who were interested only in compounds which could be purified (as by crysallization or distillation) to a degree that would permit identification. Then the growing importance of natural resins in the manufacture of oil-resin varnishes caused a more critical examination of these synthetic resinous masses, and search for suitable substitutes for such natural resins as amber, copal and dammar, led to careful study of the more promising. Notable among these were the cumaron and indene resinous products from coal-tar distillates,[2] the amber-colored resinous mixtures resulting from the reaction between phenols and aldehydes,[3] the resinous masses from petroleum oils,[4] the resin-like substance obtained by the reaction of glycerol with phthalic anhydride,[5] and the resins formed from aldehydes in the presence of alkalis.[6]

Of these products those resulting from the phenol-aldehyde reaction have been of greatest industrial importance. The cumaron resins, the glycerol-phthalic anhydride resins, and the aldehyde resins have acquired some importance while several newer synthetic resins, particularly the vinyl and the urea-formaldehyde (and thiourea-formaldehyde) resins, appear destined to acquire importance. The petroleum resins so far have found but little use.

It was early recognized that phenols and aldehydes [7] react to give more than one type of resinous product, and that after heat treatment part of the reaction mixture might be found in a hard, infusible and insoluble form.[8] The same chemical raw materials, when reacted under conditions which seemed to be nearly identical, either yielded a product which could be melted and remelted as often as desired, or yielded one which melted and then quickly hardened, while heated, to an infusible form. Since no one had learned to control the product that hardened with heat, the emphasis was placed on those products which would remain fusible and soluble under heat, and the early workers, like De Laire,[9] gave recipes for careful avoidance of the undesired, heat-sensitive resinous masses.

It remained for Baekeland [10] to show how to control the formation of the

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* The author is pleased to acknowledge his indebtedness to Dr. A. V. H. Morey and other members of the staff of the Bakelite Corporation.

infusible product, to disclose how to cause the reaction that had been studiously avoided to become the reaction of real industrial importance. A synthetic resin industry resulted when he worked out methods of control for this refractory form, such that it could be industrially handled while still in the fusible, soluble, heat-sensitive stage. These controlled resinoid products were first marketed under the trade name "Bakelite" in three different reaction stages: the "A" or fusible stage, the "B" or partially fusible stage, and the "C" or infusible stage.

It is perhaps fortunate that Baekeland chose for study the phenol-formaldehyde reactions, in the products of which transformation processes proceed rapidly at moderately high temperatures but are easily interrupted by cooling to room temperatures. The fact that the minimum reaction point is well above normal temperatures contributed greatly to his success. But much more important was his disclosure that the proportions of the reacting materials and the character of the catalysts present determine the course of the reaction, i.e. determine whether the permanently fusible form or the form that may be hardened with heat would result,[11] and furthermore, that by a proper balance of heat and pressure the "hardenable" product could be transformed in hours, instead of weeks or months, into a dense, hard, infusible, insoluble product, superior for many industrial uses to any other resinous substance, natural or synthetic.

Baekeland later differentiated between these two types of synthetic resinous masses, which differed so widely in their susceptibility to rapid and permanent change under heat, by styling those relatively non-susceptible as *resins,*[12] and those highly susceptible as *resinoids.*[13]

Thus, the *resins* may be heated and reheated and still retain approximately the same degree of hot plastic flow. In this class are included cumaron resins, aldehyde resins, ketone resins, vinyl resins, some varieties of polyalcohol-acid (alkyd) resins, and some varieties of phenol-aldehyde resins. Any synthetic resin which finds ultimate use in the fusible form may be considered in this class.

The resinoids comprise those resinous products which can be heated to a limited extent only without marked change, and which on longer or more severe heating lose most of their plastic flow and become more or less rigid even while hot. Included are the phenol-aldehyde resinoids, the polyalcohol-acid resinoids, urea-aldehyde resinoids, vinyl resinoids, and many others that are mainly of laboratory interest.

Many synthetic resins appear to lack a corresponding resinoid form, the form at present most important in the rapidly expanding "synthetic resin" industry.

Colloidal Nature.

Certain "synthetic resins," notably the phenol resinoids and phthalic anhydride-glycerol resins, find important use in the field of electrical insulation. In electrical properties and apparent structure they bear general resemblance to other insulating materials. They act like glass, for instance, to the extent of having a wide temperature range of flow rather than a sharp melting point. Glasses have been described[14] as colloidal, as desiccated jells, and classed as isocolloids. Insulators generally are in the class of isocolloids and are considered as mixtures of more or less associated polymers. Staudinger[15] describes these products as made up of "macromolecules." He considers macromolecules as long, thread-like molecular chains which exhibit colloidal properties to a varying degree. Substances whose colloidal properties are strongly emphasized, he classes as eucolloids or macromolecular colloids. He states that molecular colloids in general are not visible under the ultramicroscope. This coincides with the writer's findings relative to the synthetic resins in that, while these act in many respects like colloids, yet ultramicroscopic studies of the resinous solids, either alone or in organic solvents, are disappointing. Colloidal particles are not clearly perceptible as are, for instance, the suspended particles of colloidal gold.* The light phenomenon normally seen is a translucent haze, a more or less scanty, diffuse luminosity.

The resinoids in particular are subject to ageing similar to the colloidal ageing of systems mentioned by Rocasolano.[16] Here also the "particles are chemically unstable complexes in which there takes place continuous transformation induced by heat." In the ordinary colloidal system a stable state is reached when coagulation has become complete, but in the resinoid field this coagulation, or growth of particle size, is often complicated by a simultaneous increase in the number of coagulable molecules. These concurrent chemical and physico-chemical changes render the resinoids very complex and their behavior difficult to interpret and control. All resinoids, by polymerization, pass through the normal colloid range of particle size. The method may be defined as that of self-aggregation.

THE RESINS.

The synthetic resins may serve as substitutes for natural resins by virtue of some degree of improvement in desired properties or in cost. In general, they act in the capacity of industrial aids rather than complete industrial entities. They have made available new properties when added to rubber. They have brought increased endurance and rapid drying to the products of the resin-oil varnish industry. They have helped the cotton-lacquer industry to produce products of great industrial value. They are now found helping either process or product in such widely different fields as those of linoleum and chewing gum.

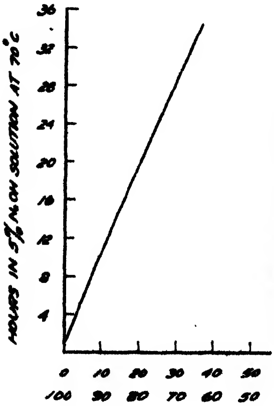

FIG. 1.

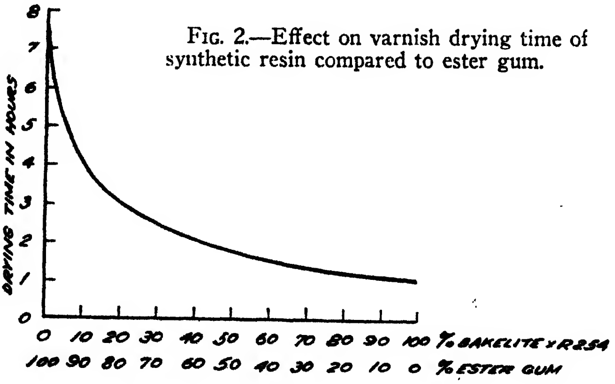

FIG. 2.—Effect on varnish drying time of synthetic resin compared to ester gum.

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* A marked difference between the refractive index of the dispersed particles and the dispersion medium is essential to their ultramicroscopic differentiation. Thus recent X-ray spectrograms of glass have demonstrated the presence in it of ultramicroscopic crystals undistinguishable in the ultramicroscope. J. A.

The use of a synthetic resin to help an industry meet a specific requirement is illustrated in Figure 1. Here is shown the increased alkali resistance imparted to a China wood oil varnish by substituting a phenolic resin, wholly or in part, for the ester gum of the formula. Figure 2 shows the setting time of this same series of varnishes, and the marked influence of small percentages of a phenolic resin in shortening this time.[17]

The use of glycerine-phthalic anhydride (alkyd) resins with drying oils to form a resin-oil varnish has lately become of some industrial importance.[18]

The Resinoids.

The peculiar mixture of organic compounds known as resinoids may be characterized as temporary hot plastics having, while heated, a constantly increasing resistance to flow and a constantly diminishing rate of flow with a given temperature and ending in practical rigidity, i.e. setting, at that temperature. The property of hardening rapidly in the heat that first fuses them, and the strong, enduring character of the resultant product, have given certain of the resinoids a prominent place in industry.

The resinoid industry is plainly much concerned with the matter of plastic flow. While the rate of flow of many plastic materials is constant, the rate of flow of resinoid plastics is not constant but varies with time and temperature. At any definite working temperature, generally over 100° C.,* the plastic flow decreases rapidly until it entirely stops and the product is said to have "set" or polymerized.

The phenolic resinoid industry has been built on the fact that its aggregation processes are not only rapid but may be controlled to a desired point, the product stored for months, aggregation then advanced by heat to a point of infusibility and the product allowed to cool. The resulting finished product is stable and remains useful for many years, some varieties remaining useful on continued exposure to temperatures as high as 125° C.

Rapid change in rate of polymerization with change in temperature does not characterize all resinoids. Low rate of polymerization for a given change of temperature has held back the industrial use of some otherwise promising resinoids for many years. In time, methods of control for all known resinoids may be perfected. At present the most nearly perfect control is in the phenol-aldehyde resinoid field. The urea-formaldehyde appears to be the next most promising group. Urea-formaldehyde products in their initial, moldable stage, however, undergo change at room temperatures, and thus as plastic raw materials have limited life. Even after these products have been given final heat treatment they appear to undergo further change and after a time tend to crack or craze. Control has reached a point, however, where they are usable for many purposes. The polyacid-alcohol synthetic products, of which the so-called glyptal resins are the best known example, have so far found their principal use in industry as resins rather than as resinoids.

When we speak of resinoids as hot plastics, we refer to the fact that their transition from being first mobile liquids and later true, rigid solids represents a wide range of temperature. It is within this temperature range that we encounter the phenomenon of plastic flow. The so-called melting points of resinoid plastics will be found anywhere within this wide temperature range. The exact position of the determined melting point will be dependent on the method employed, the rate of heating, the degree of subdivision, the time and

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* These statements do not hold below some minimum, critical temperature which is different for each resinoid.

temperature of any preheating of the specimen, and, of course, on the nature of the resinoid under test. Melting points of resinous materials are measurements of plastic flow under a set of specified arbitrary conditions and should not be confused with the exact melting points of crystalline substances.[19]

The maker of resinoids is concerned with problems in some ways analogous to those of the maker of steel, who by control of time and temperature, speed of chilling and conditions of heating is able to produce steels of different degrees of hardness from one and the same material. However, there is this important difference: the structural changes brought about in steels are reversible, thus allowing for correction of errors, but the structural changes induced in resinoids are non-reversible and any error is likely to be incurable.

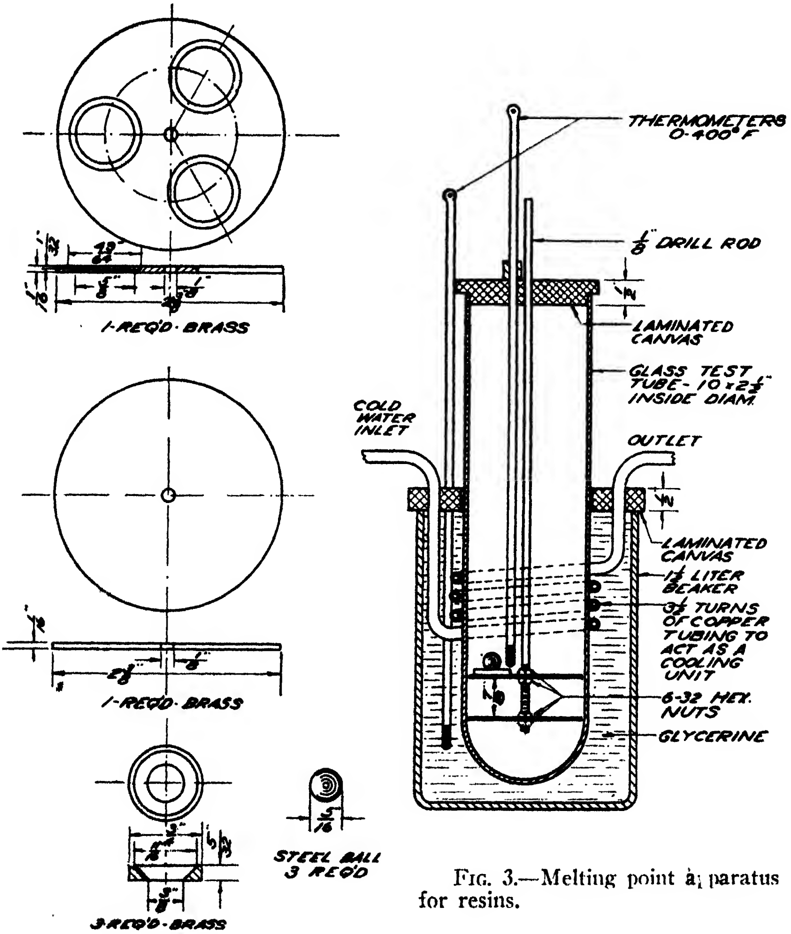

FIG. 3.—Melting point apparatus for resins.

Thus the production of resinoids, while very simple in outline, is very complex in practice. Two or more suitable organic materials are reacted under conditions which give the desired mixture of resinous organic products. Being resinous and subject to change under heat the product is not well adapted to any of the customary means of chemical purification, such as crystallization or distillation. Accordingly, a resinoid product which is to have a desired set of properties must be made directly, without purification, in a usable state of purity. This is possible only under very carefully controlled conditions. Since resinoids change rapidly under heat, a slight variation in temperature or time may cause a batch to go solid while hot, in which case the resulting useless mass must be hand-chopped from the "still."

INDUSTRIAL USES.

The resinoids find the following five main fields of use, given in the order of their importance: (1) As bonding agents for sheet materials, fibers, abrasives, graphite and other solid particles; (2) as coating materials used for protection of wood, metal, cloth, etc.; (3) as distenders and modifiers used in paints, varnishes, lacquers, etc.; (4) as heat-resistant cements such as those employed in basing electric lamps and radio tubes; (5) as solid resinoids used for their ornamental value and enduring character as in beads, pencil barrels, etc.

RESINOID MOLDING MATERIALS.

As indicated above, the resinoids have thus far found their major field of usefulness as bonding agents. They act as heat-sensitive "glues." A rock, or a piece of wood, a chunk of abrasive or of graphite, may be reduced to small particles, mixed with partially reacted resinoid and then by being forced to flow into a mold under the influence of heat and pressure may be cheaply "reassembled," that is molded into any desired shape, accurately dimensioned. The finished product may even possess properties superior to those of the original material.

Thus preparation of the resinoid molding material involves first, the handling of the initial chemical reactions so as to give a suitable bonding material, and second, the physical working of this with suitable fibrous and other added materials to a point where the behavior of the resultant molding material can be controlled within limits and its subsequent behavior closely predicted. In other words the purpose of resinoid technology is to obtain a suitably heat-reactive plastic mass which, under suitable conditions of heat and pressure, may be brought to its permanent, hardened state, fashioned into the final form desired.

The exact balance of factors required in hot plastic molding is well stated by Bingham:[20] "The material must be soft enough to take shape readily, but it must not be tacky enough to stick to the mold; it must have yield value enough to maintain its shape after removal from the mold, and after cooling it should be hard and tough."

While chemical constitution, mutual solubility of materials present, dispersion of resinoid in relation to "filler," and character and amount of lubricating materials present, if any, are factors of importance, still the working qualities of a resinoid molding material depend mainly on particle size.

Particle size comes into play in three distinct ways: (A) The molecular size of the resinoid employed, as influenced by previous polymerization; (B) the size of the fibers, and of the fiber masses as influenced by mixing, rolling and grinding; (C) the size of the mixed masses of bonding agent and fiber, as influenced by grinding and screening.

While the factors (*B*) and (*C*) seem minor as compared to (*A*),* yet they are very important in determining strength, flow, surface polish, surface color, and surface uniformity. For instance, any molding material made from

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* It is factor (*A*) which makes the resinoid molding art possible.

resinoid and fibrous filler will develop much greater flow in the mold when ground to extreme fineness. But as such fine grinding breaks the fibers present, moldings made from such material will be found to have lost in mechanical strength.

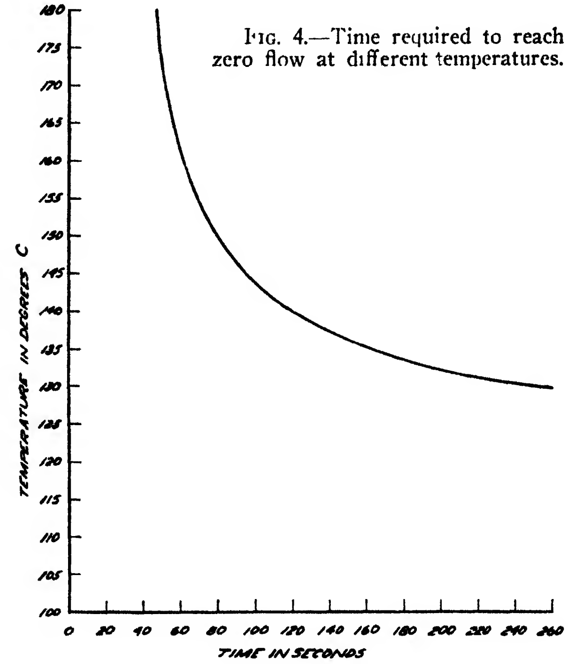

Fig. 4.—Time required to reach zero flow at different temperatures.

Some of the relations between time, temperature and plastic flow can be seen in Figure 4, which represents what happened when several samples of the same resinoid molding material were subjected to different temperatures and the time was recorded for the plastic flow to reach a zero value, that is, for the material to set or harden. As may be seen from the curve, under the constant pressure employed, a temperature of 130° C. gave a plastic flow of the resinoid material that decreased with elapse of time until at the end of 250 seconds, flow had entirely ceased. On the other hand, at 160° C. flow stopped in sixty seconds.

Figure 5 shows variation, with time, in the rate of plastic flow. A molding material in the form of coarse powder, containing approximately fifty per cent fibrous material and fifty per cent resinoid, was subjected to 100 lbs. of pressure per sq. inch, at 150° C. The rate of flow, which was noted at the end of each second, dropped rapidly from 0.40 inch per second at the end of

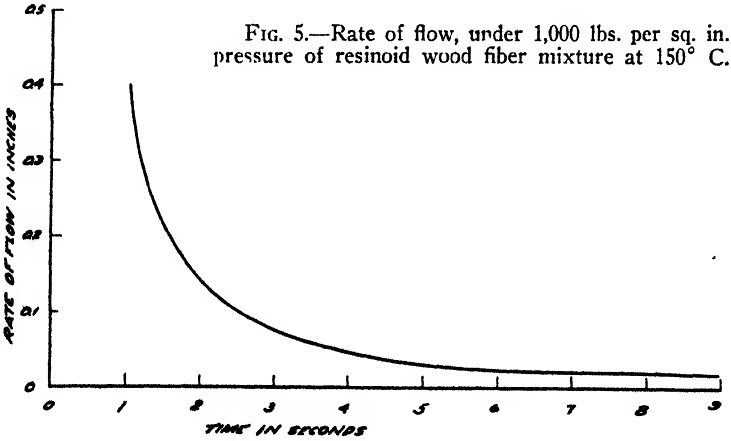

Fig. 5.—Rate of flow, under 1,000 lbs. per sq. in. pressure of resinoid wood fiber mixture at 150° C.

one second of heating to 0.13 inch per second at the end of two seconds. After four seconds the rate of flow was 0.05 inch and after ten seconds, 0.015 inch. At the end of twenty seconds the rate had reached 0.005 inch, and at the end of twenty-five seconds had entirely ceased.[21]

RESINOIDS WITH SOLVENTS.

The resinoids find extensive use also in liquid media. The "cold molding" process of using resinoids to bind fibers or solid particles is an example of partial suspension in liquids. In this process high-boiling liquids or resin-solvent mixtures are used to impart plastic flow to a mixed mass of powdered resinoid and any solid particles that are to be bonded. A good illustration is the process of bonding abrasive particles with resinoid in the production of grinding wheels. The cold molding of resinoids involves first a molding operation and second an after-heating to drive out solvents and to polymerize the resinoid. The mixed mass has at first a high rate of plastic flow, which rate decreases as the solvent is more fully taken up by the resinoid until it finally reaches a value so low that the cold-molded product may be removed from the mold and hardened by heat without deformation. Some high-boiling solvents or plasticizers may be left with the hardened resinoid for the purpose of modifying its properties, for instance, reducing its hardness and increasing its flexibility.

Resinoid "solutions" range from partial suspensions to clear liquids that give no evidence of the presence of particles under the ultramicroscope. Such clear solutions, however, exhibit the properties common to suspensoid colloids. They often pass through the zone of colloidal dispersion and one must deal with the phenomenon of *apparent* liquid viscosity. Here again we are confronted with the temporary nature of the aggregation processes. Viscosities of resinoids tend to change in kind or degree, or both, and greatly complicate the use of known viscosity laws. This is somewhat unfortunate; for many uses the value of resinoid varnishes is dependent on their viscosities which, in turn, are dependent upon the temperature, pressure, and time employed in preparation. These varnishes act like mixtures of true and colloidal solutions, and to obtain a desired industrial effect such as penetration into a porous material, this balance must be accurately regulated. By any method of measurement their viscosities are the resultant of several factors, among which are true liquid viscosity and plastic flow. The various instruments for viscosity measurement which will check for true liquid viscosities, as referred to a standard, will not check among themselves when used on these solutions.[22] However, the observed viscosities of these resinoid solutions are valuable for control purposes. Comparisons of determined viscosities are without meaning unless made on the same type of instrument and under the same carefully controlled conditions. Furthermore, the solutions must be of the same age.

According to Herschel [23] a material is considered plastic if the observed viscosity (the rate of shearing stress to the rate of shear) varies with the rate of shear, and will be considered viscous only when this ratio is found to be constant. Also, when this ratio varies, we have what is termed not true, but *apparent viscosity, apparent fluidity* and *apparent kinematic viscosity.*

Under this definition synthetic resinoids, whether cut by solvents or in solid form, are *plastic* rather than *viscous.* To be somewhat more exact, the resinoids themselves are considered as plastic, according to Bingham.[24] Their solutions, as generally prepared for industrial use, are considered as pseudoplastic, following the terminology of Williamson.[25] These solutions are characterized by exhibiting "no observable yield value or rigidity, while indicating departure from Poiseuilles' law when examined plastometrically." [26]

When resinoids are "dissolved" in solvent mixtures to give "spirit varnishes," there is ordinarily first a drop in viscosity for a short time then a gradual increase in viscosity even at room temperature. These viscosity changes are due apparently to polymerization or other aggregation changes. The change in viscosity is of course greatly accelerated by higher temperatures and slowed down by lower temperatures. In this connection it is of interest to note that viscosity changes in resinoids in solution or partial solution occur at fairly low temperatures. These changes are many times greater in solvent suspension than in the solid form of the same resinoid under the same temperature conditions. Both the initial drop and gradual increase of apparent viscosity appear to be the resultant of many factors most of which are as yet but slightly understood.*

When small particles of a plastic compound are suspended in a liquid medium, they cause a flow effect or viscosity which is different from the effect of solid non-plastic particles and different also from the effect of non-miscible liquid particles. Furthermore when the plastic compound is in itself subject to continual change in its plastic properties, one must take this plastic change into account when measuring viscosity at intervals over considerable periods of time.

In an unpurified resinous mass, like that made from phenol and formaldehyde, the intermediate form suspended in liquids consists of a mixture of raw ingredients, intermediate products, and true resinoid particles. The raw ingredients and intermediate products are continually condensing into the true resinoid form. This condensation proceeds at a decreasing rate with the decreasing probability of collision. Again the resinoid form is continually polymerizing into a more stable aggregate form, and there is considerable evidence to indicate that the polymerized molecules are continually uniting into loosely-joined colloidal type groups. In a solution where so many simultaneous changes are occurring it is certainly to be expected that the proportion of different sized particles is continually shifting, and that this influences viscosity. Even in those rare cases of resinoid solutions in which apparent viscosity remains constant over a long period of time it can be shown by the rate of penetration into fibrous masses that the particles are different at the different times of testing. A resinoid solution whose viscosity was found to be reasonably constant at intervals over a year plainly showed over the same period a constantly increasing penetration into a test paper. While the apparent viscosity was constant, it is evident that the factors which caused the resistance to flow could not have been the same at the different times of testing.

When the number, size and kind of unstable plastic particles are changing with time, these changes will be reflected back on the apparent viscosity and also on the other manifestations of flow such as penetration, change of flow with changes of pressure, etc. At times, certain obscure factors cause sudden fluctuations of apparent viscosity which are anticipated with difficulty. Again, one or more factors may predominate, and one may find an exaggerated devia-

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* Changes in the size and shape of particles, due to nematic or to other forms of molecular aggregation, may profoundly affect the working properties of products like these. Examination with the azimuth-ultramicroscope, which reveals the aggregation in vanadium pentoxide sols, should be of use. Chemical changes may take place concurrently, yielding new substances which in forming and aggregating,—or in going into solution, *must* pass through the zone of maximum colloidality referred to in Chapter I of Vol. I of this series. This zone should lie quite near the range of true solution because we are here probably dealing with large molecules which may themselves begin to approach colloidal dimensions. The observed facts seem to agree with this view. J. A.

tion from the normal; for instance, the initial drop of apparent viscosity may be lengthened out to a period of over a year. The control of certain factors, such as the proportion of the various solvents employed, makes it possible, if desired, to keep the apparent viscosity at a constant value. On the other hand by variation of the character of resinoid employed one may hold constant the rate of penetration into a fibrous material, which may be the characteristic having practical value, but in that case the apparent viscosity may vary over a wide range.

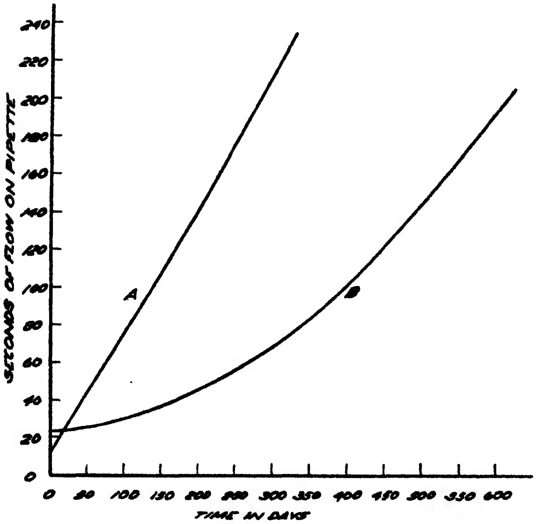

FIG. 6.—Ageing of resinoid in solvent.

Figure 6 shows progressive change, with age, of the apparent viscosities of two standard market varnishes.[27] Figure 7 shows erratic changes of apparent viscosity in experimental resinoid varnishes.

The dispersion of organic colloids in organic solvents has lately received some attention. The degree of dispersion of organophiles, including synthetic resins, has been explained[28] as having direct relation to polarity of solvent and solute. The dispersion of nonpolar organophiles is stated to be closely connected with the dielectric constant of the solvent. Rapid advance in our understanding of the viscosities of resinoid solutions may be expected, when various factors which influence their dispersion have been determined and properly evaluated. Meanwhile, though true viscosity may be expressed by simple formulas, we shall do well if by empirical modification[29] we are able to find a formula for apparent viscosity as exhibited by the ever-changing resinoids when dispersed in organic solvents.

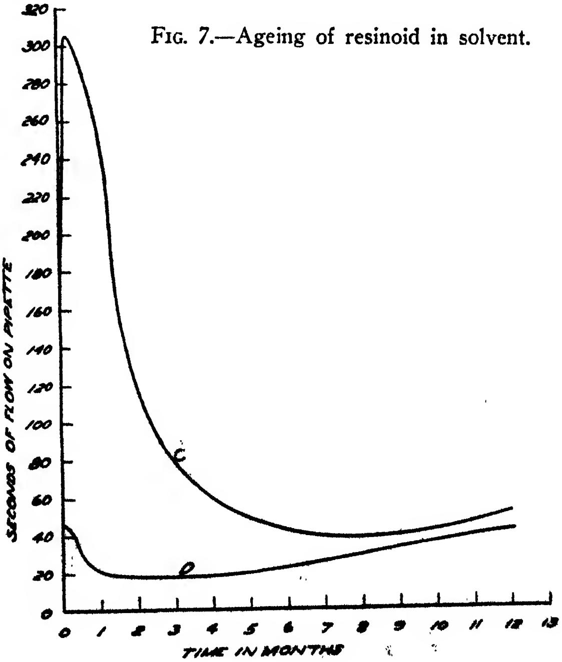

FIG. 7.—Ageing of resinoid in solvent.

CONCLUSION.

Colloids, according to Alexander,[30] are essentially substances in a labile or metastable state and the general tendency is for their interrupted aggregation processes to establish themselves if given opportunity and sufficient time. The resinoid industry finds its first major task in causing a controlled interruption of three normal aggregation processes, the first two, chemical condensation and polymerization, and the third, a physico-chemical coagulation, which is of particular interest in the case of resinoid solutions.

When one contemplates the field of resinoid chemistry, one is impressed by the importance of the factor of time. We are pleased to have inorganic chemistry complete its reactions in seconds; we encourage organic chemical reactions, in general, to move at their slow, dignified rate to a reasonable point of completion, but in the special field of resinoid chemistry reaction must proceed in definite, well regulated stages. Here the operation is under the control of a thermometer and a timepiece, with time the chief variable, and the operator well knows that industrial success depends upon his measurements of time as well as of temperature.

We have seen how the "synthetic resin" industry resulted first from discoveries made in the "discards" of organic research. First used as an amber substitute, the phenol resinoids soon developed important use as electrical insulation. In this field they have had amazing growth, yet this use bids fair to be far surpassed by those structural uses which require emphasis on lasting surface finish and resistance to corrosion along with moderate, though adequate, mechanical strength. Also, as is so often the case in chemical research, the first problem undertaken is the last to be solved, and we see the synthetic resins again displacing natural resins, as for instance rosin or ester gum, in the new, synthetic resin-oil varnishes. This they are doing by virtue of their greater effectiveness rather than as merely cheaper substitutes.

Both the synthetic resin and the synthetic resinoid industries are expanding rapidly but he would be a reckless prophet who would undertake to point out the exact direction of future growth. It does seem certain, however, that "synthetic resins" are destined to play an increasing part in our structural needs. So far the *resinoids* have found their main use in making feasible the mass production of high quality, reasonably priced, replaceable structural parts. The size of such structural units is being continually increased, with the result that the resinoids are finding use not only for furniture but also for structural parts of the house itself; not only for timing gears and ignition parts of the automobile, but for the material of the car body itself. Also the resinoids are making possible more economical shaping of structural materials by supplying more efficiently bonded abrasives, and modifications of the resinoids as well as of the *resins* are furnishing superior coatings for finishing and thereby giving longer life to other strong, but less enduring, structural materials.

Following Baekeland's early work there has been published a continuously increasing stream of patents covering synthetic resin products. The resin-like substances so far discovered and exploited have proved of such marked utility that all future resinous discoveries will doubtless promptly be subjected to careful and exacting scrutiny, and little by little the knowledge gained in the chemistry of the more easily purified colloidal substances will be applied further to improve this important group of resin-like synthetic products.

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[7] The term "phenols" is here to be understood as embracing phenol and its derivatives, such as cresol, xylenol, phenyl phenol, chlorophenol, etc., and the term "aldehydes," as embracing any aldehyde or ketone, such as formaldehyde, benzyl aldehyde, furfuraldehyde, acetone, benzophenone, etc. Of the large number of possible raw materials, phenol, mixed cresols, mixtures of cresols and xylenols on the one hand, and on the other formaldehyde, furfuraldehyde, acetaldehyde and acetone have become of most industrial importance.

[8] Kleeberg, *Ann. Chem.* **1891**, 263, 283.

[9] De Laire, French Pat. 361,539 (1906).

[10] L. H. Baekeland, *J. Ind. Eng. Chem.*, 1, 149 (1909); also *J. Ind. Eng. Chem.*, 5, 506 (1913).

[11] In the case of other synthetic resins having a "hardenable" form, such as the "alkyds," the connection between the permanently fusible form and the hardenable form has been in a measure explained, also. *See* R. H. Kienle and A. G. Hovey, *J. Am. Chem. Soc.*, **51**, 509 (1929). *Also see* R. H. Kienle, *Ind. Eng. Chem*, **22**, 590 (1930).

[12] First designated by Baekeland as Novolaks. See *J. Ind. Eng. Chem.*, 1, 548 (1909).

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[17] V. H. Turkington, R. C. Shuey, and W. H. Butler, *Ind. Eng. Chem.*, **22**, 1177 (1930).

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Into a 1,500 ml. Pyrex glass beaker is placed a Pyrex test tube suspended from a resinoid bonded "laminated canvas" cover and encircled with a few turns of a copper cooling coil. The test tube is closed with a loose, "laminated" cover from which is suspended a drill rod having at its base two brass shelves, the upper of which has holes and fittings for three brass cups. Three steel balls furnish by their weights the pressure necessary in determining the low values of plastic flow ordinarily involved. Two thermometers measure the bath and flow temperatures, respectively. The bottom of the inner thermometer is placed even with the bottom of the steel balls but not touching them. The temperature recorded by the inner thermometer at the instant that a ball drops through the resinous mass and touches the bottom plate is recorded as the melting point.

The size chosen for the steel balls was one that was found to give a temperature measurement which checked with so-called "melting points" made on resinoids prepared by grinding under anhydrous conditions. Then capillary tube melting point determinations were made using a very constant, slow rate of heating. Such capillary tube methods are difficult to check and require the averaging of determinations by various operators. The steel ball method largely eliminates variation due to this factor of personal equation.

[20] E. C. Bingham, *J. Chem. Education*, **6**, 1209 (1929).

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[23] W. H. Herschel. *See* Alexander, "Colloid Chemistry," Vol. I, this series, p. 727.

[24] E. C. Bingham, *J. Chem. Education*, **6**, 1207 (1929).

[25] R. Williamson, *Ind. Eng. Chem.*, **21**, 1108 (1929).

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[28] G. S. Whitby, *Chemistry and Industry*, **47**, 266 (1928); *see also* W. B. Lee, *J. Soc. Chem. Ind.*, **T226** (1930).

[29] Bingham, "Fluidity & Plasticity," New York, McGraw-Hill Book Co., **1922**, p. 287.

[30] J. Alexander, "Colloidal Chemistry," Vol. I, this series, p. 17.

Dispergation and Aggregation of Natural Silk in Aqueous Solutions of Neutral Salts.* †

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Before proceeding to the main subject, a brief historical introduction will be appropriate, dealing with the action of aqueous solutions of neutral salts upon those high-molecular substances which are practically insoluble in water, and capable of producing on hydrolysis compounds soluble in water, e.g., cellulose, silk, chitin, keratin and others.

Historical Introduction.‡

A systematic, experimental investigation carried out by me in 1912,[1] has demonstrated the applicability to chemically complex (high-molecular) substances, of theories concerned with preparing colloidal solutions by dispergation (peptization),[2] and also of the dispersoidological theory of true solutions.[3] The substance under investigation was cellulose, with aqueous solutions of neutral salts as dispergators.

In 1913,[4] I stated that aqueous solutions of salts should be able to dispergate, not only cellulose, but also other colloids which can hydrolyze into soluble compounds.

After the lapse of several years, this statement was confirmed by the works of other investigators. Thus, in 1921, R. Herzog and Schweiger demonstrated the dispergation of acetyl-cellulose in the concentrated aqueous solutions of a series of neutral salts.[5] Also in 1921, Herbert E. Williams wrote that concentrated calcium thiocyanate solutions dissolve not only cellulose but also acetyl-cellulose and natural silk, though they have no action upon wool.[6]

In 1925 I proved experimentally [7] that natural silk can be dispergated with ease and abundance in the solutions of a great number of salts and even in the solutions of such common salts as calcium chloride and calcium nitrate; and also that natural silk can be dispergated in, e.g., concentrated aqueous solutions of lithium iodide and lithium thiocyanate, even in the cold (e.g., at room temperature).

In 1926,[8] in collaboration with my pupil, S. Utzino, I confirmed the applicability of my theory to chitin, which was dispergated with marked readiness in hot concentrated aqueous solutions of salts. Casein has also readily dispergated in solutions of certain neutral salts. We established [9] in the same year the ability of fibrin and keratin (wool) to dispergate in hot concentrated

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* Translated from Russian by Mrs. P. P. von Weimarn.

† In this paper are briefly summed up the results of my investigations, carried out between the years 1925-1930, upon the action of solutions of neutral salts on silks; for a more detailed account *see* the papers indicated in the References.

‡ For more detailed historical data, *see* the papers enumerated in the References.

aqueous solutions of extremely soluble salts [for instance, of LiCNS and of $Ca(CNS)_2$].

The solubility of keratin (wool) in $Ca(CNS)_2$ solutions was confirmed also by L. Meunier and G. Rey;[10] these investigators also showed that the precipitate, resulting from the addition of alcohol to the solution of wool, possessed fluorescence and showed all the reactions of the initial wool.

Of course, isolated examples of dispergation in the solutions of certain salts of high-molecular substances insoluble in water were known before 1912; for instance, the solubility of cellulose in concentrated aqueous solutions of zinc chloride was known as far back as 1884 (Wynne and Powell's Patent).

But I am decidedly unaware of anyone who has expressed such a statement as was formulated by me in 1913, namely, that *any* high-molecular substance, which is practically insoluble in water and is inclined to abundant hydration and hydrolysis, must dispergate in concentrated aqueous solutions of *any* neutral salt which possesses a great solubility and capacity for hydration.

In order to avoid an incorrect understanding of this statement, I consider it important to add the following.

Of course, not every readily soluble salt taken at random from the laboratory shelf will, in its aqueous solution, with the concentration available under ordinary pressure, easily dispergate cellulose, for instance.

To obtain good results in the process of dispergation, the coherence of water in the hydrates of the salt must necessarily be dynamic (kinetic) and, moreover, its intensity must not go beyond the limits of certain medium values. If these values be reached under ordinary pressure in the solutions, then the dispergation will prove successful at ordinary pressure; otherwise, the dispergation must be brought about under other conditions, sometimes not easily attainable.

It is essential to understand that the preëminent rôle in this case is played by a *certain* state of hydration, and only a secondary rôle by the chemical nature of the salts; it should be understood, for instance, that cellulose can be dispergated in equal amounts, and with the same velocities, by concentrated solutions of several easily soluble salts, as, e.g., by salts of hydrobromic, hydroiodic and thiocyanic acids.

The states of hydration necessary for producing a considerable and rapid dispergation of chemically composite substances of the type under discussion, are not the same for different individuals, and these states are particularly dependent upon the hydration capacity of these substances; for example, hot concentrated $CaCl_2$ solutions which are obtainable at ordinary pressure dissolve natural silk colloidally in abundance, but do not dissolve even one gram of cellulose after several hours' heating in 100 cc. of the solution.

However, it must be taken into consideration, that besides a certain state of hydration of the salt, other variables also may affect the results of the dispergation process.

As a *main variable* for considerable and rapid dispergation, my theory accepts a *certain* state of hydration, and does not reject the influence also of other variables.

In certain cases, the temperature (under pressure) of the salt solutions, at which the dispergation of a chemically complex substance proceeds, is so high that the process is accompanied by a chemical decomposition of this substance. Such cases are of no industrial value; however, the dispergation taking place in these cases is of a theoretical interest, as a confirmation of the general character of the above statement.

I. DISPERGATION OF NATURAL SILK IN AQUEOUS SOLUTIONS OF NEUTRAL SALTS.

SALT-DISPERGATORS

When dispergating natural silk (silk wadding, for instance) at temperatures, and with concentrations of aqueous salt solutions available under ordinary atmospheric pressure; i.e., when high pressure is not applied, not *all* readily soluble salts, in their solutions, prove dispergators for silk.

According to my experiments, the solutions of the following salts easily dispergate silk with concentrations and at temperatures of the solutions available at ordinary pressure. The salts are arranged in order according to the periodic table, and not according to their dispergating ability.

> $LiCl$, $LiBr$, LiI, $LiCNS$, NaI, $NaCNS$; $MgBr_2$, $Mg(NO_3)_2$, MgI_2, $Mg(CNS)_2$; $CaCl_2$, $CaBr_2$,CaI_2,$Ca(NO_3)_2$, $Ca(ClO_3)_2$, $Ca(CNS)_2$; $SrBr_2$, SrI_2,$Sr(ClO_3)_2$, $Sr(CNS)_2$; BaI_2, $Ba(CNS)_2$, $Mn(CNS)_2$. And the double salts: HgI_2 with LiI, NaI, KI, etc.

The solutions of other salts which I have investigated, may be divided into those dispergating silk but slowly (the dispergation being accompanied moreover by a marked partial decomposition of the silk), and into those which *practically* do not dispergate silk at all. For instance, magnesium chloride solutions dispergate silk slowly, and a prolonged heating of the silk with the solution causes a partial decomposition of the silk. The solutions of $CoCl_2$, $Ni(NO_3)_2$, $CrCl_3$, $AlCl_3$ and the like, though producing dispergation of silk, cause a partial decomposition of the silk, which is more pronounced than in the case of $MgCl_2$.

Silk is practically not dispergated under ordinary pressure by the solutions of the following salts: Li_2SO_4, $NaCl$, Na_2SiO_3, Cs_2SO_4, $BaCl_2$, $BaBr_2$, $Ba(NO_3)_2$, $Ba(ClO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $NiCl_2$, etc.

. Those salts, the solutions of which under ordinary pressure readily dispergate silk, I have named *salt-dispergators.*

MACRO-, MICRO- AND ULTRAMICROSCOPIC OBSERVATIONS OF THE DISPERGATION OF SILK IN AQUEOUS SOLUTIONS OF SALT-DISPERGATORS.

Silk is dispergated in solutions of salt-dispergators much more readily than cellulose. I shall confine myself to the description of the following example.

One gram of cellulose fails to dispergate completely in 100 cc. of a concentrated aqueous solution of $CaCl_2$, boiling under atmospheric pressure at 135° C. even if heated for many hours; only a comparatively small part of this gram of cellulose becomes dispergated, although the fibers will have undergone some appreciable degree of swelling.[11]

Now in striking contrast to this 10 grams of natural silk (silk wadding) can be dispergated within 10 to 20 minutes, in 100 cc. of an aqueous $CaCl_2$ solution that boils under atmospheric pressure at 115° C.

Incidentally, it is important to note that by means of applying the above solutions of $CaCl_2$, it is possible to detect any adulterations whatever of natural silk, consisting of threads made up of cellulose, most particularly adulterations with artificial silk (rayon).

It is quite simple to obtain colloidal silk solutions by means of salt-dispergators. As an instance, let me describe one of my experiments on natural silk (silk wadding) dispergation, let us say, in a solution of calcium chloride.

The first thing to be done is of course to prepare a neutral concentrated aqueous solution of calcium chloride showing not the slightest *acid* or *alkaline* reaction, when tested with phenolphthalein, for instance a solution boiling under ordinary pressure at about 115° C. The simplest way to get such a solution is to let 250 grams of calcium chloride crystals (Merck's Reagent: $CaCl_2.6H_2O$) dissolve by heating in 100 cc. of distilled water. Upon letting the mixture boil for a short time, it is easy to obtain a solution of calcium chloride, boiling at 115° C. From that solution, 200 cc. are then sampled off (at 115° C.) into a tall beaker, and the beaker is placed on a piece of asbestos board, over a small flame of the gas burner; the temperature must be maintained approximately at 115° C. Then weigh 20 grams of silk (silk wadding) and introduce this whole amount, in small portions (say 1 gram at a time) into the solution, while stirring it vigorously with a glass rod (or better with a thermometer, as this permits the simultaneous reading of the temperature). Upon being introduced into the solution, the silk wadding will rapidly become slimy and dispergate.

With some experience in such manipulation, one will hardly have any difficulty in completing in 200 cc. of the solution the dispergation of the whole amount, 20 grams of silk, in the course of about 10 to 20 minutes. What is finally obtained as a result of the dispergation, is a viscous liquid of light brownish-yellow color which froths greatly when boiling. In thin layers it is quite translucent; in thick layers however, e.g. when contained in a beaker, the liquid is distinctly turbid and scarcely translucent.

On cooling the liquid down to the room temperature, no formation of an elastic jelly is observed, but merely a marked increase in viscosity. The dispergation of natural silk is effected similarly in any one of the number of other salt-dispergators mentioned above as being agents capable of readily producing colloidal dispersion of natural silk under ordinary pressure.

What is the *maximum* solubility of natural silk in the above concentrated aqueous salt solutions? The answer to this question will be the same as the answer to the question about the maximum solubility of gelatin in hot water. The *practical* limit of solubility of a substance of the type under discussion, is fixed by such amounts of these substances as will render the resulting disperse systems so viscous, that any further stirring of the solutions after the introduction of fresh portions of the substance, becomes a practical impossibility.

In the case of natural silk, this *practical* limit will be something like 30-35 grams of silk (silk wadding) per 100 cc. of the *hot* concentrated aqueous solution of the salt, the stirring being effected with the hand, by means of a glass rod.

No particular difficulties are encountered in causing 15 to 20 grams of silk to dispergate in 100 cc. of the hot concentrated aqueous solutions of salts (e.g. of $CaCl_2$, $Ca(NO_3)_2$......$Ca(CNS)_2$, NaI, LiBr and the like); but owing to the extreme viscosity of the disperse system obtained, it is not so easy to raise the concentration up to 30 grams even at temperatures between 150° to 160° C. (e.g. in the case of $Ca(CNS)_2$ solutions).

In microscopic examinations, with the bright field of illumination, it may be observed that threads become considerably swollen and then, *under suitable conditions of experimentation,* they are transformed into a *very viscous* liquid mass capable of forming drops; this liquid then dissolves in the solution of a salt-dispergator.

Ultramicroscopic observations of the process of silk dispergation give much more interesting results than microscopic. The ultramicroscopic investigations, carried out by me, have shown that every single silk thread may be divided into a multitude of tiniest fibrils and that their thickness and breadth are extremely small and lie at the limits of ultramicroscopic vision, even when observed against the most contrasted dark field of illumination. In any case the dimensions of a tiniest fibril do not exceed a few mμ.

In Figure 1 are four photo-ultramicrographs (a-d) and one photomicrograph of one single thread of natural silk, which was subjected to dispergation in a concentrated aqueous solution of one of the salt-dispergators (NaI); the magnification in all photographs is the same and equals about 350×.

From these photo-ultramicrographs it may be seen that the first stage of dispergation is a progressive swelling of the thread; and with the progress of swelling there appear in every silk thread, a multitude of fibrils, the breadth and thickness of which are of ultramicroscopic dimensions. In the thread in the photo-ultramicrograph in Figure 2 (magnification 1,200), not only a distinct fibril structure may be observed, but also some fibrils separated from the main thread by movement in the solution (in the right-hand bottom corner of the picture). It is seen that one of these separated fibrils, in its turn, can be divided into thinner fibrils (see the end of the fibril).

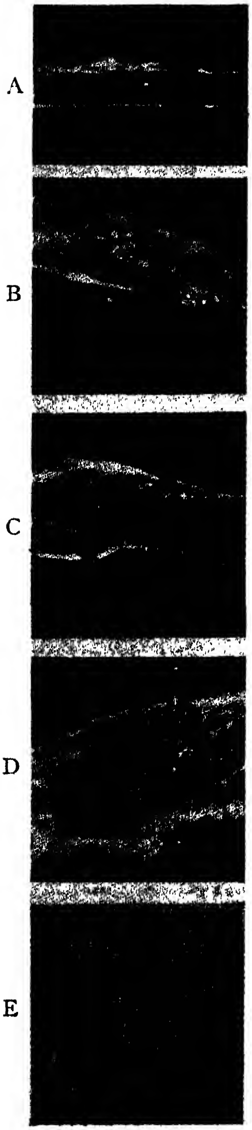

Fig. 1.
About × 350.

Fig. 2. × 1200 reduced about ⅕.

The fineness of the fibrils separating from the threads of natural silk is the same as that of a lamella, which is split off from ordinary crystals parallel to the cleavage plane. Such lamellæ consist of only a few layers of molecules.

In other words, the threads of natural silk possess what I have already termed a *fibril cleavage,* a term used in order to emphasize the relation to the cleavage of ordinary crystals.

Thus, by carrying out the dispergation process slowly, other conditions of the experiment being suitable, it is possible to demonstrate the fibril cleavage of separate silk threads; because with the growing of the swelling of the silk thread, fibrils become more widely separated. Besides this, in the photo-ultramicrograph in Figure 1 (c-d), it may be distinctly seen that the fibrils in a swollen thread are distributed in spirals; and the stronger the swelling, the more tightly are curled the spirals. And with the maximum swelling, the spiral curls are almost perpendicular to the length of the silk thread.

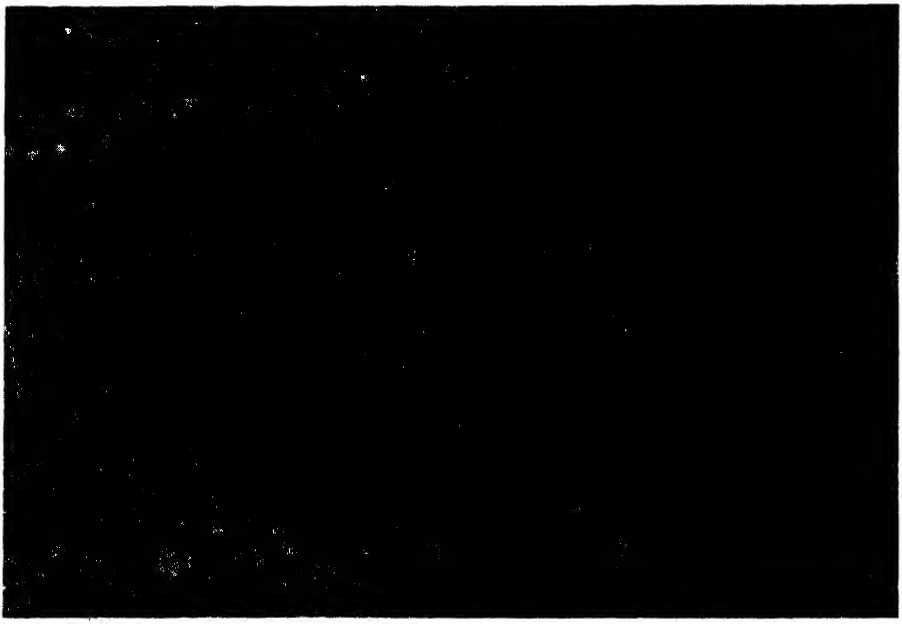

Fig. 3. About × 1,000.

A further swelling produces such a highly elastic state of the thread that it rightly may be called a rubber-like state.*

When the dispergation is carried out very slowly (e.g. in a NaI-solution) then with the progress of dispergation, the superficial layer of the strongly swollen silk thread disintegrates into perfectly spherical drops of a viscous liquid. And the spiral curls in the middle of the swollen thread, at the same time become extremely viscous semi-liquid masses of an elongated shape. They are formed almost in the same order and in the same place as were the spiral curls in the strongly swollen silk thread. In Figures 1-e and 3 (magnification 1,000) is demonstrated this stage of dispergation.

As has already been said above, a further dispergation causes the dissolu-

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* *See* my paper on the rubber-like state of matter in Vol. III, this series.

tion in the solution of the salt-dispergator, of drops of the colloidal solution, into which the silk thread has disintegrated.

In a *rapid* dispergation, it is impossible of course to observe under the microscope anything else besides the disintegration of the silk thread into pieces and a rapid disappearance of these pieces into solution.

The Distribution of Forces in Vectorial Fields of Forces of Fibroin Molecules.

The fact established by the ultramicroscopic observation and described above is that every detached silk thread may, by means of swelling, be caused to divide into a multitude of fibrils, whose cross-section is of ultramicroscopic dimensions. Further, experiment has shown that fibrils having cross-sections of ultramicroscopic dimensions, can be in their turn divided into fibrils, possessing still smaller cross-sections. This fact forces the conclusion that silk threads possess "fibril cleavage." The readiness of a silk thread to separate into fibrils, or the excellent fibril cleavage of silk, necessarily leads to the admission of the existence of a very unequal distribution of intensities in the vectorial fields of forces *of the smallest masses of fibroin which cannot be divided further without loss of chemical individuality of this substance,* or speaking briefly, of fibroin molecules.

The distribution of intensities in a vectorial field of fibroin molecules, may be imagined as having the form of an ellipsoid, extremely elongated, resembling a needle with rounded ends. In the directions of the long axis of this ellipsoid the vectorial forces reach their highest intensities; in other directions there act forces of comparatively low intensities.

It is clear that this deduction is only a logical extrapolation of the fact of the fibril cleavage of silk; because it is impossible to divide the tiniest fibril, visible under the ultramicroscope, into fibrils with cross-sections equalling those of *one single* molecule of fibroin; i.e. into fibrils with monomolecular cross-sections. It can be only established by experiment that the smallest fibril does not contain more than several molecules in its cross-section, and I hold that the extrapolation in this case from "several" molecules to "one," is in the scientific sense, not only quite permissible, but even unavoidable.

By the above-described distribution of forces in the vectorial fields of fibroin molecules, not only the fibril cleavage in the silk threads may be explained, but all the phenomena observed in the aggregation (coagulation) of colloidal silk solutions. These phenomena will be discussed later, in the course of this paper.

On the Dispergation Series of Salt-dispergators.

The temperature (beginning, e.g. from 90° C.) required for producing a marked dispergation of silk in the solutions of different salt-dispergators, varies for every salt-dispergator even when they are prepared of such concentrations that the boiling point of the solutions of *all* these salt-dispergators is the same, e.g. 120° C. The same pertains to the velocity of dispergation of silk, which varies with every salt-dispergator, etc.

On the ground of experimental data, obtained by me, it can be assumed that salt-dispergators possess different *dispergation powers,* designated by the symbol *D*. Following my experiments, salt-dispergators according to their dispergation powers may be arranged in a series known in colloid chemistry as the *Hofmeister* series.

^{D}Fluorides $<$ ^{D}Sulphates $<$ ^{D}Citrates $<$ ^{D}Tartrates $<$ ^{D}Acetates $<$
$<$ ^{D}Chlorides $<$ ^{D}Nitrates $<$ ^{D}Bromides $<$ ^{D}Iodides $<$ ^{D}Thiocyanates.

Salts of the last five acids prove to be dispergators for silk, even when their solutions are used at temperatures and with concentrations, available under ordinary atmospheric pressure. Representatives of the five other salts in this series do not, under the same conditions, dispergate silk to any marked degree. Without doubt, the dispergation of silk (as stated in the introduction to this paper) must take place also with these salts (if even with a partial decomposition of silk) when their solutions are of higher concentrations and at higher temperatures, both conditions being available only under a more or less increased pressure. It should also be added that under the influence of different variables, the members of this series may change their places.

II. On the Physico-chemical Nature of Silk Solutions in the Solutions of Neutral Salts.

On the Influence of the Concentration of a Salt, Upon the Transition of the Solutoidal Solutions of Complex Compounds of Fibroin with Salts, into Dispersoidal Solutions of Fibroin.

As is shown by R. Dubois,[12] fibroin, which is in the seripterium of the silkworm in a gummy state, dispergates (dissolves dispersoidally)* spontaneously in boiling distilled water, or in 5 to 10 per cent aqueous NaCl and K_2CO_3 solutions. But once the fibroin passes out of this gummy state, and becomes solidified into an ordinary silk thread, then, as is well known, it is insoluble either in water, or in salt solutions of low concentrations.

Aqueous dispersoidal solutions of fresh gummy fibroin, taken out of seripteria of silk-worms, were studied in detail by an Italian investigator, Carlo Foà, in 1911.[13] These solutions being of low stability, a spontaneous coagulation ensues in from 3 to 24 hours after the preparation has been made. They possess all the typical properties of ordinary dispersoidal solutions; the disperse particles, at electrophoresis, show a negative electric charge.

Of another physico-chemical nature are silk solutions in those neutral solvents, as for instance, *hot* aqueous solutions of neutral salts, which were first studied by me.[14] In order to make clear as briefly as possible the physico-chemical nature of these silk solutions, the simplest way will be to compare them with dispersoidal and true solutions of AgI in aqueous or alcoholic-aqueous solutions of, e.g., KI and $AgNO_3$.

Aqueous dispersoidal solutions of the above substance, were studied very exhaustively by A. Lottermoser,[15] while many years ago,[16] I investigated alcoholic-aqueous solutions of the same substance.†

When the concentration of KI or $AgNO_3$ is very small, we have dispersoidal solutions of AgI, in aqueous as well as in alcoholic aqueous dispersion media; on the surfaces of disperse AgI crystals, in these dispersoidal solutions, are complex compounds of the composition:

$$AgI.xKI.aH_2O, \quad \text{or} \quad AgI.yAgNO_3.bH_2O,$$

according to the excess of either component of the reaction ($AgNO_3$ + KI).

When the concentration of KI, or $AgNO_3$ is sufficiently great, then we have *true* solutions of complex molecules: $AgI.zKI.cH_2O$, or $AgI.tAgNO_3$.

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* On the subdivision of colloidal solutions into two classes: dispersoidal and solutoidal, see, e.g., my paper in *Rév. gén. colloïdes*, 7, 153 (1929).

† *See also* paper by A. Lottermoser in Vol. I of this series. *J. A.*

dH_2O; from these solutions, large crystals may be deposited of the composition, e.g.

$$AgI.AgNO_3;\quad AgI.2AgNO_3;\quad AgI.KI.$$

By the dilution of these true solutions with a sufficient amount of water, or alcohol, the complex molecules become decomposed, and a precipitate of AgI is deposited; or, if the conditions are suitable, there result the *dispersoidal* solutions of AgI, mentioned above.

Similarly, the solutions of silk-fibroin in aqueous neutral solutions of neutral salts, may, according to the conditions, give either dispersoidal solutions or true solutions (i.e. *solutoidal,** because fibroin is a chemically composite compound) of a hydrated complex "fibroin + salt."

It has been experimentally proven that the preëminent rôle in the dissolution of fibroin in salt solutions belongs to a certain state of hydration of the salt, and not to its chemical nature. It is clear that the cohesion of molecules of water in fibroin-hydrates, with that of salt-hydrates, acquires a particular significance in carrying out the dissolution under discussion.

If we designate the hydrated molecules of salt-dispergators as D.x(H.OH) and the hydrated molecules of fibroin as F.y(H.OH), then the schematic presentation of the complex molecules, present in solutoidal fibroin-solutions, is expressed as follows:

$$[D.a(H.OH)]_c\,.\,[b(H.OH).F]_d;$$

the state of hydration of these complexes is dynamic.

By the addition of a suitable amount of water, solutoidal solutions of complex compounds "fibroin + salt" may, in certain cases, be decomposed, and a dispersoidal solution of fibroin will be formed, analogous to the AgI dispersoidal solution in weak aqueous or alcoholic-aqueous KI or $AgNO_3$ solutions.

When the above *solutoidal* solutions of silk are slightly diluted with water, disperse systems are obtained which are mixtures in varied proportions, of complex compounds of fibroin with salts in a *solutoidal* state, and of fibroin particles in a *dispersoidal* state. There are also found, in such systems, solutoidally and dispersoidally dissolved products of the decomposition of the complex compounds of fibroin with salt.

THE INFLUENCE OF TEMPERATURE UPON THE TRANSITION OF SOLUTOIDAL SOLUTIONS OF COMPLEX FIBROIN COMPOUNDS WITH SALTS INTO DISPERSOIDAL SOLUTIONS OF FIBROIN

Only the solutions of a few salt-dispergators (see below) are capable of dissolving natural silk at room temperature. A great majority of the solutions of salt-dispergators can do this only at a more or less elevated temperature, most often at about 100° C. and higher. In these cases a great part of the silk, on dispergating, gives solutoidal solutions of complex compounds of fibroin with salts, and only the smaller part of silk dissolves dispersoidally, i.e. without producing complex compounds. Other conditions being equal, the quantity of silk, dissolved dispersoidally is the less, the higher the dispergation power of the salt applied. For example, in hot $Ca(CNS)_2$ solutions it is possible to dissolve solutoidally, practically all the fibroin; this solutoidal solution is perfectly transparent at high temperatures, and does not even possess traces of opalescence, when observed with the naked eye.

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* See P. P. von Weimarn, loc. cit. *Rév. gén. colloïdes,* 7, 153 (1929).

Hot silk solutions obtained by means of faintly powerful dispergators possess more or less marked opalescence. And hot silk solutions, obtained in comparatively weak dispergators, are turbid and barely translucent in thick layers.

Silk solutions, in the solutions of salt-dispergators, with the exception of only those which are obtained by certain salt-dispergators at room temperatures (see below), when cooled to room temperature, begin to develop a distinct opalescence. In case they possessed opalescence before, it becomes more marked at room temperature, and under certain conditions the opalescence transforms into a white turbidity and the solution becomes opaque.

When the experiment is carried out under such conditions that cooling these silk solutions to room temperature does not cause aggregation (coagulation) with the formation of a precipitate or of layers (separation into layers), then, upon cooling, systems are formed which are transitory from the solutoidal to the dispersoidal. The causes of this transition are the following.

With comparatively few exceptions, a great number of neutral salts dispergate silk *only* in their *hot* solutions. Cold solutions of these salts are not dispergators for silk; on the contrary, they produce aggregation (coagulation) in silk solutions, as will be seen from Part 3 of this paper.

Putting it another way, the salts can overcome the vectorial cohesion of fibroin molecules in the silk fibrils, and produce complex compounds with fibroin, only when this cohesion is weakened by a high temperature. With a drop in temperature, the vectorial cohesion of fibroin molecules with each other predominates over all other chemical cohesions of a complex compound, and the fibroin molecules begin to aggregate into dispersoidal particles, pressing out to the surface of these dispersoidal particles, molecules of salt which were combined with the fibroin molecules.

Just such a transition takes place on cooling a *true* solution of complex compounds of the type of $AgI.xKI.aH_2O$, when the concentration of potassium iodide is not too high, and the silver iodide crystals are the saturating substance.

When, notwithstanding the increased solubility of the silver iodide resulting from the formation in the solution of a complex compound, the silver iodide remains as the saturating substance, then, on cooling the solution, AgI crystals will be yielded in any degree of dispersity, dependent upon the conditions of the experiment. In this case also vectorial forces of the silver and iodine atoms which cause the formation of AgI crystals, upon a drop in temperature overcome the chemical cohesions between the atoms of the complex compounds. Thus with the drop in temperature of silk solutions in hot salt solutions, the transition takes place:

Solutoidal solutions of the complex compounds of fibroin with salts

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Dispersoidal fibroin solutions.

This transition usually proceeds at a slow rate, and therefore on cooling a solutoidal silk solution, there are formed solutions of a mixed, i.e. intermediate type, wherein a part of the complex compounds is not decomposed and is in a solutoidally dissolved state. The smaller this portion, the more nearly the nature of this disperse system approaches that of a dispersoidal solution.

III. AGGREGATION (COAGULATION) OF SILK SOLUTIONS IN AQUEOUS SOLUTIONS OF NEUTRAL SALTS.

SPONTANEOUS AGGREGATION.

Solutions of neutral salts which dispergate silk at room temperature. Salts ranged according to their aggregative abilities.

With the exception of concentrated aqueous solutions of several salts which can dispergate silk at room temperatures (LiCNS, LiI and $Mn(CNS)_2$),[17] concentrated solutions of *all* other salts, studied by me, prove to be aggregators for silk solutions at temperatures lower than those at which the dispergation of silk takes place. According to their aggregative power toward silk solutions, the salts may be arranged in the following series:

Fluorides > Sulphates > Citrates > Tartrates > Acetates >
> Chlorides > Nitrates > Bromides > Iodides > Thiocyanates.

Next I proceed to the description of various examples of aggregation.

Aggregation, with very strong concentration of salts in silk solutions. The separation of solutions into two layers.

Aqueous solutions of lithium chloride with the boiling point 130° C. readily dispergate silk wadding between 120°-125° C. In a layer of 4 cm. silk solutions prepared by dispergating 20 grams of silk wadding in 100 cc. LiI solution (boiling point 130° C.) are fairly translucent at this temperature, and have a yellow color in transmitted light. In reflected light this solution shows a strong bluish-dull-white opalescence. The following is observed when the solution is allowed to cool from 130° C. to room temperature, whilst being stirred with the thermometer in order to ensure an equal cooling.

Upon cooling, the translucency of the solution gradually diminishes, and, when the temperature falls to 105° C., the solution becomes quite opaque. At 90° C. when the solution is stirred, stripes appear, which are an indication of the beginning of separation into layers. At 70° C. the viscosity of the solution approaches that of a *fluid* dough. At 55° C. the dough becomes thickened and whilst being stirred begins to curl slightly around the thermometer. At 45° C. the solution is a ropy-plastic dough, which readily curls onto the thermometer on stirring. At 40° C., when the dough * is pressed, an almost transparent solution is squeezed out. After the lapse of several minutes (40° C.) the dough has yielded about 10 cc. of an almost transparent liquid. After standing for twenty hours at room temperature, there is seen on the bottom of the vessel, a perfectly ropy-plastic mass with a supernatant layer, approximately of 40 cc., of an almost transparent solution.

It is easy to demonstrate by microscopic examination the liquid consistency of the layer separating at elevated temperatures (95° to 85° C.), and containing complex compounds of fibroin with lithium chloride. However, the liquid consistency of this layer may be ascertained also by a direct observation of the process of separation into layers of 8 to 10 per cent silk solutions in hot lithium chloride solutions; the concentration of the salt in the solution corresponding to a boiling point of 130° C.

In this case during the separation into layers there is formed at 85° C. a layer of a viscous liquid (containing vapor bubbles) which rises to the surface

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* For the sake of brevity this form of coagula will be designated in the course of this paper as "dough."

of the lithium chloride solution. With a further drop in temperature, this quite liquid layer sinks to the bottom of the vessel, gradually assuming the consistency of the ropy-plastic dough. With the above concentration (8 to 10 per cent) of silk in the solution, the supernatant layer consists of about 70 to 75 cc. of an almost clear lithium chloride solution.

On cooling a silk solution of 30 per cent concentration, only a few drops of the lithium chloride solution appear on the surface of the dough. The greater portion of the separated lithium chloride solution is enclosed within the pores of the dough, the consistency of which is too thick to allow a *spontaneous* separation of the solution at the surface. With still higher concentration of silk in the solution, all the solution, as a whole, becomes transformed into a ropy-plastic dough (*jellied dough*) and the whole second layer of the lithium chloride solution is adsorbed by the dough; to such an extent, that not even a few drops of the lithium chloride solution find their way to the surface of the dough.

Aqueous solutions of calcium chloride dispergate silk wadding at lower temperatures than lithium chloride solutions. The comparison is carried out of course with the concentrations of the solutions of both salts having the same boiling temperature. For instance, $CaCl_2$ solutions with boiling point 115° C. readily dispergate silk at this temperature, whilst LiCl solutions with the same boiling point (115° C.) practically do not dispergate silk wadding at all at this temperature. Calcium chloride solution almost saturated at room temperature has a boiling point of 123° C. and the specific gravity of this solution is considerably greater even when compared with that of the lithium chloride solution which boils at 130° C.

For instance, silk wadding (about 10 grams) is dispergated in 100 cc. of a $CaCl_2$ solution with a boiling point of 123° C. (the dispergation requires 10 minutes for its accomplishment) and the solution is allowed to cool, under stirring, from 123° C. down to room temperature. At 50° C. the separation into layers begins (with a LiCl solution at 85° C., *see* above). After the lapse of 18 hours, a perfectly ropy-plastic dough is seen floating on the surface of the almost transparent $CaCl_2$ solution. In this case the dough does not sink to the bottom of the vessel (the sp. gr. of the solution is about 1.44 at 20° C.).

In the solutions of mixtures of salts $[Ca(CNS)_2 + LiCl, LiCl + CaCl_2]$ a similar process of separation into layers also takes place; as well as in the solutions of many more salts. For instance, a 10 to 12 per cent silk solution in NaI solution (sp. gr. at room temperature is higher than 1.8) boiling at 130° C. starts separating into layers at about 100° C. The ropy-plastic dough formed floats on the surface of the NaI solution. Silk solutions of 10 to 12 per cent, in NaCNS solution (sp. gr. at 15° C. about 1.37) boiling at 130° C., start separating into layers at about 70° C. and after the lapse of one hour (the temperature of the solution at this time drops to 30° C.) there appears floating on the surface of the almost clear NaCNS solution, a ropy-plastic dough.

The floating of the dough to the surface of the solution of sodium thiocyanate takes place only if the silk solution, when cooling, is thoroughly stirred. Without stirring, or when only slightly stirred, the dough sinks to the bottom of the vessel. The floating of the dough is accounted for by the formation, upon stirring, of a frothy foam, by which the specific gravity of the dough is lowered. Moreover, the stirring causes a partial orientation (see below) of the disperse particles of the dough, which is accompanied by the self-purification of these particles from the salt.

Of course such an influence of stirring is not limited to silk solutions in the solution of sodium thiocyanate; the same influence of stirring manifests itself also in silk solutions in solutions of other salts, when a corresponding difference exists between the specific gravities of the dough and the salt solutions.

As an example of silk solutions which, after cooling to room temperatures, do not separate into layers may be mentioned silk solutions in solutions of the following salts: $Ca(CNS)_2$, CaI_2, $Ca(NO_3)_2$, $Mg(CNS)_2$ and MgI_2. However, I have no doubt that the separation into layers at temperatures *lower* than that of the room would also ensue although at a slower rate (high viscosity), when the solutions of the above-mentioned salts, and in general of any salt-dispergator, are used in *extremely* high concentrations.

Now let us dwell awhile on the chemical composition of the ropy-plastic doughs treated above. Just after their formation, the doughs, in their greater part, undoubtedly do not consist of *pure* fibroin, but of complex chemical compounds of fibroin with salts. It is natural that in these doughs are enclosed solutions of corresponding salts in the form of small drops. A portion of the salts may be also only adsorbed by the dough, but, as I have said, the main portion of the dough consists of chemical compounds of fibroin with salts.

This deduction is based not only upon the fact that chemical compounds with salts[18] exist also for other proteins, but also upon the difference in physico-chemical properties of the above doughs, and of the disperse *fibroin* precipitates.

Doughs have a higher specific gravity than fibroin. According to J. M. Matthews the specific gravity of degummed silk (i.e. fibroin) is 1.25. The molecules of fibroin in silk are orientated in a parallel order, this being the most compact state of fibroin. The orientation of molecules in disperse precipitates of fibroin is not so orderly; they are partly disorientated, and therefore the disperse fibroin precipitates must have a specific gravity less than 1.25.

While the disperse fibroin precipitates (*see* below) do not dissolve at room temperatures in distilled water, or in weak salt solutions, the above-mentioned doughs do this readily.

On preservation in tightly stoppered vessels, the doughs undergo slow alterations, and lose their fine ropy-plasticity. The stronger the dispergation power of the salt employed, the slower this proces.

When preserved in an open vessel in a humid atmosphere, the doughs attract water, and a layer of a solution is formed above the dough. This solution does not mix with the dough as long as the concentration of salt in the dough and that in the solution does not decrease to a material extent. At this moment, the solution becomes mixed with the dough and a viscous liquid, suitable for spinning, is formed (*see* below).

The solution of salt, forming on the surface of the dough, when it is being exposed to the humid open air, may be occasionally decanted and the dough periodically stirred. As the result of these manipulations, the dough after the lapse of a certain time (from two weeks to a month, according to the conditions) becomes an *extremely* viscous slow-flowing liquid.

Aggregation with very weak concentrations of salts in the silk solutions. Gelatination of dispersoidal fibroin solutions. Silk glasses. Fibroin flocculent gelatinous precipitates.

The processes which are dealt with in this paragraph being *qualitatively* the same for the silk solutions in the solutions of any salt-dispergator, I shall confine myself to only one example, viz. the solutions of silk in aqueous sodium thiocyanate solutions.

Into a beaker containing 100 cc. NaCNS solution with the boiling point about 120° C., immersed in an electrically heated oil bath, portions of silk wadding were introduced under constant stirring. At the beginning of the experiment the temperature was 86° C., at which temperature the silk wadding already began to dispergate. At the end of the experiment the solution was boiling (about 120° C.). Fifty grams of silk wadding were dispergated between 86° and 120° C., in about two hours. A portion of this solution, still warm, was introduced into a rapidly working dialyzer (with a rapid automatic change of water). After 20 hours the dialysis was stopped. In the outside water only traces of NaCNS could be detected by means of $FeCl_3$ solution (a yellow color on the addition of $FeCl_3$ solution). Meanwhile the silk solution inside the dialyzer still showed a very weak reaction for NaCNS (an orange color on the addition of $FeCl_3$ solution). Owing to osmosis in the course of the dialysis, the concentration of silk in the solution became weaker, and was approximately 18 grams for 100 cc. of the dispersion medium. The solution was turbid and rather viscous. After 9 days the whole solution became solidified into a grayish-white elastic jelly.

The concentration of silk in another portion of the solution was increased by evaporation, to about 35 to 40 per cent. After 3 days the whole mass ot the solution became solidified at room temperature, forming an elastic jelly.

These jellies, when kept in open vessels, become synerized, i.e. they contract (e.g. the diameter of a cylindrical piece of jelly contracts to almost half its size). Gradually the jelly sets to a perfectly solid glass, which can be cut only with a knife and hammer. The cleaved surface is as smooth as that of real glass. The silk glass is transparent in a layer of 1 to 1.5 cm. In transmitted light it looks yellow or brownish yellow. I made the cutting of this glass after the lapse of almost four months from the time of obtaining the fibroin jelly.*

When the concentrations of fibroin as well as of the salt in the solution are weak, no gelatination of the solution proceeds; but white gelatinous flakes appear and settle down on the bottom of the vessel in a voluminous layer.

It is impossible to put a sharp boundary between a jelly and a gelatinous flocculent precipitate not only in the case of fibroin, but also in numerous other substances[19] studied earlier by me. Spongy jellies which, on shaking, easily break up into flakes are intermediate systems.

Jellies and gelatinous flocculent precipitates of fibroin are quite unfit for spinning. They do not possess the necessary ropy consistency and after drying up they become brittle; so much so that *thin* plates can be broken up without any strong efforts. Fibroin jellies and gelatinous flocculent precipitates practically are not dispergated at room temperature either by pure water, or by weak salt solutions.

Aggregation with mean concentrations of salts in the silk solutions. The concentrations within the limits of which fibroin solutions in aqueous solutions of neutral salts are most stable. The dependence of the higher limit of concentration upon the amount of the dissolved silk.

As has been stated in a preceding section when the concentration of the salt in the solution is extremely strong, hot silk solutions in the solutions of most salt-dispergators, on cooling, separate into layers.

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* The silk glasses possess many valuable technical properties; they are light and can be dyed uniformly, e.g., with aniline dyes. The method of preparation of these silk glasses has been patented in Japan. Patentee: The Imperial Industrial Research Institute of Osaka. Inventor: P. P. von Weimarn.

The results of the systematic investigations carried out by me have shown that there exists for every salt a limiting concentration, easily definable, which I have called *"higher limiting concentration."* Below this concentration, the silk solutions do not separate into layers on cooling to room temperatures, and they even do not in general yield precipitates after a very long time.

In other words, when the content of salts in silk solutions is below the higher concentration limits, the solutions possess at room temperature a very long stability.

As it is advisable, from theoretical standpoints, when studying two solutions, to have their concentrations corresponding to the *same* boiling point. I have defined the higher limiting concentrations of the solutions not by the per cent contents of salts, but by the boiling temperatures of the solutions.

It has already been stated in a preceding section that silk solutions in a lithium chloride solution with the boiling point 130° C., separate into layers on cooling. It was established experimentally that silk solutions (e.g. of 7 per cent) in lithium chloride solutions with boiling points between 130° to 111° C., also separate into layers on cooling. But when the boiling point of these solutions is 110° C. or lower, no separation into layers is observed whilst these solutions are being cooled to room temperatures. Silk solutions, with progressively decreasing boiling points, can be easily prepared by the dilution of concentrated silk solutions in lithium chloride solutions (b. p. 130° C.) with water or weak lithium chloride solution.

By means of similar experiments, I have ascertained those temperatures which correspond to the higher limiting concentrations; for example, for LiCl —110° C.; for CaCl—115° C.; for NaI—111° C., and for NaCNS—120° C.

The higher limiting concentration is dependent to a certain extent upon the concentration of silk in the solution. The above temperatures were fixed for the 7 to 10 per cent silk solutions (a *definite* sort of silk wadding was used). The dependence upon the concentration of silk in the solution is quite clear; because during the separation into layers there are yielded complex compounds of fibroin with salts, and not pure fibroin. And naturally, the stronger the concentration of silk, the greater is the quantity of salt taken from the solution for the formation of a complex compound. Therefore, the concentration of salt decreases with stronger concentrations of silk in the dispersion medium. And the weaker the concentration of salts, the slower goes the process of separation into layers.

Weak (up to 5 per cent) silk solutions in the solutions of neutral salts become separated into layers in those solutions having their boiling points a few degrees lower than the boiling point of the silk solutions of mean concentration (e.g. 7 to 10 per cent). Concentrated silk solutions (15 to 20 per cent) do not separate into layers, though their boiling points are a few degrees higher than that of the solutions with mean concentrations of silk.

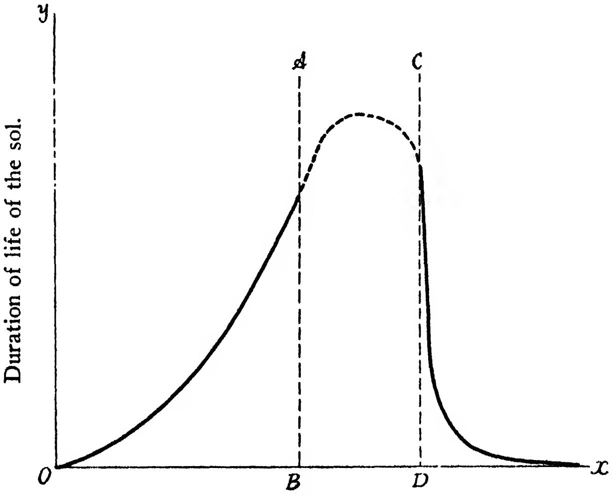
As has already been stated above, in concentrated silk solutions and in silk solutions of extremely strong concentrations, there is no layer of the solution formed, owing both to the extreme viscosity of the dough, and to the relatively scant amount of the solution yielded. Therefore it is imbibed by the dough.

The higher limiting concentration of salt is also dependent upon the sort of silk used; because e.g. inorganic admixtures in silk may have either an aggregative or dispergative influence. A strong influence is exercised upon the higher limiting concentration also by the degree of neutrality of the salt used for the preparation of the solution. This influence may be demonstrated by the example of lithium chloride solutions. By cooling 10 per cent silk solutions in LiCl solutions (b. p. 130° C.) with a weak but marked alkaline reaction (a small quantity of a LiOH solution being added) no dough is obtained; only a few dull-gray pieces of the products of silk decomposition are precipitated from the solution. However, with a solution showing a weak but distinct acid reaction (with the addition of a little HCl solution), the deposit of dough proceeds more rapidly than with an alkaline solution. In an acid LiCl solution the dispergation of silk proceeds at a slower rate than in a neutral solution. In the alkaline solution, the dispergation is accomplished with a greater rapidity; and a part of the silk forms a small quantity of non-dispergable products of decomposition.

Notwithstanding many variables influencing the higher limiting concentration of the salt, it is not difficult to define this concentration for every salt, provided *really neutral* solutions of salts are used, as well as a *definite* kind of silk.

As has been mentioned in the preceding section, with a weak concentration of salt in a silk solution, it becomes gelatinized after the lapse of several days, provided that the concentration of silk is considerable; otherwise, it yields a gelatinous flocculent precipitate.

The lower limiting concentration is far from being as definite as the higher; because from the silk solutions with mean concentrations of salt, which do not precipitate on standing for years or months, but only become more or less turbid with time, the transition is very gradual to silk solutions with weak concentrations of salt whose stability continues for weeks or days. The above-described behavior of the silk solutions is represented in the following graph (Fig. 3, *bis*).



Salt concentration in dispersion medium.

FIG. 3, *bis*.

The concentration * of salt in the dispersion medium is indicated along the axis of abscissae; along the axis of ordinates is shown the life-duration of silk solutions at room temperatures. Between the vertical lines *AB* and *CD*, lies the region of very stable silk solutions which do not yield precipitates dur-

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* The concentration is equal to the general concentration of the salt in the solution, minus that quantity of salt which has united with the fibroin for the formation of the complex compounds.

ing several years; beyond the line *CD* are placed those silk solutions which separate into layers either before they reach room temperatures, or on standing at room temperatures. When the concentration of silk is not strong (less than 5 per cent), the separation into layers causes the appearance of slimy translucent flakes, which collect in semi-liquid, vaseline-like layers on the bottom of the vessel, or on the surface of the solution, dependently upon the specific gravity of both layers.

With mean concentrations of silk (up to 15 to 20 per cent) in the solution, the layers possess the consistency of a ropy dough; whilst with strong concentrations of silk (25 per cent and stronger) all the solution becomes solidified to a ropy-plastic dough, i.e. the solution is transformed into the systems [20] which I have called resin-like (ropy) jellies or jelly-doughs.

The chief constituents of the fresh slimy or doughy layers, yielded by the silk solutions placed to the right of line *CD*, are complex compounds with salts. To the left of line *AB* are silk solutions which either yield on standing white gelatinous flakes (with weak concentrations of silk), or which gelatinize as a whole mass into elastic jellies (when the concentration of silk is stronger). In the course of time, owing to syneresis and drying up, these elastic jellies transform into transparent glasses. The chief constituent of these precipitates is fibroin.

AGGREGATION RESULTING FROM THE INFLUENCE OF VARIOUS FACTORS

Salts Aggregators; Strong and Weak Aggregators

As has been already mentioned above, silk solutions in those salt solutions which readily dispergate silk in a hot condition, on cooling separate into layers when the concentration of salt exceeds the concentration which I have called the higher limiting concentration. Also the addition to the stable silk solutions (between lines *AB* and *CD* in the graph) of salt solutions of such excessive concentrations causes the coagulation (aggregation) of the silk solutions. A few examples of such aggregation sufficiently illustrate the case. In these experiments the *mixing solutions were at room temperatures* (15° to 18° C.).

(1) 25 cc. of a 10 per cent silk solution in LiCl solution (b. p. 110° C.) were added under constant stirring, to 25 cc. of LiCl aqueous solution (b. p. 130° C.). The mixture at once became white and dimmed. The dimness was caused by the formation, in the liquid, of very small slimy flakes. After the lapse of 20 hours a layer of a slimy consistency was formed on the bottom of the vessel; the supernatant solution was almost perfectly clear.

(2) 50 cc. of a 20 per cent silk solution in CaCNS solution (b. p. 130° C.) were added, whilst being stirred, to 50 cc. LiCl solution (b. p. 130° C.). The aggregation began immediately, and a ropy-plastic dough was formed on the bottom.

(3) 35 cc. of a 20 per cent silk solution in $CaCl_2$ solution (b. p. 115° C.) were added, under constant stirring, to 65 cc. $CaCl_2$ solution (b. p. 118° C.). A dim white liquid resulted. The aggregation progressed slowly. After 24 hours the solution to the amount of 55 cc. from the bottom formed a collection of slimy flakes which had partly coalesced. The supernatant layer, of 45 cc., was a perfectly transparent solution.

In comparison with the salts the solutions of which, regardless of their concentrations and temperatures, do not dispergate silk under *ordinary* pressure, those salts the solution of which under ordinary atmospheric pressure are dispergators for silk at elevated temperatures prove to be *poor aggre-*

gators at room temperatures. The former salts may be rightly called *powerful aggregators.*

Naturally no sharp boundary line can be drawn between the salts of weak and those of strong aggregative power, because there exist salts whose aggregative power may be characterized as *medium.*

The solutions of readily soluble fluorides, sulfates, citrates, tartrates and acetates are *strong* aggregators for stable silk solutions, because they do not dispergate silk, when taken in any concentration and at any temperatures whatsoever, under ordinary atmospheric pressure. Such salts as NaCl, $Ba(NO_3)_2$, etc., are aggregators of mean capacity. The arrangement of salts according to their aggregative capacities has already been presented elsewhere in this paper.

Organic Aggregators

Every organic substance-dehydrator, as e.g. alcohols, acetone, tannin solutions and the like, produce aggregations of stable silk solutions similarly to the solutions of salt-aggregators. Solutions of salt-dispergators in alcohols and similar organic liquids possess greater aggregative ability than *aqueous* solutions of the same salts.

Examples of the Course of the Aggregation, Proceeding under the Influence of Strong Aggregators. On the Processes Causing the Aggregation of Silk from the Solutions

The process of aggregation, taking place in the solutions of silk (fibroin) by the addition to these solutions of alcohol or of solutions of salt-aggregators, is highly interesting both from the scientific as well as from the practical viewpoints.

Let me now describe such an aggregation process, as it took place in the special case of an aggregation, produced by ethyl alcohol in a solution of silk (fibroin), with a concentrated $Ca(NO_3)_2$ solution as dispersion medium (this solution was prepared in the following manner: 10 grams of silk wadding were dissolved at a temperature of about 115° C., in 100 cc. of a $Ca(NO_3)_2$ solution, boiling under ordinary pressure also at about 115° C.).

Suppose we are given 100 cc. of the above solution (at about 50° to 25° C.) contained in a tall beaker, and that in a measuring cylinder we have 500 cc. of absolute ethyl alcohol (at about 25° to 20° C.).

Let us first add to the above solution as much alcohol as will prove sufficient to produce a certain amount of white precipitate. On examining this precipitate with the naked eye, we shall see at once that it possesses a filiform structure; it appears to consist of filaments, capriciously interwoven with each other. And now, if we go on adding the remaining quantity of alcohol to the solution, while constantly stirring the contents of the beaker with a glass rod to which we impart a circular movement, we shall observe the following phenomena:

The filamentous precipitate will spool up round the glass rod (the individual threads glueing together) and form at its end something like a coil of threads intercrossing and sticking to each other. And if we take the above roll of threads by its lower end and begin to draw it out, while twisting it at the same time, it permits being drawn into a string or a thread, a few millimeters in thickness and about two meters in length. Under a certain degree of tension, the thread begins to display a beautiful satin gloss.

In Figures 4 and 5 are shown two photographs of such threads. In Figure

FIG. 4.

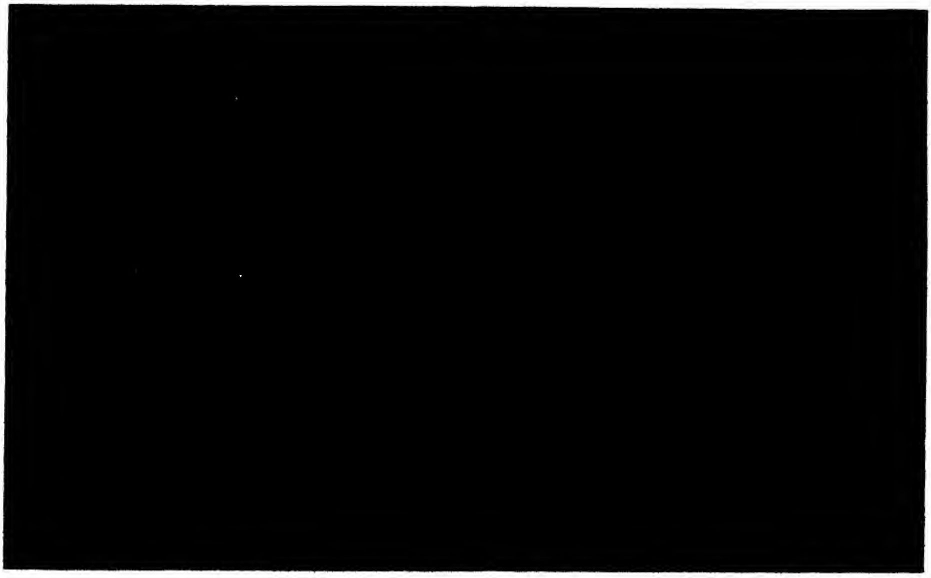

FIG. 5.

4, the glass rod is seen (held in the right hand), with a part of the thread-roll sticking to its end; the thick thread, extending from that roll to the left hand which holds its other end, is very distinctly seen on the dark ground of the photograph. And in the picture in Figure 5 the thread has been given a still greater extension; the left hand which holds its end (not shown in the picture) is stretched out almost to the full length of the arm.

This thick thread can easily be flattened by drawing it out into a thin translucent ribbon or film, which brings into prominence the character of the structure of the silk (fibroin) coagulum, a structure consisting of thin filaments glued together.

An extremely interesting phenomenon is the phenomenon of changes in the condition of the silk coagulum (fibroin). These changes occur in proportion as the dehydration of the coagulum goes on, that is to say in proportion as it is acted upon by the alcohol or by some other aggregator, e.g. Na_2SO_4 aqueous solution (according to the percentage concentration of the alcohol or of some other aggregator used, and of the time during which the coagulum has been kept submerged in the aggregating medium).

In that sequence of changes in the condition of the silk coagulum, through which it has to pass, in proportion as its degree of dehydration gradually increases, we may witness the realization of every possible transition stage marking the gradual conversion from the condition of an extremely viscous syrup through that of a gluey mass, to that of an elastic rubber-like jelly (*in this condition, an elastic extension to twice or even four times the former length is possible*)—and thence to that of masses possessing consistencies like those of animal tendons, till it finally reaches the state of an altogether solid mass, so solid that, when present in thin sheets, it may be broken into pieces.

The case now under consideration furnishes us with overwhelming, *prima facie* evidence that the process of transition from the condition of a syrupy or gluey mass to that of an elastic jelly is essentially a process of partial dehydration.

Thus it is established experimentally that the aggregation of silk from its solutions, and the solidifying of the silk coagula, are caused by two processes: the dehydration of complex compounds of silk with salts, and their decomposition into salt and fibroin, with further dehydration of fibroin.

IV. OBTAINING THREADS (SPINNING) FROM SILK COAGULA AND FROM SILK SOLUTIONS.

GENERAL.

I have obtained silk threads either from silk coagula, obtained by pouring silk solutions in the solutions of salt-dispergators, into concentrated solutions of aggregators, or by means of coagulating very thin streams of silk solutions forming within the solutions of aggregators (for more details, see below). Threads of good quality are obtained by both these methods, provided the conditions are suitable. The second method is more adaptable to industrial uses, although for the application of this method many alterations or rather additions are required in the modern machinery used for spinning artificial silk prepared by the viscose method.

It is not difficult to obtain beautiful silk threads of any length desired, but with a relatively weak tensile strength; to obtain threads possessing great tensile strength is as yet a problem which requires the very careful consideration of a series of factors, which are therefore very important and are dealt with in this Chapter.

COAGULATION BY STRETCHING OR COAGULATION BY MOTION. NEGATIVE FLUIDAL STRUCTURES AND THE ORIENTATION OF FIBROIN DISPERSE PARTICLES.

In his highly interesting paper, the Italian investigator, Carlo Foà [21] (quoted above) has shown that the coagulation of a thread of natural silk in the course of spinning the cocoon by the silk-worm, is caused by stretching (Zugkoagulation). On the basis of the coagulation caused by stretching, are manufactured the so-called "Fil de Florence" and "Crins de Florence." [22]

The latter threads are obtained from seripteria of silk-worms; the seripteria being removed from the silk-worms, after they have been soaked in acetic acid. Under the coagulative influence of acetic acid, fibroin in the seripterium assumes a condition like dough. At this moment the seripterium (about 2 inches in length) is taken by each end, and stretched as far as the plasticity of the coagulum of fibroin permits; and "Crins de Florence" result with a length of from 15 to 20 inches.

This method was known in China from a very early date; in Europe from 1760.

Carlo Foà has not explained the underlying cause of the coagulation (aggregation) by stretching, which, in my opinion, lies in the following. As already stated, the intensities of forces in the field of forces of a fibroin molecule may be imagined to be distributed in the form of an ellipsoid, extremely elongated, similar to a thin needle with rounded ends; i.e. the intensity of forces in two sections of a fibroin molecule is considerably greater than in all other sections. And as a result of such structures of the fibroin molecule, all vectorial disperse particles of fibroin are extremely negative * ultramicrocrystals; on the ends of their long axis cohesion is considerably stronger than elsewhere. On setting in motion the liquid or semi-liquid mass containing molecules and particles of the above description, there are formed structures, which I have called negative fluidal structures.[23] In motion, the disperse particles, drawn out in one direction (the drawn-out molecules also), are orientated in the direction parallel to each other, similarly as are the logs of trees floating along the river. And being orientated in parallel fashion, the particles have more chance to become united at the points of maximum cohesion.

The parallel orientation of particles which are drawn out in one direction may be accomplished not only by means of stretching a doughy silk coagulum, but by any other mechanical treatment, which can effect the shifting of the coagulum particles in one definite direction. It can be done, for example, by pressing the coagulum, by rubbing its surface in the direction parallel to its length, etc.

On the ground of these experiments, I proposed [24] to call the coagulation of this kind by a more general term *"coagulation by motion,"* instead of coagulation by stretching.

In Figures 6 and 7 are given photo-ultramicrographs of threads which I have obtained by stretching the doughy silk coagula, and by subsequently rubbing them lengthwise; the coagula were prepared by pouring silk solutions in the solutions of neutral salts, into the concentrated solutions of aggregators. The longitudinal filamentous structures of these threads are perfectly distinct in the photo-ultramicrographs.

The process of "coagulation or solidifying by motion" can be successfully

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* On the classification of crystals into positive and negative, see p. 42 of my paper in Vol. I of this series.

FIG. 6. About × 200.

FIG. 7. About × 200.

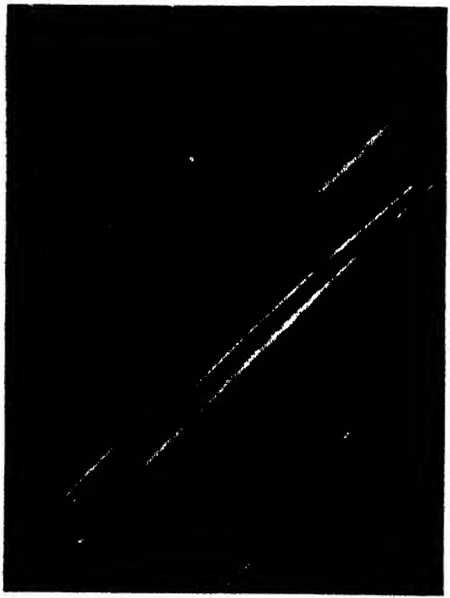

FIG. 8. × 62, crossed Nicols.

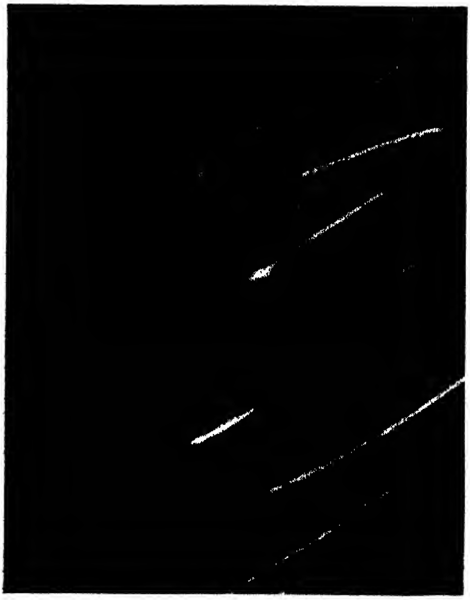

FIG. 9. × 62, crossed Nicols.

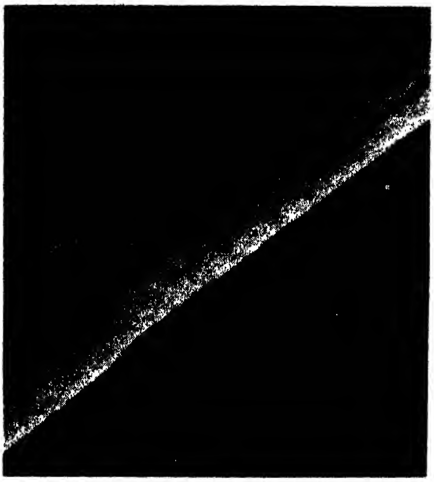

FIG. 10. × 62, crossed Nicols.

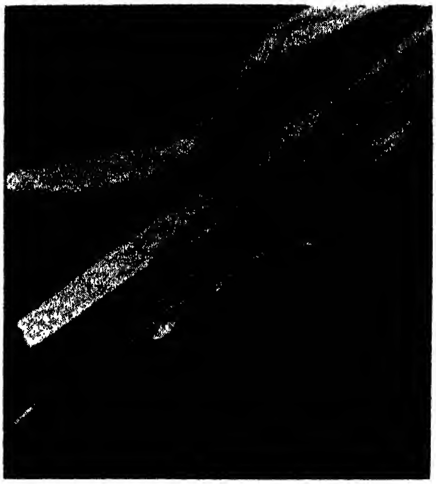

FIG. 11. × 62, crossed Nicols.

studied microscopically in polarized light. I shall confine myself to the description of only one instance.

A small piece of a coagulum-dough, prepared by pouring a small quantity of a *warm*, concentrated silk solution (of more than 20 per cent concentration) in a NaI solution, into aqueous sodium citrate solution (4N concentration) of room temperature, was *strongly* stretched and the *perfectly soft*, rather thick thread obtained was fixed by its ends to the edges of the object-glass. Then the preparation was covered with a large cover-glass.

In Figures 8 and 9 are represented the photomicrographs in polarized light (crossed Nicols) of the preparation. The structure of the threads, consisting of the thinnest fibers, is evident. It looks as if numerous more or less parallel microscopic streams of a viscous liquid have been impressed on the photomicrograph. In Figure 9 is seen a piece of the preparation with a foreign body which chanced to enter the coagulum. The arrangement of microscopic stream-threads around this obstacle is very characteristic.

In a strongly drawn out coagulum bright interference colors appear in the course of time; as is seen from Figures 10 and 11 (crossed Nicols) threads drawn out of this coagulum do not differ essentially from those of natural silk in the brightness of their interference colors and in their fibril cleavage (see Figure 11, the torn end of a thread). For comparison in Figure 12 (crossed Nicols) are demonstrated a thread of natural silk (on the left) and

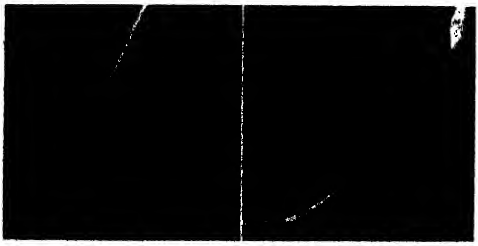

FIG. 12. × 62, crossed Nicols.

an almost equally thin thread obtained by me by the coagulation of silk from its solutions in aqueous NaI solutions.

THE STRENGTH OF THREADS IS ACCOUNTED FOR BY THE MAXIMUM ORIENTATION OF FIBROIN PARTICLES. WEAK JELLY-LIKE THREADS, BRITTLE ON DRYING, RESULT FROM THE MINIMUM ORIENTATION OF FIBROIN PARTICLES.

In the preceding pages it was pointed out that silk solutions in the solutions of neutral salts, when the concentrations of the latter are weak, yield fibroin either in the form of gelatinous flakes, or, in case of the concentration being rather strong, the solutions in their whole mass become gelatinized. By syneresis and drying up of the gelatinous flakes, they are transformed into brittle masses. Jellies gradually become perfectly transparent solid glasses, which are brittle like real glass; and naturally a glass thread may be easily broken.

Fibroin jellies and gelatinous flakes can not be stretched. In this they present a sharp contrast to the ropy-plastic coagula-doughs, discussed above. It is easy to spoil a coagulum dough and make it a brittle solid by the extraction of salts. And only by the stretching of the coagulum of a suitable consistency (see below) can long thin threads be obtained.

When the disperse fibroin particles in any section of the thread will not orientate themselves in parallel fashion on stretching, but will remain more or less unorientated, then in these places, after the washing and drying of the thread, at first a jelly will be formed and later a glass. Therefore such threads, though in a fresh condition, they seem satisfactory in appearance, become brittle after the lapse of a certain time. It is sufficient to neglect only this one condition of the maximum orientation of the fibroin disperse particles in threads, and, even if all other conditions for the obtaining of strong threads are strictly observed (see below) strong threads can not be obtained.

With the example of silk—fibroin may be demonstrated better than with any other substance, the striking dependence of the physical and mechanical properties of a system, upon the degree of orientation of the constituent disperse particles. With the maximum orientation, strong pliable threads are produced; with the minimum—glass.

TWO METHODS OF SPINNING. THE IMPROVEMENT OF WEAK THREADS BY MEANS OF MECHANICAL ORIENTATION OF FIBROIN PARTICLES.

Both methods are based on a common principle, namely on obtaining from silk solutions in the solutions of neutral salts, a ropy-plastic coagulum that can be transformed into a silk thread by a more or less rapid stretching, i.e. through "coagulation or solidifying by motion."

The difference in the two methods lies in the means by which the coagulum is stretched into a thread. As already stated, the first method consists in obtaining a coagulum of consistency suitable for stretching, by means of merely pouring a small quantity of the silk solution in a solution of any salt-dispergator into a concentrated solution of an aggregator. As soon as the coagulum assumes that consistency which on further stretching will result in solidification, a small piece of the coagulum is drawn out in a thread as fine as possible. The stretching is begun under the solution of the aggregator and continued in the open air. The thread obtained is suspended in a drawn out condition by its ends and allowed to remain quiet for some time. During this period, portions of the solutions left between the fibrils in the thread bedew the surface of the thread in the form of drops. The thread gradually loses its high elasticity and its consistency approaches that of a thread of natural silk. By rubbing the thread in the longitudinal direction with two fingers, at the time when it is still highly elastic, a rapid loss of elasticity is effected, and the thread acquires the luster of natural silk and the tensile strength of the thread increases.

Though it may seem surprising, it is an empirical fact, that the rubbing of the thread with the fingers can easily effect a parallel orientation of the highly disperse particles of fibroin and even of its molecules.

The same orientation, with the subsequent loss of elasticity may also be accomplished by rolling with a glass rod the thread placed on a glass plate. In this case, the thread will appear flattened, but in luster and strength, it is not inferior to the thread obtained by the longitudinal rubbing with the fingers. In the latter case, however, the almost round cross-section of the thread is preserved, as the rubbing may be performed equally along all the surface of the thread. Finally, the orientation may also be effected by repeated stretchings and *spontaneous* contractions of the thread while it is still in the elastic state.

When the thread becomes quite solidified, it must be thoroughly washed, first in cold water, then in boiling water and finally in a boiling 8-15 per cent solution of a neutral soap. Washed once more thoroughly in hot water and dried in the open air, the preparatory stage of the thread is finished. My experiments have shown that when the thread has been prepared with all necessary precautions (see below) it has remained without any noticeable alterations for four years. According to my experiments, threads properly prepared, can be easily and uniformly dyed.

The second method, being very simple, is very important for the establishment of the most suitable practical conditions for industrial spinning. It is as follows:

Into a tall cylinder is poured a solution of any substance-aggregator, the specific gravity of this solution being less than that of the silk solution in the solution of the salt-dispergator. The silk solution is poured onto the surface of the solution of the aggregator in small drops, by means of a dropper with its end in the form of a very thin tube.

The concentrations of silk, of the salt-dispergator and of the aggregating substance being rightly selected, a ropy-plastic coagulum is formed on the surface of the drop, and this coagulum, by virtue of the weight of the drops, goes down to the bottom of the vessel, forming an extremely fine thread on its way. This thread is then taken out of the solution of the aggregator and treated according to the above description.

In the case when the specific gravity of the silk solution is less than that of the solution of the aggregator, the drop naturally does not sink to the bottom of the vessel. Then the procedure must be somewhat modified, viz. a very thin layer of the silk solution is poured onto the surface of the solution of the aggregator and then shot (e.g. lead shot), of small diameter, are thrown on the top of the liquid. The shot, coming into contact with the film of the ropy-plastic coagulum, drag it down in the form of very fine threads. By varying the specific gravities of drops in the first example and that of the material of the shot in the second, the rate of stretching the coagulum into thread can be also changed as desired, and the influence of the rate of stretching upon the quality of threads may be thus studied.

As already stated, in general the study of the forming threads by this method may prove very valuable for the industrial spinning of silk solutions in the solutions of neutral salts.

Several instances of forming threads by the second method follow:

A twenty per cent silk solution in calcium chloride solution (b. p. 115° C.) or in calcium nitrate solution (b. p. 115° C.) was diluted to half strength with water, i.e. a ten per cent silk solution was used. The solution was poured drop by drop into an ammonium acetate solution (50 grams ammonium acetate + 50 grams water). The threads thus obtained were strong enough to be washed within a few minutes; and after a short drying in suspended condition, at room temperature, these threads stretched and treated by rubbing them with the fingers, will endure e.g. a half an hour's boiling in water, without any noticeable change in their strength.

With the solution of the same aggregator, stable threads were also obtained from a twenty per cent silk solution in a sodium thiocyanate solution (a 50 per cent silk solution in the solution of sodium thiocyanate was diluted with a suitable amount of water), and from a 15 per cent silk solution in the solution of calcium chloride (a 30 per cent silk solution in $CaCl_2$ solution was diluted with water 1 : 1). The solutions in all these experiments were of room temperature.

Threads can be also produced (by drop and shot methods) from the silk solutions in the solutions of weaker aggregators, as, e.g., saturated sodium chloride solution; but these threads suffer disintegration immediately after immersing them in water. In this case the process of coagulation is very slow and after being not less than 24 hours in the solution of the coagulator, the threads become strong enough to suffer washing in water without destruction.

Threads from, e.g., 20 to 10 per cent silk solutions in sodium thiocyanate solutions, after they have remained for 24-48 hours in the solution of the aggregator (NaCl), have the elasticity of an elastic dough, which under extension above a certain limit becomes ropy. These threads possess no silk luster; their color is snow-white. However, after repeated stretchings and spontaneous contractions, and subsequent rubbings of their surfaces with two fingers, these weak threads acquire considerable strength and silk luster. The metamorphosis in the properties of silk threads resulting from the above manipulations, is really very striking.

It should be also noted that threads, even when not wholly solidified, very often become separated in the longitudinal direction (along the whole length of the thread) into thinner threads, i.e. they display a fibrillar cleavage.

For industrial applications, great speed in spinning is very essential; and this is only possible when the solidifying of the thread in the spinning bath also proceeds at a great speed.

The speedy solidifying of threads may be easily effected in three ways:

A. The concentration of *silk* being constant, the concentration of salt in the silk solution may be reduced by means of the ultrafiltration (keeping the same volume of the solution by the addition of water) or dialysis (keeping the same volume of the solution by evaporation).

B. The concentration of *salt* being constant, the concentration of silk in the solution may be increased.

The stronger the concentration of silk and the weaker that of the salt in a solution, the more rapidly proceeds the solidifying of threads in the solution of a given coagulator. However, the concentration of salt (see the graph, Figure 3 bis) should not be decreased below a certain limit; otherwise, brittle glass-like threads result on drying.

C. By the application of the most powerful coagulators, i.e. of solutions of fluorides, sulfates, citrates, and tartrates. However, these coagulators can be applied only to silk solutions in the solutions of salts of the alkaline metals, because with the above acids, the earth-alkaline metals give salts which are either more or less soluble (citrates, tartrates) or else completely insoluble, with excess of the coagulator.

The application in practice of these three courses does not offer any difficulty, and silk solutions may be spun with greater speed on the machines used for spinning, e.g. of viscose silk. However, the tensile strength of the threads, obtained with such machines, does not reach that which is possessed by the threads with the maximum orientation of disperse particles, obtained by the above-described laboratory methods.

ONE EXAMPLE OF THE INFLUENCE UPON THE TENSILE STRENGTH, OF THE ORIENTATION OF FIBROIN PARTICLES IN THREADS.

In my first of the series of papers * dealing with the production of threads from silk coagula, I wrote that "certain threads obtained by me possess even greater tensile strength than those of natural silk." These threads were prepared according to the first method described in a section above.

Here I wish to describe one example of the production of strong threads by the *second* method. By this example is demonstrated quite clearly the influence of the orientation of fibroin particles on the tensile strength of threads.

For the preparation of threads I used a solution of silk wadding in an aqueous sodium thiocyanate solution. Fifty grams of silk wadding were dissolved in 100 cc. of the sodium thiocyanate solution having a boiling point 120° C. The solution obtained was diluted with distilled water (40 cc. of the silk solution + 75 cc. water); the mixture was heated to boiling and then allowed to cool to room temperature. The solution was used either immediately after preparation, or after a longer or shorter time during which it was kept in tightly stoppered vessels.

For the experiments described hereafter, I used a solution which was prepared eleven months before; and notwithstanding this the results were quite successful. For the spinning liquid I used an aqueous cadmium sulfate solution, containing in 100 cc. of the solution, 50 grams of $CdSO_4.8/3H_2O$ (extra pure, Merck).

The specific gravity of the silk solution being less than that of the spinning liquid, "the shot method" had to be applied, and in order to get also relatively thick threads rather large lead shot was used, having a mean diameter of 1.6 mm.

Several drops of the silk solution onto the surface of the spinning solution contained in a test tube 2 cm. in diameter (the depth of the layer of this solution, 11 cm.) were poured and the shot were placed *immediately* upon the solution. In corresponding places each shot carries down to the bottom of the test tube, in the form of threads, the ropy-plastic silk film-coagulum which is formed.

The shot must be placed upon the silk solution immediately, because the consistency of the film-coagulum changes very rapidly: after one minute the shot can carry the thread formed down to the bottom of the test tube (i.e. to the depth of 11 cm.); after two minutes, the shot with the thread does not reach the bottom by one-fourth of the height of the column of the solution; after three minutes the shot with the thread sinks to about one-third of the distance

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* P. P. von Weimarn, *Repts. Imp. Ind. Research Inst. Osaka*, Vol. 7, No. 5, p. 20 (1926).

TABLE 1. *Properties of Natural and of Fabricated Silk Threads.*

Numbers	Method of Preparation of Threads	Degree of Orientation of Fibroin Particles in Threads	Degree of Dryness of Threads	Time in Hours Between the Preparation of Thread and Its Test	Breadth of Thread in mm.	Thickness of Threads in mm.	Forms of Cross-sections of Threads	Breaking Load in gm. for One Single Thread	Tensile Strength in kgs./mm.²	Remarks.
1.	Natural silk (Silk wadding used for the preparation of the colloidal solution)	Very considerable.	Air-dry.		0.0135	0.0108	Irregular.	4	27	Determination of the tensile strength of the strongest threads from silk wadding was carried out; many threads in the same sample of silk wadding possessed considerably smaller tensile strength.
2.	1 hour in spinning solution; after washing the thread was dried in air for 18 hours.	Very small.	Though the thread appears dry * in reality it contains much H_2O.	18	0.36	0.36	Almost a perfect circle.	28	0.3	Upper, thicker part of thread was taken for experimentation; during washing and further manipulations, no stretching or rubbing was exercised. The thread was soft, jelly-like.
3.	Method 1 (see the text).	Only the superficial layer of the thread shows considerable orientation.	Not completely air-dry.	24	0.108	0.081	Irregular.	80	9	Micro- and ultramicroscopic investigations have revealed that the inner part of the thread consists of a jelly-like mass; only the thin superficial layer possesses considerable orientation of fibroin particles.
4.	Method 1.	The same as in No. 3.	The same as in No. 3.	24	0.145	0.083	Irregular.	140	11	The same as in No. 3 but the orientated superficial layer is somewhat thicker; the inner part of the thread is jelly-like.

5.	Method 1.	The same as in No. 3.	Considerable content of moisture.	½	0.153	0.0225	Approaching a rectangle.	70	20	By a strong rubbing with the fingers and nails the thread is flattened; the quantity of jelly inside the thread is small.
6.	Method 1.	Considerable.	Wet.	240	0.09	0.018	Approaching a rectangle.	32	20	Previously to testing, the thread was immersed for 1 hr. in distilled water. The tensile strength of the thread was determined whilst it was in a moist condition.
7.	Method 1.	Considerable.	Almost air-dry.	240	0.252	0.0135	Approaching a rectangle.	75	22	By a stronger rubbing the thread prepared was successfully made thinner than thread No. 5. After breaking, it was perceived that *one* end of the thread had split into several.
8.	Method 1.	Very considerable.	Almost air-dry.	240	0.09	0.018	Approaching a rectangle.	43	26	After breaking it was perceived that one end of the thread had split into five threads of different thicknesses; certain of them being of only several thousandths of a millimeter thick.
9.	Method 2 (see the text).	Very considerable.	Considerable content of moisture.	½	0.0315	0.0135	Approaching a rectangle.	11.5	27	
10.	Method 1.	Very great.	Wet.	24	0.072	0.018	Approaching a rectangle.	48	37	Previously to testing, the thread was soaked for half an hour in distilled water. The tensile strength was determined whilst the thread was still moist.
11.	Method 2.	Very great.	Not completely dry.	About 12	0.0675	0.0135	Approaching a rectangle.	37	40	
12.	Method 1.	Very great.	Almost air-dry.	240	0.099	0.018	Approaching a rectangle.	22	12	The thread possessed high fibril cleavage. Under stretching, at the point of future breaking, the thread had split into four minor threads which were afterwards broken separately, not at the same time (see the text).

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* As is known, silk with 30 per cent content of its weight of moisture still appears dry.

TABLE 2. *Natural Silk.*

Numbers	Kinds of Silk	Tensile Strength kgs./mm.^{2}	
		Dry	Wet
1.	Raw silk	50.4	40.9
2.	Silk, boiled off	25.5	13.6
3.	Silk, dyed red and weighted	20.0	15.6
4.	Silk, blue-black, weighted 110%	12.1	8.0
5.	Silk, black, weighted 140%	7.9	6.3

TABLE 3. *Artificial Silk.*

	Methods of the Preparation of Threads	Tensile Strength kgs./mm.^{2}	
		Dry	Wet
A.	Chardonnet's collodion, undyed	14.7	1.7
B.	Lenher's collodion, undyed	17.1	4.3
C.	Cuprammonium, undyed	19.1	3.2
D.	Viscose, early samples	11.4	3.5
E.	Viscose. latest samples	21.5	7.0

between the top of the solution and the bottom; and after four minutes, only a small hollow is produced by the shot in the film-coagulum.

Notwithstanding the fact that even after a few minutes in the spinning solution the threads acquire a consistency permitting careful washing in cold water and further treatment by stretching and rubbing after they have half dried at room temperature, it is nevertheless advisable to increase considerably the period of time during which the threads remain in the spinning solution; because manipulating threads which are weak, which easily stick together, and which have been not long enough in the spinning solution, is extremely difficult.

Threads which permit a considerable subsequent stretching were obtained by me as follows: (1) The threads were allowed to remain in the spinning solution for 12-18 hours; after which time the threads were rinsed in a *slow* stream of water, in order to keep them relaxed. Afterwards the threads were subjected to stretching and rubbing with the fingers. (2) After one hour in the spinning solution, the threads, without washing, were placed for 12 to 18 hours on a filter paper, and then were subjected to stretching and rubbing with the fingers.

The treatment according to the second method (using the lower thinner parts of the threads, about 5 cm. in length) resulted in extremely fine and strong threads; because the original threads (about 5 cm.) could be stretched to four times this length, or even more; whereas threads obtained according to the first method, very rarely permitted so great an elongation. All these experiments were carried out at room temperature (15° to 17° C.).

In Table 1 are summed up the results of several measurements of the tensile strength of threads obtained by me, with different degrees of orientation of their fibroin particles. Some of the threads the tensile strength of which was determined, were in an air-dry condition, while others were moist or not quite air-dry.

The measurement of the cross-section of threads was carried out with the "Stufen-Micrometer" of the firm Leitz (Wetzlar). The micrometer was carefully verified by means of an object micrometer (0.01 mm.).

As the calculation of the surface of the cross-section of a thread was made, not from the actual surface, but from the surface of a rectangle described around the cross-section, the values obtained were greater than the true values and therefore the numbers for tensile strength given in Table 1 should be considered as being smaller than the true values; provided we are certain that other possible measurement errors do not influence conversely the numbers obtained.

Under No. 1 (Table 1) is given the result of the measurement of a single thread of silk wadding, which was used for the preparation of the colloidal silk solution; one of the strongest threads was measured. Many of the silk threads taken from this wadding were weaker and certain of them were so weak that they were torn whilst being fastened to the tensile strength testing machine.

Taking the above-said into consideration, from the comparison of the number indicating the tensile strength of the silk wadding thread, to the number in Table 2,* indicating the tensile strength of boiled off silk (No. 2), it is clearly seen that the numbers of both tensile strengths are near to each other.

Thread No. 2 was prepared as follows: after remaining for one hour in the spinning solution, the thread formed by means of dropping a shot onto the silk coagulum, was carefully (in as relaxed condition as possible) washed under a slow stream of tap-water, during several minutes, in a vertical position and then the thread was placed on a filter paper where it was left for about 18 hours. The upper, thicker part of the thread was taken for the determination of tensile strength. Before the test the thread was not subjected either to stretching or to rubbing.

The thread which was white and possessed no silk luster, was of a soft jelly-like consistency. The tensile strength of this thread is low and equals only 0.3 kgs. for mm.^{2} Its torn ends have shapes of frustrums of cones, the diameters of smaller sections of which are equal to 0.162 mm., i.e. the thread possesses marked plasticity and exhibits distinct elongation when loaded. Even if we take for the calculation of tensile strength, the relation of the breaking weight to the smaller section, we have a tensile strength equal only to about 1.4 kgs./mm.^{2}

Stretching and rubbing of the surface of the thread after it has been taken out of the spinning solution and washed with water, result in a striking increase of the thread's tensile strength. Even comparatively brief stretchings and rubbings are sufficient for increasing the tensile strength to between 8 to 12 kgs./mm.^{2}

In Table 1, under Nos. 3 and 4, are given the results of the measurement of such threads. These relatively thick threads seem quite satisfactory in appearance they show silk luster, etc., but their tensile strength equals only about one-third of that of threads of boiled off silk.

Micro- and ultramicroscopic investigations carried out by me immediately revealed the cause of the insufficiently high tensile strength of these threads. It became clear after the investigation, that only in the thin superficial layer of the thread, are the fibroin particles orientated; whilst inside this thin envelope is a jelly-like mass of fibroin. These threads may be likened to a fine bough of a shrub; the envelope consisting of orientated fibroin particles may be compared to the bark, and the wood-mass—to the jelly-like fibroin.

In Figure 13, a, is a scheme of the cross-section of thread No. 4; it was drawn from the data given by the micro- and ultramicroscopic observations.

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* Tables 2 and 3 are taken from "International Critical Tables," New York, McGraw-Hill Book Co., 1927, Vol. II, p. 234; the number in Table 3 bearing an asterisk is taken from the book of Clément et Rivière, "Matières Plastiques," Paris, 1924, p. 77.

In the observations under a dark field illumination (ultramicroscopic condenser Leitz) the outer edge of the cross-section of a thread appears perfectly homogeneous, resembling glass of high quality, whilst the inner part of the thread is distinctly opalescent, bluish-white. Under a bright field illumination, striations along the thread are quite visible (an indication of the fibril cleavage), but they appear most distinct when observed under a dark field (see Figure 13, b).

When the thickness of the layer of orientated fibroin particles is known, there is no difficulty in calculating the approximate tensile strength of this part of the thread. The thickness of this layer in thread No. 4 is about 0.0165 mm. and the tensile strength is about 29 to 30 kgs./mm.^{2}

The thickness of the layer consisting of orientated fibroin particles may be increased by stronger stretching and rubbing of the thread, whereas the thickness of the jelly-like content of the inner part of the thread is thereby decreased. This immediately causes an increase in the tensile strength of the thread to 20-22 kgs./mm.^{2} (Table 1, threads Nos. 5 and 7).

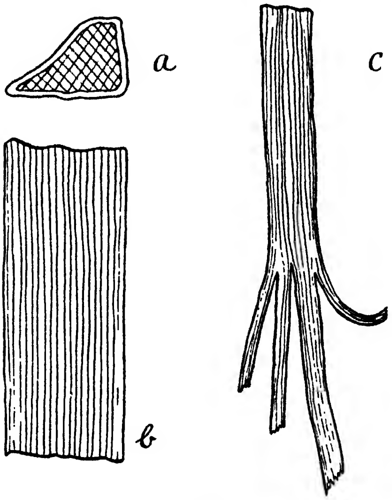

Fig. 13.

A complete elimination of the jelly-like layer in relatively thick threads is extremely difficult; and in order to accomplish this, at least one dimension of the thread—the thickness—under stretching and rubbing (with the fingers and then with the nails), must be able to assume dimensions not exceeding several hundredths of a millimeter, e.g. not more than 0.02 mm.

Of course this conclusion pertains only to the treatment of threads with the fingers; it is quite probable that by means of certain mechanical devices, it would be possible to produce thicker threads possessing high tensile strength.

But only in *thin* threads, by the application of the above-described method, was I able to obtain values for tensile strength between 26-40 kgs./mm.^{2}

According to my experiments * relatively thick threads become brittle with time. The cause of it lies in the fact that the jelly-like inner content of the thread gradually undergoes syneresis and dries up, becoming glassy; in the relatively humid laboratory air this process sometimes takes months.

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* P. P. von Weimarn, *Reports*, Vol. 8, No. 6, p. 18-19 (June, 1927).

At any rate, threads with a jelly-like inner content cannot stand drying; in proportion as they yield water, the threads lose their pliability and finally become brittle.

As was stated above, a comparatively weak tensile strength is accounted for by the presence of jelly in the inner part of the thread. Another cause underlying the breaking of threads under a load less than that which might be expected from the strong orientation of the fibroin particles, is of a different character. It is the splitting of threads into thinner threads, prior to the moment of their breaking.

When the fibroin particles in threads obtained by the above method, are highly orientated, then the fibril cleavage in these threads is stronger than in natural silk threads produced by silk-worms. Therefore, when these threads are being fixed to the tensile strength testing machine, they split into several thinner threads. Often the splitting is not noticed at first by the experimenter and becomes evident only at the moment of the breaking of the thread. In this case it is very difficult to have *all* the thinner threads stretched evenly during the determination of their tensile strength, and consequently the breaking takes place first in those threads which are more highly stretched, and then very rapidly in those less stretched.

Naturally under such conditions, the breaking weight appears considerably less than in the case when there has been no splitting of the thread, or when the stretching of the separated threads during the experiment is perfectly equal.*

Because of the splitting and unequal stretching of the separated threads during the breaking experiment, thread No. 12 (Figure 13, c) in Table 1, notwithstanding the very high degree of orientation of its fibroin particles, showed tensile strength equal only to 12 kgs./mm.^{2} The result of the microscopical study of the torn ends of the thread (split into four threads of different thicknesses) and of the measurement of the separated threads, leads to the conclusion that the thread under investigation, if it were not split, would possess a tensile strength between 30 and 36 kgs./mm.^{2}

No such an extensive decrease in tensile strength was observed when after breaking, *only one end* of the thread was separated into several threads (threads Nos. 7 and 8); probably due to the fact that these separated threads were more uniformly stretched during the test than in the case of thread No. 12.

Further it is of interest to dwell on the difference in tensile strength of threads prepared by me, when they are in air-dry and in wet conditions.

As is seen from Tables 2 and 3, moisture affects natural silk threads to a much lesser degree than it does the threads of artificial cellulose silk. But all the same, the tensile strength of wet natural silk threads is 20 or even more per cent lower than the tensile strength of dry threads of natural silk.

The tensile strength of threads obtained by me from colloidal silk solutions according to the method described in this section, is lowered only slightly even after the threads have remained from half to one whole hour in water (see Table 1, threads Nos. 6 and 10). I think that the slight influence of moisture upon the tensile strength of threads in this case is due to their slow process of swelling.

There are three reasons for the slowness in swelling of threads or their slight tendency to swell: (1) a very strong orientation of fibroin particles in

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*** In testing metals and crystals the presence of minute flaws reduce the strength as determined experimentally below the strength calculated theoretically. See paper by Alexander and McBain in this volume. J. A.**

the threads, (2) a weak capacity for imbibing water as a result of the presence on the surface of threads of greasy substances from the skin of the fingers, and (3) the adsorption of so strong a dehydrator as sulfate.

Those threads prepared by me whose fibroin particles were less orientated, possessed correspondingly higher capacities for swelling, and in accordance with this, the tensile strength of these threads in a wet condition was markedly decreased, in comparison with that of the same threads in an air-dry condition. The greater is this difference in the tensile strength, the less orientation there is of the fibroin particles in threads. Hence a conclusion emerges *that the tensile strength differs very little for air-dry and wet threads,* provided that the orientation of the fibroin particles in these threads is perfectly regular.*

From the data collected in Table 1, it is seen that the tensile strength of threads obtained by me is not only greater than that of the boiled-off silk (silk wadding) which I used for dispergation, but it is even greater than the tensile strength of certain other kinds of real silk; these observations agreeing with those expressed by me already in 1926 (*loc. cit.*).

Correspondingly higher values for tensile strength must be obtained for threads with still higher orientation of their fibroin particles than in the case of the threads in Table 1. However the measurement of the tensile strength in such highly orientated threads has been beset by certain difficulties which I hope to overcome in the future.

The fact is that as a result of *long* and *repeated* rubbing of the thread (which is necessary in order to achieve the highest possible orientation of fibroin particles) there are obtained threads possessing an extremely high fibril cleavage, which makes the measurement of the tensile strength difficult. Due to high cleavability, the threads either split along all their length into very thin threads, the thickness and breadth of certain of which threads are equal only to several thousandths of a millimeter, or they split only in some places; in the latter case, although to the naked eye the thread appears intact, a microscopic investigation (sometimes even with a magnifying glass, 10×) reveals distinct pores, arranged parallel to the length of the thread.

Therefore I cannot give here numerical data concerning the tensile strength of these threads, as the determination of their tensile strength and especially the determination of the actual surface of their cross-sections, presents many difficulties which have yet to be overcome.

Unfortunately our testing machine (employing water as a weight) is too rough for the work with the extremely fine threads which without great difficulty I succeeded in obtaining; the dimensions (thickness and breadth) of these threads range between several thousandths of a millimeter, and owing to the very high degree of orientation of fibroin particles in these threads, they must possess a high tensile strength. Although owing to the above-mentioned difficulties I cannot at present state exactly the higher value for the tensile strength † of threads of the *highest quality* obtained by my method, I can with full certainty assert that the tensile strength of threads with the orientation of their fibroin particles approaching a perfect regularity, must considerably exceed the tensile strength of the best kinds of silk produced by silk-worms.

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* In page 715 of J. M. Matthews's book "The Textile Fibers," New York, John Wiley & Sons, Inc., 1924, 4th Ed., are given Hassack's measurements of real silk threads in the dry and wet conditions. The numbers for tensile strength in both cases are equal, viz. 37 kgs./mm.^{2}; unfortunately there is no indication of the kind of real silk which was investigated.

† For instance, I defined the breaking weight for one of such threads, which was equal to 330 grams. The thread was thin, but relatively broad; its cross-section could not be exactly measured owing to the difficulties already mentioned in this paper. However, the tensile strength of this thread is undoubtedly greater than the tensile strength of threads in Table 1.

THE CHIEF CONDITIONS NECESSARY FOR OBTAINING SILK THREADS WITH MAXIMUM STRENGTH.

1. The silk for the solution must be previously thoroughly cleansed from admixtures, especially those which can give insoluble compounds with the coagulators. The presence of such compounds in threads affects their strength.
2. The dissolution of silk in the solutions of salt-dispergators must be carried out as rapidly as possible and at temperatures as low as possible; preferably below 100° C., or only a little higher. A long subjection of the silk solution to temperatures above 100° C. causes a marked hydrolytic decomposition of silk. The presence of the products of hydrolysis in the threads reduces their quality.
3. With both these conditions taken into consideration, threads of the maximum possible strength are obtained only when the orientation of the disperse fibroin particles in the solidified threads has reached the maximum. The last condition is of most importance, because without observation of this condition, no *really strong* silk threads can be obtained.

CONCLUSION.

From an economic standpoint, for the application to industry of my method of forming silk threads, solutions of calcium salts, especially of calcium chloride, are most suitable. However, because of the reasons above mentioned such strong aggregators as fluorides and sulfates cannot be used for the coagulation of silk solutions in the solutions of calcium salts.

In my opinion the most convenient solvents for silk are solutions of sodium thiocyanate. Silk can be dissolved in these solutions at temperatures even somewhat lower than 100° C. Moreover, the application of such strong coagulators as fluorides, sulfates, citrates and tartrates does not in this case meet with any objections.

As I have already pointed out, the use of viscose silk machines for the preparation of threads obtained according to my method, cannot give threads possessing maximum strength. Machines of another construction are required for this purpose, which must be equipped with special devices not only for stretching but also for rubbing with definite force all over the surface of threads in the longitudinal direction.

But here ends the region of colloid chemists and the creative activity of mechanical engineers must begin; and I am sure that before long, satisfactory results will also be reached in this respect.

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EDITOR'S NOTE

Prof. Dr. P. P. von Weimarn has called my attention to the fact that the statement of Dr. E. G. Acheson on page 551 of Vol. III concerns "deflocculation," the dispersion of colloidal aggregates, already pre-existing, which as the footnote beginning on page 549 indicates is simply another word for "peptization," a term coined by Thomas Graham. Berzelius (1824-5) "deflocculated," or peptized SiO_2 with alkali carbonates, and the process was known to many others, e.g., Kuhn, W. Spring, T. Graham. So far as I know, Von Weimarn was the first to demonstrate by systematic experimentation, the transition conditions governing change from crystalloid to colloid, and *vice versa*. Graham, however, well knew that a substance could exist in either state, for he wrote: "The mineral forms of silicic acid deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition."

Technologically Useful Properties of Casein.

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Casein is the principal member of an important class of proteins, the raw material from which it is obtained is readily available, and it is easily separated in what, among proteins, is considered a high degree of purity. It has accordingly been the subject of many scientific studies. Nevertheless the technological uses of casein do not owe their development directly to scientific activity; they have come instead from invention and empiricism. Success in working with casein often has been derived more from art than from rational deduction, and theory has been the result of discovery rather than its cause.

The hiatus between "pure" and "applied" research in the technology of casein cannot be attributed to the antiquity of the practical uses of casein, for none of these uses achieved material importance until comparatively recent times, when modern chemistry had long since become a potent factor in industry. This hiatus must rather be attributed to the fact that scholars have studied casein chiefly from the points of view of organic and biochemistry and the physical chemistry of its dilute solutions, while industrialists have been concerned primarily with its concentrated sols and jellies. As a matter of fact the chemical individuality of casein proves to be of secondary interest in its technology, because its uses depend primarily upon the characteristic properties of certain colloidal states in which many other substances besides casein can also be obtained. Unfortunately colloid scientists have not yet succeeded in setting up quantitative criteria for defining these states of matter adequately and consequently we still apprehend them for the most part only qualitatively. Lack of suitable technic for evaluating results has seriously deterred the application of scientific methods in developing the industrial uses of casein.

Under the circumstances the method of trial and error no doubt succeeded in establishing practicable processes and formulas in less time than more erudite styles of research would have required. It is the writer's opinion, however, that simple pioneering will prove less fruitful in the future and that significant improvement of present products must be achieved through a more arduous probing of fundamental principles. Unless the technological applications of casein are now studied in a thoroughly scientific manner casein may be unable to hold its own against its many competitors.

The Place of Casein in Industry.

Casein is used in industry principally in coatings for paper, glue for woodworking, plastics, paints, and insecticide sprays. Although there is also a large number of miscellaneous uses to which casein has at some time been put or for which it has been shown to be suitable, the amount of it actually used for

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* Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

such purposes is small. Applications of casein in pharmacy and in foods are outside of the scope of the present discussion. Reliable descriptions of the technology of casein by specialists in its manufacture and in each of its applications have been published elsewhere.[1] Only a brief survey of these applications can be given here.

The writer's personal experience with the industrial uses of casein has been confined to the field of woodworking glues; for information about its other uses and its manufacture he has drawn largely upon Edwin Sutermeister, George H. Brother, Albin H. Warth, and Arnold O. Dahlberg.

The Manufacture of Casein.[2]

The casein of commerce, which is made from skim milk, is a by-product of the dairy industry. The process of manufacture consists essentially in precipitating the casein as a curd, separating the curd from the whey, washing it, pressing out the free water, grinding the moist curd, and then removing imbibed moisture through kiln drying. Since precipitation and separation may be effected in different ways with consequent variation in certain important properties of the product, it is customary to classify caseins according to the method of manufacture.

Rennet casein.—Rennet casein is made by curdling fresh skim milk, held at 35.5° C., with the enzyme rennet. At a critical stage in the coagulation, recognized through experience, the curd is cut or broken up by agitation and the mixture is heated to 65.5° C. The whey is then drained and the curd washed, pressed, ground, and dried at about 45° C. Rennet casein of good quality has a very high ash content and its alkaline solutions are very viscous as compared with those of other kinds of casein.

Naturally soured casein.—All other kinds of casein are precipitated by acidifying skim milk. In making naturally soured casein, which is sometimes called lactic-acid casein, acidification is effected by fermentation of the lactose in the milk by the ever-present *Bacterium lactis acidi.* The skim milk may simply be held in a vat at 26° to 32° C. until it curdles, and the process may then be speeded by adding a small amount of sour whey held from the previous day's production. Another method is to hold over enough sour whey so that on mixing it with the skim milk coming directly from the cream separator the casein precipitates at once. To separate the curd the temperature is raised to 43° to 54° C. as soon as the correct degree of acidity has been reached. A more granular curd, easier to wash, is obtained if instead of heating the curdled milk in the vat the mixture is passed through a steam ejector [3] in which the steam not only heats it but also stirs it vigorously. After separation the curd is washed, pressed, ground, and dried. Naturally soured casein usually has both a medium ash content and a medium viscosity, while if it is made by the ejector method these two features may be low.

Sulfuric-acid casein.—Sulfuric-acid casein is made by heating skim milk to about 50° C. and adding sulfuric acid while stirring the mixture thoroughly. Just enough acid is added to cause the curd to separate sharply, leaving a clear whey. The curd may then be washed, pressed, ground, and dried. When small creameries lack facilities for the final operations and wish to ship wet curd to a central drying plant they may adopt the cooked-curd method. In this method, after the whey has been drained the curd is covered with water and heated directly with steam to about 78° C., whereupon the curd collects in a semi-fluid, plastic mass. Sulfuric-acid casein is usually high in ash and in viscosity.

Hydrochloric-acid casein.—When the whey is desired for recovering lactose,[4] the casein is precipitated with hydrochloric instead of with sulfuric acid because sulfuric acid forms calcium sulfate, which crystallizes with the lactose while calcium chloride is sufficiently soluble to remain in solution. Hydrochloric-acid casein is usually high in ash and in viscosity. The viscosity is especially high if the cooked-curd procedure is followed.

Grain-curd casein.[5]—Grain-curd casein is made by adding dilute hydrochloric acid (1 *N* solution) to skim milk at 34° C. until test of a sample of expressed whey indicates an apparent pH of 4.6 with methyl red. The curd under these conditions has a granular character that permits very thorough washing. Much more acid is used, however, than in making ordinary hydrochloric-acid casein. Grain-curd casein is low in ash and in viscosity.

Pure casein.—Pure casein for scientific investigations has generally been made either by the method of Hammarsten[6] or by that of Van Slyke and Baker.[7] Pure casein is very low in ash and in viscosity.

The Testing of Casein.[8]

Since commercial caseins vary widely in some of their properties and the kind of casein preferred by some industries is not considered satisfactory by others, there is need of an acceptable system of testing on which to base purchase specifications and acceptance. Many consumers feel that the methods proposed so far are not adequate and that the only reliable test is to make a trial batch of the product in which the casein is to be used. It must be admitted that chemical tests alone are insufficient, but a combination of chemical and biological tests may accomplish the purpose. However, more experimental work will be needed to establish a system of testing for each of the uses of casein.

The most significant chemical test of casein is the ash content, because there is a connection between this content and the viscosity of alkaline solutions of casein.[9] In general the higher the ash content the greater the viscosity of solutions that are comparable in all other respects. Probably the calcium content of the ash would prove more directly indicative than the total ash content of the casein. The relation can be only approximate at best, however, for other characteristics of the casein, particularly its deterioration through hydrolysis or biological action, may also affect viscosity.

For some uses it is important that the content of butter fat be as low as possible, in which event a fat determination is desirable. The sugar content is a good indication of the thoroughness with which the curd was washed. The nitrogen content is higher in casein of good quality than in an inferior product. A test for acidity, or capacity for combining with alkalies, has proved of interest. Since casein is hygroscopic, a determination of moisture content is a necessary part of any chemical test.

Results of chemical tests of caseins of different kinds are given in Table 1.[10] Physical tests have been used to a certain extent, although their significance is doubtful. Color, freedom from observable dirt, odor, and fineness may be important. Standardized solubility tests in a solution of borax have been described;[11] caseins made at high temperatures, such as cooked-curd caseins, leave an undissolved residue or form a jelly instead of yielding a mobile sol. Standardized tests of the viscosity of alkaline solutions, however, have proved instructive[12] only when the solution chosen is one playing a part in the use for which the casein is intended. A test for adhesive strength,[13] or rather for the amount of casein needed to make a coating of the strength required, has proved useful in the paper industry. In choosing casein for woodworking glues, tests of joint strength have not been very valuable because strong joints can be made even with glues containing inferior casein, provided that suitable gluing technic is employed.[14] However, such joints may be lacking in water resistance or in permanence.

TABLE 1. *Proximate Analyses of Some Caseins Made by Different Methods.*[*]
(The column of principal interest is the ash content.)

Kind of Casein	Number of Samples Analyzed	Moisture	Fat (Moisture-free basis)	Ash (Moisture-free basis)	Nitrogen (Moisture-fat-, ash-free)	Acidity
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Cc./g.*
Pure casein, Hammarsten	2	8.71	0.11	1.89	15.54	7.5
Pure casein, Van Slyke	3	8.13	0.16	0.33	15.18	8.1
Grain cured	11	9.48	0.33	1.65	14.84	9.9
Naturally soured, ejector method	18	7.87	0.27	2.15	14.84	8.7
Naturally soured, domestic	12	7.70	0.88	3.46	14.38	9.7
Naturally soured, Argentine	8	8.20	1.10	3.87	14.66	11.5
Sulfuric acid, pressed curd	23	7.97	1.41	3.92	14.42	10.4
Sulfuric acid, cooked curd	18	8.16	0.65	4.45	14.40	7.5
Hydrochloric acid, pressed curd	14	7.37	0.56	4.52	14.39	8.7
Hydrochloric acid, cooked curd	8	9.44	0.18	4.71	15.03	5.2
Rennet	3	8.29	0.63	7.97	14.41	7.9

[*] Browne, *Ind. Eng. Chem.* 11, 1019 (1919).

Casein is subject to infestation by molds, bacteria, and insects. It may thereby be rendered unfit for some of its uses without the revelation of that fact through chemical or physical tests. Biological tests are therefore necessary. Good casein should give a mold count of not more than 100 per gram and it should not become putrid in less than 72 hours when subjected to the Warth incubation test.[15] This test is simple; 15 grams of casein and 90 cc. of sterile water are placed in a 200 cc. sterile flask and kept at 38° C.

The Manufacture of Casein Plastics.[16]

For practical purposes, plastics are solids that can be softened enough to permit amalgamation into bodies of desired size and to allow shaping to desired forms, by such means as heating and pressing, molding, bending, or extruding, and can then be made rigid and mechanically strong. Casein competes in this field with many other materials of diverse chemical nature, such as other proteins, cellulose esters, natural and synthetic resins, and rubber. Processes for making casein plastics differ widely in mechanical features but for the present purpose only the essential changes undergone by the casein need be discussed.

Rennet casein, with 7.5 to 8.0 per cent ash, is preferred for making plastics. After it has been ground to a moderately fine powder, it is mixed thoroughly and enough water is added to swell and soften the granules of casein. If a transparent, colored plastic is desired, acid aniline dyes are dissolved in the water. Pigment colors, "fillers," and a plastifying agent may also be incorporated during the mixing. The plastifier facilitates or is thought to facilitate subsequent conversion of the granular powder into a homogeneous mass and, with substances like glycerine, may also improve the elasticity of the finished product. According to the patent literature a great many substances of different kinds serve as plastifiers.

The moist, granular mixture is next converted into a plastic mass by simultaneous application of heat and pressure, together with mechanical kneading. In order to make a strong product it is essential that the mass be worked by a rubbing or flowing of the material over or into itself, somewhat after the fashion of rubber compounding. The machinery for accomplishing this has much to do with the success of the process. The soft plastic is finally extruded in the form of rods, and either pressed into sheets or molded in desired shapes.

The plastic is next soaked in aqueous formaldehyde, which reacts with the casein and profoundly alters its properties. Without the formaldehyde treatment the material on drying would be brittle, soluble in alkalies, and excessively hygroscopic. The reagent makes the product tough and insoluble and greatly reduces its hygroscopicity. The soaking is a slow process, requiring two weeks to six months according to the size of the mass and the temperature and concentration of the solution. It is essential that the formaldehyde diffuse uniformly and completely through the plastic so that the product will be homogeneous.

The final step is seasoning to reduce the moisture content to 8 or 10 per cent. This is also a slow process, depending upon diffusion outward through the jelly. The loss of moisture involves shrinkage, which sets up internal stresses in the mass wherever there is a gradient in moisture content. If the drying is unduly hastened the material may break, or it may become brittle. There is likely to be warping during seasoning, but the shape may be restored by subsequent heating and pressing.

Casein Paints.[17]

Casein may be used as the binder for cold-water paints where, analogous to the linseed oil in oil paints, it forms the matrix of the coating in which the pigments are embedded and bound to the underlying surface. Casein competes with animal glue for this purpose but has the advantage of being more easily rendered insoluble in water so that the paint coating may be washed. Casein paints, however, offer much less resistance than oil paints to the passage of moisture and are therefore inferior as protective agents for wood or metal exposed to the weather. Most water paints are used indoors, though casein paints find some use out of doors.

The manufacture of casein paint is merely a matter of grinding and mechanically mixing dry ingredients, which the consumer ultimately stirs into water for use. Sulfuric- or hydrochloric-acid casein of fairly high ash content seems to be preferred. It must be ground to a fine powder so that it will dissolve rapidly. Besides the pigments, of which whiting is usually the principal one, there must be reagents to establish the correct alkalinity of the solution for dissolving casein and a coagulating agent to make the casein subsequently insoluble. Slaked lime performs both of these functions because its solubility and its strength as a base quickly establish a sufficient alkalinity when it is added to cold water and because calcium ions in solution slowly change casein sols into jellies. It is common practice, however, to add also a small proportion of some sodium salt such as trisodium phosphate which, in the presence of lime, increases the alkalinity slightly by forming sodium hydroxide and thus insures more rapid and more nearly complete solution of the casein. Sometimes dextrine or starch is incorporated to retard settling of the pigments after the paint has been mixed with water, and a preservative like zinc sulfate or mercuric chloride may be added to prevent biological deterioration of the casein during storage. [Certain moths lay eggs in casein, and the maggots then eat it. J. A.]

Casein for Paper Coatings.[18]

Casein plays much the same part in coatings for paper that it does in water paint; namely, it forms a matrix to bind minerals together and hold them on the paper. The purposes of such coatings are to provide a surface of the required degree of smoothness and absorptiveness for ink and to give the sheen desired. Competitors of casein in this field are animal glue and starch. Paper coatings require a higher standard of precision in controlling the properties of the product than is necessary in water paints.

Mixtures for coating paper are commonly prepared from casein and the other ingredients immediately before use. The casein is first dissolved in water with the aid of alkalies, the insoluble minerals are then incorporated, the mixture is applied mechanically to the paper, and the coated paper is dried and finally polished by calendering or other means.

Naturally soured casein of low ash content is preferred for paper coatings. It should be ground to a moderate degree of fineness, that is, so that almost all of it will pass through a sieve of 20 meshes to the inch but more than half of it will be retained on a 60-mesh sieve. Coarse casein dissolves slowly while very fine casein is likely to gather together in lumps with dry, undissolved casein in their centers. The casein is first soaked in part of the water long enough for the particles to be thoroughly softened. The alkali is dissolved in the rest of the water and the solution added to the casein suspension, which is stirred and may be warmed slightly until the casein dissolves. It is essential that all of the casein dissolve and a solution of low viscosity is desired. The alkali is generally one or more of the following: Borax, ammonium hydroxide, sodium carbonate, trisodium phosphate, and sodium hydroxide. Considerably more alkali is added than is required to neutralize the casein, consequently the solution is distinctly alkaline and in general more strongly so the more completely hydrolyzed and dissociated the alkali chosen.

The mineral substances are next mixed with water and the casein solution is added to them. Enough of the casein solution must be used to attach the coating firmly to the paper, but too much casein reduces the absorptiveness of the paper for ink and also dulls the sheen obtained on calendering. The amount of casein required varies with the kind of mineral and with such properties as the size of the mineral particle. Minerals commonly used are china clay, blanc fixe, precipitated chalk, and satin white (the product of precipitation of calcium hydroxide with aluminum sulfate). The choice of minerals largely controls the finish of the paper. Tinting colors may also be added, as well as waxy or oily substances to prevent foaming or to improve the finish of the paper.

Machines for applying the coating mixture vary. In general, after the coating has been spread on one or both sides, the paper is passed through squeeze rolls to remove excess mixture, and the surface is then smoothed by the action of brushes. For satisfactory results the mixture must be kept uniformly in a suitable consistency and there must be as little foam as possible. The consistency of the coating mixture is by no means determined by the viscosity of the casein solution but apparently depends very largely upon the way the mineral substances are dispersed in this solution.[19] There is clearly an important relation between the alkalinity of the casein solution and the consistency of the coating mixture, for some minerals cannot be used in strongly alkaline solutions while others cannot be used in weakly alkaline ones.

When the alkali used in making the casein solution is nonvolatile the coating is not waterproof unless the casein is rendered insoluble. Satin white has a tendency to do this. The casein can be rendered insoluble also by treating the coated paper with metallic salts like zinc sulfate, chrome alum, and lead acetate. A more general procedure, however, is to add a small amount of dilute formaldehyde solution to the coating mixture, taking care not to add enough to cause the mixture to thicken before it can be used up. Sometimes hexamethylenetetramine is added instead of formaldehyde because on heating in the calenders it gives off formaldehyde, which reacts with the casein.

Casein Insecticide Sprays.[20]

The efficient application of toxic sprays to the surfaces of leaves and of fruits requires that a "spreader" be incorporated in the solution containing the poison. The function of the spreader is to maintain adequate wetting of the surface while the water evaporates so that the solids will remain as a thin film completely coating the surface instead of gathering at isolated spots. Soaps make good spreaders but soluble proteins are effective at lower concentrations. Casein has the advantage that, in conjunction with lime, it leaves a film that is not readily washed off again by rain water. A mixture of finely ground casein with three times its weight of lime makes a good spreader. About three quarters of a pound of spreader is sufficient for 100 gallons of spray. The spreader is dissolved in a small quantity of water before adding it to the other ingredients.

Casein is also used as an emulsifying agent in making oil sprays. A pound of the casein-lime spreader may be dissolved in a gallon of water, 8 gallons of oil added, and the mixture agitated thoroughly until an emulsion results.

Casein Glues.[21]

In the field of woodworking glues casein competes with animal glue, starch glue, blood-albumin glue, and vegetable-protein glues like soya-bean glue. The principal advantage of casein glue is the fact that it may be made water-resistant more conveniently and with less expense than animal glue or blood-albumin glue. Casein glue is not equal in water resistance to good blood-albumin glue, but it is less expensive and does not have to be heated while the joint is being pressed. Casein glue is not so cheap as starch glue, but starch glue is not at all water resistant. Soya-bean glue is cheaper than casein glue and is nearly as water resistant, but it has not yet been made equal to casein glue in joint strength, particularly in the joining of hardwoods.

Woodworking glues are aqueous sols having a viscosity such that they can be readily applied to wood by the various mechanical glue spreaders in common use. Dry wood withdraws moisture promptly from these sols, causing them to attain a consistency suitable for withstanding the joining pressures necessary in gluing operations. Upon further dehydration the sols yield strong, elastic jellies that adhere firmly to wood. The concentration of the sol must be sufficient to leave a continuous layer of dry jelly, with no voids, between the two surfaces joined.

Naturally soured casein has generally been preferred for glue making. However, satisfactory glues have been made from all kinds of casein, including rennet casein, although it is necessary either to change the proportion of water or to adjust the usual formula in other ways if glue of uniform viscosity and working life is to be made from caseins that vary in ash content. In general, the higher the ash content of the casein the more water is required to make a glue of given viscosity.

Casein glues may be either "wet-mixed" or "prepared." Wet-mixed glues are made by the consumer from casein and other ingredients just before use. They have the advantage of permitting the use of reagents that are not compatible with dry powders, such as ammonium or sodium hydroxide and commercial sodium silicate. Prepared glues are mechanical mixtures of finely ground casein with dry, powdered reagents in such proportions that the mixture need only be stirred into cold water immediately before use.

In practice, water-resistant casein glues always contain lime, which serves two purposes. When the glue solution is first prepared the lime takes part in the chemical reactions that establish its alkalinity. Once the casein is in solution an excess of lime over that consumed in these reactions slowly changes the sol into a jelly, unless hydrolysis in very strongly alkaline glues destroys the casein before the jelly forms. The rate at which gelation proceeds determines the working life of the glue, that is, the length of time during which it remains within the range of viscosity suitable for application in gluing operations. The jelly is irreversible except that, if kept moist, the casein eventually hydrolyzes and the jelly then becomes liquid again.

A reagent is commonly included in the mixture for controlling the alkalinity of the glue solution. Any sodium salt, the corresponding calcium salt of which is materially less soluble than calcium hydroxide, will serve as a reagent because, when the mixture is thrown into water, the reagent and the lime dissolve and react, precipitating the calcium salt and forming sodium hydroxide in the solution. The precipitate does not settle but remains dispersed in the viscous solution, perhaps peptized by the casein. Since an excess of lime is always present, the amount of reagent added determines the alkalinity of the solution.

Sodium fluoride, trisodium phosphate, and sodium carbonate or mixtures of them are reagents in common use. Sodium fluoride releases its equivalent amount of sodium hydroxide very promptly when the mixture is brought into contact with water, with the result both that the casein dissolves quickly and that the viscosity of the glue is at first low; the viscosity soon begins to rise through the action of the calcium. Trisodium phosphate, on the other hand, reacts more slowly, so that with it the glue is less strongly alkaline at the start, the casein goes into solution less rapidly, and the viscosity of the glue decreases during the early part of the working life as the remaining amount of sodium hydroxide is set free. By mixing sodium fluoride and trisodium phosphate in varying proportions it is possible to exercise a considerable measure of control over the change in viscosity of the glue during much of its working life.

Any of the preceding reagents can be used in wet-mixed glues, of course, but other reagents are also possible. In Europe ammonium hydroxide is often used as the principal source of alkali, accompanied by considerably less lime than is customary in this country. Such glues are very low in alkalinity and require much more than the usual amount of water to give them the right viscosity. Sodium silicate is a reagent of exceptional properties because it not only reacts with lime to form sodium hydroxide, but also introduces colloidal silica and silicates into the mixture; this silica acts as a buffer to keep the alkalinity relatively low and also prolongs the working life of the glue by retarding gelation.

The alkalinity of the glue solution dominates certain important properties. Glues of relatively low alkalinity require much more water than more strongly alkaline glues to give a solution of suitable viscosity. The working life is longer the higher the alkalinity. Stronger jellies are formed and, when kept wet, the jellies take longer to reliquefy the lower the alkalinity. Of particular importance is the fact that casein hydrolyzes more rapidly in glues of higher alkalinity, and hydrolysis may become so rapid that the mixture fails to form a jelly at all. Joints made with such glues late in the working life, may lack water resistance and the water resistance of joints made early in the working life is less permanent than it would be if the alkalinity were reduced. At best the alkalinity of casein glues is undesirably high, commonly lying in the region of pH from 12 to 14.

Measurements more precise than former ones have shown that the dispersed calcium salts precipitated by reaction between lime and the reagent definitely retard gelation, giving the glue a longer working life than it would have if the same degree of alkalinity were produced by direct addition of sodium hydroxide. The solids also affect the strength of the jelly formed at the end of the working life.

Soluble copper salts are often added to casein glues for the purpose of increasing their water resistance. Such glues have the violet color of colloidally dispersed copper hydroxide. The addition of carbon bisulfide to casein glues increases the water resistance, but copper salts and carbon bisulfide may not be used together.

In mixing casein glues, thorough stirring is necessary although it must be done in a way that precludes foaming. Bakers' dough mixers prove very satisfactory. Prepared glues are mixed by slowly adding the powder, in correct proportion by weight, to cold water while stirring it in the mixer. Solution of the casein should be complete within 30 minutes and the glue should have a working life of 4 to 8 hours. Where water resistance is important, glues that fail to congeal should not be used and glue found liquid on the morning after mixing should never be used directly or even incorporated in a fresh mixture. In making wet-mixed glues the casein, which should be ground only to moderate fineness, is soaked in water until the particles are swollen and softened, and is then stirred during the addition of the remaining ingredients, which usually are dissolved or suspended in water. The order of addition of the ingredients may be important; for example, lime is always put in and given a few minutes to act on the casein before sodium silicate is added.

COLLOID CHEMISTRY IN THE USES OF CASEIN.

A satisfactory treatment of the colloid chemistry of casein as it affects the industrial uses of casein is not possible with the information now available. The following discussion is intended to arouse curiosity rather than to satisfy it.

General Chemical Considerations.

Casein has generally been considered a distinctly individual chemical substance.[22] Apparently this view is not correct, for casein seems to consist of a mixture of substances differing in solubility [23] and in molecular weight.[24] Moreover the molecular weight differs markedly in accordance with the method of preparation; for example, about one-third of a casein made by Hammarsten's method had a molecular weight of 375,000 while most of a casein made by the Van Slyke and Baker method had a molecular weight between 75,000 and 100,000 when dissolved at room temperature, although if it was heated to 40° C. while dissolving it the molecular weight rose to 188,000, with no molecules as light as 100,000. The "molecular weight" referred to is the physicist's rather than the chemist's term, that is, it is the relative weight of the smallest particles that move independently under such forces as gravity or centrifugal sedimentation. To the chemist these particles are perhaps micelles capable of further subdivision into smaller units having the chemical characteristics of the substance, which would be the chemist's molecules. Whether all the molecules so obtained from each micelle of casein would be identical in composition is as yet open to question. From chemical considerations, all more or less dubious, molecular weights for casein that vary from about 3,000 [25] to 192,000 [26] have been estimated. The combining equivalent is higher when the temperature is raised.[27]

Many workers consider casein, in common with the proteins in general, to be an amphoteric electrolyte, combining stoichiometrically with acids or with bases.[28] Others regard the relation with acids and bases as one of adsorption.[29] It has been suggested that the combination is stoichiometric between pH 2.5 and 10.5 but is adsorptive beyond those limits.[30] Evidence recently offered indicates that dry casein forms a definite compound (or mixture of similar compounds) with gaseous hydrogen chloride but that it takes up gaseous ammonia only by adsorption.[31] The debate between the stoichiometrists and the adsorptionists is further complicated by the difficulty of deciding whether particles that may have a molecular weight as high as 375,000 are in homogeneous solution among molecules of water with a weight of 18 to 54 or whether the mixture contains two phases,[32] one colloidally dispersed in the other. Whatever nomenclature may be chosen to describe it, there is no doubt about the fact that acids or alkalies added to water containing casein are partitioned between the casein and the water, part of each increment of acid or base being bound by the casein and the rest remaining free to raise or lower the pH of the aqueous solution. The titration curves with alkalies [33] are inflected in a manner suggestive of compound formation, but uncertainty about the chemical individuality of casein and its combining equivalent render such evidence inconclusive. The titration curves for casein with alkalies are not strictly reversible through the pH range of 4.6 to 10.5; there is a hysteresis loop between the curve obtained on adding alkali and the back-titration curve obtained on adding acid.

Formaldehyde reacts chemically with casein to form a product having a solubility and other physical properties distinctly different from those of casein.[34] Carbon bisulfide also forms a compound with casein.[35] The organic chemistry of both reactions is still obscure, as is also that of the reactions with acids and bases.[36]

The Precipitation of Casein from Milk.

As it exists in milk, casein is intimately associated with calcium oxide and calcium phosphate,[37] which make up the principal portion of the ash content of casein. These constituents are not to be considered extraneous, like fat or lactose, but are intimately associated with the casein, profoundly affecting its properties. The extent of this association between casein and inorganic constituents is a function of the pH, becoming less as the milk increases in acidity until at the isoelectric point, pH 4.6,[38] the casein is free. Accordingly the nature of casein varies with the acidity of the milk from which it is precipitated. Of the commercial products, rennet casein retains the largest amount of the inorganic constituents. If the milk is allowed to become somewhat acid before adding the rennet the ash content of the casein is reduced correspondingly. Grain-curd casein, because it is precipitated as nearly as possible at the isoelectric point, contains the least ash.

The mechanism of the precipitation of casein with rennet is not yet understood. An older view [22, 37] considers that it involves a splitting of the molecule, yielding para-casein, which has a lower molecular weight than casein and differs in solubility and in combining power. A more recent view [39] holds that it is primarily colloidal coagulation with little or no change in molecular weight. Acids precipitate casein because only caseinate ions or casein micelles charged by adsorption of hydroxyl ions are soluble and on neutralization the free casein separates. Weak organic acids are often much less soluble than their salts. For a moderate range in values of pH that begins at the isoelectric point the solubility of casein increases in direct proportion to the amount of alkali bound by it.[40] The fact that casein does not begin to separate when only part of the bound alkali has been neutralized by acid must be attributed to peptization of the free casein by the caseinate ions still remaining in solution.[41]

In precipitating casein with acids the inorganic constituents are removed only incompletely because (a) as a rule only enough acid is added to bring the milk to the point of precipitation, which is still short of the isoelectric point, (b) the back-titration curve lags behind the curve for combination with alkalies, and (c) the interior of the pieces of curd require more time to come to equilibrium with the surrounding milk than is usually allowed in commercial operations. Since naturally soured casein permits longer contact between curd and acid milk, it has less ash than casein precipitated by adding sulfuric or hydrochloric acid, and if the naturally soured milk is passed through a steam ejector, better contact is obtained and the ash content of the product is still lower.

The precipitated casein is a curd, that is, it consists of shreds of swollen jelly whose size and physical state depend upon such factors as local variation in concentration and temperature and mechanical conditions of stirring while the curd is separating as well as upon the pH of the acid milk. At the isoelectric point the swelling of the jelly is a minimum and the curd forms relatively fine grains that do not tend to stick together. On departing from the isoelectric point in either direction, swelling increases and the curd softens and tends to clump. Heating softens the curd still more, making it possible in the cooked-curd process to fuse the shreds into a tough, coherent mass.

The swollen curd lends itself to removal of free water through pressing. Subsequent drying of the imbibed water involves diffusion outward through the particles of jelly, some shrinkage, and hardening. Unless the curd is torn into shreds of suitable size the drying will take place very slowly.

Sols of Casein in Monovalent Alkalies.

Dry casein swells again when brought into contact with water or an aqueous solution, and there is also an evolution of heat. The degree of swelling varies with the pH of the water and is minimum at the isoelectric point. Combination of the casein with calcium or other di- or polyvalent metal or with formalin or carbon bisulfide reduces the amount of imbibition and swelling, sometimes greatly but never entirely.

The aqueous solution in contact with swollen particles of casein dissolves some of the casein.[40] At the isoelectric point the amount so dissolved is very small but it increases rapidly as the solution is made more alkaline. If the solution is made sufficiently alkaline, the concentrations of casein in the aqueous phase and of water in the jelly increase until the two phases are alike in composition and the casein is uniformly dispersed as a sol. Casein can be dispersed in some acids also, but sols on the acid side of the isoelectric point have found no application in technology. When the casein is combined with calcium, that is, when a high-ash casein is used, a higher degree of alkalinity is necessary to effect complete dispersion than is needed for a low-ash casein.

The alkaline sols of casein have the viscosity that is characteristic of strongly hydrated lyophile colloids. As the concentration of casein increases the viscosity increases, at first slowly, and then ever more rapidly. The sols of importance in technology are all very viscous casein glues having, for example, viscosities of the order of tens of poises. The casein solutions used in paper coating and in paints are somewhat less viscous. The viscosity is markedly affected by many factors besides concentration and pH, such as temperature, the age of the sol, the method of preparing the sol, and the presence of other substances, especially of electrolytes. The ash content of the casein, as usual, is of importance, the higher the ash content the more viscous the sol, other factors being comparable.

In general the viscosity of casein sols increases rapidly with the alkalinity, reaching a maximum of pH 9.2, after which it falls off again sharply.[42] The viscosity at the maximum varies materially with the cation of the hydroxide furnishing the alkalinity; thus the maximum viscosity decreases in the order $NH_4OH > KOH > NaOH > LiOH$. If the alkalinity is furnished by a hydrolyzing salt like sodium phosphate, sodium fluoride, sodium carbonate, or sodium silicate, the maximum viscosity still occurs at pH 9.2, although its magnitude varies for the different salts. Ammonium hydroxide and borax, however, are striking exceptions in that the viscosity curve with ammonium hydroxide does not recede after attaining its maximum, and borax has its maximum at pH 8.1. In explanation of the peculiar behavior of ammonium hydroxide it has been suggested that the decline from the maximum of the curves for other alkalies is due to the hydrolysis known to take place at higher alkalinities, during which ammonia is split off, and that ammonium hydroxide represses this hydrolysis by mass action. The abnormality of borax has been attributed to formation of a complex between boric acid and polyhydroxyl groups of casein, similar to the complex between boric acid and polyhydric alcohols, whereby the boric acid becomes a much stronger acid.

Sols of casein in alkaline solution containing only monovalent cations are not truly viscous[43] and do not obey Poiseuille's law unless the concentration of casein is low.[44] Such behavior is usually taken as evidence of structure within the sol; in other words, the sol may be regarded as an exceedingly weak and swollen jelly. If such sols are heated moderately in course of preparation the viscosity is much greater than it is if the sol is prepared at room temperature.

The consistency of suspensions of finely divided solids in casein sols, such as paper-coating mixtures, departs widely from the flow characteristics of viscous liquids and is not predictable from the apparent viscosity of the sol before a suspended solid is added.[12] The apparent viscosity of the suspension may indeed be much lower than that of the original casein sol.[19] The size and shape of the particles of solid and the tendency of the casein sol to peptize[45] or to flocculate them undoubtedly directly affect the consistency of the suspension and consequently the finish it gives a coated paper. The strongly basic mineral satin white is incompatible with weakly alkaline casein sols, such as those in borax, while china clay works well in the weakly alkaline solutions. With clay and no doubt other minerals as well, the finer the particles of the clay the more casein required to furnish sufficient binder for the coating. The facts that blanc fixe and chalk make coatings with matte finish, clay makes one with moderate gloss, and satin white one with still higher gloss are probably connected closely with the nature of the dispersion of the minerals in the casein sols.

Sols of Casein that Contain Calcium Hydroxide.

The addition of di- or polyvalent cations to alkaline casein sols either precipitates the casein promptly as a curd or causes the sol to change more or less rapidly into a rigid jelly. Whether a curdy precipitate or a jelly is obtained depends primarily upon the concentration of the cation responsible for the change, as is also the case with the rate of formation of a jelly. Either a generally high and continued concentration or a locally high concentration, while the addition is being made, yields a curd. Because of the slight solubility of the hydroxides of most di- and polyvalent cations, few of them can be added in appreciable amounts to alkaline casein sols; those available are practically limited to the alkaline earth metals and magnesium. Calcium hydroxide, both because lime is cheap and because it happens to have a suitable solubility, is by far the most important in casein technology. It is usually added in excess of the amount required to react with the casein and to saturate the solution, so that the concentration of dissolved calcium hydroxide may be considered constant.

Casein sols containing suspended lime begin to increase in viscosity soon after they are prepared, at first slowly, and then with increasing rapidity until finally they form jellies.[43] The time required for gelation to take place depends principally upon the concentration of the sol, its alkalinity, the presence of suspended solids or other colloids, the ash content of the casein, and the temperature. The rate of gelation is faster the higher the concentration of the sol, particularly so at very high concentrations. At very low concentrations, such as those used in insecticide sprays, jellies are not formed. Gelation is slower the higher the pH, but the change in rate is not great until about pH 12.5, above which the rate of gelation is diminished rapidly. In sufficiently alkaline sols gelation fails to take place at all. Suspended solids such as calcium phosphate or calcium fluoride, the minerals used in coating paper, or the pigments in water paint, retard gelation materially. Other colloids like colloidal silica and silicates are particularly effective in retarding gelation so that casein glue made with sodium silicate may have a longer working life at pH 12 than a glue lacking the silica would have at pH 13.[46] Gelation takes place more quickly in sols made from casein of high ash content than in sols made from low-ash casein. Gelation proceeds more rapidly when the temperature is raised.

If less calcium hydroxide is incorporated in the sol than the amount required for combination with the casein and for saturation of the water, gelation takes place more slowly and weaker jellies are obtained. If such sols are used as glues the joints are less water resistant than they are when sufficient calcium hydroxide is present. Calcium salts act like the hydroxide in causing gelation, their rate of activity diminishing with their solubility. Magnesium hydroxide, which is less soluble than calcium hydroxide, acts less rapidly in causing gelation and an excess of it may be suspended in sols of lower alkalinity than those that will suspend an equivalent excess of calcium hydroxide.

Formaldehyde causes casein sols to gel so rapidly that a curdy precipitate is formed. But if a small amount of a dilute solution of formaldehyde is added, with care taken to distribute it quickly throughout the sol by rapid stirring, gelation is retarded sufficiently to yield a jelly.

Sols of casein containing calcium hydroxide in excess prove to be truly viscous in the sense that the observed viscosity is independent of the rate of shear.[43] They remain so even when very concentrated or when approaching very closely to the condition of a jelly. Sols having a viscosity greater than 2,000 poises and yet truly viscous have been found. Sols of animal glue change sharply from a viscous to a plastic condition when the viscosity is less than 500 poises.[47] Presumably sols of casein containing large amounts of suspended solids, such as casein paints, are no longer truly viscous. The flow characteristics of those casein glues that contain substantial amounts of suspended solids have not yet been investigated.

The surface tension of alkaline casein sols is the same as that of water when the surface is first formed and for about 6 seconds thereafter.[48] It then decreases slowly for many hours, indicating that casein is gradually concentrating at the surface. When casein sols are placed upon the surface of strongly acidified water, in which casein is practically insoluble, the casein spreads out in a monomolecular film 6 to 7.5 A.U. thick.[49] On pure water the film spreads slowly and it is much thicker than monomolecular. The effectiveness of casein in making emulsions of oil and water is apparently due to its ability to form stable films at the oil-water interface.[50] The films are often thick enough to be visible. The emulsions may be of the oil-in-water or the water-in-oil type, depending upon the nature of the oil, its specific gravity, the relative proportions of oil and water, and the kind of alkali used to dissolve the casein. NaOH tends to form water-in-oil emulsions under circumstances that would produce oil-in-water emulsions with $Ba(OH)_2$.

Casein Jellies.

Sols of casein when spread upon porous, absorptive surfaces, such as dry wood or paper, promptly separate into two parts, one an aqueous solution of the alkali and any soluble constituents present, no doubt containing some casein, which penetrates deeply beneath the surface, and a layer of more concentrated sol left as a film upon the surface.[51] Any suspended solids remain in the film. Withdrawal of moisture from the film by the hygroscopic wood or paper proceeds rapidly until the sol changes into a jelly. On further drying the jelly becomes stronger and harder, finally taking on the characteristics described by Freundlich as those of a xero-gel.*

The jellies formed through holding casein sols containing calcium hydroxide in bulk until they congeal are at first weak but they become stronger as time passes until they reach a maximum in jelly strength.[46] Most of them then begin to weaken and, if kept with all their moisture, finally become liquid again. By removing the water from the jelly through evaporation the course of events may be interrupted and a strong, hard xero-gel, which lasts indefinitely if kept dry, may then be produced. If it becomes moist again, however, the progress of events is resumed.

The maximum strength of such moist casein jellies depends upon the water content, the temperature, the alkalinity, and the presence of suspended solids or of other colloids. Jellies are stronger the less water they contain and the lower the temperature. Solids suspended in the sols may affect the maximum jelly strength markedly and may retard the subsequent decline from the maximum, often greatly. There are great differences in the effects produced by different solids, the reasons for which have not yet been investigated. Casein jellies may be made containing colloidal silica, in which the jelly strength slowly rises beyond the limits of measurement with the Bloom gelometer and remains there for many days. It is probable that such jellies owe their strength, after the first few days, to the silica rather than to the casein.

Jellies of casein containing lime or formaldehyde are irreversible in the sense that without deep-seated chemical decomposition of the casein they can not be restored to sols. When they reliquefy on ageing, the casein has been decomposed chemically. Nevertheless casein jellies are elastic in that they exchange moisture with the surrounding atmosphere until they reach an equilibrium with the prevailing relative humidity, and the volume and physical properties of the jelly vary continuously with its moisture content. Thus a film of a typical casein glue in equilibrium at 27° C. was found to have the following relation between moisture content (based on the weight of the glue when oven dry) and relative humidity:[46]

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* Freundlich defines "Xerogels" as "gels formed by drying, and very poor in liquid but nevertheless coherent." (Hatfield's translation, page 660.) J. A.

Moisture content of glue, per cent.......	48	33	26	20	14	11	8	7	6
Relative humidity of ambient air, per cent	90	80	70	60	50	40	30	20	10

When plotted, these data follow the curve characteristic of elastic jellies,[52] which when completed is S-shaped. The amount of moisture imbibed undoubtedly varies greatly with the composition of the jelly, especially at the higher relative humidities. Formaldehyde-treated casein is materially less hygroscopic; a typical casein plastic took up only 18 per cent of water after soaking for 22 days.[10]

Change in volume accompanies the change in moisture content of casein jellies, but the adjustment in volume is not constrained to fixed ratios between length, width, and thickness. Thus a coating of casein or a layer of glue may change in volume by becoming thicker or thinner, while in length and width it conforms to the dimensions of the surface to which it adheres. Inequalities of moisture content within a large mass of jelly set up internal stresses and may cause warping, cracking, or the phenomena of case hardening.

Casein jellies are mechanically stronger and harder the less moisture they contain. They also become less distensible and less flexible as the moisture content decreases. The weakening that takes place when moisture is absorbed, however, is materially less with casein jellies than it is with such substances as animal glue.[53] Even in an atmosphere of 95 per cent relative humidity, films of casein glue have been found to have a strength in tension of about 2,000 pounds per square inch. The water resistance of casein glues and coatings is a question of the mechanical strength of the swollen jellies, not of their solubility in water.

Warm, swollen jellies of casein, under certain conditions, attain a consistency that enables shreds of jelly to flow together under suitable mechanical working, forming a single body of jelly. The physical characteristics of flow and the chemical nature of casein that make such action possible have not yet been studied systematically. It has been supposed that the inorganic constituents of casein have much to do with its plastic properties but there is some evidence against that view.[37] Differences in plasticity of the casein may instead depend upon whether the casein has been changed before precipitation from the strongly hydrated emulsoid into the weakly hydrated suspensoid condition.[54]

Hydrolysis in Casein Sols and Gels.

Since unmistakable signs of hydrolysis of casein are evident soon after the preparation of sols more alkaline than pH 10.5, any explanation of the behavior of the strongly alkaline sols of technologic importance must certainly take hydrolytic cleavage into account.[55] The nature of the relation between pH and the viscosity of sols, the rate of gelation of sols containing calcium hydroxide, the maximum strength of jellies, and the rate of decline in jelly strength after the maximum has been passed, suggest that in these casein systems we are dealing with two reciprocal processes, one of which tends first to increase the viscosity and finally to congeal the sol, while the other tends to tear down the jelly structure and reduce the viscosity of the sol. The second is clearly the hydrolytic cleavage of the casein into simpler proteins, polypeptides, and amino acids. The first, of gelation tendency, may be a synthesis similar in nature but opposite in direction to the hydrolytic decomposition. In other words, the irreversible casein jellies may bear much the same relationship to the original casein that collagen bears to gelatin.

Proof that hydrolysis goes on rapidly in casein glues during their working life and after they form jellies, has been obtained by subjecting them to formol titration by the Sörensen method.[46] The content of ammonia and of free amino nitrogen increases steadily as time passes. The rate of hydrolysis so measured increases in direct proportion to the hydroxyl ion activity in the glues, which is measured by the hydrogen electrode.

It has not yet been possible to demonstrate the nature of the changes in casein sols that are responsible for the tendency to gelation.

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Tanning; and the Modern Theory of Colloid Swelling

By Em. Prof. Henry R. Procter, D.Sc., F.R.S.

It is now many years since the attention of the writer was drawn to the curious phenomena of "pickling." In its simplest form, skins are swollen in an acid solution, and then transferred to a strong salt-brine, in which they not only lose their swelling, and become extremely "flat," but if dried out in this state, are found to be converted into a white leather which, it is true, will not stand wetting, but is soft, porous and opaque like kid. The pickled skins, as they come out of the salt bath are of course wet, but only in the same sense as a wet towel, from which the water can be squeezed or wrung, while in the unpickled skin the fibers themselves are swollen with liquid which can hardly be expelled by pressure. If the same process be applied to sheets of swollen gelatin jelly, which contain no pores, they become hard, transparent and horny.

Before the end of the last century, the writer commenced a series of systematic experiments to elucidate the causes of these changes, mostly using gelatin instead of hide to avoid the difficulty of liquid contained between the fibers, the quantity of which was not easily estimated. He soon found that the degree of swelling was entirely dependent on the concentration of the acid solution, though not in any simple direct proportion, but rapidly rising to a maximum in very dilute solutions, and then diminishing with increasing concentration in a hyperbolic curve, and though not then able fully to explain the cause, he was able to deduce a mathematical equation which completely represented the curve. It was evident that the swelling was in some way due to osmotic pressure, but it was hard to see how this pressure could arise. Osmotic pressure is the force with which a dissolved salt seeks to diffuse from a stronger into a weaker solution, and it is generally demonstrated by the use of some membrane through which water can pass, but which opposes the passage of the salt, which therefore pushes against it: but in this case there was no such membrane, and all the substances in the solution of salt and of acid were able to freely pass through the jelly. It was not until Prof. Donnan in 1911 published his important discovery of "membrane-equilibria" that the key to the problem could be found. Donnan found that if a colloid salt were separated from a solution of its acid by a membrane through which the acid could freely pass, while the colloid base could not, the distribution of the acid did not become the same on both sides of the membrane, as would have been expected, but remained less on the side which contained the salt, since the latter ionized into a colloid base (cation), and an anion the same as that of the acid, which by its osmotic pressure opposed the entrance of the anion of the acid; and the hydrogen ion of the acid, since it could not enter without its accompanying anion, was also kept out. Equally the anion of the salt was compelled to remain on the salt side by the electrochemical attraction of its colloid cation which could not pass through the membrane. To take a concrete case, suppose a gelatin solution on one side of the membrane, (say parchment-paper), and dilute hydrochloric acid on the other. The acid will pass through and form gelatin chloride, which will ionize into a positive gelatin-ion, and Cl′, which cannot leave the salt solution alone, but will oppose the entrance of an equal quantity of the Cl′ of the HCl, and therefore of the H^+, which cannot leave the acid solution without its accompanying Cl′. The result will be, neglecting any un-ionized substances, that on the salt side there will be a larger quantity of ionized Cl, and a smaller quantity of H than on the acid side, where they are necessarily equal. Ultimately the two sides must be in complete electrochemical equilibrium, as the acid solution can pass freely through the membrane, and there must be no greater tendency for it to pass one way than the other. Now the condition of such an equilibrium is that the $H^+ \times Cl'$ on the one side must be equal to the $H^+ \times Cl'$ of the other. Also the osmotic pressures on both sides should be equal, but osmotic pressure depends not on the equality of products of the + and — ions on each side, but on their total sum, irrespective of their electrochemical character. We have shown that on the side of the acid the H^+ and Cl′ are necessarily equal, while on that of the salt, the Cl′ is in excess, and a very slight mathematical consideration will show that under these conditions it is impossible for both conditions to be realized simultaneously. If we look at it geometrically, the sum of the sides of a rectangle will always be greater than those of a square of equal area, and the more different are the lengths of the two adjacent sides, the greater their combined length will be in proportion to those of the equal square. Applying this reasoning to our colloid solution, the greater the difference between the H^+ and Cl′ ions, the greater will be their combined sum as compared to those of the acid with which they are in equilibrium, and as the osmotic pressure depends on their number, there will always be a greater osmotic pressure on the colloid side of the membrane. If there is an actual fixed membrane this osmotic pressure can be directly measured; and this has been done by Loeb,* and found to agree with calculation. The case of a jelly is however somewhat different. The surface of the jelly serves as a membrane, since the Cl′ ions cannot pass outside it, but it is not fixed, and the pressure tends to swell it and absorb the acid solution with which it is surrounded. This again lessens the difference of pressure, since as more and more of the acid passes into it, the proportional difference between its H^+ and Cl′ becomes lessened, but there is always an excess pressure in the jelly, and the swelling would go on to infinity and complete solution if there were no opposing force. Such a force however exists in the cohesion or internal attraction of the jelly itself, and the swelling reaches a definite maximum when this cohesion exactly balances the remaining excess of osmotic pressure. This cohesion differs in different samples of gelatin, and probably also in different hide-fibers, but it is also very dependent on temperature, since it disappears at about 30° C. when the jelly melts, and the solution mixes with the surrounding acid. As the temperature approaches this point, the maximum of swelling increases, though a certain amount of heat is evolved in melting, and according to a usual physical law the swelling should therefore be lessened by rising temperature. It will be obvious that the maximum of the difference of osmotic pressure will occur when the difference of H^+ and Cl′ in the jelly is also at a maximum, and this will happen when the proportion of ionized gelatin chloride is greatest as compared to that of free acid in the jelly. This occurs when the external acid has a hydrion concentration of about $pH = 2.4$, whatever the acid, that is, a normality of .004*N* of actual free hydrogen ion, while the jelly itself will be $pH = 3$, or .001 *N*. The reason for this will be

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* *See* paper by Jaques Loeb in Vol. II of this series. *J. A.*

more fully explained when we come to consider the hydrolysis of salts of weak acids and weak bases.

There is another consequence of the unequal distribution of Cl′ and H^+ in the jelly and the external acid which must be mentioned, as it is probably of great importance in the theory of tanning. The Cl′ is trying to escape from the jelly, while the H^+ attracted by it is trying to get in, but as neither can pass the surface, they form a "double layer" there of Cl′ within and H^+ without, and as these ions have equal and opposite electric charges, they cause an electric potential at the surface, which is positive outside, and consequently will attract other particles negatively charged. Tannins consist of colloidal particles, with negative charges, and are consequently attracted, and it is quite probable that this, and not any actual chemical affinity is the cause of the combination of tannins with gelatin or hide fiber, which only takes place normally in slightly acid solutions. When gelatin or hide is in an alkaline condition it is negatively and not positively charged.

So far, for the sake of simplicity, we have only considered the acid compounds of gelatin and collagen (or hide-fiber), but the actual chemical constitution of both of them is that of a chain of amino acids. Amino acids are amphoteric, that is they are capable of acting either as acids or bases, according to the alkalinity or acidity of the solution in which they are dissolved. Glycocol or aminoacetic acid is like ordinary acetic acid in which one of the hydrogen atoms attached to the second carbon is replaced by the $—NH_2$ group, thus on the one hand possessing the —CO.OH characteristic of organic acids, and on the other that of an ammonia in which one of the hydrogens is replaced by a more complicated organic radical. It thus has the capacity of attaching itself to another amino acid, the acid "head" of the one attaching itself to the alkaline "tail" of a second; and proteins consist of chains of amino acids attached in this way, with apparently an acid group at one end and an alkaline at the other end of the chain. Whether such a chain acts as an acid or a base is entirely dependent on the alkalinity or acidity of the solution in which they are. Obviously there must be a point at which the two tendencies are equal,—the "isoelectric point," at which in Loeb's opinion there is no ionization and the protein forms neither acid nor alkaline salts, while the present writer inclines to the view that it combines equally with both, but to so small an extent that this can no longer be proved by analysis. Both views are possible, but the latter is somewhat supported by the fact that at the isoelectric point, there is a very perceptible fixation of neutral salts from tolerably concentrated solutions, which suggests that both the anion and the cation are combined.

The isoelectric point of both gelatin and collagen is about pH $= 4.7$, or $N/50000$ of actual free ionized acid. Wilson has suggested that there is a second isoelectric point in more alkaline solution, but his observation seems to require further confirmation. Loeb has shown very conclusively that below the isoelectric point, (that is in more acid solution), only acid salts, chlorides, sulfates, acetates, etc. can be formed, while above it, in more alkaline liquids, only gelatinates and collagenates of bases can exist. These alkaline salts behave as regards swelling and surface-potential quite in the same way as the acid salts, though the actual swelling curve is a little different for reasons which need not be discussed here, and the surface-potential is negative instead of positive. Loeb has shown that both in acid and alkaline swelling, divalent acids and bases produce only about half the swelling of monovalent; and this is a point of great practical importance, since divalent acids, such as sulfuric or oxalic can produce only about half the maximum swelling given by monovalent acids, such as hydrochloric or nitric, and similarly soda will swell about twice as much as lime or baryta,—(it must be borne in mind that the concentration producing maximum swelling is only about $N/400$ of the *actual ionic* concentration, and this is very different from the ordinary total normality, which in a strong acid like hydrochloric nearly corresponds to the actual ionic normality, while acetic acid is so little ionized, that it is impossible to use a strong enough solution in practice). An observation which is easily made in the tannery is that the addition of a sodium salt, (even the neutral sulfate which does not increase the alkalinity) considerably increases the swelling in the limes.

It has been shown in a previous page why the increase of concentration of the external acid or alkaline solution beyond a certain point leads to a diminution of swelling, because although the proportion of the gelatin salt goes on increasing till the whole of the gelatin (or hide-substance) is converted into the salt, the external osmotic pressure becomes more nearly equal to that in the jelly; but some explanation of why this conversion into salt is only gradual and at no point complete is required, for this has proved one of the greatest difficulties in the acceptance of the theory by old-fashioned chemists, some of whom denied that, as there was no definite end point, the combination could be really a chemical one, but belonged to an indefinite class which they styled "adsorptions." We are all familiar with the fact that if we add standard hydrochloric acid to a solution of lime or soda, we come suddenly to a definite point at which litmus changes from blue to red, methyl orange from yellow to pink, and phenolphthalein from red to colorless, and all these changes are practically simultaneous. If, on the other hand we add acid to an alkaline solution of gelatin, the change is a very gradual one, and there is a considerable interval between the fading of the phenolphthalein red, and the appearance of a full red in the methyl orange, and no definite end-point can be fixed. The same thing occurs, though to a less degree, if we try to titrate acetic acid with caustic soda,—there is a considerable interval between the change of methyl orange and that of phenolphthalein. This always occurs when we are dealing with a "weak" (that is a little-ionized) base, or a "weak" acid, and the reason is known as "hydrolysis." Pure water is one of the least ionized of known electrolytes, but even it ionizes to a very minute extent into H^+ and OH', and this ionization is constant,—if we remove the ions formed, fresh ones immediately take their place, and this goes on *ad infinitum.* Supposing we have an acetate in solution, it ionizes largely into H-ions and acet-ions, and a minute proportion of these will combine with the free ions in the water, reforming acetic acid and the base, and as these ions are instantly replaced, the process will go on till a very appreciable quantity of the acetate has been decomposed. The acetic acid however being extremely "weak," scarcely ionizes, and immediately reverts to un-ionized acetic acid, which has no acid properties, as these are wholly due to the free H-ion, while the base, if a "strong" one such as soda, remains ionized and the solution becomes distinctly alkaline. Such cases are very common: we all know that sodium carbonate, though theoretically a neutral salt, behaves as strongly alkaline, because carbonic acid is extremely weak; and alum tastes distinctly sour because alumina is a very weak base. Thus a solution of gelatin chloride in water, would at once be largely decomposed into free hydrochloric acid, and neutral un-ionized gelatin. The only condition under which gelatin chloride can subsist in water is that there should be so large a proportion of hydrochloric acid present, that the tendency of the hydrolyzed gelatin to recombine with acid should be as great as that of the gelatin chloride to hydrolyze; and thus any acidified gelatin solution is a mixture of a definite proportion of the chloride and of neutral gelatin, and the combination is only theoretically complete when the proportion of free hydrochloric acid is infinite. Procter has shown that if the concentration of actually ionized acid in the solution is x, the proportion of uncombined gelatin to combine will be $\frac{x}{x + k}$, where k is a constant called the hydrolysis-constant, from which the dissociation-constant of gelatin can be calculated. As k is a very small quantity, it will be seen that the value of the fraction rises at first rapidly towards 1, but never reaches it till x becomes so large that k can be disregarded. If however the quantity of acid actually combined at different concentrations is determined, it can be calculated what quantity of gelatin is required to combine with 1 mol of hydrochloric acid; and this is the combining equivalent of gelatin for acids, if viewed as a monovalent base. Wilson and Procter calculate this as 768, and that of collagen as probably less by one molecule of water. This figure is very much lower than those which have been assigned by some other chemists as the molecular weight of gelatin from physical considerations, but the physical molecular weight may be that of a molecule consisting of several or many of the smallest chemical individual represented by the combining equivalent, and at least for practical calculation the latter is the more useful quantity.

Probably a little fuller explanation of the meaning of the phrases "weak" and "strong" acids and bases may be welcome here to some of my readers, though to many others it is superfluous. All acids are sour, and have some other properties in common, for which we distinguish them as acids. This common property is due to the possession of one, or sometimes several atoms of hydrogen, which on solution in water can separate with a + electric charge: that is become hydrogen ions. In the "strong" acids, such as hydrochloric, nitric and sulfuric, this takes place instantly and almost completely, so that even a moderately dilute solution of hydrochloric acid consists almost entirely of H^+ ions, and Cl' ions, free to move independently in the liquid, though they cannot leave it. In the case of a "weak" acid like acetic, this dissociation takes place only to a very small extent, though it increases as the solution is diluted, and in theory, at infinite dilution is complete. An $N/8$ solution of acetic acid contains 7.5 grams in the liter of the acid, but of this only about 11.5 mg. is actually active acid, the rest being held in reserve, as un-ionized acid with no acid properties. If however we use up this small portion of active acid, in neutralizing lime or in swelling hide, a further equal quantity instantly ionizes, so that the process can be repeated *ad infinitum* till all the acid is used up. Thus the equivalent of weak acid does just as much work in the end as one of a strong acid like hydrochloric, but it does it gradually, holding a large part of its acid-strength in reserve, just as in the lime pit, the large excess of undissolved lime does not itself act upon the hide, but serves as a store to keep up the strength till all is used. Exactly the same thing applies to a weak alkali like ammonia. Though, unlike lime, it all goes at once into solution, it only comes into activity as it is used up. A further very useful property of weak acids and alkalies is that they are rendered still weaker by the addition of their neutral salts, so that acetic acid, by the addition of acetate of soda, can be rendered so weak as to be hardly sensibly acid, and will not swell hide, but yet will neutralize its full quantity of a strong alkali like lime; and quite the same as true of weak alkalies like ammonia, which is similarly weakened by the addition of ammonium chloride.

Probably the greatest service which modern protein chemistry has as yet rendered to the tanner is that of directing his attention to the enormous importance in his industry of the small changes in acidity or alkalinity lying near the isoelectric point of gelatin, and which lies between "neutrality" as shown by phenolphthalein and that indicated by methyl orange. At phenolphthalein neutrality (slight alkalinity) the collagen is negatively charged, and normal tannage cannot take place, as it has no attraction for the negatively charged tannins. At that of methyl orange, distinctly more acid than the isoelectric point, collagen is positively charged, and forms acid salts, so that it can not only readily combine with the tannins, but swells a good deal, though not to its maximum, and forms acid salts, while on the other side of the isoelectric point, it can only form collagenates with bases, and will swell slightly on the alkaline side. The depleting action of bates and drenches depends to a large extent on their degree of alkalinity between these two points. The minimum swelling is actually at the isoelectric point, but the curve rises slowly on the alkaline side, and as the best alkalinity for the action of the tryptic ferments lies on that side, the best pH for most sorts of bating is from pH 6 to 8. The acidity for tanning must always be at a pH lower (that is more acid) than pH 4.7, but what will actually be the best depends somewhat on the sort of leather. If the tanner desires plump leathers he will keep his liquors about pH 2.4, while for soft and thin ones, a higher pH will be used. For this and similar purposes much use is now made of "buffers," generally mixtures of weak acids or alkalies with their neutral salts, which are added to the liquor and only ionize to the acidity desired. In this way the pH can be kept practically constant, though it must not be forgotten that the presence of neutral salts affects, and generally lessens the swelling power of liquors. An instance of this sort is the Stiasny neutralizing liquor for chrome-leather which consists of a mixture of free ammonia and ammonium chloride, so adjusted that, while it will remove surplus acidity, it cannot become so alkaline as to injure the leather. No doubt the old tanners often unconsciously and accidentally used the same principle in their bates and drenches, "mellow" liquors and old limes. The acids were all weak and organic, such as lactic, acetic and butyric; and the alkali ammonia; and the salts formed by their action on hide and lime accumulated in the solutions, formed a natural buffer mixture. In the bran-drench this was further supplemented by the fact that the organisms producing acids could only thrive within narrow limits of pH, and an effect precisely similar to drenching is produced by a suitable mixture of lactic or acetic acid with sodium or calcium acetate or lactate. For this reason it is desirable in deliming with weak acids, to use the same liquor repeatedly or continuously, as its action is more gradual and gentler than that of a fresh solution. If strong acids are used, the solution should be very dilute, and the acid, added in successive portions, should be sufficient in quantity to combine with the whole of the lime, or a proportion of an alkaline acetate, lactate or sulfite should be added, which will act as a buffer. Boracic acid is so weak itself that it needs no buffer, but its lime-salt is rather insoluble, so that if the same solution is used repeatedly, there is danger of the fixation of calcium borate on the hides, which will cause discoloration, like calcium carbonate, in the liquors; and not only for this reason, but from its high cost, it is advisable to use it, if at all, only as an addition to other acids.

Tanning.*

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There is probably no branch of chemical industry in which the relationship to colloid chemistry is so obvious as in the manufacture of leather. The animal hide appears to partake of the nature of a gel with an active surface which, after the preparatory work is done on it in the beam house, is in a particularly adsorptive condition. The tanning materials have, despite the variety of their chemical natures (vegetable tanning materials, basic chromium or alum or iron salts, unsaturated fatty acids, etc.), one common attribute, namely their semicolloidal condition. It is thus evident that the process of tanning invites inspection from a colloid point of view. It does not follow, however, that this point of view is the only right one, for all the changes which the hide goes through before the actual tanning begins, can also be studied on the basis of the amphoteric nature of the proteins which compose it. Likewise the tanning process itself can be pictured as a purely chemical process (salt formation or the building up of complexes and the like). We are in many cases forced to the belief that the various theories of tanning do not differ so greatly in their fundamentals and that it is the method of expression that gives the appearance of difference.

In the following review of the subject the colloid viewpoint will be favored. The subject matter is best divided under three headings: (1) The skin and its preparation for tannage; (2) the tanning materials; (3) the action of the tanning materials on the skin, i.e. the tannage.

THE SKIN AND ITS PREPARATION FOR TANNAGE.

A thorough exposition of the anatomical structure and chemical composition of the skin would exceed the limits of this review.

For an understanding of the processes leading to the formation of leather it will suffice to take the following facts as proven.[1] The skin is composed of the epidermis and the corium. The epidermis is a distinct layer differing both anatomically and chemically from the corium. On this fact is based its easy removal. Even in the egg we find the origin of the epidermis in the outer seed leaf (ectoderm) while the corium originates in the inner seed leaf (mesoderm). In the epidermis we can recognize several layers, of which the mucous layer (*stratum mucosum*) and the horny layer (*stratum corneum*) are the most important. This division is purely arbitrary since there is a steady migration of cells from the bottom layer (*stratum germinativum*) outwards to the top layer. Thus we find that the new cells built by cell division push the old ones ahead of them. These old cells gradually lose their cylindrical form, becoming flattened, harder and dying. They finally are rubbed off as dry flakes. A differentiation between particular layers such as *stratum granulosum* and *stratum lucidum* has no significance for skins used in tanning

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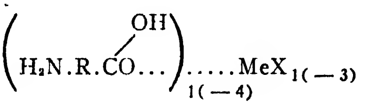
* **Translated by Dr. Thomas Blackadder, New York City, U. S. A.**

as these layers are only recognizable in particularly thick and hairless portions of the epidermis such as the human sole. The connection between the epidermis and the corium is established by threads of protoplasm, which extend from the *stratum germinativum.* These threads form the connection between the base cells of the epidermis and the papillary layer of the corium. The epidermis dips down into the body of the corium, giving place for hair follicles, grease and sweat glands which extend down into the skin. These are removed along with the epidermis when this is loosened either by decay or by the action of lime or sodium sulfide, whereby the acid albuminoids (Cytose) of the protoplasmic threads are destroyed thereby dissolving the connection between epidermis and corium. The loosening of the hair results from the thick hair root becoming soft and slippery while the pockets are simultaneously enlarged by swelling.

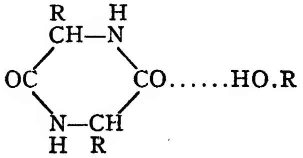
While the epidermis is of great value to the living skin as evidenced by its living cells, still the corium is the real protective layer and is also the layer which has the greatest interest for the tanner. In the corium two layers are recognizable, the papillary layer and the reticular layer. The papillary layer is composed of fibers of collagen, and among these a network of elastic fibers and lastly a network of blood vessels, nerves, muscles and latent cells, which are the source of new growth when the living skin is broken. The reticular layer is purely a protective layer without any living function. Both layers are alike built up in an elaborate arrangement of interlacing fibers of various thickness. These fibers are again composed of numbers of individual fibrils. This interlacing pattern shows a remarkable elasticity which is due to the shifting of the fibers among each other rather than to an elasticity of the fibers themselves. The reticular layer is composed of a coarser network than the papillary layer and in turn we find the outside of the papillary layer next to the epidermis is composed of an extremely fine network which gives the grain a remarkable hardness and durability and leads to the belief of a surface layer of different chemical composition[2] (the so-called hyalin layer). On account of the greater development of surface in this surface layer the grain can take up considerably more tannin than the reticular layer and the avoidance of this over-tannage of the grain is one of the problems of tanning.

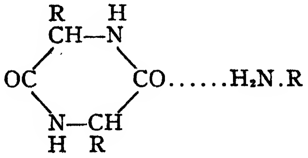
In addition to the hide structure we must also take into consideration the chemical composition and properties of the collagen composing the hide. Collagen denotes not so much a definite compound as a convenient term for representing a number of compounds whose properties are similar but nevertheless discernibly different. The leather chemist is concerned only with the collagen of the hide, but the osseine of the bones and the albuminoids of cartilage and fish scales are also to be included in the term collagen. Since all forms of collagen are insoluble and only rendered soluble by peptization or hydrolysis, it is only possible to distinguish between these forms by differences either in the conditions necessary to convert collagen into gelatin, or in the decomposition products formed by hydrolysis. In this connection it is well known that bone collagen is more difficult of conversion to gelatin than hide collagen and this latter in turn more resistant than fish collagen. Furthermore even in the case of hide collagen great differences are found according to the kind of animal, its age and sex and even the portion of the body from which the skin is taken. The collagen of a young animal is more easily gelatinized, also swells more and is more easily attacked by ferments than that from an older animal. Likewise the collagen of the male is more resistant than that of the female, while collagen from the flanks is more susceptible than that from the back. If such differences are to be explained by differences in the protein molecule, a specific composition must be assumed for each type of collagen. A more satisfactory viewpoint is arrived at if we adopt the following conception of the structure of collagen.[3]

We have reason to assume the components of the collagen molecule to be peptones which in turn are built up of amino acids. The bonding of the amino acids occurs chiefly through formation of peptides. Concerning the manner in which the peptones are linked together we have at present incomplete knowledge. It is obvious that the bond between the peptones must differ from the bond between the amino acids composing the peptones. This explains the action of swelling neutral salts (thiocyanates, iodides) which cause a distinct splitting up of collagen without the formation of new groups reacting with formaldehyde. The behavior of the proteins towards various ferments also leads us to distinguish between bonds uniting the peptones and bonds uniting the amino acids. The action of pepsin is predominantly a peptizing one (severing the bonds between peptones), the hydrochloric acid exerting the main part of this action. The tryptic ferments, on the other hand, have a hydrolyzing action on the peptide groups, the specificity of this action being greatly influenced by the constitution of those parts of the protein molecule which border on the peptide group. This distinction between peptization (severing the bonds between peptones without formation of groups reacting with formaldehyde) and hydrolysis (severing of peptide-linkage with formation of groups reacting with formaldehyde) makes it necessary to assume different kinds of linkages in the two cases. The view held by the author assumes that only the amino acids are linked together by primary valence forces, forming the peptones, these latter being held together by secondary valence forces. The collagen is thus to be understood as a molecular compound of peptones, analogous to the molecular compounds between amino acids or diketopiperazines on the one hand and neutral salts or phenols or amino derivatives on the other hand, as shown by the following examples.[4]

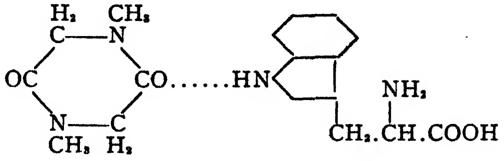


$$\left(H_2N.R.\overset{OH}{C}O\ldots\right)_{1(-4)}\ldots\ldots MeX_{1(-3)}$$

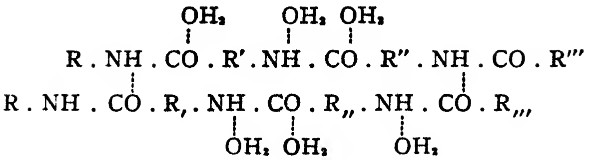




A striking example for the combination between decomposition products of proteins is the molecular compound of sarkosin (dimethyldiketopiperazine) and tryptophane (β-indolalanin).



From this example there is but a small step to the assumption of secondary valence forces holding the peptones (polypeptides) together.



$$\begin{array}{l} R.\underset{\vdots}{NH}.\overset{OH_2}{\overset{\vdots}{CO}}.R'.\overset{OH_2}{\overset{\vdots}{NH}}.\overset{OH_2}{\overset{\vdots}{CO}}.R''.\underset{\vdots}{NH}.CO.R''' \\ R.NH.\overset{\vdots}{CO}.R_{,}.\underset{OH_2}{\underset{\vdots}{NH}}.\underset{OH_2}{\underset{\vdots}{CO}}.R_{,,}.\underset{OH_2}{\underset{\vdots}{NH}}.\overset{\vdots}{CO}.R_{,,,} \end{array}$$

The formula given here shows not only the linkages between two peptones, but also the hydration of each peptone and the relation between hydration and intensity of forces holding the peptones together. The more water molecules are bound to the peptide groups of the peptone, the less secondary valences will be available for the linking together of the peptones and *vice versa*.

In conformance with these remarks we find that swelling hastens or precedes the breakdown of a protein into peptones as if the swelling were a preliminary step in the breakdown. Envelopes of water around the peptone molecules appear to be enlarged during swelling with a resulting loosening of the structure until a complete disintegration occurs. We further find that the collagen from the skins of younger animals is richer in water and more easily broken down while the removal of water either by means of alcohol or drying out will bestow a greater resistance to the peptization of proteins. This action is similar to that which has been demonstrated in the case of numerous inorganic gels.[5]

Any electrolyte (acid, alkali, neutral salt) which forms molecular compounds with the collagen, thus engaging secondary forces, which previously were active between the peptones, will produce a peptizing effect.

Apart from any attempt to locate the seat of secondary valence forces between peptones, the analogy between a protein and the colloidal state of any simple chemical compound may be pointed out. Just as in a colloidal solution of an element (e.g. sulfur or gold) or of a simple chemical compound (e.g. ferric hydroxide or silicic acid), we have particles definite as to composition, dimensions and stability, which particles are composed of aggregates of many molecules, held together by forces other than primary valence forces, so we can picture the protein complex as being an aggregation of peptone molecules. Also, just as in the case of increased dispersion of a colloid, the aggregates become smaller and more numerous, so in the case of peptization of a protein the peptone complexes become smaller and smaller until finally they result in individual peptone molecules. The peptization is thus not a question of the severing of primary valences as would be the case of the decomposition of a chemical compound. Rather it is a question of the loosening of bonds of a weaker kind, which from their nature and magnitude, we may assume to be of the nature of secondary valence forces. A distinct difference between the protein and the colloid sulfur particle is, that the latter is built up of similar molecules while the former may have molecules of different composition in its structure.

The relationship between swelling and peptization is particularly noticeable in the effect of those neutral salts which have a swelling action such as thiocyanates and iodides. We find no evidence of any hydrolysis, but a distinct evidence of peptization. This peptization is shown in the case of pure, ashfree gelatin which shows an increased power of diffusion through membranes. Further the gelatin loses its power of muta-rotation, the specific rotation of the gelatin solution at 15° C. being lowered as much by addition of a thiocyanate as if the solution had been warmed, thus pointing to an increase in the state of dispersion.[6] We also find that while the presence of thiocyanates or iodides accelerates the peptization due to trypsin, they do not further the hydrolytic action as measured by the formol titration.[7]

In the light of the above explanation of the structure of collagen we conclude that there are two ways in which the various collagens can differ from each other. Firstly there may be differences in the composition of the peptones which enter into the aggregates forming the collagen. Secondly there may be differences in the closeness of the bonds holding the peptones together in the collagen micelles.

The first possibility has to be considered when comparing collagens of different origin, e.g. collagen of the corium of mammals and fish collagen. But we have no reason to assume that the various collagens of mammals—and these are the only collagens the tanner has to deal with—are built up from different amino acids; at least the results of hydrolytic decomposition give us no inkling of it. More probable is the second alternative to explain the differences in the corium of calf, sheep, ox, goat, etc. According to the above explanation the differences in those collagens are due to variations in the intensity of the forces holding the peptones together.

This view allows us to understand the importance of the degree of swelling which the hide undergoes during the processes before actual tannage. It explains this influence not only as regards the properties of the leather finally obtained, but also as regards the conversion of collagen into gelatin.

The idea that the conversion of collagen into gelatin must be understood as peptization rather than hydrolysis is also held by O. Gerngross,[8] who supports this view by the following arguments:

> Equal amounts of hydrochloric acid are taken up by hide powder and gelatin out of solutions of HCl + NaCl (NaCl to prevent swelling). Equal amounts of acid are taken up by formol-tanned hide powder and by formol-tanned gelatin out of solutions of $H_2SO_4 + Na_2SO_4$. Prolonged heating of a gelatin solution alters many physical properties of the gelatin without altering the capacity for binding HCl. Pronounced alterations in the viscosity, melting point, jelly strength and binding strength of the gelatin are often accompanied by only small increases in the formol titration number, pointing to peptization and only slight hydrolysis. The Röntgen spectrum of stretched gelatin corresponds with the Röntgen spectrum of collagen.[9]

In the following description of the processes which the hide must undergo before actual tanning, the distinction between hydrolysis and peptization given above will be chosen as a working hypothesis. These processes deal chiefly with the freeing of the corium from the epidermis, and have the further aim of bringing the corium to the proper state desirable for the particular kind of leather. In these preliminary processes hydrolysis has to be limited to the non-collagen portion of the hide (principally to the proteins of the epidermis); the collagen of the connective tissue should not be attacked by hydrolysis, it should however not remain entirely unaffected, the important point being a very slight degree of peptization which must be far from leading to soluble degradation products, but still capable of loosening the system of peptones called collagen to a degree demanded by the particular kind of leather.

The hides or skins are first soaked in order to free them from dirt and salt which has been used to preserve them and further to bring them to the desired degree of softness, workability and swelling. In the case of skins and hides which have been preserved by drying we meet with more difficulty and it is often necessary to assist the soaking by chemical or mechanical means. Among the chemical means soda or sodium sulfide is commonly used while less often we find acids used, such as formic acid or, lately, emulsifying agents, which combine softening with antiseptic action. The old-fashioned method of allowing the hides to ferment slightly has been succeeded by use of pancreatic enzymes under such conditions that hair loosening is not produced. Mechanical means comprise the flexing of the hides or skins in rotating drums or stocks or in striking out machines. A thorough study of the most favorable conditions for the efficient preservation and the subsequent soaking of raw hides has been carried out at the University of Cincinnati under the direction of G. D. McLaughlin.[10] *

The soaked skins and hides must now be freed from the epidermis and from the adipose tissue. The first is brought about by hydrolysis of the mucous layer and by softening of some keratins of the hair root, so that the hair may be mechanically plucked. The difficulty lies in attacking those more delicate keratins of the hair root without damaging the more resistant keratins of the hair itself. Alkali (especially lime) solves this problem, but requires several days before sufficient hair-loosening is attained. Sulfides hasten the process of hair-loosening, but attack the keratin of the hair. Experiments by which a preliminary treatment with sodium hydrosulfide is followed by a treatment with lime, have proved promising.[11] Enzymatic methods are also likely to solve the problem, and pancreatic enzymes are in practical use for loosening the hair after a sufficient alkaline swelling of the skin.[12] An old process of unhairing, called "sweating," consists of suspending the hides or skins in chambers, the temperature and humidity of which are suitable for the action of hair-loosening bacteria.

After liming or sweating, the skins or hides pass along to suitable machines which remove the hair with the epidermis and also the loosened "flesh" on the underside of the corium. A washing follows to partly free the corium from the materials used in the liming process. To accomplish this process of "deliming," the skins or hides are treated with acids or acid salts or ammonium salts. By this treatment the alkaline swelling is much reduced or even completely removed according to the kind of leather desired. Strong mineral acids (HCl, H_2SO_4) can only be used for superficial deliming, as acid-swelling of the outer layer (grain) which must be avoided, begins before the alkali from the interior of the skin is neutralized. Even the weaker organic acids (lactic, butyric, acetic acid) involve this danger of swelling, if deliming is continued until the middle of a fresh cut shows no more reddening with a drop of phenolphthalein. It was generally acknowledged that buffers of such acids with their salts (e.g. lactic acid + calcium lactate, formed by the action of a preceding addition of acid to the limed hide) will not cause acid swelling as long as the pH-value of such buffers is higher than 4 (that is, the limit of swelling capacity of a pure acid solution). This view has proved to be erroneous, the skin taking up the acid of such buffer solutions preferably, so that swelling will not be prevented unless the salt concentration is of such magnitude that a pickling process (*see* later) is accomplished.[13] Boric acid and other acids of similar weakness (acid salts like sodium bisulfite may be included in this class) can be used in excess without causing any acid swelling. Ammonium salts (first proposed in 1858 by Zollikofer) are now much in use, because they allow complete deliming without any swelling of the grain.

For many purposes (all light and upper leathers) the more or less completely delimed skin, called "pelt," undergoes a treatment called *bating*. This consists principally in the action of tryptic enzymes (of bacterial or digestive origin) and transforms the swollen, somewhat rubbery condition of the skin into slackness, smoothness and superficial slipperiness. Until recently dog dung or hen manure provided the bating enzymes, but these distasteful sources

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* See Prof. McLaughlin's paper in this volume. J. A.

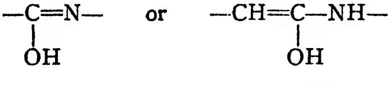
of ferments have now almost completely been replaced by the use of pancreatic glands or extracts from them. Ammonium salts are added to complete deliming and to bring the pH-value of the bating liquor down to the favorable figure of 8.

The two main actions of the bate are hydrolysis of any remaining traces of the epidermis (hair bulbs, etc.) and a slight peptization of the collagen of the connective tissue, thus providing for softness, elasticity and stretch in the finished leather. Other actions of the bate, e.g. the saponification or emulsion of natural fats (after hydrolysis of the fat cell-membrane) or the alteration of the elastic fibers (the elastin loses the property of being colored by resorcin-fuchsin) are of minor importance. The bating effect on the fibers is probably due to a slight peptization of the collagen (opening of secondary valence bonds between peptones and forming peptone complexes of minor magnitude than originally present before bating). Similar changes in the state of dispersion have been observed when acting with thiocyanates on gelatin. In the case of collagen, parallel changes could occur and escape detection, as long as no soluble products of decomposition were formed. We do know that excessive bating or unsuitable conditions in the bating process will cause a more or less thorough peptization of the collagen with a resulting destruction of the skin and production of soluble decomposition products.

This is also the case if neutral salts of a swelling and peptizing capacity like thiocyanates are added to the enzymatic bate. The use of ammonium sulfate as a deliming agent is therefore preferred to the use of ammonium chloride because calcium chloride formed as a product of deliming increases the peptizing effect of the bate while calcium sulfate is not acting in this dangerous direction.

The actions of acids, alkalis, neutral salts and ferments on the proteins of the hide play such an important rôle in the preparatory treatment of the hide before tanning, that a study of the mechanism of these actions seems necessary.

Acids combine with the basic groups of the protein (amino-, guanidyl-, imidazole-, etc., groups) but not with the peptide groups; this can be seen by the titration curves of polypeptides (see Figs. 1 to 6) which show no increase of combined acid by increasing the number of peptide groups in the polypeptide molecule. Alkalis on the other hand combine not only with the acid groups of the proteins (carboxylic groups), but also with the peptide groups which very likely react in the tautomeric form



$$-\underset{\displaystyle OH}{\underset{|}{C}}=N- \quad \text{or} \quad -CH=\underset{\displaystyle OH}{\underset{|}{C}}-NH-$$

There is no acid but much alkali fixed by the polypeptide after addition of the amount equivalent to the amino or carboxylic groups present.[14]

Neutral salts are fixed in a minor degree by the proteins of the hide than acids or alkalis; it is most probable that molecular compounds are formed by saturating partial valences of the protein on the one side and of the neutral salt on the other side. From the practical point of view the swelling produced by electrolytes (acids, alkalis or neutral salts) is more important than the amount of electrolytes fixed by the hide.

The theory of electrolyte-swelling of proteins is rather complicated. One important factor is the osmotic pressure exerted by the protein-electrolyte-compound, this compound being of the nature of a colloid-electrolyte, that is, an electrolyte with one colloidal ion. It makes no difference if this com-

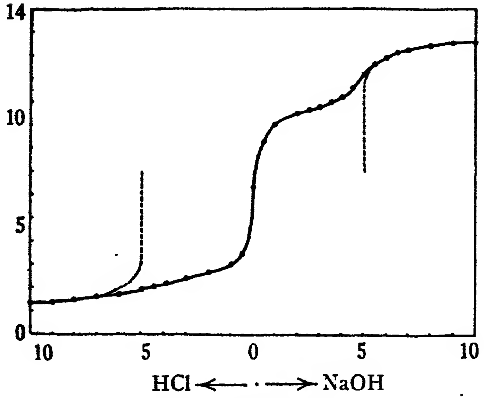


Fig. 1.—Glycocoll.

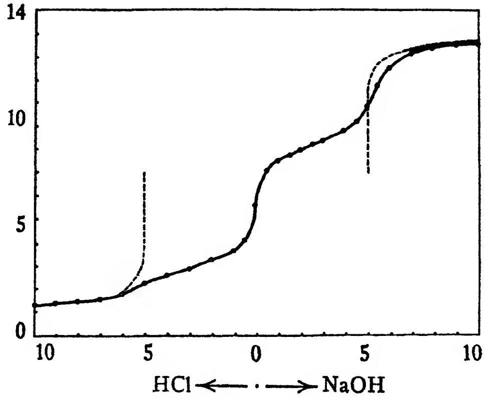


Fig. 2.—Glycylglycin (Dipeptide).

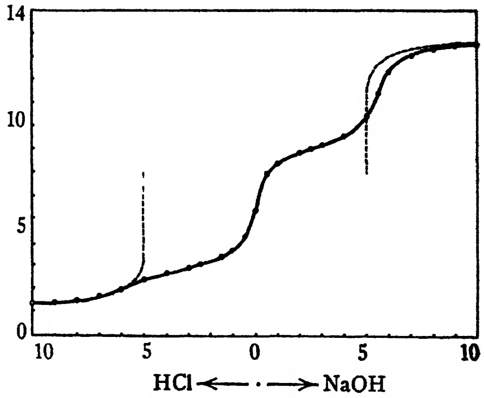


Fig. 3.—Diglycylglycin (Tripeptide).

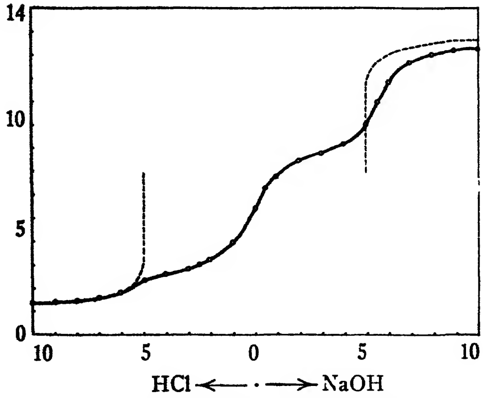


Fig. 4.—Triglycylglycine (Tetrapeptide).

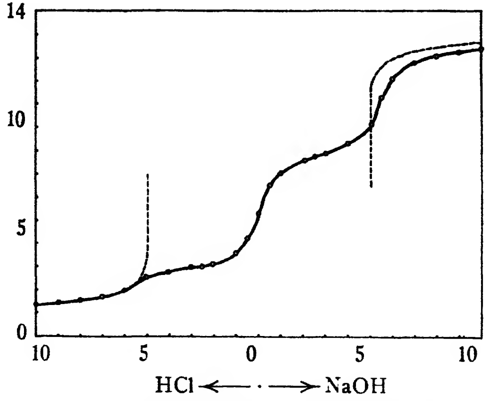


Fig. 5.—Tetraglycylglycine (Pentapeptide).

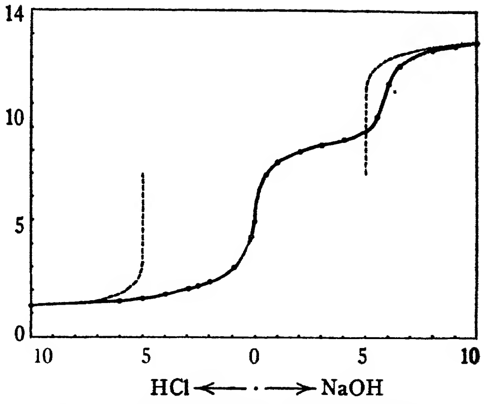


Fig. 6.—Pentaglycylglycin (Hexapeptide).

pound is formed by salt formation or by the formation of a molecular compound. According to H. R. Procter and J. A. Wilson[15] such a compound must act according to Donnan's law of membrane equilibrium.* This law was established for the case of a colloid-electrolyte-solution being separated by a semipermeable membrane from a solution of an electrolyte with one common ion. It also holds for the case of a protein compound without any membrane, e.g. in the case of gelatin chloride in presence of hydrochloric acid. The Donnan equilibrium demands that the product of $[H^{\cdot}] \cdot [Cl']$ in the gelatin jelly must be equal to the product of $[H^{\cdot}] \cdot [Cl']$ in the external solution.

$$[\dot{H}]_{in} \cdot [Cl']_{in} = [\dot{H}]_{out} \cdot [Cl']_{out}$$

$[H^{\cdot}]$ and $[Cl']$ are alike in the external solution but not in the gelatin on account of some chlorine ions being paired with gelatin ions. As a result the product on the right hand side of the equation is built up of equal factors (corresponding to a square) while the product on the left is built up of unequal factors (corresponding to a rectangle). As the osmotic pressure depends on the sum of the diffusible ions, it will be greater in the gel than in the external solution because the perimeter of the rectangle is greater than that of the square of equal area. Hence water enters the gel and causes swelling.

The greater the positive charge of the gelatin produced by the fixation of the hydrion of the acid, the greater will be the swelling. HCl solution, stronger than *N*/50, will repress the ionization of gelatin chloride, thus diminishing the positive charge and therefore also diminishing the degree of swelling. Addition of other chlorides, e.g. NaCl, will act in a similar way and cause a marked repression of swelling. The actual swelling curve of gelatin when acted upon by HCl is in very good concordance with the claim of this theory. In a similar way the alkaline swelling can be explained by the formation of an alkaline salt of the protein and a Donnan-equilibrium established between this salt and the alkali in the external solution.

There are, however, other factors besides those considered by Procter and Wilson which can play an important rôle in connection with the problem of swelling.[16] These factors are: (1) the fixation of the anion of the acid (or the cation of the alkali) used; and (2) the peptizing action of the electrolyte on the protein. By fixation of the anion of the swelling acid, the positive charge produced by the combination between gelatin and hydrion is reduced and consequently the swelling diminished. This is the case with sulfuric acid and with organic acids, the anions of which are distinctly taken up by gelatin or collagen. Of greater importance is the peptizing influence of the electrolyte. This action diminishes the forces by which the peptones or peptone complexes are held together in the gelatin (or collagen) molecule and therefore reduces the cohesive forces which are opposed to swelling. The result is an increase of swelling, the amount of which can be called peptization swelling. From the study of the swelling effect of neutral salts it is known that equimolar solutions of different salts (of the same pH-value) act very differently according to the position of the anion in the Hofmeister series. Thiocyanates and iodides have a distinct dispersing effect, while sulfates and phosphates have even less dispersing effect than water. This neutral salt effect increases with increasing concentration of the solution, and it is obvious that the same effect will be exerted by the anions of acids in the

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* See paper by H. R. Procter in this volume. J. A.

case of acid swelling. Consequently the swelling by organic acids must be favored by the peptizing effect of the anions of these acids (and by the peptizing effect of the un-ionized portion of these acids as well), and this accounts for the great difference in the swelling curves of hydrochloric acid and acetic acid. In the case of hydrochloric acid, the fixation of hydrions is the predominant factor because chlorine ions are fixed only to a negligible extent and because peptization is not noticeable at the applied concentration. Hence the equation derived from Donnan's law by Procter and Wilson, viz. $e = -2x + \sqrt{4x^2 + f^2}$ * is in accordance with the experimental facts.

If, however, instead of dilute hydrochloric acid, an organic acid of the same pH-value but—consequently—of higher molar concentration is used, the swelling will not obey the demands of the formula of Procter and Wilson, because other factors (the fixation of anion and the peptizing action of the acid) will show considerable influence on the degree of swelling. It has been a mistake to base every reasoning on the pH-value and to neglect other factors; this not only applies to the problems of swelling and pickling but also to many other problems connected with the leather industry.†

Tanning Materials.

In the following discussion of both vegetable and chrome tanning materials we shall note how both the chemical nature and the state of subdivision must be considered from the point of view of leather making. These two kinds of tanning materials deserve most consideration as they play the most important part in commercial practice.

All vegetable tanning materials have the common property of converting the animal skin into leather, but in addition to this they possess individual properties which show themselves in the different qualities of leather each material produces. The tanner knows that he cannot use the same tanning materials in the production of sole leather as he would use in the production of upper leather or fancy leather. While the kind of skin and its preparation for tanning have a large influence on the properties of the finished leather, still the choice of the tanning material also plays a distinct part in the final result, and it is this influence of the tanning material which is of interest to the chemist. The chemist naturally will first look to differences in the chemical constitution of the tannins for an explanation of this influence and we are therefore deeply interested in all research which leads to an explanation of the structure of the tannins. Unfortunately this domain of chemical research is so extremely difficult to traverse and our progress in it is very slow. So much so, that today the only tannins which have been thoroughly investigated are those related to the tannin of nut galls and such tannins are not commercially applicable or valuable. Among materials which are closely related to the tannins we know the structure of only catechin and ellagic acid. We know very little concerning the important tannins present in oak bark, pine bark, hemlock bark, oak wood, chestnut wood, quebracho wood, sumac, valonea, myrabolans and others. The changes which occur in the primary tannin of the leaf before it ever arrives in the wood or bark or fruit, make the study even more difficult and in the opinion of K. Freudenberg,[17] we can

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* e = the difference of ionic concentrations inside and outside the protein, and consequently a measure of the osmotic pressure which causes swelling.

x = the electrolyte concentration in the external solution.

f = the concentration of the protein salt formed by the acid.

† Biological problems are also vitally affected. *See* papers in Vol. II of this series dealing with this aspect, especially those on proteins; e.g. by T. B. Robertson, M. H. Fischer, Jacques Loeb, and editor's notes in connection therewith. J. A.

not expect an early understanding of the chemical constitution of the tanning materials. This is even more true of the secondary products of transformation appearing in tan liquors. We must therefore seek in colloid chemistry an understanding of the individual properties of the various tanning materials. The tanning properties, the astringency, the speed of diffusion, the degree of adsorption and the reversibility of the adsorption (ease of washing out of the tannin) are properties depending more on the degree of dispersion and other colloid properties than on the chemical constitution.*

Solutions of tanning materials are distinctly polydisperse systems containing particles ranging from molecular size (phenolic non-tans of the type of gallic acid) up to coarse suspensoids which cause the cloudiness in incident or transverse illumination. If now we undertake to fractionate these particles according to their size and express these fractions as percentages of the total tanning present, we will obtain relative figures so long as our method is uniform, and these figures will vary according to the tanning material present. Such a fractionation is conceivably possible in different ways. We might, by employing ultrafilters of various pore dimensions, separate particles of certain definite dimensions just as in sifting analyses we use sieves of various meshes to separate particles of various sizes. This method however is beset with difficulties in that the ultrafilter, unlike the sieve, acts as an adsorbing agent, and further during the filtration the dimensions of the pores change and this affects the speed of filtration. We succeed better by fractional salting out of the particles and re-dissolving of the precipitates obtained. In connection with this procedure we have of course to consider that salting out depends not only on the size of the particle but also on the degree of hydration. Since, however, the degree of hydration is related to the particle size (smaller particles have obviously larger water envelopes than larger particles) the principle of fractionation according to particle size by this method is by the same token further validated.

Now it has been shown [18] that different amounts of tannin will be precipitated from different tanning material infusions when these are one-third, two-thirds and completely saturated with common salt. It has also been further shown that the individual fractions from any one infusion will differ from each other in surface development, color, ease of removal from tanned hide powder by subsequent washing, sensibility towards electrolytes and also toward gelatin as a precipitant. Since these properties are a measure of that still-vague term, astringency and also of tanning power, we have here a distinct relationship between the size of the particle and the tanning action. In fact this simple procedure of salting out gives us a ready method for the comparison of various tanning materials. We can also recognize by this procedure the effect of sulfiting on quebracho extract whereby the heating of the extract with bisulfite causes an increase in the dispersion of the particles even to the extent of converting tannin to non-tannin when dispersion is carried too far. Astringency disappears at high dispersion.[19]

We can also, by this method, distinguish and decide what infusions are highly dispersed and suitable for the early stages of tanning and which are less dispersed and suitable for the later stages. In the early stages we desire diffusion and little astringency and require more highly dispersed particles than in the later stages. Dilution causes an increase in dispersion, and the "golden rule," according to which we commence tannage in weak infusions and gradually proceed to stronger infusions, is only a special case of the gen-

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* Some aspects are treated in a paper on "Degree of Dispersion as an Influence in Tanning," by Jerome Alexander, *J. Am. Leather Chemists' Assn.*, Aug. 1923. J. A.

eral principle that high dispersion is necessary at the commencement of tannage and that as tannage proceeds the dispersion should gradually become lower. Experience has taught us to handle our tannage counter-current fashion. That is, the hide must encounter an infusion which contains little tannin but which is rich in non-tannins and thence enter infusions which are stronger in tannin and more astringent. This practice appears to be validated in the light of the above views for experiments have shown that not only dilution but also the presence of phenolic non-tannins (gallic acid) causes increase of dispersion and thus a reduction of astringency. By application of such methods we can avoid a too-rapid tanning action at the start together with all its disadvantages. Another force acting to cause greater dispersion is the presence of the organic acids resulting from acid fermentation of tan liquors, which acids are also important on account of their influence on swelling. These acids are to be distinguished from mineral acids which act against an increase of dispersion. We can, in fact, judge all the many additions which the tanner is in the habit of making to his liquors and vats from the standpoint of their influence on the degree of dispersion of his infusions.

In the case of chrome tanning the relationship between the chemical constitution of the tanning agent and its tanning effect is better understood than in the case of vegetable tanning, and even there the relationship between the degree of dispersion (size of particle) and the tanning power is obvious.[20]

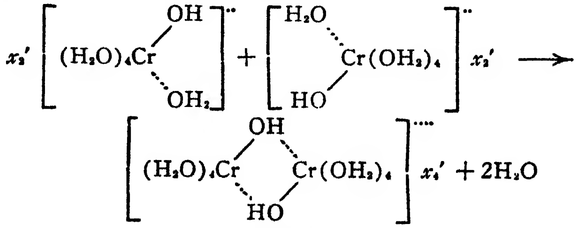
In the light of Werner's theory of complex salts, the chrome compounds can be divided into the following groups (see Table I), in which $a = \mathrm{OH_2}$ or $\mathrm{NH_3}$ or any substitute (like urea, ethylenediamine, pyridine, etc.), x = an acid radical (e.g. $\mathrm{Cl}, \mathrm{NO_3}, \mathrm{SO_4}/2$, etc.) and k = an alkali metal (e.g. potassium).

TABLE I. *Classification of Chrome Compounds.*

1. $\left[\mathrm{Cr}\ a_6\right]^{\cdots} x_3'$
2. $\left[\mathrm{Cr}\ {x \atop a_5}\right]^{\cdot\cdot} x_2'$
3. $\left[\mathrm{Cr}\ {x_2 \atop a_4}\right]^{\cdot} x'$
4. $\left[\mathrm{Cr}\ {x_3 \atop a_3}\right]$
5. $\left[\mathrm{Cr}\ {x_4 \atop a_2}\right]' K^{\cdot}$
6. $\left[\mathrm{Cr}\ {x_5 \atop a}\right]'' K_2^{\cdot}$
7. $\left[\mathrm{Cr}\ x_6\right]''' K_3^{\cdot\cdot}$

$$\left[\mathrm{Cr(OH_2)_6}\right]^{\cdots} x_3' \longrightarrow \left[\mathrm{Cr}\ {\mathrm{OH} \atop \mathrm{(OH_2)_5}}\right]^{\cdot\cdot} x_2' + \mathrm{H}x \longrightarrow \left[\mathrm{Cr}\ {\mathrm{(OH)_2} \atop \mathrm{(OH_2)_4}}\right]^{\cdot} x' + 2\mathrm{H}x$$

formation of hydroxo compounds by hydrolysis.



formation of polynucloid ol-compounds by the process of olation.

Group I is of interest from the point of view of tanning as far as $a = \mathrm{H_2O}$. The hexaquochromisalts $[\mathrm{Cr(OH_2)_6}]^{\cdots}x_3'$ do not tan themselves but form basic salts by hydrolysis, which basic salts (hydroxochrome compounds) are converted by secondary changes into ol-compounds of tanning power.

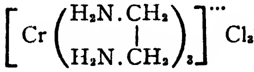
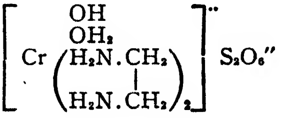
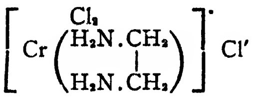
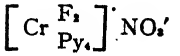
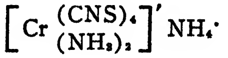
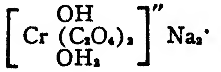
These ol-compounds, the molecular weight of which can be increased by increasing the degree of basicity and by ageing or heating, are the real tanning agents in the chrome liquor. The astringency depends on the size of the molecule and only those chromic compounds which cause a semi-colloidal character of their solution are valuable as tanning agents.

Groups II and III represent very frequent examples of chrome salts, e.g. chromic chloride or chromic sulfate, formed by heating a solution of the hexaquo salt. By this treatment, one or more acid radicals enter into the chrome complex. These acido-aquo-chrome compounds undergo hydrolysis as described for group I and the hydroxo compounds thus formed are converted into ol-compounds which act as tanning agents.

Chrome compounds with tanning capacity can also be obtained from chrome salts belonging to group IV-VI in so far as aquo groups are present which allow hydrolysis and as far as ol-compounds are produced by secondary changes of the hydroxo compounds. The chrome compounds belonging to group VII have no tanning power whatever.

Table II gives a list of chromic compounds which have no tanning capacity.

TABLE II. *Non-tanning Chrome Compounds.*

1.	$[Cr\,(OCN_2H_4)_6]^{\cdots}Cl_3'$	Hexa urea chromic chloride (belonging to Group I: $[Cr\,a_6]^{\cdots}\,x_3'$)
2.	 $\left[Cr\begin{pmatrix}H_2N.CH_2\\ \vert\\ H_2N.CH_2\end{pmatrix}_3\right]^{\cdots}Cl_3'$	Triethylenediamine chromic chloride (belonging to Group I: $[Cr\,a_6]^{\cdots}\,x_3'$)
3.	 $\left[Cr\begin{matrix}OH\\ OH_2\\ \begin{pmatrix}H_2N.CH_2\\ \vert\\ H_2N.CH_2\end{pmatrix}_2\end{matrix}\right]^{\cdot\cdot}S_2O_6''$	Hydroxoaquodiethylenediamine chromic dithionate (belonging to Group II: $\left[Cr\begin{matrix}x\\ a_5\end{matrix}\right]^{\cdot\cdot}x_2'$)
4.	 $\left[Cr\begin{matrix}Cl_2\\ \begin{pmatrix}H_2N.CH_2\\ \vert\\ H_2N.CH_2\end{pmatrix}\end{matrix}\right]^{\cdot}Cl'$	Dichlorodiethylenediamine chromic chloride (belonging to Group III: $\left[Cr\begin{matrix}x_2\\ a_4\end{matrix}\right]^{\cdot}x$)
5.	 $\left[Cr\begin{matrix}F_2\\ Py_4\end{matrix}\right]^{\cdot}NO_3'$	Difluorotetrapyridine chromic nitrate (belonging to Group III: $\left[Cr\begin{matrix}x_2\\ a_4\end{matrix}\right]^{\cdot}x'$)
6.	 $\left[Cr\begin{matrix}F_3\\ Py_3\end{matrix}\right]$	Trifluorotripyridine chrome (belonging to Group IV: $\left[Cr\begin{matrix}x_3\\ a_3\end{matrix}\right]$)
7.	 $\left[Cr\begin{matrix}(CNS)_4\\ (NH_3)_2\end{matrix}\right]'NH_4^{\cdot}$	Tetrarhodanatodiammin-ammonium chromiate (belonging to Group V: $\left[Cr\begin{matrix}x_4\\ a_2\end{matrix}\right]'K^{\cdot}$)
8.	 $\left[Cr\begin{matrix}OH\\ (C_2O_4)_2\\ OH_2\end{matrix}\right]''Na_2^{\cdot}$	Hydroxodioxalatoaquodisodium chromiate (belonging to Group VI: $\left[Cr\begin{matrix}x_5\\ a\end{matrix}\right]''K_2^{\cdot}$)
9.	$[Cr\,(CNS)_6]'''\,(NH_4)_3^{\cdot}$	Hexarhodanato-triammonium chromiate (belonging to Group VII: $[Cr\,x_6]'''\,K_3^{\cdot}$).

In all of these non-tanning chrome compounds we find: No aquo groups are present in the chrome complex (*see* 1, 2, 4, 5, 6, 7, 9); the complex is stable and resistant to the influences during tanning; no hydrolysis takes place in aqueous solution, the solution showing neutral reaction (*see* 1-9). It must be pointed out that no relation seems to exist between the electrical charge (sign and magnitude) of the chrome complex on the one hand and the tanning capacity on the other, because non-tanning chrome salts may belong to any of the groups mentioned in Table I (1-7). This conclusion is corroborated by the fact, that chrome salts with tanning power have been found to belong to any of the groups 1-6 as shown in Table III.

TABLE III. *Tanning Chrome Compounds.**

1. Ol-compounds formed from $\left[\mathrm{Cr}\begin{matrix}\mathrm{OH}\\(\mathrm{OH_2})_5\end{matrix}\right]^{\cdot\cdot}x_2'$, $\left[\mathrm{Cr}\begin{matrix}\mathrm{OH}\\x\\(\mathrm{OH_2})_4\end{matrix}\right]^{\cdot}x'$, $\left[\mathrm{Cr}\begin{matrix}\mathrm{OH}\\x_2\\(\mathrm{OH_2})_3\end{matrix}\right]$ } belonging to Group 2, 3 and 4.
2. Ol-compounds formed from $\left[\mathrm{Cr}\begin{matrix}(\mathrm{OH})_2\\(\mathrm{OH_2})_4\end{matrix}\right]^{\cdot}x'$, $\left[\mathrm{Cr}\begin{matrix}(\mathrm{OH})_2\\x\\(\mathrm{OH_2})_3\end{matrix}\right]$
3. Ol-compounds formed from $\left[\mathrm{Cr}\begin{matrix}\mathrm{OH}\\(\mathrm{SO_4})_2\\\mathrm{OH_2}\end{matrix}\right]''K_2$ † belonging to Group 6.
4. Ol-compounds formed from Hydroxosulfato-, hydroxosulfito- or hydroxo-oxalato Chrome salts, in which the Chromium complex is negatively charged, belonging to groups 5 and 6.

The chrome tanning liquors used in practical tanning are made from chrome alum by adding sodium carbonate and common salt or by reducing bichromate with any suitable reducing agent (SO_2, $NaHSO_3$, sugar, organic waste products of different kinds, etc.); they contain basic chromium salts of different basicity, different degree of olation and different stability of the chromium complex, and the solutions are further distinguished by different acidity and percentage of neutral salts, all of the named factors being of influence on the kind of tannage produced.

THE ACTION OF THE TANNING MATERIAL ON THE SKIN.

A complete catalog of all methods of preparing leather is so comprehensive that it would be impossible to state a general principle of tannage capable of comprising all of them. We have firstly the important commercial methods, including vegetable tannage, mineral tannage with chrome and aluminum salts, and oil tannage. Secondly, we have a group of methods which are in less common usage, such as tannages with formaldehyde, synthetic tanning materials, iron salts, quinone, etc. Lastly, we have countless possible methods of tannage with halogens,[21] titanium,[22] and bismuth[23] salts, salts of the rare

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* $x = \mathrm{Cl}$, $\mathrm{So}_4/_2$ etc.

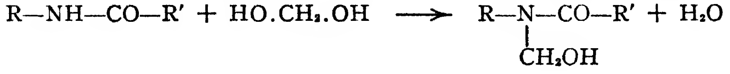
† The Ol compound of this salt is formed by evaporating solutions of mixtures of chromium sulfate and potassium sulfate. Though crystallizing from a warm solution, the dissolved substance shows colloidal behavior. Immediately after dissolving it does not penetrate a parchment membrane; by ageing or heating the chromium complex is altered and a dialysing chrome salt is formed.

All solid chrome tanning extracts as well as all residues prepared by evaporating chrome sulfate solutions (such products being on the market under the name of chrome sulfate) contain substances of this or like type. A freshly prepared solution of these extracts gives no precipitate with NH_3 nor with $HCl + BaCl_2$. Addition of $BaCl_2$ (without HCl) forms a precipitate of the barium salt $\left[\mathrm{Cr}\begin{matrix}\mathrm{OH}\\(\mathrm{SO_4})_2\\\mathrm{OH_2}\end{matrix}\right]\mathrm{Ba}$. After ageing or heating the solution regains the capacity of being precipitated by NH_3 and by $HCl + BaCl_2$.

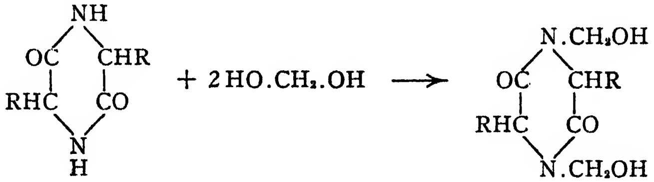
earths,[24] silica,[25] picric acid,[26] magnesium carbonate [27] and other insoluble materials,[28] and alcohol-soluble materials which remain in the pores after evaporation of the alcohol.[29] It is possible to prepare leather (that is, to transform skin into an imputrescible and to some extent water-resisting material with a certain degree of flexibility) in a number of ways which differ very radically. When for instance a skin is shaken with a suspension of an insoluble material, such as copper phosphate or zinc hydroxide among others, enough of the material will be mechanically worked into the pores so as to give a product of leather-like nature though not of commercial value. Again a skin dehydrated in alcohol and immersed in an alcoholic solution of stearic acid will, after evaporation of the alcohol, yield a product which by mechanical means (staking) can be softened until it resembles a white leather, similar to alum tawed leather. In such cases we must view the action that takes place as a filling up of the interstices without either any chemical action on the collagen or any primary adsorption coupled with secondary changes in the adsorbed material. On the other hand the tannages secured by means of vegetable, mineral or oil tanning materials must be accepted as being of a different nature. In these cases the common property of the tanning materials is their semi-colloidal nature. While significant, this does not mean that the tanning action is based on this property alone. Lastly in the case of the tannage secured by the action of formaldehyde or the halogens we can only believe that the action is a purely chemical one.

The chemical character of the formaldehyde tannage follows from the fact that all materials of a polypeptide structure as well as simple amino acids have their acidity raised through the action of formaldehyde. This action depends on the conversion of basic groups into groups of neutral character as shown by the following equations: [30]

$$R{-}NH_2 + OCH_2 \longrightarrow R{-}N{=}CH_2 + H_2O$$



$$R{-}NH{-}CO{-}R' + HO.CH_2.OH \longrightarrow \underset{\displaystyle CH_2OH}{R{-}\underset{|}{N}{-}CO{-}R'} + H_2O$$



The acid groups present in the proteins are thus allowed to exert their influence on the character of the chemical compound, undiminished by the basic groups originally present. In the case of soluble substances (amino acids, soluble polypeptides) this action of the formaldehyde can be controlled by titration, while in the case of insoluble substances like collagen, the diminished power of acid fixation offers a measure of the effect of formaldehyde.[31] The action of formaldehyde is favored by a distinct alkaline reaction of the medium; this applies to amino acids as well as to proteins, and explains the fact that formaldehyde tannage must be carried out in alkaline liquors (pH = 7 to 9).

This latter condition applies also to the quinone tannage. Quinone appears to react in a purely chemical manner with collagen according to L. Meunier and A. Seyewetz,[32] the discoverers of this method of tannage. This opinion is shared by W. Fahrion[33] and in fact by the majority of leather chemists. Another conception of the process is based on the view that quinone in the weakly alkaline solution, which is most favorable to the tannage, undergoes a change forming products of semi-colloidal character which possess tanning properties.

The theories of vegetable and chrome tannage may be discussed in somewhat greater detail. Vegetable tannage has been long associated with the astringent taste of the material used for tanning. De la Lande,[34] to whom we owe the first book (1764) of any value on tanning, perceived nothing more in tanning liquors than a "powder which has an astringent and drying property." This anthropocentric-physiological tanning theory, as it was termed by Ebert,[35] was first expressed by Galenus in the second century and is comprehensible, when we consider that in those days the only tannages known were vegetable and oil, while of these the oil tannage was not considered a real tannage. Both vegetable tanning materials and alum, introduced into Europe as a tanning agent by the Moors in the Middle Ages, possess the astringent taste. It is remarkable, however, that no attention was paid to the fact that the hide takes up tannin and gains in weight during tanning. It was seemingly owing to Lavoisier's influence that this fact gained recognition. At any rate it was Armand Seguin, a contemporary of Lavoisier, who in 1795 put forward the first theory of tanning worthy of the name.[36] Seguin had noticed that glue caused a precipitation from an infusion of oak bark.[37] He recognized in this a combination of glue with tannin and took the view that tannage was the result of an analogous combination between tannin and hide. H. Davy[38] came to a similar view independently of Seguin at about the same date and this view seems to have become quite common. We note that Seguin did not go deeply into the nature of the combination, while Dumas and Berzelius, who also studied these matters, avoided any definite expressions as to the formation of a chemical compound. Davy and Pelouze, however, spoke definitely of a chemical compound, while Stenhouse[39] went so far as to differentiate between the chemical constitutions of sole and upper leathers. It was tacitly understood that the chemical compound was a salt formed from the hide as a base and the tannin as an acid.

In 1858 Friedrich Knapp[40] first made a stand against a purely chemical conception of the subject. He based his views on experiments wherein, by repeated immersion of a prepared skin in alcohol, dehydration was obtained and after evaporation of the alcohol and simple mechanical treatment (staking) a material was obtained similar to white alum leather. Such a material reverted to the original raw state on wetting, but Knapp found that treatment with an alcoholic solution of stearic acid with subsequent evaporation of the alcohol, gave a leather which retained its nature despite rewetting and which also resisted decomposition when kept for a long time under water. From his experiments, therefore, Knapp was led to the view that tanning was concerned with a dehydration of the fibers of the skin, a separation of these from each other and then a coating of the fibers with a substance insoluble in water, so that on drying the fibers would not stick together and at the same time be protected from putrefying.

Knapp's theory of fiber coating won rapid recognition and in great measure displaced the purely chemical viewpoint. Gradually, however, the purely chemical viewpoint came to the front again and W. Fahrion[41] was its particular advocate. He originated the so-called oxidation theory according to which the skin must be first oxidized before it can combine with tannin. This view was first developed in connection with the chamois tannage (oil tannage) and then carried over to the other methods. In chamois tannage the skins are drummed with fish oil and then allowed to lie in piles, when tannage occurs accompanied by a strong development of heat. This operation of drumming with oil followed by the action of the oxygen of the air is repeated until finally a leather is obtained which is freed from excess oil by pressing and treatment with soda solution. There is no doubt that in this process an oxidation of the oil occurs and that it is the oxidized oil which tans. The greater part of the oil can be extracted out of the chamois leather by various solvents and this extracted oil shows a much lower iodine value, a reduced solubility in petroleum ether and an increased acid value. A small proportion of the oil is so firmly held that it cannot be extracted, and can only be recovered by destruction of the leather with alcoholic potash solution followed by acidifying this solution and shaking out with a grease solvent. This hidden fat, Fahrion considered as the true tanning agent, and he held that it had entered into chemical combination with the skin. Fahrion now further assumed that peroxy-fatty acids were formed by the oxidation of the fatty acids of the oil and that these transferred oxygen to the skin, thereby becoming reduced themselves to hydroxy-fatty acids. The chemical combination then took place between the hydroxy-fatty acids and the oxidized skin. This view of tannage has been adapted by Fahrion to other modes of tannage. He pictured, for instance, that vegetable tannage was of the nature of the quinone tannage in that the vegetable tannin was firstly oxidized to a quinone which then gave up oxygen to the skin with finally a chemical union between the oxidized skin and other quinone molecules. Fahrion himself later gave up his oxidation theory, but there are many leather chemists who still hold these views in one form or another—so much so that we still find patents being issued for tanning processes in which air is introduced into the tanning liquors or where tannage is proposed to be furthered by aid of oxygen from the air or hydrogen peroxide.

The colloid theories of tanning began to appear as the study of the colloid phase progressed, and particularly when the study of the phenomena occurring in the surface layer spread widely. Tannage would thus rest firstly on an adsorption of a semicolloid body on the skin fibers, followed by secondary changes which render the adsorption process irreversible. These secondary changes need not necessarily be a chemical union between adsorbent and adsorbed material, i.e. collagen and tannin. We can in most cases see a fitting explanation when we limit ourselves to changes which occur in the adsorbed tanning material itself. Such changes would be included in dehydration, polymerization, oxidation or a change from a sol to a gel form on the part of the tanning material. As an illustration of a secondary change in an adsorbing surface, let us mention the dyeing of silk (or charcoal) with fuchsin.[42] The adsorption process appears to be irreversible, for water will not remove any of the fuchsin. Alcohol, however, will remove all the color from the silk, washing it perfectly clean. The silk can be re-dyed in a water solution and again washed clean with alcohol and the cycle be gone through repeatedly without any loss in weight on the part of the silk. The fuchsin, however, which is present in the alcohol, is no longer identical with the original fuchsin, but is now a polymerized product of the original fuchsin. Other processes which can be included in the term adsorption catalysis are recognizable in the oxidation of amino acids, formic acid, glycerin, etc., on the surface of charcoal; the hydrolysis of cinnamic acid on hide powder; the destruction of phenyl thiocarbamide by shaking it with charcoal and so on. It would seem proper therefore to expect analogous changes to occur during tannage where the highly developed surface present in the collagen plays the part of the adsorbing layer.

We are further led to a colloid viewpoint with regard to vegetable tannage by our knowledge of the phenomena connected with the precipitation of gelatin by tannins. This precipitation is commonly accepted as analogous to the tanning of collagen and based upon the mutual neutralization of the electrical charges of the two colloidal bodies concerned, viz. gelatin (or collagen) and tannin. The following equations show the analogy as well as the difference between this conception and the theory of salt formation.

$$\text{Salt formation:}\quad \underset{\substack{\text{Gelatin}\\ \text{(or collagen)}\\ \text{acting as}\\ \text{a base}}}{G^{\cdot}\,OH'} + \underset{\substack{\text{Tannin}\\ \text{acting as}\\ \text{an acid}}}{T'H^{\cdot}} \longrightarrow \underset{\substack{\text{Gelatin-Tannin-precipitate}\\ \text{or collagen-tannin}\\ \text{precipitate (leather)}}}{GT + H_2O}$$

$$\text{Colloidal precipitation:}\quad [G_n G]^{\cdot}\,x' + [T_m T]'\,\dot{H} \longrightarrow [G_{n+1} T_{m+1}] + \dot{H}x'$$

In this equation G_n means the aggregate of gelatin molecules forming one colloidal particle, which by adsorption of one molecule of gelatin salt received a positive charge. T_m means the aggregate of tannin molecules forming one colloidal particle, which by adsorption of one molecule of ionized tannic acid received a negative charge. The precipitate formed is due to the neutralization of charges and shows how the quantitative relation of the two components depends on the size of the aggregates of the colloids originally present.

This conception does, however, not fully satisfy the claims of a theory which strives to express all experimental data. It misses the necessary condition of the chemical character of the two components. Not any colloidal or semi-colloid solution of a substance with negatively charged particles has the capacity of tanning, nor are all tanning agents negatively charged (*see* chrome tannage). There must be a kind of affinity between hide and tannin, but not necessarily an affinity expressed by primary valencies to be mutually saturated, but by secondary valencies of suitable character on both sides.

Just as in the conception of F. Haber [43] and of I. Langmuir [44] and W. D. Harkins [45] unsaturated secondary valencies of surface molecules are essential for the adsorption process, the tanning process is dependent on these same conditions. K. Freudenberg [46] was the first to draw the attention to this fact. He showed that amines (ammonia, hydrazine, hexamethylene tetramine, quinoline, etc.) form crystalline molecular compounds with phenols (pyrocatechin, resorcinol, pyrogallol, phloroglucinol, etc.). These compounds are composed of the two components in the proportions of 1 : 1 or 2 : 1 or 3 : 1. Freudenberg also draws attention to the molecular compounds which result from combination of oxygen bases with phenols. As oxy-bases dimethylpyrone and camphor may be mentioned, and the analogy between such compounds and those formed between tannin (representing the phenol class) and cinnamic aldehyde, vanillin, or dimethylpyrone (representing the oxy-bases) is worthy of notice. As we proceed from the simple phenols to the tannins on the one hand and from the simple amines to the proteins on the other, we arrive finally at the tannin-gelatin precipitation as the analog of the molecular compounds mentioned above.

It has been pointed out that a purely colloidal conception of the tanning process cannot satisfactorily explain the complexity of experimental facts. It is likewise necessary to say, that the ability to form molecular compounds is also insufficient to produce the tanning effect. Both factors, the ability of manifesting secondary valencies and a sufficient size of the particles present in the tan liquor, must combine in order to accomplish the tanning effect.

As an instance of the influence of the size of the particle we can consider that tannin gives a precipitate with gelatin while neither gallic acid nor sugar do so. Pentadigalloyl glucoside is colloidally dispersed in water, whereas the components gallic acid and sugar are soluble as crystalloids. Again the crystalloid monomolecular α-silicic acid does not precipitate gelatin, while its polymer, the colloidal β-acid, does precipitate gelatin. Still more can we differentiate between the action of different sizes of the particles in the case of a solution of a vegetable tannin. Such solutions are polydisperse, containing particles of various sizes. If now we take an infusion of wattle bark and add salt to one-third, two-thirds and complete saturation, we can fractionally precipitate the infusion, the successive fractions each containing particles of a different magnitude. When we redissolve the three fractions separately and test them for their tanning action, we find that the first fraction, which was most easily salted out, is adsorbed by hide powder much more firmly than the second fraction while the last fraction, which was not salted out at all, is adsorbed so loosely as to be almost completely removed by washing. Difference in the chemical constitution of these fractions will hardly serve to explain these differences. There are, however, great differences in the particle size of the fractions and in this instance the particle size and tanning power run parallel.

Through such observations and others of similar nature we are impelled to stipulate two kinds of properties as necessary for tanning action: 1. The ability to be adsorbed, which we may express as an ability to form secondary valence compounds with hide substance; 2. A molecule (or molecular-aggregate) of dimensions large enough to class it as semicolloidal, is necessary in a tannin.

From this viewpoint we can comprehend not only vegetable tannage but also chrome tannage. The study of this latter has shown that both positively and negatively charged complex chromium ions are suitable for tanning insofar as they contain hydroxyl groups with secondary valency forces capable of combining with suitable groups of the collagen molecule, and insofar as the chromium complex is of sufficient size to cause a semi-colloidal character of the solution. The size of the molecule of the tanning agent must, however, not exceed certain bounds because a highly colloidal tanning solution will not penetrate into the hide and will consequently fail to tan the interior fibers of the hide.

In the case of chrome tannage the relation between chemical composition and colloidal character of the solution is clearer than in the case of vegetable tannage because the process of olation which is responsible for the formation of polynucleoic chrome compounds and consequently for the increase of the molecular weight of the basic chrome compounds can be traced by chemical methods (see above).

Table IV[47] shows the analogy of vegetable tannage and chrome tannage as regards the two principal conditions for tanning, viz. the capacity of forming molecular compounds with the collagen of the hide and a sufficient size of the molecule of the tanning substance.

From this conception of the tanning process it follows that neither a purely chemical nor a purely colloidal view can completely satisfy the needs of a theory of tanning. Both views must be combined and the time is past when the "chemical" and the "physical" conception of tanning represents an irreconcilable antagonism.

TABLE IV. *Analogy of Vegetable and Chrome Tannage.*

Chrome salts with one Cr in the molecule (low molecular weight) Phenolic non-tans (e.g. gallic acid)	Crystalloid, no tanning effect
Basic chrome salts (ol-compounds) with several Cr atoms in the molecule (medium molecular weight) Vegetable Tannins	Semicolloid, OH-groups with full secondary valences; good tanning effect
Basic chrome salts (ol-compounds) with many Cr atoms in the molecule (high molecular weight) Phlobaphenes	Colloid, no satisfactory tanning effect

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Tanning.

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Leather is the product formed by the action of a tanning material upon animal skin; this process is termed tanning. Raw undried skin is characterized by its tendency towards rapid decomposition; tanned skin by its stability. Tanning may be accomplished with either organic or inorganic tanning agents.

The importance of leather in the world's economy becomes apparent when we consider shoes, harness, belting, automobile and furniture upholstering, and its many other uses.

Tanning preceded agriculture. It reached a high development in ancient Egypt, China, Greece and Rome. Ancient and modern literatures contain many references to the art, made, for instance, by writers in the Old Testament, by early Chinese sages, Homer, Æsop and later by Shakespeare. The first copy of the Koran is said to have been written on leather, while the armor of the Roman Legions was made in part of leather. In the roster of scientists who have worked in the field are found the names of Paracelsus, Lavoisier, Davy, Berzelius, Liebig and Emil Fischer. Pasteur's father was a tanner.

There is probably no scientific field richer in unsolved problems than tanning; it beckons to the thinker in many branches of chemistry—organic, inorganic, physical-colloidal and physiological, as well as to the bacteriologist and histologist. The composition of most of the vegetable tannins is unknown; the supposed composition of skin is open to the same questions which other animal tissues offer; convincing evidence as to the exact nature of the forces causing the hydration and dehydration of skin in the presence of acids, alkalies and salts is still to be found; while of the actual mechanism of the combination between skin and tanning material we actually know very little. Important bacterial and enzymatic phenomena are scarcely yet recognized, while histological research is only begun. This condition of ignorance and uncertainty is partly due to the slowness of the tanning industry to appreciate the necessity of fundamental research, and also to the lack of experimental knowledge and the persistency of theoretical reasoning based upon inadequate experimental evidence, together with an insufficient acquaintance with modern science on the part of some workers and inadequate knowledge of tanning practice at the hands of others.

Any attempt to deal with the science of tanning in a quantitative fashion is, therefore, impossible, and an outline of the few known facts, with an indication of their probable significance must, in our present state of knowledge, suffice. We will merely, therefore, first give a brief description of the practical methods of tanning, followed by a statement of the known experimental facts, and then indicate the possible applications of these facts towards a general theory.

PRACTICAL METHODS.

The character of the finished product depends upon the kind of skin employed; thus for example, the heavy skin (or hide) of cattle is generally used for sole, harness, upholstery, or belting leather, while light leathers are made from the skins of smaller animals, such as calf, sheep, or goat. The general steps involved in the tanning of all skins are the same; the differences lie in process details, which are determined by the character of leather desired. The several stages in leather manufacture are: (1) death of animal, (2) curing of the skin, (3) soaking, (4) unhairing, (5) preparation for tanning, (6) tanning, and (7) finishing. We will briefly describe these steps.

(1) *Death of Animal.* Until recently it was not known what a direct relation existed between the time elapsing between slaughter and cure and the value of the skin for tanning. Animals may be butchered in abattoirs or on the farm. The time elapsing between death and curing may be long or short; the significance of this will be dealt with later.

(2) *Curing of Skin.* The object of curing is to minimize the decomposition of the skin after its removal from the carcass, which results from the action of the proteolytic bacteria which cover its surfaces. Three general curing methods are employed: (*a*) drying the skin, (*b*) treatment with a salt, such as sodium chloride, and (*c*) a combination of *a* and *b*. Salt diffuses into the skin and partially dehydrates it. The salt also retards bacterial decomposition.

(3) *Soaking.* Upon arrival at the tannery, the skin is soaked in water or a solution of a chemical for from two hours to two weeks; this time varies with the skin's condition and the class of leather desired. The object of soaking, in general, is to rehydrate the skin and to remove extraneous matter from its surfaces, as well as the salt which it contains, in the case of salted skins. Furthermore, soaking removes certain undesirable protein substances from the skin also.

(4) *Unhairing.* The soaked skin is placed in a saturated calcium hydroxid solution and remains therein, until the hair may be easily removed by mechanical means. The lime solution dissolves or decomposes certain skin constituents, thus loosening the hair. The action of the lime solution may be hastened by the admixture of a soluble sulfid, such as sodium, when double decomposition and hydrolysis ensue, with the formation of sodium hydroxid and calcium sulfhydrate. In addition to its depilatory action, lime swells the skin, and distends and separates the fibrils which compose the corium structure (thus producing greater reactive surface) and partially saponifies the fatty bodies of the skin. It also brings about certain other necessary chemical changes in the skin. Hair and wool removal are sometimes accomplished through bacterial decomposition of certain skin constituents; this process is difficult to control. Unhairing may also be accomplished through the action of certain artificially prepared enzymes on the skin.

(5) *Preparation for Tanning.* When the skin leaves the depilatory solution and has been treated mechanically for the removal of hair, certain epidermal material and adipose tissue, it is prepared for the tanning process proper. This preparation may consist, in the case of heavy skins, of a short

soak in cold water, in order further to hydrate the skin and to partially dissolve its surface lime, or it is given a weak bath of an organic acid, such as lactic, in which a portion of the lime of the skin is removed; this is termed "deliming." In case of light skins, the chemical deliming processes just described may be substituted for by what is termed "bating." This consists, in part, of the action of pancreatic enzymes on the skin, whereby an enzymatic digestion of certain skin constituents occurs and a physical change in other skin constituents is brought about, as recently shown by McLaughlin, Highberger, O'Flaherty and Moore.[1]

(6) *Tanning.* In the case of vegetable-tanned leather, the unhaired skin is placed in a weak, mellow tan solution. This solution is repeatedly replaced by a stronger, fresher solution, until after a period of days, weeks, or months the skin no longer absorbs the liquor components and is said to be "tanned." By the word "mellow" is meant the absence of astringency and this quality ensues upon the ageing, fermentation and decreasing tannin content of a liquor, especially when in contact with skin substance. Thus, as tannage proceeds, the skin comes into contact with increasingly astringent liquor. The tanning process described may be hastened by agitation of the skin and tanning liquor in slowly revolving drums. Mineral tanning consists in treating the unhaired skin with a basic mineral salt, such as basic chromium chloride or sulfate, or with aluminum salts. Tanning may be accomplished by impregnating skin with unsaturated oils, whereby the skin fibers are probably mechanically coated and the subsequent oil oxidation products possibly unite with the skin. Formaldehyde also has the power of uniting with skin and forming leather.

(7) *Finishing.* This process consists in treating the tanned skin mechanically so as to secure a solid, firm body, or a soft, pliable product, as desired; in both cases the proper lubrication of the leather with oils strengthens and preserves it. The dyeing of colored leathers is part of the finishing process.

Experimental Knowledge.

Let us consider first the skin, and second, the tanning materials.

Skin.

Skin is the outside covering of animals and performs several functions, among which are protection of the animal's body, partial regulation of its temperature and the elimination of a portion of the body's waste products. The physical and chemical character of skin varies with the kind of animal, its age, and environment. For example, cattle exposed to the elements and to the rigors of the range develop a thicker, tougher skin than is the case with dairy cattle.

Morphologically, animal skin may be divided into epidermis, corium and adipose tissue. These three divisions are subject to subdivision, which, for the present purpose, need not be considered. The epidermis, or outer layer, is removed prior to tanning proper. The corium is connective tissue, composed of interlacing bundles of fibrils and constitutes the largest proportion of the skin weight. The adipose or fatty tissue connects the corium and the animal body.

The composition of skin has been approximately determined by Rosenthal[2] and also by McLaughlin and Theis[3] and Theis.[4] The isolation of its various protein constituents presents the same difficulties and uncertainties found in the examination of other animal tissues. We can employ empiric biochemical methods and isolate numerous bodies and classify them according to their response or lack of response to the tests employed. Whether distinct compounds are thus isolated is yet to be settled. There is, however, no doubt that the character of the epidermis differs from that of the corium, both physically and chemically. Epidermis is of keratinous nature and differs from the underlying corium both in ultimate composition and in response to distinguishing tests, as well as in its solubility in alkalies. Corium is composed mainly of water and collagen, together with small quantities of elastin, mucoid, and bodies responding to the tests employed for albumin and globulin. Both corium and epidermis contain, also, physiologic salts, and fatty bodies, the amount and character of which vary with the animal's age, sex, and species. Of particular interest is the fact that only a portion of the fatty bodies present in skin is extractable with ordinary fat solvents; the skin must be subjected to hydrolysis before the remainder is extractable. This fact indicates a union of protein and fatty bodies, as shown by McLaughlin and Theis.[5] Unpublished experiments in this laboratory have proved that animal skin contains *glycogen,* which disappears rapidly after the animal's death.

When an animal dies, life processes, as such, cease, but the skin continues to live; that is, the respiration of the skin proceeds for from five to eleven hours, in the case of steer. Shiro Tashiro,[6] working in this laboratory, has found that the length of this period is affected by temperature, whether the epidermis or the adipose surface is exposed to the atmosphere, and by the extent to which the tissue dries out. The various parts of a skin's area differ as to death point and this, in turn, varies with the species and age of the animal. If, under given conditions, a steer skin lives for seven hours after the animal's death, a calf skin lives approximately five hours, and sheep and lamb three and one-third.

Following the animal's death a rapid post-mortem change occurs in its skin; this is evidenced by the formation of non-volatile acid, as shown by McLaughlin.[7] Repeated qualitative tests have shown the presence of lactic acid, though whether lactic is the only acid formed is unknown. The source of the lactic acid is not yet established, but it may be either glycogen or mucoid, or both. Coincident with acid formation is a decrease in the ability of the skin to swell in an alkaline solution, such as $Ca(OH)_2$. Its leather potentiality is adversely affected, also.

Shortly after slaughter, bacterial invasion of the skin also proceeds.[8] Thus it becomes evident that prompt, proper curing of the skin is imperative, since otherwise, as practice has shown, the skin decreases in tanning value; that is, the resultant leather is less in quantity and poorer in quality. All evidence points to the fact that the great bulk of all the chemical changes occurring in skin from the death of the animal until the skin enters the lime are the direct or indirect result of bacterial action.

Only recently has it been shown that if fresh steer hide is soaked in distilled water, a rapid outward diffusion of its mineral constituents occurs. As these salts are lost, the ability of the skin to swell is reduced.[9] On the other hand, if the soaking medium is a "physiological solution" of the skin mineral constituents, swelling power is retained. This finding is analogous to some of the well-known effects of "physiological salt solutions" on other animal tissues. [Ringer's solution is a type. J. A.]

The water content of skin bears a direct relation to its swelling capacity. Salt-cured steer skin contains approximately 40 per cent of water, and, in this condition, has a rather definite swelling capacity. If the skin dries out further before swelling, its power of imbibition decreases uniformly with the extent of such drying, to a certain point.[10]

All evidence points to the fact that before tannage can proceed properly the skin must be hydrolyzed, though the optimum point is still unknown, but is now under investigation in this and other laboratories. This hydrolysis may occur during the time elapsing between death and curing, during curing, or during soaking or liming. We do know that, should hydrolysis become pronounced, the value of the resultant leather is decreased. It is quite possible that the studies mentioned may show a relation between amino and carboxyl (and other) groups and tanning, as well as the effect of de-aminization and de-carboxylization.

The subject of skin swelling is of paramount importance in leather manufacture, because the phenomenon is seen in certain of the important steps of tanning, and because the ability or inability of skin to swell (whether a swollen state is ultimately desired or not) is the best index known of the skin quality. Numerous theories of the mechanism of protein swelling have been formulated and will be dealt with by other authors in these volumes. Suffice it to say here, however, that thus far, unfortunately, none has received quantitative proof as regards *skin* swelling, nor has any influenced practical tanning, so far as we are aware. It is to be hoped that some of the various theories may find future application. It may be that (as has been emphasized by M. H. Fischer [11]) one of the chief impediments towards progress in this field is the fact that many workers endeavor to apply, *in toto,* the findings of experiments on dilute solutions of gelatin or other proteins to systems of the opposite type: water-in-protein. In skin swelling, we do not deal with dilute water solutions of skin protein, but with solid systems, containing from twenty to ninety per cent protein.

Procter,[12] * to whom the science of tanning owes a great debt, was the first to attempt the application of Donnan's Membrane Equilibrium to protein swelling and later with J. A. Wilson evolved a general swelling theory. Jacques Loeb,[13] † some years later, adopted and extended Procter and Wilson's work and derived a theory under which he rather dogmatically states all protein swelling must occur. From the results of his experiments, Loeb contends that only the valency and not the nature of an acid anion determines swelling, provided the internal pH of the swollen jelly be the same for different acids at equilibrium. This internal pH is determined after dissolving the swollen gelatin in a large excess of water, thus forming a dilute solution or system. Thus, under the experimental conditions noted, all acids functioning as mono-basic show equal swelling, while those functioning as di-basic swell one-half. Conversely, all mono-acid bases swell equally, and di-acid bases one-half. In other words, the "Hofmeister series" is illusory.‡ The recent experimental work of other investigators has shown, however, that Loeb's sweeping and dogmatic generalizations must be greatly modified, and that the series of Hofmeister does not, as Loeb repeatedly contends, rest upon any inadequate technique of Hofmeister and his followers. Carefully complying with all of Loeb's experimental conditions, this laboratory [14] has found that the swelling of skin corium is not merely a valency function but is influenced by the nature of the anion or cation employed; Stiasny and Ackermann [15] have confirmed the Hofmeister series in an investigation of the effect of neutral salts on the action of

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* *See* his paper in this volume. J. A.

† *See* Vol. II of this series. J. A.

‡ Loeb's swelling theory, carried to its logical conclusion, holds that, since all mono-basic acids swell equally at the same internal pH, and since this swelling depends upon the ionization of the "protein salt," it follows, then, that gelatin chloride, nitrate, formate, lactate, etc., all ionize equally.

trypsin on skin; Ostwald, Kuhn and Bohme[16] have shown that the swelling of gelatin does not follow the Loeb theory and Gustavson[17] has confirmed the Hofmeister series in the case of hide powder.

It must not be forgotten, however, that the work of Procter, Wilson and Loeb represents the first real attempt to explain the *mechanism* of protein swelling and to derive mathematical laws which will rationally explain the process, thus obtaining a really scientific elucidation. It may well be that future experiments and modifications will clear up the disputed points. It is the author's belief that this must await, however, a clearer understanding of the structural chemistry of the proteins.

Tanning Agents.

Vegetable Tanning. Certain plant tissues contain bodies which, when extracted with a solvent, are termed "tannin." Tannin is characterized by its ability to combine with animal skin. Botanists are not agreed as to the rôle of these bodies in plant life, nor is it clear what relation the extracted bodies bear in composition to the parent substance in the living plant. Tannin remains largely an enigma to the organic chemist, since heating, distillation, or attempts at crystallization have proved impracticable. The tannins have been empirically divided by Stenhouse and others into two groups, characterized by their behavior towards certain qualitative tests. According to one classification of such division, tannin bodies giving blue-black coloration with ferric salts are pyrogallol derivatives, and those giving green-black are catechol. But this division is arbitrary, because many natural tannins seem to be combinations of the two types, and because most phenols and certain of their derived acids behave similarly towards ferric salts. All natural tannins thus far examined yield either catechol or pyrogallol or both, when heated to 200° C. Further classifications have been made by Perkin[18] on the basis of the reaction of the tannins to various reagents and by Freudenberg[19] on the basis of their structural formulas. A detailed exposition of the voluminous literature on the subject of tannin composition would lead us too far afield, and the interested reader is referred to texts on the subject. In passing it should be noted that the classic work on this subject is that of Emil Fischer and his co-workers. Fischer and Bergmann[20] attempted the synthesis of gallo-tannin acid and produced a compound which they showed to be pentadi-galloyl-glucose, which is so nearly related to gallo-tannic acid that the synthesis may be assumed to be complete.

Tannins are, so far as is known, colloidal dispersions, in aqueous solution. All aqueous tannin dispersions are presumed to be negatively charged, in the state in which they are employed in tanning.

The "astringency" of vegetable tannin solutions is of great importance and has been the subject of much speculation. The hypothesis of Procter and Wilson[21] assumes it to be a function of the potential difference of the negative charge of the tannin particle and the positive charge of the skin, as well as the potential difference between the solution immediately in contact with the tannin particles and the bulk of the surrounding solution. Grasser[22] has attempted to throw light on this subject through investigation of the electrochemistry of tannins, but has obained rather inconclusive results. Thomas and Foster[23] have investigated the problem and have measured the potential differences of various tannin solutions and obtained interesting results, though they point out that the values obtained are not absolutely correct. It is probable, however, that potential differences must be considered as one of a number of factors governing astringency. McLaughlin and Porter[24] have shown the specific influence of the presence of added electrolytes in modifying a tan liquor's astringency. Of greatest importance, probably, is the degree of dispersion of the tannin system, to which reference has been made by many workers,* but which has been more especially emphasized by Moeller,[25] by Schultz[26] and by Stiasny.[27] Until recently, no reliable method of dispersion-estimation has been available, but the ultra-filtration experiments of Browne,[28] with certain modifications, promise a practical solution of the problem in the future.

Both laboratory determinations and practical experience have proved that the pH value is one of many factors determining the action of a tan-liquor; considered alone, pH value means little. This is because the "pH" may result from the presence of any one of a number of acidic substances some of which are desirable in vegetable tanning, others being undesirable. Adequate methods for the identification and estimation of these substances have, until recently, been lacking. This need has recently been successfully met by the work of Cameron and McLaughlin.[29]

As we follow the complicated process of vegetable tanning, certain phenomena, at least, are always found. Different vegetable tannins vary in their speed of tanning, and in the qualities they impart to the finished leather. The amount of tannin fixed by hide varies with (1) the concentration of the tan solution, (2) the weight relation of tan solution to hide, (3) the time of contact, and (4) the pH of the tan liquor. Von Schroeder and Paessler[30] showed that tannin absorption by hide is affected by the concentration of the tan solution. Their experiments have recently been repeated and their findings confirmed by Thomas and Kelly.[31] It is the variation of tannin fixation under different conditions which makes a quantitative determination of its reaction with protein difficult. Vegetable-tanned sole leather may contain seventy parts of tannin combined with one hundred parts skin substance and appear completely tanned, yet the author has allowed hide to remain in a typical tan solution for four years and found a fixation of 125.

Mineral Tannins. Many inorganic compounds combine with skin to form leather, the best known of which are the salts of chromium, aluminum, and iron. Salts of the alkali metals and of the alkaline earths produce leather, under a broad definition, but the product is unstable.

Chromium salts have found wide application in the manufacture of certain types of leather, chiefly that made from light skins. Basic chromium sulfate is the salt most employed, although basic chloride may be used also. The skin may be tanned by either the "two-bath" or the "one-bath" process. In the former case the skin is soaked in a solution of sodium or potassium bichromate, in the presence of an acid, for example hydrochloric, whereby KCl and CrO_3 are formed. The CrO_3 combines with the skin which becomes yellow in color. The skin is then passed into a "reducing" solution, that is, a solution of sodium thiosulfate, acidified with HCl, the sulfurous acid formed reducing the CrO_3 to the basic state and the resulting $Cr(OH)Cl_2$ tans the skin, which becomes a greenish blue. In the "one-bath" process a chrome liquor already rendered basic is employed. Some authors contend that the active chrome salt is the basic sulfate regardless of whether hydrochloric or sulfuric acid is used in the reducing solution. The exact nature of the active chrome compound is still an open question. R. W. Griffith[32] considers it

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* *See also* article entitled "Degree of Dispersion as an Influence in Tanning," by J. Alexander, *J. Am. Leather Chem. Assoc.*, August, 1923.

probable that in the one-bath process the chrome salt, either chloride or sulfate, is dialyzed, the hide absorbing the chromium base and liberating the free acid. Many different types of reducing agents may be employed. Well-tanned chrome leather is not affected by boiling water. The chrome process is much quicker than vegetable tanning.

Aluminum salts give less stable leather than do those of chromium, although the aluminum-skin compound increases in stability with time. Alum tannage has a rather extensive use.

Iron salts produce leather which, up to the present time, has mainly been of theoretical interest, since its quality does not compare sufficiently favorably with chrome leather to render the lower cost of iron salts a factor of importance.

Theoretical.

It is only to be expected that a field containing all the complexities of protein chemistry and bacteriology, the little understood tannins and the complications of chrome liquors should be fruitful of hypotheses. Theories of today may tomorrow be obviated by newer knowledge arising in a seemingly unrelated field. It is necessary that this be borne in mind when criticizing those who have had the courage to steer a course.

The investigator in tanning science, like the medical worker, is first confronted with the proteins. No *chemical* theory of tanning will rest upon a sound basis until more is known as to: (1) the initial composition and molecular structure of skin, (2) what protein groups combine with simple electrolytes or with tanning agents, (3) how the liberation or activation of these groups may be brought about and (4) something of the *nature* of the combination between the reactive protein groups and the tanning agent. Any purely *physical* theory of tanning must first prove that stoichiometrical relations do not exist and that the presence or absence of acidic or basic protein groups are without appreciable effects. When the final story is written, it will probably be found that both chemical and physical processes occur and that the predominance of either the one or the other varies with conditions and the type of tanning process.*

Reviewing very briefly the past and present theories of tanning, we may start with that of Knapp, who, in 1858, regarded vegetable tanning as a purely physical process, whereby the skin fibers were "coated" with or by tannin, which prevented their adhesion upon drying. Stiasny advanced the theory that tanning was essentially an adsorption process accompanied by secondary chemical reactions. Fahrion proposed a chemico-physical explanation which included the oxidation of the skin fiber prior to tannage. Bennett regarded tanning as essentially an adsorption process. Moeller advanced a modification of Knapp's physical theory. Wood suggested the purely chemical nature of tanning, assuming the combination of vegetable tannins to be with the amino groups of the skin and chrome with the carboxyl. Wood later abandoned this view, suggesting the reactions to be of the nature of a "colloidal precipitate." All of the foregoing theories lacked satisfactory experimental proof which would enable them to be applied broadly. The advances during the past decade in protein chemistry, physical chemistry and our understanding of valence have made possible investigations which, although by no means complete or con-

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* No sharp line of demarcation can be drawn between "chemical" and "physical" forces. This point is discussed in Vol. I of this series. Broadly speaking *chemical* combination is a special type of the wider physical combination. J. A.

clusive, have greatly broadened our theoretical outlook on the whole problem. Prominent among those who have carried on these researches are Stiasny, Wilson, Thomas, and Gustavson.

The tanning theory of Procter and Wilson, like that of Wood, assumed purely chemical forces to be involved; positively charged skin neutralizing negatively charged tannin, from which the anomalous conclusion necessarily followed that, if chrome tannage were chemical, the positively charged skin and positively charged chromium combined. In attempting to explain and reconcile this contradiction (since skin and chrome are both actually positively charged in tanning practice) Wilson[83] suggested that even though the charge of the skin were predominantly positive there would still remain a small number of negatively charged groups. These groups would be neutralized and precipitated and the further ionization of the protein would continue to furnish this small number of negatively charged groups until tannage is completed. Thompson and Atkin,[84] on the other hand, suggested an explanation in the presence of negatively charged colloidal chromium complexes in certain types of chrome solutions. These points will be dealt with later. Thomas and his co-workers[85] studied the quantitative combination of skin and chrome and assumed 3.38 grams to be the minimum amount of chromic oxide required for the complete tannage of 100 grams of collagen. This is based upon Wilson's[86] assumption that the equivalent weight of collagen is 750, hence $\frac{(152 \times 100)}{6 \times 750} = 3.38$. By varying time of tannage and concentration of chrome liquor, they obtained approximate multiples of this figure up to 26.60 grams, which they describe as an "octo-chrome" compound. Moeller,[87] on the other hand, was unable to obtain any such maxima, but found 37.25 grams Cr_2O_3 fixed per 100 grams collagen from a dilute, and 48.19 grams from a concentrated chrome solution.

A difficulty attaching to the Procter-Wilson theory of vegetable tanning was found in the fact that combination occurred on both sides of the iso-electric point of the collagen; which was, of course, contradictory to the theory.

The more recent studies of Stiasny and his co-workers and of Gustavson have done much to theoretically clarify the disputed points in chrome tanning, while Thomas and his collaborators have discovered important additional factors in vegetable tanning.*

Stiasny[88] summarizes his work with the statement that the migration direction of the chrome complex is of no great importance since a chrome liquor of purely cathodic chrome complexes or one with purely anodic may tan equally well. Of much more importance than the nature of the charge are: (1) the composition of the chrome complex, (2) its stability when dissolved in water, (3) its degree of dispersion and, (4) the existence of free secondary valences; and, if these lead to the formation of molecular compounds on the surface of the skin fibers, adsorption results. His views regarding vegetable tanning are substantially the same as for chrome. Stiasny[89] has also advanced the interesting speculation that the peptones—the building stones of the collagen complex—are very probably held together by a different type of linkage than that of the amino acids within the peptone molecule. Therefore, it is quite possible that the nature of the connections between peptones within the protein molecule is not through groupings which depend upon the saturation of primary valences, but consist of much looser bonds, in which the peptones

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* **See paper by E. Stiasny in this volume. J. A.**

play an independent rôle. It is quite conceivable that this loose connection between the peptones becomes more tenuous during swelling of skin, due, perhaps, to the enlargement of the watery envelope existing around each single peptone molecule. According to this, it is evident that swelling could be regarded as a preliminary stage in the peptonizing—i.e. the decomposition into peptones—of the skin proteins.

The recent investigations of Gustavson [40] have proved of great importance to our theoretical understanding of chrome tanning, and have enabled him to suggest a number of interesting speculations. His experimental results and those of Stiasny confirm each other in many respects.

Gustavson believes chrome tanning to be mainly a chemical process, but feels that it is still an open question whether molecular or primary valency compounds result, although the great stability of chrome leather supports the view of primary valency being involved. He points to the importance of the degree of aggregation of skin protein and its degree of activation (liberation of basic and acidic groups). He, like Stiasny, finds the migration direction of the chrome complex to be of minor importance, but feels that the presence of colloidal chrome constituents is not a general requirement, since purely crystalloidal chrome solutions tan satisfactorily. His experiments indicate that acidic protein groups are the chief vehicle of chrome tanning and basic groups of vegetable, and he shows that tanning skin with chrome increases its capacity for combining with vegetable tannin. This phenomenon is evidently an activation of basic groups, probably by the breaking up of the inner structure of the protein molecule, thus removing acidic groups and liberating and activating the basic. Gustavson [40] is in agreement with Stiasny as to the importance of the constitutional nature of the chromium salts as the principal regulator of its tanning property, but does not feel its degree of dispersion to be of great importance.

As previously mentioned, the Procter-Wilson chemical theory of vegetable tanning, when investigated by Thomas and his collaborators, failed to explain the fact that tannin fixation occurred on both sides of the iso-electric point of the skin protein (collagen). It would have been expected that, since the iso-electric point of skin is at about pH 5.0, fixation would not occur if the acidity of the tannin solution were pH 5.0 or less, whereas experiment showed it occurs in tan liquors as alkaline as pH 11.0. Thomas explains the fixation between 5.0 and 7.7 pH, in the light of the two iso-electric points for skin which Wilson and Kern found, *viz.* 5.0 and 7.7. (This second iso-electric point has been quite properly questioned by Atkin and by the author,[41] who point out that in determining it, Wilson and Kern employed buffer solutions and hence are dealing with two variables: the swelling action of the H^+ or OH^- ion and the antagonistic and shrinking action of the salt present.) Seeking an explanation for the fixation at alkalinities greater than pH 7.7, Thomas [42] showed that "pure" tannin is not fixed beyond pH 8.0. He further showed that commercial tannins contain quinone like bodies and that it is the latter which are fixed at the higher alkalinities. His experiments also strengthen the view that vegetable tanning is largely a combination with the amino (or imino) groups, since deaminization of the protein reduces tannin fixation. There remains a considerable fixation, however, after deaminization, from which we may conclude that, if vegetable tanning is really a chemical process, protein groups other than the amino or imino radicles must be active.

In conclusion we would re-emphasize that any great advances in the pure science of tanning must await a better knowledge of the chemistry of the skin proteins. Numerous research workers are now occupied with the chemistry of skin proteins, chief among which may be mentioned Bergmann and his co-workers. The bacteriology and histology of skin is receiving special attention in this laboratory.

Any significant advance in the technology and practice of tanning will be possible only at the hands of men well trained scientifically, who have also become thoroughly conversant with practical methods of manufacture. Such men will apply the significant scientific work of others. The variables in tanning are many, since no two skins the tanner receives are in the same state. As a result, the great bulk of research work which has been performed with gelatin or hide powder (ground and denatured hide) and the mathematical formulas derived therefrom, constitute interesting reading, but they have had, as yet, practically no bearing on or value in the commercial production of leather.

It is not unreasonable to expect that the next decade will witness the solution of many questions which now perplex us, and that tanning will take its proper place among scientifically controlled processes. The scientific knowledge which will make this possible cannot but be of value in the realm of pure science and in other technical fields.

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Colloid Chemistry and Photography.*

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The Forms of Silver Halide and the Ripening Process.

Silver halide occurs in photographic layers in every conceivable colloid chemical form, from the highly disperse silver chloride of print-out papers, and the so-called "grainless" silver bromide of plates for Lippmann interference photochromy, as also the silver iodide of Daguerreotypes, up to the definitely crystalline grains of high speed "instantaneous" plates.

In pure aqueous solution the highly disperse silver halides can be obtained by ionic reactions in very dilute solutions as opalescent or milky fluids. A. Lottermoser [1] was the first to investigate this thoroughly. Silver chloride, free from binder, and apparently highly disperse, seems to have been obtained by Herschel.[2] He prepared a silver chloride milk from very dilute solutions with special precautions, and allowed it to settle on glass plates. Herschel demonstrated with such silver chloride layers the influence of excess silver nitrate on the sensitivity to light. Victor Schumann [3] used silver bromide free from binder in his experiments on the preparation of plates sensitive to the ultraviolet. All such layers free from protective colloid are very difficult to operate photographically since they easily fog. This has also been described by Herm. Weiss.[4]

Colloid silver bromide has frequently been prepared as a gelatin-emulsion, and in the form of Lippmann emulsion even attained a certain practical significance. A suitable "grainless" emulsion may be obtained by pouring together 300 cc. each of 10 per cent gelatin solution containing respectively 4.5 grams potassium bromide and 6 grams silver nitrate at 35° C.† If only the ripening experiments, now to be described, are to be performed with this emulsion, it may be prepared without harm in full daylight. Nor is it necessary for these experiments to wash the emulsion. While the silver bromide sols free from binder (unprotected) are naturally flocculated by electrolytes, the gelatin emulsion is fully protected against all acids and neutral salts; on the other hand, silver halide *solvents,* such as bromides and especially *ammonia* rapidly exert a strong action. If a little ammonia is added cautiously to samples of the grainless emulsion, and these are then warmed a short time to boiling, the originally clear and transparent emulsion soon becomes opaque and white, and by longer cooking it can be observed without optical instruments that a relatively coarse "grain" has been produced. According to a principle of W. Ostwald small particles have a greater solubility than larger ones; thus the smaller particles present in the original silver bromide emulsion are first dissolved by the ammonia, and opportunity is given to the larger particles for further growth in the solution so formed, which is supersaturated with respect to these larger ones. This process of increase of particle size is termed in photographic technology *ripening.*

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* Translated by Dr. S. E. Sheppard, Rochester, N. Y.

† This is a typical example of double colloidal protection; *see* paper on this by J. Alexander in Vol. I of this series. J. A.

In order to demonstrate the main action in the ripening process very strikingly dry plates, preferably lantern slide plates, may be fumed over ammonia. In this way, in consequence of the slower action the details can be very thoroughly studied. Flat dishes are filled nearly to the edge with concentrated ammonia solution. The dry plates are laid on these, and in the course of a few hours it can be observed that the structure of the silver bromide has altered, ultimately with the formation of a coarse grain. Microphotographs of such structures by the author were reproduced in the *Kolloid-Z.,* **9,** 240 (1911), and a thorough study of the processes was made later by Sheppard and Trivelli.[5] Silver chloride and silver iodide behave similarly. However, the solubility of silver iodide in ammonia and its consequent tendency to increase of particle size is small, while the ready solubility of silver chloride corresponds to a very considerable tendency to coarsening of the grain, which is of particular importance for printing-out processes.

Most commercial high speed dry plates show on sufficient magnification in the microscope definitely crystalline forms or at least the transition from more spherical structures to tetrahedra and octahedra.[6] These forms represent the end-product of the ripening process, consisting in a *recrystallization* of the silver bromide.

Silver bromide precipitated from aqueous solution can be broken down again to homogeneous uniform emulsions of colloid particles by *peptization;* to effect this the precipitated silver bromide is warmed with gelatin and soluble bromide or ammonia. Such peptized layers give a very remarkable characteristic curve and pronounced tendency to *solarization.*[7]

To prevent false impressions it must be noted that in the industry ripening is not carried out by starting with such a highly disperse silver bromide as is present in the Lippmann emulsion. The high dispersity of the "grainless" emulsion is obtained by securing a very small amount of silver bromide for a large amount of gelatin, and a low total concentration of silver bromide. It is true that the solubilizing ammonia can effect in this case a very considerable increase of grain, but nothing like to the extent desired for high speed emulsions, because the "nucleus range" is not sufficiently large enough to attract sufficient "nutrient material." In practice emulsion layers are used in which about 2 to 3 parts of gelatin at the most are used with 1 part of silver halide, while in grainless emulsions the gelatin content is much greater. Consequently in the preparation of coarse-grained emulsions the precipitation is effected at the start with much higher concentration of silver salt, and a fairly coarse grain is immediately obtained. The concentration ratios in general play in emulsion technique, a very special rôle, which has however, like everything else, up till now been only empirically recognized.

The totality of the practically attainable increase of sensitiveness of gelatino-silver bromide has another very important component beside the increase of grain size; this consists probably in a purely *chemical* action of the gelatin solution on the silver bromide, namely in a trace of *reduction.* The reduction theory of ripening first proposed by J. M. Eder, R. Abegg and other investigators was more exactly studied by the author[8] and its correctness shown in a very simple manner. If finished dry plates are treated with suitable silver solvents, e.g. chromic acid solution, it is found that with increasing ripening the silver bromide layers appear to contain increasing amounts of silver, although quite minute and naturally not detectable analytically, which are removed by the silver solvent. With the removal of these reduction nuclei the light sensitiveness of the layers sinks, for high speed plates to one-thirtieth or one-fortieth, for less ripened ones to a correspondingly less amount. A control experiment with a plate of very low degree of ripening, which showed no loss of sensitiveness on similar treatment with silver solvents, shows that no secondary process is responsible. In order to give at least some approximate numerical ratios, it may be remarked that the increase of light sensitiveness of the grainless Lippmann emulsion up to approximately 500 to 1,000 times takes place without reduction of the silver bromide, but that the last and highest degree of sensitizing is apparently to be ascribed chiefly to traces of reduction. For such grains already superficially reduced a smaller amount of light can afford the minimum (threshold value) of silver nuclei necessary for the initiation of the development process, than in layers of grains, which do not contain the traces of silver due to ripening.

For further particulars on the ripening process and the rôle of the gelatin thereby see *Sheppard* and *Mees,* "Investigations on the Theory of the Photographic Process," London, **1907.** Lüppo-Cramer, *Kolloid-Z.,* **10,** 182 (1912).

THE PHOTOHALIDES AND THE LATENT IMAGE.

If the sols of the silver halides are coagulated in the presence of colloidal silver, e.g. by dilute sulfuric acid, and the mixed gel thus obtained treated with nitric acid, there are obtained beautiful red, blue or violet colored substances, the so-called *photohalides;* these contain, according to their mode of preparation, small amounts, never more than fractions of one per cent, more silver than the formula weight of the silver halide. Exactly analogous photohalides may be obtained by direct adsorption or dyeing of silver halide with colloid silver. These colored silver compounds are nothing more than adsorption compounds, in which the silver bromide has taken over the rôle of the fiber in the dyeing process.

Even before the investigations of the American, M. Carey Lea,[9] to whom we owe the first information on the preparation and properties of these photosalts, it was known that the colored products formed by illumination of silver chloride and silver bromide are notably resistant to oxidizing agents. Carey Lea recognized at once therefore, that his colored silver salts, obtained without light action, by purely chemical means, must be identical with the photochemical products; for this reason he termed these salts quite generally photo-salts: photochloride, photobromide, photoiodide.

Carey Lea himself, and most other investigators in photographic chemistry assumed that in the *photohalides* there was contained not silver but a *subhalide.* Since in the meantime the controversy over this question has been decided quite in favor of the author's silver adsorption theory, it is quite unnecessary to discuss the old question again in any detail. The author's theory[10] is considered today so taken for granted by many writers as to be self-evident, that the writer is generally not named in connection with it; it is necessary, therefore, to recall the fact that it was first necessary for me to carry on a campaign lasting years for the recognition of the adsorption theory. The *suggestion,* that in the photohalides and the latent light image not hypothetical subhalides, but silver must be contained had indeed often been expressed (R. Abegg, R. Lorenz) but many purely photographic reactions seemed to speak against the conception. [*See* paper by R. Lorenz, Vol. I, this series. J. A.]

I was able to produce the photohalides in the form of regular homogeneous gelatin emulsions. Such an emulsion is the only material with which the reactions occurring in photography can be carried on, since the salts, free from protective colloid, change too rapidly and irregularly on reduction for a thorough study of the phenomena to be possible with them.

The synthetically prepared photochloride and photobromide layers were rapidly reduced by the developer without exposure to light, provided that in their preparation the excess silver was not removed with too strong an oxidizing agent. It was, in fact, discovered that it is not the *insoluble firmly adsorbed* silver which induces development, but chiefly the portion of the adsorbed silver which is still soluble in strong chromic acid, etc., and which acts as nucleus. Quite similar relations are found with the latent image; it is partially destroyed by oxidizing agents, but another part remains undestroyed. This is what we find with many other adsorption compounds of quite different chemical nature.

Fuller details concerning the photohalides may be found in: Lüppo-Cramer, "Kolloid Chemie und Photographie," 2nd Ed., Dresden, **1921**. On crystallized photohalides compare the interesting investigations of W. Reinders, *Chem. Weekblad.* **1910**, Nos. 46 and 48; also Lüppo-Cramer, *Phot. Korr.* **1911**, 311; *Kolloid-Z.* **2**, 297, 353 (1908). For the simplest methods of preparing Carey Lea's photohalides, see *Kolloid-Z.* **2**, 361 (1908). On the development of photohalide emulsions and their color sensitivity, *Phot. Korr.* **1909**, 273, 397, 415, 426, 493, 526; **1910**, 128; **1911**, 33, and *Kolloid-Z.* **7**, 304 (1915). On photobromide formation by ripening, *Kolloid-Z.* **17**, 26 (1915). On the quantitative and topographic relations of the latent images and the reaction of nucleus exposure, *Kolloid-Z.* **12**, 42 (1913). A comprehensive study by the author is: "Das latente Bild," Halle, **1911**.

On the so-called color adaptation of the photohalides compare Lüppo-Cramer, "Kolloid-chemie und Photographie," 2nd ed., Dresden, **1921**, p. 7.

ADSORPTION PHENOMENA AND PROTECTIVE ACTIONS WITH THE SILVER HALIDES.

As is well known, A. Lottermoser has shown that by ionic reactions in very dilute solutions silver bromide sols may be obtained of *opposite charge* according as an excess of silver salt or bromide is present.* If the positively charged silver bromide sol with silver salt excess is required, the bromide salt solution must be poured into the silver salt solution; to obtain the negatively charged silver bromide sol with bromide excess, the opposite procedure is necessary. Such oppositely charged silver bromide sols, according to the author's investigations, behave remarkably differently toward *dyes:* Basic dyes flocculate the negatively charged silver bromide sols prepared with excess bromide, but not those with excess silver salt, while acid dyes behave the other way, i.e. flocculate the sols prepared with excess silver salt, but not those with bromide excess.[11]

As the silver sol prepared according to Carey Lea's ferrocitrate method is negatively charged, it precipitates a positively charged silver bromide sol at once and so forms in the simplest manner a photobromide with all its characteristic properties. Basic dyes also precipitate photobromide from a mixture of similarly charged (negative) sols of silver bromide and silver.

The *protective actions* of dyes are also interesting. These phenomena were first described by the author, and later confirmed by others. The protective action of the dye is particularly notable when opposed to the ripening action of ammonia in a highly disperse gelatino-silver bromide emulsion; it is, however, very general, both with basic and acid dyes, and independent of the sign of the charge of the silver bromide. The only condition is that the dye be not used in too small amounts.

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* *See* paper by A. Lottermoser in Vol. I of this series. J. A.

To 200 cc. portions of 5 per cent gelatin there were added respectively 7.2 cc. of 10 per cent KBr solution and 10 cc. of 10 per cent $AgNO_3$ solution. The silver salt solution was then poured into the bromide solution at 45° C. For each experiment 100 cc. of such highly disperse grainless emulsions were mixed with 10 cc. of a dye solution 1 : 1000, and then 0.5 cc. ammonia (sp. gr. 0.91) added. The dye-free control emulsion was treated with 10 cc. of water or alcohol, according to the solvent of the dye, to equalize the volumes.

While the dye-free emulsion became turbid immediately after the addition of the ammonia, and in a few minutes completely opaque at the thickness of a test tube, the dyes hinder the ripening of the silver bromide practically completely, even after 24 hours standing of the emulsion at room temperature. The actual protective colloids such as gelatin, albumen, etc., act similarly, but the action of dyes is stronger than that of albumen.

The enormous protective effect of dyes against the ripening of the highly disperse silver bromide by ammonia within a gelatin emulsion is of particular interest. The ripening of silver bromide by ammonia is one of the most typical "Ostwald ripening" effects, i.e. increase of particle size by intermediate solution. The interference with this ripening might take place in two different ways: either the velocity of solution, or the renewed crystallization might be affected by the dye. W. Reinders has already shown, in dealing with the retarding action of gelatin on the reduction of silver chloride, that the rate of solution of silver chloride in ammonia is *not* retarded. Consequently Reinders sees in the retarding action on the reduction a prevention of the crystallization of the silver from its supersaturated solution, after the fashion indicated by the investigations of R. Marc on the crystallization of potassium sulfate and other salts from dye solutions. The peculiarly strong interference with ripening due to dyes in the experiments described, is probably to be referred less to a reduction of solubility than to an influence on the recrystallization of the transiently dissolved silver bromide on the nucleus surfaces, contaminated by dye, i.e. on a poisoning of nuclei, in the sense of *G. Bredig.*

The adsorption of the dye by the silver bromide and the effect on the crystallization process are naturally of importance for *optical sensitizing* of photographic plates; furthermore, the retardation of development by dyes, discovered by the author in the course of the development of his *desensitizing process* with dyes [12] belongs in this region of phenomena.

Colloid Silver.

The methods of preparation and properties of colloid silver are sufficiently dealt with in the general literature of colloid chemistry, so that it is unnecessary to describe them here. A silver sol sufficiently pure for many photographic purposes may be obtained most simply and surely by Carey Lea's reduction method with alkaline dextrin solution. Lea dissolved in 2 liters of water 40 grams caustic soda and 40 grams dextrin (the yellow form is much preferable to the purified) and adds to this a solution of 28 grams of silver nitrate. A transient turbidity due to silver oxide rapidly gives place to a quite clear brown-red colored silver sol. From long experience I recommend taking only half as much water for the solution of the dextrin and of the alkali and when the reduction has taken place to precipitate the colloid from solution with an equal volume of alcohol and then to redissolve it in water.[13]

The author first gave a method of preparing all the colors of colloid silver in gelatin in *durable form as a color scale.*[14] For this purpose it is not necessary to purify the nuclear silver sol; one proceeds as follows:

Add 20 cc. of 10 per cent caustic soda solution and 45 cc. of water to 20 cc. of 10 per cent solution of yellow dextrin. Then add 15 cc. of 10 per cent silver nitrate solution.

A purified gelatin is prepared by thoroughly washing emulsion gelatin with distilled water. 20 cc. of 10 per cent silver nitrate solution are added to 500 cc. of the 2 per cent gelatin solution at 30° C., and 5 portions each of 100 cc. are measured off.

The above-mentioned unpurified silver sol is diluted 30 times; of this there is added to the 5 portions of silver nitrate in gelatin solution (a) 10, (b) 0.5 cc. (c) 2 cc. (d) 5 cc. (e) 10 cc. Then to each mixture is added 4 cc. of 10 per cent hydroquinone in alcohol.

After some 20 minutes the reaction is ended; by transmitted light the preparations appear: (a) gray-blue, (b) blue, (c) red, (d) yellow-brown, (e) green. By variation in the amount of innoculating sol all intermediate color steps may be obtained. After dilution of the freshly prepared sols with an equal volume of 10 per cent gelatin solution and drying on glass plates, much finer colors are obtained, the whole scale being pushed to the blue end of the spectrum: the yellow brown sol appears red, the red violet to blue, the violet blue; the green sol, however, becomes a reddish brown, reverting to green on moistening. As a side issue it may be noted that the color of the sols depends on the kind of gelatin, its content of chlorides and phosphates. For further investigations of the colors of silver, see: *Kolloid-Z.* **8**, 97, 240 (1911); **9**, 73; 14, 186 (1914); *Phot. Korr.* **1915**, 1, 136. See also *K. Schaum* and *H. Lang, Kolloid-Z.* **28**, 243 (1921); *K. Schaum and Th. Marx, Kolloid-Z.* **31**, 64 (1922).

In the ordinary photographic processes this very markedly colored silver occurs chiefly only in the printing out *process* and in the form of *dichroic fog.* In *print-out* layers we have to deal with silver chloride of very high dispersity, on the border of microscopic visibility. Consequently the silver particles which can be formed on reduction are very small. On exposure to light only red to violet and blue tones are obtained. If, however, certain unripened emulsions are thoroughly washed with distilled water before exposure, which removes all organic silver salts, then the residual silver chloride turns orange yellow.[15] The color of the unfixed print-out paper is always unitary, i.e. the more strongly exposed portions of the image do not show any different color from the more weakly exposed. On the other hand, the author[16] was able to obtain on certain gelatino-silver bromide plates of medium size of grain, after impregnation with silver nitrate, a scale which after fixation showed all colors from yellow over red to blue, proceeding from the least to the most illuminated fields.

On certain unfixed gelatino-silver chloride print-out papers it is possible to obtain pure *black* silver by "light ripening," if the layers swollen in water vapor are exposed in a humid atmosphere for a long time to sunlight.[17] Black silver of this kind is peptized by simply warming in water, to a yellow silver sol.

The tinting of silver halides with colloid silver, leading to Carey Lea's photosalts, can be regarded as exactly analogous to dyeing. The analogy goes so far, that silk and wool can be dyed with colloid silver.[18] In the product obtained by dyeing the silver halide with silver the silver behaves so far like a dye that the silver halide becomes *optically sensitized.* This discovery was actually made by Ed. Becquerel in 1840, hence 30 years before the discovery of orthochromatic photography. It is true that in this case even up to the time of H. W. Vogel people were satisfied that the hypothetical subhalides were in question. Becquerel found incidentally that print-out papers, i.e.

layers having beside silver chloride a soluble silver salt, were intensified by a subsequent exposure under yellow or green glass, i.e. "developed." This experiment succeeds with any commercial printing-out paper. The author[19] published pictures, as given by such an experiment following Becquerel.[20]

Synthetic photohalides also show sensitivity over the whole visible spectrum and beyond, so that J. M. Eder[21] on the basis of his spectrographic experiments made with my preparations termed *colloid silver an ideal panchromatic sensitizer.* It is of special interest also that X-rays and similar forms of energy induce the panchromatizing of silver bromide more easily than ordinary light,[22] which goes to show that the silver formed by these rays has a higher dispersity than that due to light. In all the optical sensitizing effects produced by radiant energy the original subdivision, or size of grain, of the halide plays a great part. Compare Lüppo-Cramer, "Die Röntgenographie," Halle, **1909.**

In certain abnormal variations of development there is formed in place of the ordinary black silver gel a more or less *colored* silver. Such colored forms may also be produced in gelatino-silver halide in absence of photo-nuclei, and lead to the so-called *"colored fogs"* or *dichroic fogs.* In practice colored fog occurs mostly in consequence of contamination of the developer with the fixing "hypo," but also when a much diluted developer, or a slow-working developer containing much bromide works too long on a plate or paper.

Since the silver is yellow at its greatest dispersity, and with increasing particle size becomes red, violet and blue, there may be observed in the formation of this colored fog the transition yellow, red, blue, as the fogging increases.

A heavy production of dichroic fog on underexposed plates often leads to a special kind of *reversed* images, since the colored silver reduced in the unexposed parts of the image gets a greater opacity than the normally produced black silver in the exposed regions. This reversal phenomenon is termed "pseudo-solarization."[23]

Fundamental studies on the forms of silver occurring in photographic processes were published in 1895 by R. Ed. Liesegang,[24] and extended later by Lüppo-Cramer.[25]

ADSORPTION PHENOMENA IN THE SILVER OF NEGATIVES.

It has already been remarked that negatively charged silver sol is flocculated by positively charged silver bromide sol. In quite analogous manner the silver sol is precipitated by all *basic dyes.* This action of basic dyes on colloid silver explains both a peculiar acceleration of development due to basic dyes, as also a fogging action of basic dyes sometimes occurring with high speed plates. These reactions are of practical interest for work with color-sensitive plates.[26]

Both silver sols and the gels formed therefrom by coagulation absorb thiosulfate strongly. The black silver of photographic negatives also adsorbs thiosulfate. If normally developed negatives are first hardened in chrome alum prior to fixation and then fixed, with definite precautions, in concentrated alkaline bromide solution, it is possible to obtain the silver of the negatives free from adsorbed substances. If such images are then bathed in thiosulfate solution, thoroughly washed, and then the silver dissolved by means of chromic acid mixture, nitric acid, or persulfate, there remains a strongly yellow-brown colored residue, which on closer investigation is found to be *silver sulfide.* This residue, mixed with silver halide, is present in every negative as usually fixed in thiosulfate.[27]

Special investigations by the author have further shown that the adsorption of thiosulfate by the silver of the negative is in the last instance the cause of the *characteristic reduction process* with *persulfate.* The silver of a negative is in the more faintly exposed portions more finely divided (of greater dispersity) than in the high lights. The shadows therefore adsorb relatively more thiosulfate than the high lights, consequently the high lights are more rapidly attacked than the shadows. I can only refer here to my very numerous papers on this question, in which several peculiar reactions of the "negative" substance are described. The gist of it, and literature references are to be found in a summary article by the author in *Phot. Korr.* **1914**, p. 241; in this the interesting papers of Stenger and Heller are comprehensively cited and reviewed. Quite recently papers have appeared, in which the persulfate problem is thoroughly discussed in connection with the views of *Stenger* and *Heller*, on the one hand, and of the author, on the other. These articles are by G. I. Higson[28] and S. E. Sheppard.[29] While the former seems to give preference to the catalytic theory, Sheppard, on the basis of his very extensive investigations, is more inclined to Lüppo-Cramer's conception.

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Colloids and Photochemistry

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The relation of colloids, as disperse phases of matter, to photochemical change is an intimate one, and important both in nature and for industry. Absorption of light and photochemical reaction commence at the surface of a system; since colloids are distinguished by large surface development, opportunity is given for a relatively more uniform and effective action of light, above all in the cases of solids and of liquids of high viscosity, where equalization of action is not readily effected.

A large factor in this is what is known as *irradiation,* or diffuse internal reflection. Consider a block of homogeneous solid, with a plane surface exposed to light. If, as frequently happens,* the photo-product itself has a greater absorption of the active light than the original reactant, then the photolytic action is soon brought to an endpoint or stationary state. Suppose on the other hand that the same mass of material be broken up—dispersed, into particles suspended in a transparent medium. Light will penetrate further into the system by internal reflection, from one particle to another, and a greater amount of photolysis become possible. However, it does not follow that this increase will become a maximum for particles of colloidal dimensions. In the case of substances which are poor conductors of electricity, and therewith have relatively low absorption coefficients (for light), when the particles approach in dimensions to a wave-length of light—say about 500 $m\mu$—then the phenomena of diffraction become very important. Light waves whose lengths are several times those of the particles pass around and through, while the shorter waves of dimensions of the same order or less than those of the particles are much more deviated and reflected. According to the Rayleigh's theory of scattering, the extinction of light in such a turbid medium is given by the formula:

$$I = k\frac{n v^2}{\lambda^4}$$

where I is the intensity of light, n the number of scattering particles per unit volume, v the volume of a particle, λ the wave length, and k a constant. This formula has been found to hold[1] fairly well in the case of non-metallic (non-conducting) particles small compared with the wave length.

Few or no attempts seem to have been made to determine the possible *increase* in light consumption by a photo-sensitive system of this character, compared with a less disperse system. The problem is complicated by conditions of relative sensitivity of the particles themselves, and the (true) selective absorption. Data and mathematical treatment will be found in papers by F. E. Ross.[2]

We have prefaced this sketch with these rather photophysical than photochemical considerations because the fundamental photochemical law, the specific application of the principle of conservation of energy, is the law of absorption; only the light which is absorbed by a substance is photochemically

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* For example, in the darkening of silver salts in light.

active.[3] It is from the marriage—if originally little more than a *mariage de convenance*—of this principle with the law of mass action that there are obtained the formal equations of photochemical reaction *kinetics*.[4] Moreover, it is by the discovery of the mechanism of light absorption by the atom, the molecule, and the molecular aggregate, that there will be obtained the basic and intimate law of photochemical *energetics*. The known principle of *photochemical equivalence*, due to Einstein,[5] is a weighty contribution, which may be regarded as the nucleus on which the working theory may be crystallized out, rather than the final law. It is possible that it is in the hitherto somewhat neglected field of photochemical kinetics in *colloid* systems that some of the missing elements of photochemical, and even photophysical, theory will be found.[6]

An indication of this is perhaps given by the number of cases in which the photochemical change in initially homogeneous systems appears to involve as first step the production, in gases or solutions of "reaction nuclei." In this connection then may be cited particularly the work of F. Weigert [7] on photochemical reactions of solids are actually reactions at a gas-solid interface; densation phenomena produced in gases and vapors by ultra-violet light and X-rays [8] properly belong here. In fact, we may note that in much recent theory of chemical reaction velocity and catalysis [9] the suggestion is made of the existence (but without discussion of the origin) of a reaction-nucleus [10] in which many molecules of both reactants and products are conceived as gathered in quasi-monomolecular unity.

If we endeavor to disentangle how much is to be assigned here to the molecular structure of gases and liquids, on the one hand, and to the nature of radiation, on the other, we find a situation resembling that typified in the riddle of the hen and the egg. Admitting the kinetic theory of gases and liquids, then the statistical theory of fluctuations applied to these provides for minute random and transient aggregates of molecules [11]—which tend to be "ripened" or "developed" in the neighborhood of critical points, e.g., critical temperatures of liquefaction or of desolution (precipitation). These systems are, in colloid terminology, iso-colloid, or at least, iso-disperse. On the other hand, if light or directed radiation, fall on a gas, it would seem probable that such aggregates would be the initial reaction nuclei. For in them the density of radiation would be increased, and propinquity would permit greater catalytic effects. On the other hand, if a discrete, quantum character be verified for radiation (in transmission) the *chance* of effective impact of a quantum on a molecule might *originate* such groups, or again, would increase as such "groupings" occurred.

In all gas-reactions, surfaces of contiguous solid phases, e.g., of containing vessels, may play a dominant part. Since the phenomena at surfaces involve *adsorption*, a colloid chemical factor exists here.*

In the green-leaf synthesis of carbohydrates, the surface relation of the chloroplasts to the CO_2 is of capital importance. Bovie [12] has suggested that adsorption and orientation of CO_2 molecules is an initial phase of the process. The great importance of traces of gases for the photoelectric sensitivity of metals [13] should be noted. Conversely, it may be remarked that many photochemical reactions of solids are actually reactions at a gas-solid interface; where too little attention has been paid to the gas-phase.[14] Oxygen, and more still, ozone, can play a part in the photochemical decomposition of the silver halides.[15]

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* To be weighed in the light of the Langmuir-Harkins theory of orientation in monatomic and monomolecular layers.

Summarizing roughly the foregoing: in systems of the type gas/solid, there are formally two classes (1) where the gas is contained or dispersed in the solid (2) where the solid is dispersed in the gas. In principle, no difference exists in regard to colloid factors influencing a photochemical reaction; these factors are adsorption and dispersity, and while increase of dispersity permits a higher integral adsorption, it is adsorption which maintains dispersion. Where solid catalysts are used in photochemical gas reactions, it is probable that greater relative efficiency could be secured by subdivision of the catalyst down to colloidal dimensions and circulation in the insolating vessel.

In systems of the type: gas/liquid, similar postulates are admissible. The apparent production of heterogeneous photocatalytic nuclei in gases may occur entirely *de novo,* or may be a kind of photo-ripening of molecular associations or groupings occurring in any case according to the principle of fluctuations.

SPECIFIC PHOTOCHEMISTRY OF COLLOIDS.

In the following a number of specific photochemical reactions of colloids are noted without attempt at exhaustiveness. For convenience they will be described under two main heads: (1) Photo-peptization and photocoagulation; (2) Photosensitizing.

(1) Many instances have been reported of change of dispersity produced by light. Bredig and Pinsel [16] suggested that the developable "latent image" in photographic plates was due to a mechanical disintegration of silver halide crystals. Actual disintegration is observed in a case of silver iodide; the phenomena were fully studied by C. Schultz-Sellack [17] and later by H. Scholl.[18] A very thin continuous layer of silver iodide is obtained by exposing a silver mirror to iodine vapor. This becomes turbid and varicolored on exposure to intense light, and is easily shown, as for example by rubbing,[19] to be actually mechanically disintegrated. Scholl (*loc cit.*) showed that the action is catalyzed both by iodine and by oxygen. At one time it was believed [20] that this and other such disintegrating or peptizing light-actions were due to a direct mechanical effect of light on matter. In 1910-11, The Svedberg observed [21] that a number of metals—mercury, silver, lead, copper, tin—could be disintegrated quite rapidly by ultra-violet and X-rays, more slowly by ordinary light. "If a pure silver plate is laid in a flat glass dish, covered with a thin layer of water or pure alcohol, and exposed at a distance of a few centimeters to the rays of a Heraeus quartz-mercury arc, after a few minutes the liquid shows in the ultra-microscope the characteristic appearance of a colloid solution." However, the mechanical disintegration is really the consequence of a preliminary photochemical reaction. It was found by Nordenson [22] that there is initially a photochemical oxidation process—involving peroxide formation. Similarly the photo-disintegration of silver halides follows the photochemical liberation of halogen, and may be regarded as caused by the pressure of the released halogen.[23] With photopeptizations may be classed, if only *pro forma,* the reduction in viscosity of cellulose solutions and of rubber sols. M. Nakano [24] states that the viscosity of cuprammonium solutions of cellulose is much affected by exposure to light; it is suggested that depolymerization of the cellulose aggregate is brought about, but it is known that the presence of oxygen has much to do with the change of viscosity.[25] Solutions of nitrocellulose, in acetone and other solvents, lose viscosity, and the solid breaks down, in ultra-violet light.[26] The influence of light, particularly ultra-violet light, in depolymerizing rubber, and thinning rubber sols, has been frequently

observed. H. P. Stevens[27] has noted that the syneresis of vulcanized rubber gels in benzol is increased by light.

A very old photographic reaction which has important colloid chemical aspects is the insolubilization of asphalt by light. Nièpce, early in the nineteenth century, coated sheets of metal with a solution of asphalt in lavender oil; he found that the parts exposed to sunlight became insoluble in the usual solvents, whereas the unexposed portions became soluble. J. Errera[28] has quite recently shown that the most sensitive fraction of asphalt, considered as a polydisperse system, is not that in molecular dispersions, but the colloid disperse portion. "When chemically analyzed, this colloidal part appears to be richest in sulfur, the valences of which being a factor of polymerism. According as their degree of association is greater or smaller we find in asphalt the intermediate stages between molecular and colloidal asphalt. Sunlight seems to have a coagulating action."

Numerous examples of what is broadly termed "photocoagulation" are known. The action of ultra-violet light in colloidal platinum sols was observed by E. B. Spear and coworkers.[29] Exposure to a 220-volt Cooper-Hewitt quartz-mercury arc at 15 cms. greatly accelerated coagulation of a Bredig Pt-hydrosol, 10 hours being more effective than 6 months to daylight. Coagulation by NaCl was accelerated by ultra-violet light. The action of tropical sunlight in coagulating colloidal metal sols was observed by P. P. Gangaly and N. R. Dhar.[30]

Hydrosols of sulfides and oxides were also coagulated in 60 hours in the absence of protective colloids. With the photocoagulations may perhaps be classed E. Hatschek's[31] observation of anomalous Liesegang stratifications produced by light, as when $Pt(NO_3)_2$ is allowed to diffuse into agar gels containing KI. Alternate extra wide and normal bands were produced in light—diurnal illumination—which were absent in darkness, the extra wide bands being superimposed on those of normal width.

The coagulating effect of ultra-violet light on albumen and other proteins is well known.[32] In some respects analogous to photocoagulations, but commencing with molecularly dispersed systems there may be mentioned the important group of photopolymerizations and condensations of organic compounds,[33] of which several lead to essentially colloid bodies.

(2). *Photosensitizing* (Photocatalysis)

It is probable that many photocoagulations may be regarded as initiated by photoelectric effects, i.e., neutralizations of positively charged micelles by photoelectrons. These may be emitted either by the substance itself or by a sensitizer. Thus N. P. Peskov[34] finds that anthracene exerts a sensitizing action on the coagulation of hydrosols of Pt, or As_2S_3 and other substances; he suggests that such colloids could act as indicators for photoelectric effects. As attention is directed to the subject, it is likely that many more instances of the relation of colloid subdivision to photocatalysis will be recognized. M. C. Zenghelis[35] has observed that the activity of gases is increased by fine subdivision; CO_2 is reduced by H_2 when the gases are dispersed by passing through porous membranes, formaldehydes and reducing sugars being formed. It is stated that the reaction is accelerated by light. R. Audubert[36] states that on diluting alcoholic solutions of sulfur with water, light of short wave length speeds the agglomeration of the particles formed, light of long wave length (beyond the yellow) retards it. H. Freundlich and A. Nathansohn[37] find that sols of As_2S_3 are more sensitive to electrolytes after illumination. Colloid sulfur is formed. The increased electrolyte sensitivity is found in the dark after insolation, a marked case of photosensitizing. This is in some ways analogous to the cases of photosensitizing in gases noted by Weigert (*loc. cit.*). A more typical case of the production of a colloidal (heterogeneous) catalyst by photochemical reaction in a solution is shown by the decomposing action of light—especially ultra-violet—on hydrogen peroxide in potassium ferrocyanide solution.[38] This continues after insolation has ceased, due to the formation of a hydrous ferric oxide catalyst.

In this connection it may be noted that a vastly important rôle, as photocatalysts active in the evolution of living from non-living matter, was assigned by B. Moore [39] to colloidal oxides of metals. Experiments of A. Bauer and A. Rebmann [40] have, however, failed to confirm Moore's specific results with colloidal uranyl and iron oxides as photocatalysts in the formation of formaldehyde from CO_2 and water.

From what has been said so far, it appears that the photochemical reactions of colloids are determined by the light-sensitivity proper to the molecule of the substance, but modified by the colloidal condition of this. The plenitude of colloid chemical aspects in photography illustrates this (q.v.) for the photochemical reduction of the silver halides.

Colloids and Phototropy.

In a text-book of photochemistry, published in 1914, the present writer drew attention to the greater probability of phototropic accommodation in the colloid state of matter.[41] This was stated in very generalized terms, but it is at least gratifying to find that an important rôle has been assigned quite independently to the colloidal state in relation to photochemical change by F. Weigert [42] and this in consequence of his recent remarkable discoveries on the action of polarized light. In certain systems, namely gelatin emulsions of photochloride of silver, and dyes in collodion, plane-polarized light produces changes most succinctly described as "adaptation of the material system to the color and polarization of the exciting radiation." It is pointed out by Weigert that photochemistry, and indeed chemistry in general, in their present development, have no specific category for such changes, which are in essence identical with *physiological adaptation*. Ultramicroscopic experiments on the photochloride systems [43] have shown that the individual molecular species present have as such nothing to do with the adaptation. No quantitative chemical change could be detected, and it was concluded that the changes occur between numerous neighboring molecules associated in very small micelles. In well-developed, pure crystals, the condition of completely haphazard molecular orientation (molecular chaos) is not fulfilled, so that accommodation to a given color and vibration plane is never possible. Provisionally Weigert interprets these modifications of matter by radiation to a "photokinetic deformation" of the electron orbits of neighboring molecules. None the less he properly indicates their fundamental connection with the primary events in photochemical change. In the writer's opinion, the existence of a true photomechanical action of light on matter, interdependent with but not resultant on photochemical change, must still be regarded as awaiting proof.

As we have seen, much supposed evidence for direct photodispersion of colloids has been found inadequate (*vide supra*). In the discussion concerning photo-accommodation by the writer [44] color adaptation was associated with the colloid state of the photo-halides in a very general way, although a fairly definite synergy of photomechanical and photochemical actions of the absorbed energy was proposed. A much more explicit scheme was proposed by Weigert, with adoption of the Einstein quantum equivalence principle (as regards absorption). Weigert has proposed [45] that the quantum of absorbed energy may be regarded as taken up partly as increase of inner energy, partly as increase of translational (kinetic) energy of the molecules:

$$h\nu = \Delta E_i + \Delta E_k$$

the increase of inner energy, ΔE_i, conceived as an inner photoelectric effect, constitutes the primary photochemical even, while ΔE_k, the increase of kinetic energy, is the part inducing the photomechanical changes.

While the writer is at present unconvinced of the existence of a direct photomechanical or photokinetic potential of light on matter, the importance of Weigert's demonstration of adaptation remains unaffected. Biologically, these investigations may be of great significance in regard to the development of pigmentation in organisms, and of optical sense organs. At the commencement, a local pigmentation sensitive to light—it is to be asked how in the vegetable kingdom this develops into the main mechanism of nutrition, in the animal kingdom into the principal sense directing locomotion.*

The great field of the effects of radiation upon organisms [46] necessarily requires much further specific work upon the action of light of colloids. The important work of Selig Hecht [47] has shown that many physiológical adaptations, such as vision in higher animals, and photosensitivity in lower organisms, follows mathematical laws in line with photochemical change. These normal reactions, as well as the pathological actions of light, take place in colloidal systems. It is possibe that some general law may be found from the action of light upon the equilibrium of colloids. Loeb [48] has demonstrated the general importance for such systems as the proteins of "membrane equilibrium." This equilibrium is an ionic, i.e., an electrochemical one, and it is not impossible that it is directly affected by radiation, through photoelectronic action.

A General Colloid Chemical Factor in Photochemical Change.

The view so far expressed here, that colloid chemical factors in photochemistry are only subsidiary, and only entail modifying circumstances for the primary photochemical event may need revision. The fundamental importance of adsorption for catalysis points to this, in a general way. A more specific interpretation of this is the tendency to regard catalysts as identical with photochemical sensitizers.[49] A still more specific indication of the possible fundamental importance of the colloid chemical factor in photochemistry is suggested by the recent important work of K. Fajans and his collaborators [50] on the influence of adsorption upon the spectral sensitivity of silver halides.

The relation of ion adsorption, a specific, if not the specific, colloid chemical event, to the photosensitivity of silver halides, is developed on the following grounds.[51] In the photochemical decomposition of the crystal lattice formed from silver ion and bromidions the primary products are silver and bromine atoms; hence individual bromide ions must have given up their valency electrons to silver ions of the space lattice, a process which may be termed an inner photoelectric effect.*

The energy-difference between the initial condition in which the electron finds itself prior to its excitation by light, and its final state after transfer to a silver ion is a measure of the work afforded by radiation. Let it be assumed that the initial state of the electron is generally the same, as follows from

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* This conception is the necessary reinterpretation of the older view that the photochemical decomposition "split" the molecule "AgBr" into $Ag + Br$. Since the silver halides are typical heteropolar compounds, forming space-lattices of Ag^+ and Br^- without privileged pairs, a restatement was necessary. This appears to have been perceived and noted at much the same time by Fajans (1921) and by Sheppard and Trivelli (*Phot. J.*, 1921).

consideration of the electro-static potential of the lattice points, which is given additively from the proper charge of the ions and the arrangement of the charges surrounding them; then the positive potential of the silver ions forming part in the usual way of the uppermost plane lattice of the crystal, and surrounded by bromide ions, is lower (and hence its tendency to capture electrons less) than the potential of the adsorbed silver ions isolated in position on the uppermost plane lattice. The transfer of an electron to the latter can therefore occur on reception of a smaller amount of light energy than is necessary for the corresponding transfer of electrons in the normal lattice layer. In accordance with the Einstein equivalence principle, for the inner photoelectric effect as primary photochemical reaction, this is expressed as a lowering of the $h\nu$ value of the light, consequently as extension of the spectral sensitivity toward the red. For the experimental results supporting this hypothesis, reference must be made to the original. More recent work of Fajans and Fromherz[52] indicate that the extension of light absorption due to adsorption of deforming ions is not so much a shift of the absorption limit as an increase of the total absorption. This means that the *number* of absorbing molecules, or ions, has been increased, and is very possibly associated with disturbance of the space lattice of the absorbing crystals.[53]

QUANTUM THEORY AND PHOTOCHEMICAL CHANGE IN CRYSTALS.

The colloid state may be regarded as synonymous with "dispersed states of matter," above molecular dimensions. The author prefers to regard such systems as pseudo-colloids, reserving the term colloids for the macromolecular systems originally contemplated by Graham.[56] But keeping to the conventional usage, it may be noted that the particles in solid dispersions, even when ultramicroscopic, are generally still crystalline, according to X-ray spectroscopy. The photochemical behavior of such colloids then is largely determined by that of microcrystalline solids in light. It has been shown recently, in the case of heteropolar crystals, such as silver bromide,[57] that the quantum of radiant energy just sufficient to decompose the substance is determined by the lattice energy of the crystals, as well as the electron affinity of the anionic component. This may be generally expressed by an equation of the form

$$h\nu = e\phi + E_{x^-} - P$$

where $h\nu$ is the quantum value of the longest wave-length absorbed, $e\phi$ is the electrostatic part of the lattice energy, E_{x^-} is the electron affinity of the anion, and P is a term expressing the effective electron attraction of the immediate environment. On Pauling's theory, this cannot involve any transaction incompatible with the rapidity of the quantum absorption. Pauling finds the P term can be expressed as the "electron affinity of the crystal," which is calculable from the diamagnetic permeability. This conception has been discussed by Sheppard and Vanselow. The determination of the wave-length limit of the absorption is beset with considerable uncertainty, so that conclusive decision is not possible on this ground. But that the general argument from the electrostatic lattice energy is sound appears from Hilsch and Pohl's evidence[58] that the wave-length *maximum* of the longest wave absorption band in the alkali halides can be calculated from the expression

$$h\nu_{\text{max.}} = e\phi + E_x - I_{me}$$

where I_{me} is the ionization potential of the metal atom. The first products of ultraviolet illumination of alkali halide crystals are alkali metal atoms and halogen atoms. Subsequent processes, such as heating, etc., may aggregate these to polyatomic nuclei and eventually colloid particles. On the other hand, radiation by X-rays produces immediately large polyatomic aggregates of the order of colloid metal particles.

These processes are of fundamental importance for the photodecomposition of the silver halides, and the formation of the photographic latent image.

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Color Photography.

H. Mouquin, D.ès S.*

While the photographic emulsion has made it possible to confer an achromatic permanence on visual images, their monotony causes them to suffer in both fidelity and beauty. This organic demand for more complete ocular stimulation through color is responsible for perhaps the largest portion of research activity in two major industries: Printing and the Cinema.

And yet it is a curious reflection that the (temporary) fixation of color, by photo-reduction of silver halide films prepared on reflecting surfaces, predated Daguerreotypy by at least two decades.† This color process depends on the fact that a light ray suffers a complete reversal of phase on specular reflection at an interface. Accordingly, when the incident and reflected beams interfere, there is set up a standing system of nodes and antinodes at intervals of half a wave-length. Furthermore, if the reflector be coated with a photosensitive material, photoaction proceeds only at the points of phase reenforcement, and a parallel series of laminae composed of the photo-product are thus formed. In the case of silver halides these will be of metallic silver. And, since the alternations appear at characteristic distances for each wave-length, they will selectively reflect those rays whose frequency coincides with that used to produce them—all other frequencies being suppressed by interference. Unfortunately, however, unresolved light destroys the lamination by reducing the remainder of the halide. Lippmann surmounted this difficulty by employing exceedingly fine-grained collodion emulsions backed by a layer of mercury (in order to ensure proper optical contact). It was thus possible to preserve the stratification by dissolving out excess halide. But, despite this advance, the process remains little more than a scientific curiosity. To begin with, it requires an emulsion which should be at once very fine-grained and exceedingly fast, colorless, homogeneous (non-scattering) and panchromatic. The best emulsions yet prepared are all too slow to be practicable. In addition, the effect of color is obtained only by viewing the plate at certain critical angles. In consequence the method has failed to materialize commercially.

Nor, indeed, do any of the proposed "ideal" solutions of the color problem show immediate promise of emerging from the limbo of abstract possibility; and all current attempts depend on the fact that the retinal perception of any spectral region may be excited by proper combination of three primary hues. These fundamental tones may ultimately be produced in one step, e.g., by photographing with light-sensitive dyes such as the diazo compounds; but such colors are fugitive by hypothesis, and no means of fixing them is known at present. In practice, then, we are reduced to an indirect method which employs a speedy but color-blind silver halide emulsion, the required color differentiation being procured by interposition of sharp-cut filters. Two general methods for accomplishing the latter may be distinguished:

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† In the *Farbenlehre* (1810), Goethe remarks: ". . . if a spectrum produced by a prism is thrown onto moist silver chloride paper, and the printing be continued for fifteen minutes, I observe the following: in the violet the chloride is reddish-brown (sometimes more violet, sometimes more blue) and

I. The "Separation Negative" technique in which, as the name implies, three negatives are separately exposed through red, green and blue filters, and later used in the production of dyed positives; and

II. The "Screen" processes, in which a single composite negative is photographed through a tri-colored mosaic, or "screen," of microscopic filters placed in contact with the photo-sensitive emulsion. Positives made by transferring to a second screen require no subsequent staining, since the tinted mosaic forms an integral part of the picture.

It should be noted that in separation negative procedure a desired shade is obtained by *subtracting* its complement from white light. This is demanded by the fact that the three color-positives must be superposed in order to yield a complete image on projection; and for accurate superposition it is imperative that the originals should have been exposed simultaneously and isosterically, which desideratum has evoked an impressive display of patented ingenuities. Conversely, when screen positives are projected, the colors are produced *additively;* that is by a reblending of the beams that issue from contiguous elements on the mosaic.

It may not be amiss at this point to direct attention to some rather interesting applications of colloidal chemistry made in the manufacture of polychrome prints from separation negatives. These prints are produced by impregnating either (*A*) the silver image, or (*B*) the gelatin matrix, with a relatively transparent and selectively absorbed stain.* The various methods for accomplishing (*A*) thus far developed are:

1. **Toning.**—This involves an alteration in either the *constitution* or the *dispersity* of the print grains, and is perhaps the most obvious method of producing chroma. As an example of the first may be mentioned conversion of the silver to its sulfide; of the second, the color dependence of Carey Lea sols on particle size.

In the polysulfide routine[1] colloidal sulfur is deposited; and more recently, toning with such diverse substances as mercury, copper, iron, molybdenum, uranium, cobalt, and tin, has been tried with success. But these precipitated materials have a tendency to give muddy prints and are all too opaque to project well. Furthermore, since the resulting color is a function of particle size as well as of composition, accurate reproducibility is difficult. Nevertheless, the comparative simplicity of the process has tempted contemporary workers to extend and improve the older toning methods with very encouraging results.

2. **Mordanting.**—In this case, lake formation occurs at the superficies of the print grains. Since the silver is initially converted to its iodide, or replaced by a metallic ferrocyanide or other quasi-colloidal complex, in order to adsorb more efficiently, the first step in this process is essentially the same as toning. Transparency is usually increased by dissolving out the image deposit after staining.

E. R. Bullock[2] has treated the problem of adjective dyeing from the standpoint of mutual precipitation of oppositely charged colloids, and points out the influence of gelatin pH.

A. Seyewetz,[3] and more recently H. B. Weiser,[4] have dealt with these

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this coloration extends well beyond the limit of the violet; in the blue the chloride takes a clear blue tint which fades away becoming lighter in the green. In the yellow I usually found the chloride unaltered; sometimes, however, it had a light yellow tint. In the red or beyond the red it looks a rose or lilac tint." Subsequent work,[22] carried out by halogenating polished silver plates, would seem to indicate that his failure to procure true rendition for shorter wave lengths but good reproduction in the red was conditioned by the poor reflecting powers of paper for higher frequencies. Furthermore, the color of silver halides changes with time during reduction; and, since the reaction rate differs for various wave lengths, this time factor would tend to mask the purely photo-optical effect.

* These do not exhaust the possibilities, since separation negatives may also be colored optically, e.g., by the use of gratings of the proper constants, as in R. W. Wood's method.[19]

mordanting procedures *in extenso,* and the interested reader may be referred to their numerous publications.

3. **Developing with dye intermediates.**—Since the photographic image is not constituted of pure silver, but also contains oxidation products from the developer, its color will depend somewhat on the latter's composition. We may take advantage thereof by developing with substances that oxidize to suitable dyes in the process. Thus, indoxyl easily passes to indigo blue; and thio-indoxyl to the corresponding thio-indigo red. In other cases a leuco form is produced and converted to the dye by subsequent treatment. This technique has been developed particularly by B. Homolka.[5]

Another indirect dyeing procedure due to J. H. Christensen has some exciting possibilities. It depends on the fact that colloidal silver will catalyze the bleaching of many dyes by weak reductants. By stratifying two or more emulsions charged with the appropriate dyes, multi-colored images are obtained after a single exposure and development.

In case (*B*) mentioned above, where the matrix itself must be colored, successful production of a chromatic print depends on the fact that the dye-imbibing power of pectous materials is locally altered by tanning. The tanning may be carried out in either of two ways:

1. **By a chemical reaction involving the colloidal silver image.**—The local insolubilization of proteins by bichromates in the presence of the image deposit forms the basis of everyday tanning procedure.* Yet, as a search through the general literature will reveal, photographic chemists betray a deplorable lack of understanding of its mechanism. This in spite of the tremendous strides toward the explanation of chrome tanning that have been made in the leather industry.[6–10] According to these findings, the sequence of events occurring at the image deposit when a photograph is immersed in the tanning bath is as follows:

First, a relatively unstable chromium complex of semi-colloidal dimensions is formed at the silver interface. Then, through the agency of water (precisely as in leather tanning), the secondary valence forces of the chromium radicle come into play, and a Werner compound is formed, in whose coordination-sphere the water-soluble groups of the protein are firmly fixed. The well-known resistance of such conjugated complexes to chemical change adequately accounts for the irreversibility of this type of tanning. It should be observed that instability, or reactivity, and not charge, is the essential characteristic of the original complex formed at the silver-gelatin interface.

It is obvious that many secondary factors such as pH, neutral salt effect, and the specific action of the "bleach," will influence the formation as well as the subsequent behavior of the reacting groups. This, together with the general complexity of the system, has served to keep us in ignorance of the precise molecular constitution of the interacting species; but the accumulated evidence leaves little doubt that the postulated mechanism is essentially correct.†

Since the innumerable ozobrome and relief processes in use today are all based on chrome-tanning, the photographic chemist may profit by following the leads indicated above.

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* Many other forms of chemical tanning are available for photographic purposes. The tanning action of developers, notably pyrogallol, has long been recognized. "Negative" tanning is exemplified by the action of ferric chloride. Since the ferrous salt formed at the grain boundary has no appreciable tanning action the image is left softer than the portions where ferric hardening has continued unimpeded. Again, liquefaction of the matrix by catalytic decomposition of hydrogen peroxide at the silver grain may be used to produce an etched negative image.

† This is not the place to consider an alleged distinction between Werner complexes and Duclaux micelles. It is interesting to note however that gel tanning can be effected with colloidal chromium oxide sols as well as with the Werner compounds.[11]

2. **Photo-tanning.**—This method depends on the regional solarization of bichromated colloids; and the critical definition thus obtained is responsible for its wide use in motion pictures. But it was not until the vexatious problem of exact reproduction of delicate gamma from the original negative had been solved that photo-tanning could be employed with success. To appreciate the difficulties experienced, it may be well to contrast the behaviors of glue and gelatin when so treated.*

The principal difference between these lies in their aqueous solubility. In the case of glue, unexposed areas remain soluble in cold water; and the depth to which hardening proceeds depends on the tone-density of the negative. Hence in the ideal case the matrix left after washing is isosclerotic and of varying thickness. But, since gelatin is not water-soluble at ordinary temperatures, it should give a print of uniform thickness and varying hardness. Inasmuch as final color-density will depend on either or both these factors (thickness of the tinted stratum and dye concentration therein), the mechanism of color reproduction in glue and gelatin media will quite naturally be radically different.

In practice, however, the total range of hardness (and hence of dye-imbibing capacity) of the primary photo-tanned gelatin print is not as extensive as the scale of density in the original negative; and the result is an irretrievable loss of gamma. Moreover, in the glue print (exposed, as usual, through the back in order to anchor the matrix to the base), there exists a gradient of increasing hardness under the isosclerotic surface, which is governed by the extinction coefficient of the bichromate.

It has been possible to minimize these defects in the "Imbibition" processes (largely developed by F. E. Ives). In these, the photo-tanned image is charged with dyes which are then transferred mechanically to the final surface, a mordanted and partially hardened gelatin film, by pressure.† Such a transfer depends on surface dye concentration alone and demands a heterosclerotic printing face, such as can be obtained with gelatin. Successful use of this last named material, however, necessitates improvement of its gamma range.

This has been effected by focussing attention on surface conditions, since in imbibition processes all detrimental effects occurring in the interior of the matrix, such as excessive hardening, may be ignored. By printing through the support, the actinic rays are compelled to traverse a layer of light-restraining material incorporated in the coating. Finely divided silver bromide, for example, emphasizes contrasts appearing on the negative by scattering the incident light through the print gelatin. At the same time, this prevents the actinic ray from penetrating through the surface too rapidly.

However, the chief point of theoretical interest in photo-tanning is the mechanism responsible for the formation of the tanning complex. Since the reaction proceeds in the visible, absorption of energy from incident radiation could be mediated only by loosely-bound electrons. This type of linkage, moreover, characterizes all coordination complexes, the bichromates among others. The immediate consequence of illuminating such a system is to increase the reactivity of the resonating groups. And in the case under consideration, light probably effects a scission in those bichromate complexes undergoing adsorption-strain at the surface of the colloid; the liberated chromium radicle forming an insoluble complex with the water-soluble groups

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* Here the glue has a *low* jelly strength, while that of the gelatin is *high*. J. A.

† Registration is simplified by reenforcing the printing matrices with a metal backing. This is possible only because final printing is not done by transparency.

of the protein, just as in chemical tanning.* It should be possible to learn more about the precise nature of the complex formed on illumination of bichromate solutions by employing the Permutit technique developed by Gustavson.[12] [See also the several papers on tanning in this volume. J. A.]

This brief survey of methods utilized in producing separation-negative prints would be incomplete without some reference to the difficulties encountered in the final superposition of the dyed positives. And these difficulties are intensified in motion picture work, where physical distortion of the flexible film base has effectively prevented the employment of more than two separation-negative colors. An attempted remedy has been to simulate the effect of superposition by relying on persistence of vision; the three color-positives being flashed before the eye in rapid succession. But this is attended by two undesirable consequences: eye-strain due to "color bombardment"; and the chromatic haloes around moving objects known as "color fringes." It should be remarked in passing that, since the last-named device entails physiological super-position, it is in effect an *additive* separation negative procedure. The simultaneous side-by-side projection of three positives [20] constitutes still another exception to the general rule. But the elaborate equipment required for this variety of optical registration has prohibited its general adoption.

This difficulty in superposing images is not encountered in screen processes, of which perhaps the best known are the Lumière and the Agfa. In the former, the mosaic is composed of stained starch grains whose interstices are filled with carbon; in the latter, of dyed plastic particles pressed into contiguity. Each of these represents a triumph in colloidal chemistry; yet both contain an inherent defect which makes it impossible to produce good quality prints with their aid. To begin with, it is not feasible to attempt the coincidence of units which not only are distributed in a haphazard manner, but also show great variation in size and shape. Their irregularity precludes the possibility of employing the "scanning" method of coincidence, since the excessive displacement required results in considerable loss of definition.† Such failure to obtain registration involves an inevitable loss of color value as well as an increase in graininess when printing is attempted. Positive transparencies ‡ are consequently made by reversing the negative, i.e. dissolving out the image and redeveloping the remaining halide, instead of printing onto a second screen. [Lumière plates give excellent lantern slides but on close examination of the enlarged image, the starch grains may be seen. J. A.]

A great advance towards getting good registration has resulted from the introduction of structured plates bearing relatively coarse and regularly disposed geometrical patterns. But this, although it allows production of an indefinite number of screen positives from a single negative, has not lent itself to the manufacture of motion picture film. To begin with, the continual solvent shrinkage and mechanical stretching to which the elastic film base is subjected during staining make it impossible to obtain the registration given by rigid backings. And it is consequently necessary to resort to the scanning

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* I am indebted to Mr. A. Spector for this particular interpretation, which is based on a photochemical investigation he is at present conducting in the Laboratories at Washington Square College, New York University.

† The scanning method of printing consists in slightly displacing the negative screen with respect to the positive, either mechanically or optically, in order to insure coincidence of two similarly colored elements at some time during the exposure.

‡ Color prints on paper are invariably prepared from separation negatives as, e.g., in lithography, or with carbon tissue. In other words, printing on opaque supports from screens involves the intermediate production of three clichés. Incidently, a diazo-type process may find readier application in reproduction from screens than in direct dye photography, since exposure could be prolonged.

method of coincidence. For this purpose a mosaic of regular structure[*] is best suited; especially if composed of parallel lines, since the latter require no more than a unidirectional scanning displacement of about the same order of magnitude as one tri-color element, and thereby preserve the definition. In addition, linear screens have less boundary per unit area than any other kind. There are consequently fewer boundary intersections in printing, and less diminution of transparency. However, the minuteness of the color elements demanded by the excessive magnification used in cinema projection, together with the flexibility of the support, render the methods used for producing geometric screens on glass inapplicable to screen film,[†] and it has consequently been necessary to develop an entirely new technique to cope with the situation.

Parenthetically, an attempt to circumvent these difficulties, namely the Keller-Dorian, Berthon process,[23] deserves mention here. In this ingenious optical modification of the screen principle, advantage is taken of the plasticity and thinness of the support, one face of the film being embossed with a parallel series of minute semi-cylindrical lenses through which the light must pass before reaching the coat of panchromatic emulsion on the back. In addition, the objective used is provided with a special filter of three co-planar primary color elements which lie parallel to the lenticulations on the base.

The mechanism of color reproduction by this process depends on the fact that any optical image is essentially discontinuous, and is, in the case at hand, composed of tri-colored point-images of the aperture. The alignment of cylindrical lenses occupying the focal plane of the system has two important functions: to magnify the chromatic point-images to a resolvable size; and secondly, to arrange the color components of the latter in contiguous parallel lines on the emulsion—thereby preventing the image units from overlapping, as well as gaining the advantages of a linear screen. By projecting the black-and-white positive thus obtained through the taking-filter an additive polychrome picture is obtained. This, however, necessitates the use of the same optical system for projection as for recording and is obviously a disadvantage —although not so serious a one as the persistent failure of the screen to yield positives except by reversal. The origin of the latter difficulty (which is common to all optical methods) is the lack of physical intimacy between the color elements and the image deposit. "Scanning" consequently requires an exceedingly intricate, and cumbersome, optical armamentarium.

The orthodox linear screen methods consequently remain in possession of the field as far as prints are concerned. Perhaps the most satisfactory of these is the Warner-Powrie process,[13] which owes its success to the introduction of two interesting innovations:

A. **Parallax Printing.**—On this screen the color elements are composed of three successively dyed series of photo-tanned glue lines. As said, distortion of the plastic base makes it impossible to allocate such lines with precision by procedures involving the mechanical displacement of a mask. The latter is therefore temporarily printed on the back of the film. And by projecting the interlinear spaces through the thickness of the support at various angles—depending on the direction of the incident beam—a tri-colored

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[*] Nevertheless, *irregular* mosaic screens on flexible base, notably "Lignose" film,[21] have been successfully marketed. It is interesting to note in this connection, that discontinuities of structure are noticed less on geometric screens than on irregular ones with elements of equal size. One is seldom conscious, for example, of the coarse but regular divisions on a newspaper half-tone cut, although they are plainly discernible.

[†] However, since the composition of this paper, a "rigid" screen-plate process, the Dufay, has been successfully applied to film (24). Basically this is a mechanical procedure, and the number of color elements is necessarily restricted to some 750 to the linear inch.

assemblage of juxtaposed glue-enamel lines is produced on the opposite side. Thus the film shrinkage incidental to the dyeing, washing, and recoating demanded by each color series is compensated for by an equivalent shrinkage of the mask.

In practice, it is sufficient to deposit a tri-color filter bearing 1,500 lines per inch, this being beyond the limit of resolution under normal conditions of viewing.

B. **Dual Tanning.**—The direct incorporation of such highly concentrated dyes as are required by the extreme thinness of the glue lines almost completely destroys the photosensitivity of bichromated mixtures. Consequently staining must *follow* insolubilization. But since the screen undergoes three distinct dyeings and washings it is essential that the lines stained one color should not imbibe those subsequently applied. This requirement is fulfilled by treating each color set with tannin. The latter agent secures the water-soluble amino groups of the protein in a complex analogous to that previously formed in the chromium-carboxyl tanning.

Furthermore, in order to prevent "bleeding," the dye must be colloidally dispersed.[14] The glue lines are therefore dipped alternately in acid and basic dye baths. This results virtually in the formation of a lake.[15]

Finally, before coating with balanced panchromatic emulsion, the entire surface is covered with a uniform layer of glue enamel. Since the refractive index of this stratum is identical with that of the lines, all superficial irregularities are smoothed over, and no haze due to general light-diffusion can take place.*

Accurate control of line width is obviously essential in this process. And, since this is markedly influenced by over- or under-exposure, the sensitivity of the bichromated colloid becomes of paramount importance. Moreover, since the photo-chemical behavior of these materials is altogether different from that of the silver halide emulsions, it is impossible to gauge their photospeeds with sufficient accuracy by the usual sensitometric methods. The procedure employed involves printing the spaces of an arbitrarily chosen diffraction-grating on the experimental coating through a "log shutter." Subsequent micrometric measurements establish the correct exposure.

Since sensitivity varies as an inverse power of coating-thickness, the factors affecting the latter—such as, viscosity, density, time of draining and drying, and speed of coating—must be carefully controlled. The sensitivity of a particular coating is therefore meaningless unless its thickness is defined. (This may be estimated colorimetrically or gravimetrically for solutions of known composition.)

In addition to this purely physical factor of thickness, one must consider the actual composition of the bichromated glue:

By carefully adjusting the protein concentration—which arrests crystallization—it is possible to incorporate a much larger quantity of the actinic salt than is required in ordinary photo-mechanical usage. This serves not only materially to speed up the entire process, but also enhances the light-restraining effect of the yellow bichromate.

Moreover, as would be predicted from the mechanism proposed for photo-tanning, the final moisture content of the coating will significantly alter its sensitivity. Hence atmospheric temperature and humidity must be carefully regulated.

Again, reaction velocity may be augmented by increasing the critical instability of the system; either by the incorporation of catalysts,[16] or by ageing—which depends on the exo-energetic aphotic reaction—or, finally, by promoting the "continuation" reaction † by

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* It will be appreciated that such losses become serious in the case of corrugated film stock.

† This photochemical after-effect is presumably a heterogeneous reaction initiated by nuclei diffusing from the insolated area, and is readily observed in the ultramicroscope. It obviously determines the maximum interval which may elapse between exposure and removal of the excess bichromate by washing. It may be added that such nuclear diffusion probably plays the major rôle in "Carbro" contact printing.

means of water vapor or secondary exposures.[17] When so processed, however, the behavior of the colloid becomes exceedingly erratic and unmanageable.

The acquisition and utilization of this type of detailed information in most modern procedures has largely eliminated the "rule-of-thumb" element that characterized the older methods. But the very multiplicity of this knowledge robs it of its major force. It need hardly be insisted that procedures so encumbered with technical complexities are still somewhat embryonic. Thus, in the cinema, where separation-negative colors are limited to two compromise-primaries, the defective reproduction of tone must be compensated for by artificial lighting and make-up. And yet, strangely enough, the more accurate renditions given by screen positives are no unmixed blessing, since natural color values are generally too low to appeal to the average audience. The latter situation is further aggravated by the opacity of the silver image.

This, then, is the present status of the problem: color can be reproduced photographically, but only with the expenditure of considerable effort. Further progress must depend almost entirely on the development of a simple and wieldy technique.

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Notes on Colloidal Phenomena in Paint and Varnish Products.

By Henry A. Gardner,

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On examining samples of prepared paints that have been stored for long periods of time, the oil floating on the surface will often appear to be extremely pale in color as compared to the rather dark amber color of the raw linseed oil used in grinding. Apparently the foots and some of the coloring matter in the oil are adsorbed by the pigment particles, thus allowing the oil to become very clear and unusually light in color. As a result of such observations, the writer has assumed that pigments will show varying degrees of adsorptivity. In order to determine the possibilities in this direction, a few dyestuffs were experimented with. In dilute aqueous solution, they were shaken with a number of pigments. Almost immediate discoloration of these dye solutions was observed when in contact with some pigments, and practically no change with others. As a result of this work a method of tests was developed whereby dried pigment was placed in contact with a standard aqueous dye solution and the extent of adsorption determined by means of titration with titanous chloride.*

The results on a large number of white and colored pigments showed wide variance in the degree of absorption and adsorption.

From experiments of the above type, it is possible that practical applications may be developed. Thus, for instance, they would suggest that processes might possibly be developed for incorporating practically all dry pigments in oil to paste or ready mixed form, without the use of grinding apparatus. It is well known, for instance, that white lead pulp containing large percentages of water may be easily incorporated with oil by adding oil and agitating the pulp, whereby the water is expelled and the pigment incorporated with the oil to a smooth condition. White lead, however, is probably the only pigment at the present time that is being made into paste form in this manner. Its ease of incorporation by this method is probably due to the basicity of the pigment particles which exert a very much greater surface attraction for linseed oil than for water. Believing that a brief study of the wetting properties of pigments with different liquids might afford some information in this connection, the following series of tests were made:

Twenty dry pigments were selected for test. Into test tubes were placed 10 cc. each of two different types of immiscible liquids. Into each test tube was then placed an amount of dry pigment equivalent to the size of the head of a match stick. As the pigment dropped through the upper layer of liquid, its speed decreased when it reached the line separating the two liquids. In many instances reactions would occur at that line, which would subsequently allow the pigment to either drop through to the bottom liquid

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* *See* Circular No. 295 of the Educational Bureau, American Paint and Varnish Manufacturers' Association.

or remain suspended at the interface. Upon shaking the tubes for a few seconds, an emulsion-like mass would be formed, which would gradually separate into two layers. The pigment would either go into one layer or would be suspended at the interface. Very rapid movement of the temporary emulsified particles would take place for several seconds, a miniature battle being waged between the liquids to determine which would wet the solid. That the result of the battle would not be due entirely to the gravity of the materials is indicated by the fact that pigments of practically the same gravity might be found to finally rest at the bottom of the lower liquid or in the upper liquid, according to the surface attractions presented. After these experiments were made, it was found that some similar work was done by Hoffmann with a number of dry substances but with liquids that are applied less to the paint and varnish industry than those experimented with in the present writer's work. Hoffmann's experiments are described on page 102 of Bancroft's "Applied Colloid Chemistry." He found, for instance, that if powdered glass is treated with water and then shaken with kerosene, the glass goes into the water phase. If, however, the dry glass powder is first allowed to stand for a long time with kerosene, some of the glass powder will remain in the interface, but vigorous shaking will cause the water to displace the kerosene.

It is conceivable that processes might be developed, whereby pulp colors coming from the washing tanks, and probably relatively free from adsorbed air particles, might be wetted with much greater ease than dry particles, the surface of which had adsorbed air or gases and which would then be resistant to wetting with oil. Such pulp colors, if properly agitated with oil under certain conditions, possibly in the presence of added chemicals * to lower the surface tension effects, might readily be incorporated with the oil. Experiments in this direction apparently offer promise. The fineness of the pigment, the amount used, and the acid value and temperature of the liquids are factors which would probably exert influences in such phenomena.

The results of the tests are shown in the following tables.

TABLE 1. *Pigments Added to Tubes Containing Toluol and Water.*

Upon adding pigments, all settled gradually in snowflake fashion to the bottom of the tubes, with the exception of Nos. 10, 14, 15, 16, 17, and 18, which remained at the interface. After shaking, the pigments remained suspended in the layers indicated by X.

		Upper Layer Toluol	Lower Layer Water
1	Antimony Oxide		X
2	Zinc Oxide	X	
3	Lithopone	X	
4	Leaded Zinc (5% Lead)	X	
5	Basic Lead Sulfate	X	
6	Basic Lead Carbonate	X	
7	Barium Titanox		X
8	Calcium Titanox	X	
9	Pure TiO_2	X	
10	Magnesium Silicate	X	
11	Calcium Carbonate	X	
12	Red Lead	X	
13	Indian Red	X	
14	Toluidine Toner		X
15	Raw Sienna		X
16	Raw Umber	Some at interface	X
17	Graphite	At interface	
18	Carbon Black	X	
19	Fuller's Earth		X
20	Light Green 25% on Barytes-Clay Base	Some at interface	X

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* Aqueous soap solutions are suggested.

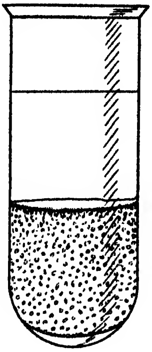

FIG. 1.

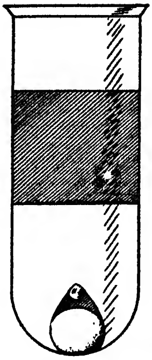

FIG. 2.

FIG. 3.

FIG. 4.

1.—Before Shaking: Upper layer, toluol; lower layer, water. Lithopone pigment rests at interface and is gradually dropping like snowflakes into lower layer.

2.—Before Shaking: Upper layer, linseed oil; lower layer, water. Lithopone pigment dropped rapidly in spherical shape to bottom layer and carried with it a globule of linseed oil which is endeavoring to become detached and float back to surface. A bubble of air is occluded at the apex of the oil.

3.—After Shaking: Upper layer, mineral spirits; lower layer, water. Toluidine pigment has gone into water phase, occluded in a web-like structure of mineral spirits, giving a honey-comb appearance. Pigment will gradually rise to interface.

4.—Immediately after Shaking: Aluminum powder with turpentine and water. The powder resists wetting with water and is rushing with a swirling vortex motion toward the surface. After a few minutes, it will be found resting in the bottom of the upper turpentine layer at the interface with clear turpentine above and a clear layer of water below.

TABLE 2. *Pigments Added to Tubes Containing a Mixture of Mineral Spirits and Water.*

Upon adding pigments, the general tendency was for them to remain largely at the interface, with slight amounts settling slowly in snowflake form to the bottom. Pigments Nos. 2, 5, 11, 14, 16, 17, and 18 remained entirely at the interface. Upon shaking, the pigment remained suspended in the layer indicated by X.

		Upper Layer Mineral Spirits	Lower Layer Water
1	Antimony Oxide		X
2	Zinc Oxide	X	
3	Lithopone	X	
4	Leaded Zinc (5% Lead)	At interface	
5	Basic Lead Sulfate	At interface	
6	Basic Lead Carbonate	X	
7	Barium Titanox	At interface	
8	Calcium Titanox		X
9	Pure TiO_2	X	
10	Magnesium Silicate	X	
11	Calcium Carbonate		X
12	Red Lead	X	
13	Indian Red	At interface	
14	Toluidine Toner	At interface	
15	Raw Sienna		X
16	Raw Umber		X
17	Graphite	X	
18	Carbon Black	At interface	
19	Fuller's Earth	At interface	
20	Light Green 25% on Barytes-Clay Base	At interface	

Fig. 5.

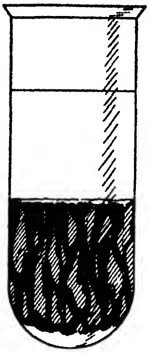

Fig. 6.

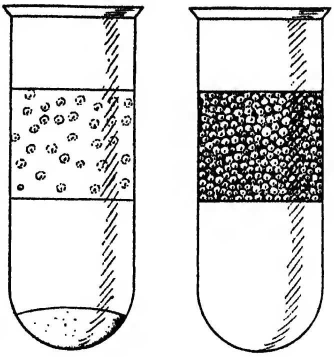

Fig. 7.

5.—Before Shaking: Upper layer, linseed oil; lower layer, water. White lead pigment as it drops through the oil leaves a series of milky threads caused by the wetting action of the oil. It then drops rapidly in a spherical shape to bottom of water layer. Occluded oil and air are seen in a struggle to rise toward the surface.

6.—Before Shaking: Upper layer, alcohol; lower layer, linseed oil. White lead pigment drops with rapidity through the alcohol and upon striking the oil starts to diffuse downward in heavy milky threads, showing rapid wetting action of the oil upon the pigment which may have become fairly air-free by the alcohol bath.

7.—After Shaking: Both tubes contain upper layer of turpentine and lower layer of water. To left hand tube zinc oxide was added. To right hand tube titanium oxide was added. Air and water have become entrained with the titanium pigment. Much of the zinc pigment is at bottom of tube. Some is still in upper layer.

Table 3. *Pigments Added to Tubes Containing Water and Linseed Oil Layers.*

Upon adding pigments, they suspended to some extent throughout the upper oil layer, then gradually started to diffuse through the lower water layer. Pigments 13, 15, and 18 remained in the upper oil layer for a very substantial period of time before diffusing slowly into the latter layer. Upon shaking, the pigment remained suspended in the layer indicated by X.

		Upper Layer Linseed Oil	Lower Layer Water
1	Antimony Oxide		X
2	Zinc Oxide		X
3	Lithopone	Very cloudy	X
4	Leaded Zinc (5% Lead)..........		X
5	Basic Lead Sulfate...............		X
6	Basic Lead Carbonate *...........		X
7	Barium Titanox	X	Some pigment at bottom
8	Calcium Titanox	X	Some pigment at bottom
9	Pure TiO_2	X	
10	Magnesium Silicate		X
11	Calcium Carbonate		X
12	Red Lead		X
13	Indian Red		X
14	Toluidine Toner	X	X
15	Raw Sienna	X	
16	Raw Umber	X	
17	Graphite	X	
18	Carbon Black	X	
19	Fuller's Earth	X	Some suspended below oil layer
20	Light Green 25% on Barytes-Clay Base		X

* Under proper conditions and with sufficient agitation the lead should go into the oil phase.

TABLE 4. *Pigments Added to Tubes Containing Slightly Alkaline Water and Linseed Oil Layers.*

Upon adding pigments, they dropped rapidly through the oil layer to the water layer, and then quickly to bottom of tube. Upon shaking, the pigment remained suspended in the layer indicated by X.

		Upper Layer Linseed Oil	Lower Layer Water with 0.5% Ammonia
1	Antimony Oxide	Very cloudy	X
2	Zinc Oxide	Very cloudy	X
3	Lithopone	Very cloudy	X
4	Leaded Zinc (5% Lead)	Very cloudy	X
5	Basic Lead Sulfate	Very cloudy	X
6	Basic Lead Carbonate	Very cloudy	X
7	Barium Titanox	X	X
8	Calcium Titanox	X	X
9	Pure TiO_2	X	X
10	Magnesium Silicate	Very cloudy	X
11	Calcium Carbonate	Very cloudy	X
12	Red Lead	Very cloudy	X
13	Indian Red	X	Some pigment at bottom
14	Toluidine Toner	X	Some pigment at bottom
15	Raw Sienna	X	Some pigment at bottom
16	Raw Umber	X	Clear
17	Graphite	X	Clear
18	Carbon Black	X	Clear
19	Fuller's Earth	X	Clear
20	Light Green 25% on Barytes-Clay Base	X	X

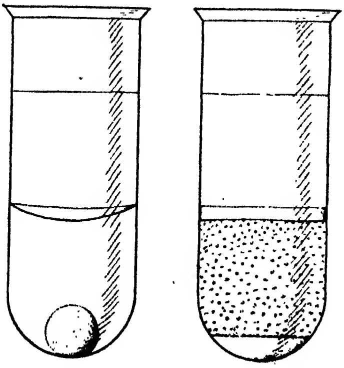

FIG. 8.—Before Shaking: Both tubes contain upper layer of turpentine and lower layer of water. To left hand tube white lead pigment was added, and lithopone to right hand tube. Lead pigment settled rapidly to spherical mass. Lithopone pigment rested first at interface and "snowed" down gradually.

Separating Fine and Coarse Particles.

When a pigment is added to a mixture of water and some immiscible liquid like mineral spirits, and shaken therewith, it is probable that the organic liquid floating on the top more readily wets the finer particles which are kept in suspension in the upper layer, while the coarser particles are wetted by the water and drop out. This principle is used in separating the carbon from the coarse slate particles in powdered coal and also in removing zinc and other ore-bearing minerals from less valuable ore, by oil flotation. The writer has shaken 100 grams of Pennsylvania mineral brown with 100 cc. of mineral spirits, and then added 100 cc. of water. After vigorous shaking, the material separated into two layers, the upper layer of mineral spirits containing a fairly bright red mass of pigment (12.5 per cent), and the lower layer of water a dark dull red mass of pigment (87.5 per cent). The relative fineness of these two groups of pigment was as follows: Per cent retained on 325 mesh screen —Upper layer from mineral spirits, 0.04 per cent; lower layer from water, 1.0 per cent. This would suggest a method of separating fine from coarse pigments, without the usual elutriation method.

TABLE 5. *Pigments Added to Tubes Containing Linseed Oil and Alcoholic Resin Solution Containing 33% by Weight of Rosin.*

Upon adding pigments, they dropped with great rapidity through the resin solution to the oil, and then dispersed throughout the oil readily Upon shaking, the pigment remained suspended in the layer indicated by X.

		Upper Layer Alcohol-Rosin Solution	Lower Layer Linseed Oil
1	Antimony Oxide		X
2	Zinc Oxide		X
3	Lithopone		X
4	Leaded Zinc (5% Lead)		X
5	Basic Lead Sulfate		X
6	Basic Lead Carbonate		X
7	Barium Titanox	Very cloudy	X
8	Calcium Titanox	Very cloudy	X
9	Pure TiO_2		X
10	Magnesium Silicate		X
11	Calcium Carbonate		X
12	Red Lead		X
13	Indian Red	Very cloudy	X
14	Toluidine Toner		X
15	Raw Sienna	Very cloudy	X
16	Raw Umber	Very cloudy	X
17	Graphite	Very cloudy	X
18	Carbon Black	Very cloudy	X
19	Fuller's Earth	Very cloudy	X
20	Light Green 25% on Barytes-Clay Base		X

Adsorption Effects in Paints.

The liquid with which various pigments are wetted in the manufacture of paints probably gives to the finished paint distinctive properties. Thus, for instance, if a paint made with three or four different pigments is prepared by grinding each of these pigments separately in oil, or grinding some in oil and others in varnish, and then mixing the various pastes together to make the paint, a product is produced which will probably give different results than if the pigments are mixed in the dry condition and are ground together in one liquid or in a mixture of liquids. In the latter method finely divided pigments like zinc oxide may coalesce with coarser pigments and give to them the distinctive properties they possess.

The above assumption would also suggest that the addition of varnish to an oil paint would produce a product that would give different results than one made on the same formula in which the pigments were first ground in varnish and then mixed with oil. Differences in the keeping qualities and even the durability might be expected. Similarly, if pigments are first milled with a dilute solution of rubber dissolved in toluol or gasoline in order to thoroughly wet the surface of the pigment and surround each particle with a rubber coating, this mass, when further mixed or ground in linseed oil, produces a different product than one in which the mixture is made otherwise. Reactive pigments such as red lead, when thus treated with rubber and later mixed with linseed oil, have shown in laboratory experiments markedly less settling and reactivity. This principle of wetting pigments with various protective colloids previous to grinding in oil, is one that should receive much further consideration and experimentation.*

Wetting Phenomena.

Bancroft has pointed out that if a small amount of oil is poured upon a compact surface of dry sand, the oil will readily wet the sand. If the sand is first wet with water and the oil then poured on, the oil may draw up in the form of drops and accomplish no wetting action. If, however, the sand is well dried, the oil can readily be adsorbed, and complete wetting of the sand particles is possible. Similarly with pigments, dampness present on the particles prevents wetting and interferes with the making of paint.

Pigments are often difficult to wet with oil, because of the envelope of air or gas around the particles, that has been adsorbed by the pigment surfaces. High-acid linseed oils apparently more readily displace this coating than do low-acid oils. If the pigments are first heated to remove moisture, they are wet more easily. Subjecting the pigment to a vacuum will accomplish removal of the air and much of the gas. It is well known that black carbon pigments are very difficult to wet with water, but if they are first heated or so treated as to remove the adsorbed films of hydrocarbons and air, they may be wet more readily. A mixture of heavy bodied linseed oil and mineral pigments previous to adding raw oil, will often reduce their resistance to wetting.

Fig. 9.—Dry pigment mass upon which have been placed drops of linseed oil. Note depressions caused by oil and rapid adsorption. On right, wet pigment mass upon which have been placed drops of linseed oil. Oil does not readily wet surface and tends toward spherical form.

Various finely divided pigments, especially those produced by the fume process, may adsorb gases present during the process of manufacture. For instance, carbon black may contain a very high percentage of gas. When 100 pounds of it is ground in oil and the gas eliminated by the action of the plates, there may be present in the mixture considerably less than 100 pounds of actual black, the balance being eliminated in the form of gas. Similarly with some white pigments produced by sublimation in contact with sulfur gases, there may be present upon the pigment particles as high as 0.2 per cent of adsorbed sulfur dioxide.

Grinding.

In a rather comprehensive study of the fineness of the particle size of white and colored pigments, it was indicated that most paint pigments are so fine that the grinding action that might be accomplished by plate mills such as are used in the manufacture of paint, is practically negligible. The plates simply break down the agglomerates, so that the pigment particles can be

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* Two articles that have come to the writer's attention on the subject of colloid chemistry as applied entirely to paints and varnishes are as follows:

"Varnishes, Paints, and Pigments," by R. S. Morrell, page 102, Third Report on Colloid Chemistry and Its General and Industrial Applications. Department of Science and Industrial Research, British Association for the Advancement of Science.

"Fundamentals of Colloids as Applied to Paint and Varnish," by E. W. Fasig, as delivered before the Toronto Convention of Paint and Varnish Production Managers' Club.

wetted by the oil and the oil adsorbed to disperse the pigments to a smooth paint. Only by repeated grinding through the mill for several passes can any real coarse particles be reduced to an appreciable extent. When paints are not thoroughly ground, and the pigment particles are not properly wetted, they may later agglomerate and precipitate out to the bottom of the cans. Examination of these agglomerated particles indicates extremely dry surfaces in some instances. The introduction of a very small amount of free fatty acids, soaps or of bodied oils as dispersing agents will often prevent such trouble.

Oil Absorption.

The amount of oil required for pigment saturation or wetting is directly proportional to the specific surface of the pigment mass existing at the point of saturation. As the specific surface of the mass is relative to its degree of particle subdivision or fineness, the oil absorption factor also measures to a great extent the fineness of the pigment. The oil absorption factor being relative to the surface condition of the pigment is possibly to some extent independent of its chemical composition or specific gravity. As the surfaces of a pigment are being wet with oil, the pigment mass remains relatively dry and crumbly, and will not smear when brought into contact with a piece of glass. At that point, however, where all the pigment particles become wet, the mass immediately forms a paste of a soft nature, which will then smear when brought into contact with glass.

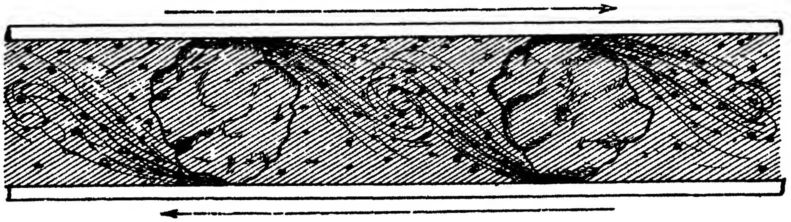

FIG. 10.—Imaginative view of a pigment of very finely divided particle size and linseed oil being passed through burr stone plates of grinding mill. Large lumps represent aggregates of pigment which are broken down to individual particles by the rotary motion of the plates. The individual particles are so small that no actual grinding is accomplished by the plates, the distance between which is far greater than the size of the pigment particles.

Texture of Pigments.

The texture of a pigment is of great importance. It can be determined by milling the pigment with a small amount of a mixture of equal parts of bodied oil and of mineral spirits or turpentine. After thorough grinding on a slab with a muller, the paint so produced is floated on a piece of sheet glass and allowed to drain in an upright position for three or four hours. A soft pigment will disperse thoroughly throughout the mass and make a smooth coating. A hard pigment or one with a fritted surface will drop down and show aggregates of coarse particles due to agglomeration. The running and sagging of red lead paint brushed upon vertical surfaces is generally due to coarse particles. Finely divided red lead seldom shows such defects.

Fineness and Strength.

Small amounts of color are adsorbed by large amounts of white pigments. It has been pointed out by Bancroft that a large amount of coarse pigment can be stained to a brilliant color with a small amount of finely divided color, or that a small amount of finely divided pigment can be stained to the same degree with a great amount of the same color. For instance, he found that 8 mg. of lampblack would stain 10 grams of dolomite that was about 40 mesh in size, whereas 654 mg. of lampblack were required to stain 10 grams of dolomite that was finer than 200 mesh. All of this indicates the part played by the specific surface of a pigment. It also points to the necessity of fine grinding of colors in order to get the maximum strength.

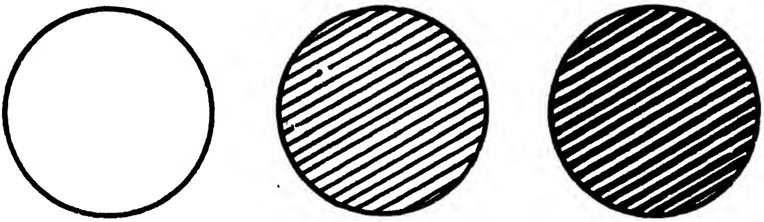

Fig. 11.—View illustrating effect of adding a coarse or a fine tinting color to a white pigment. First circle may illustrate white pigment. Second circle may illustrate white pigment to which 5% of coarse tinting color has been added. Third circle may represent white pigment to which 5% of finely divided tinting color is added. The greater tinting strength of the finely divided pigment is indicated.

Adsorption Phenomena.

The adsorption or the coalescence of certain pigments by others is of great interest, since upon this principle depends the preparation of some of the most important white pigments used in the paint industry. This is notably true of lithopone and of Titanox, in which there is usually present from 70 per cent to 75 per cent of barium sulfate which of itself has practically no hiding power in oil. The zinc sulfide or titanium oxide, in each instance, probably coats over the particles of barium sulfate, the finished pigments having almost as great hiding power as zinc sulfide or pure titanium oxide. This same coating action explains why a pigment made by precipitating 20 per cent of pure chrome green on 80 per cent of barium sulfate has much greater coloring value per pound than would be suggested by the composition.

In a recently devised process, coal containing a high percentage of ash, when mixed with water and subsequently with fuel oil, will, upon proper agitation, throw down the ash in the water and the oil will become absorbed by the coal.

Plasticity and Yield Value.

A paint or an enamel is plastic, and a certain amount of force is necessary to change its shape. This force which is required to produce flowing properties is termed yield value. Substances, such as bodied oil, may be added to a paint to increase the dispersion of the pigments and lower the yield value.

When a cubic inch of raw linseed oil is poured upon a horizontal glass plate, after a while it will flow out in an ever widening circle to an area of about 7½ inches in diameter, showing great mobility. When a similar volume of spar varnish is poured upon the plate, the area of flow may be only 6 inches. If an equal weight of pigment is ground with the raw linseed oil and it is then poured upon the plate, it may flow out only to the extent of about three inches, showing that it has been made very plastic through the introduction of the pigment, and has assumed a high yield value. If the same weight of pigment is then ground with a spar varnish, the paint thus formed may flow out to an extent of about five and one-half inches, or almost as much as the original varnish. This indicates that the yield value caused by the introduction of the pigment has been lowered to a great extent through the dispersing action of the polymerized oil in the varnish. This experiment teaches one that the flowing or spreading value of a paint may be regulated to a great extent through the addition of dispersing agents such as varnish or bodied oils. Similarly, high or low yield values may be obtained in enamels through the use of various thinners of different composition, or combinations of these thinners.

Fig. 12.—View showing raw linseed oil paint poured upon a glass plate. Paint has flowed out to area of three inches. View on right shows the same paint containing heavy bodied oil in the liquid portion. Paint has flowed out to a much greater area.

Rubber Solution.

Ordinary crude rubber is a very highly colloidal substance. When about 5 per cent is dissolved in 95 per cent of benzol, a very thick, jelly-like mass is developed, which can hardly be poured. Through this mass, some sort of structure is shown. If, however, the rubber is first milled to break down the protective structure surrounding the rubber particles, it can then be dissolved in the same amount of benzol to form a clear solution of low viscosity. In other words, the solubility of the rubber has been increased by breaking down the protective films around the particles. The fact, however, that only about 5 per cent of rubber may be obtained in solution would indicate its high degree of polymerization or aggregation. By chlorinating it and thus depolymerizing the mass, as great an amount as 15 per cent may be obtained in solution.

Electrical Charges.

Pigment particles are usually electrically charged. If several different types of these particles are present and they are all charged negatively, the particles may repel each other and be maintained in permanent suspension. If, however, a substance is added, in which the particles are charged positively, the positively and negatively charged substances may neutralize each other

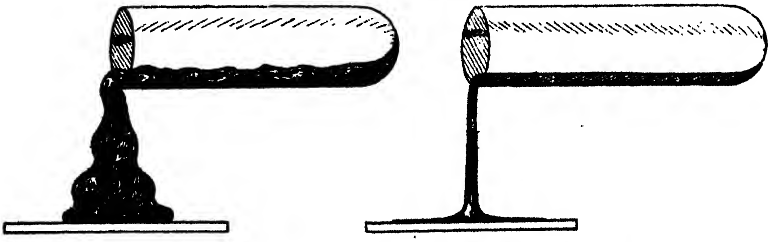

Fig. 13.—Tube on left contains solution made with 5% of crude rubber dissolved in 95% of benzol. Note structure throughout mass and resistance to pouring. Tube on right contains 5% of *milled* rubber in 95% of benzol. The structure of the rubber has been broken down by milling, and it forms a very mobile solution that pours readily.

and the whole mass agglomerate. The addition of some substance that will coat over the particles and prevent neutralization of such charges, may stabilize the mixture. A protective colloid of the glue or resin type will often prevent such effects.

The addition of various pigments to rubber latex affords an interesting subject for experimentation. The writer has found that when white lead, zinc oxide, and similar opaque pigments are stirred up with rubber latex, the latex immediately coagulates and precipitation of a solid white rubber mass occurs. Even though the pigment is washed free from acid or traces of metallic salts, this result will take place. It is probably due to positive charges of electricity on the pigment particles neutralizing negative charges on the rubber latex, or *vice versa*. On the other hand, certain pigments such as silica may be mixed and ground with rubber latex without any difficulty. These pigments apparently have the same type of electrical charge as the latex particles. Similarly, when rubber latex is added to certain oils or volatile organic thinners used in paint, almost immediate precipitation of the rubber occurs. In this instance, it is probable that the organic solvent added may dissolve the protective colloid around the rubber latex and thus leave the particles free to coalesce.

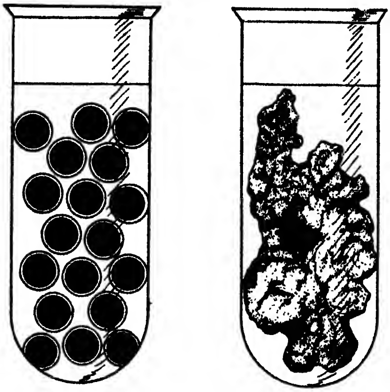

FIG. 14.—Possible structure of rubber latex. Each individual particle of rubber is shown surrounded by a thin film of resin which acts as a protective colloid. Particles may be electrically charged and are probably in violent motion in the water suspension. Millions of particles may be contained in a few cubic centimeters. View on right shows effect of adding a white pigment of opposite electrical properties to the rubber latex. Charges neutralize each other, and a mass of pigmented rubber is precipitated out. Similar effects are obtained by adding turpentine or some similar solvent for the resin which, being dissolved, allows the rubber particles to coalesce to a solid mass.

Leafing Effects.

Paints made of aluminum powder have been found very useful for certain purposes. They hold back aniline stains and similar products which would bleed through ordinary paint. The floating or leafing effect of the aluminum pigment is responsible for its protective action. Thus, for instance, although it is of very much greater gravity than any paint liquid used as a binder, certain portions of it will, when stirred with such a liquid, immediately float to the surface and remain there to form a continuous aluminum film. This can be demonstrated by adding a small amount of aluminum powder to even such a dark-colored liquid as coal-tar. When flowed upon a sheet of glass, the film will appear like a sheet of aluminum. If one looks at the under side of the glass, a black coating will be apparent. A few grains of aluminum powder, when stirred up with such light liquids as mineral spirits or turpentine, will show a very large percentage floating on the surface, due to non-wetting of the particles. This effect is not entirely due to the presence of stearic acid on the aluminum powder, as it may be observed on grades free of stearic acid.

Suspension Effects.

Certain volatile thinners are better suspending mediums for some white pigments than other thinners. For instance, if a small amount of lithopone is suspended in a quantity of mineral spirits produced from a highly saturated oil, almost complete settling may take place at the end of twenty-four hours. Other types of mineral spirits containing, for instance, percentages of cyclic compounds, may cause the pigment to be so sustained that the amount of settling in twenty-four hours may be very much less. Advantage of this may be taken in the manufacture of certain dipping paints where suspension must be more or less permanent even in the presence of high percentages of mineral spirits. The addition of small amounts of metallic stearates will also aid in this direction. Such substances act as deflocculators.

Aluminum stearate is used quite widely in the manufacture of certain types of paints and coatings to increase the viscosity or body of the solutions and delay settling. There is a great difference, however, in the results that can be obtained with different kinds of aluminum stearate, some of which are entirely unsatisfactory. When a dozen different samples were dissolved in the proportion of ten parts to ninety parts of crude paraffin oil, and then allowed to cool, great differences were observed in the gels produced. Some were solid masses of great stability, whereas others were quite mobile. Upon pressure, some broke down into small granular lumps. Others appeared like soft vaseline and exuded the petroleum oil. The presence of traces of alkali, for instance, may transform one that is solid into one that will be very liquid and smeary.

Marked settling may occur in some types of paints, but it is not always due to pigments of the heavier type, but rather to pigments that have resisted the wetting action of the oil. Pigments of rod-like structure, such as asbestine, are suspended to a better extent than those not of this shape. Pigments of small particle size do not, as a rule, settle as rapidly as those of larger size, as they present so much more surface for the suspending action of the liquid. Viscous liquids that exert high internal friction offer more resistance to the settling of pigments than those that have been greatly thinned with solvents or those which are of very low viscosity. If the viscosity of a liquid has been artificially increased by the addition of a small amount of aluminum soap, such as aluminum stearate, suspension is obtained for longer periods of time.

Gelling by Absorption.

If certain kinds of pigment are mixed with highly acid resin varnishes, adsorption of the resins on the surface of the pigment particles may in some instances be sufficient to cause the entire mass of paint to solidify to a gel-like structure. One of the interesting features about paints that have become partly solidified, such as red lead ground in slightly acid oil, is the fact that they may sometimes be made usable again through the addition of a large quantity of the same fatty acids or resins which in small quantity caused their solidification. The writer knows of an instance where several thousand gallons of stiff, unusable paint were remade by this method and used satisfactorily.

When certain highly polymerized oils are added to paint liquids, they seldom form true solutions but are kept in colloidal suspension, highly dispersed throughout the liquid. Any slight changes in these liquids, due to the introduction of certain ingredients, may cause the oil polymers to aggregate. This is often shown when highly polymerized oils are over-thinned solely with thinners of the petroleum type and used in flat drying coatings. Perfectly clear mineral spirits floating over the surface of the agglomerated oil in contact with the pigment has been observed by the writer. The use of some thinner of an unsaturated nature or of a small amount of pine oil will often prevent such an occurrence.

Granulation.

One of the most interesting conditions that may be observed in certain types of paint that are stored for a long period is so-called "granulation." This is indicated by the presence of flake-like particles at the juncture between the settled pigment and the oil. These flakes, which resemble "corn flakes" in appearance, may be one-half inch in length. They are translucent and range in texture from a soft, mushy consistency to a firm, brittle, shell-like mass. Sometimes their presence is accompanied by small granules or particles of pin-head size, adhering to the sides of the can at the area covered by the oil.

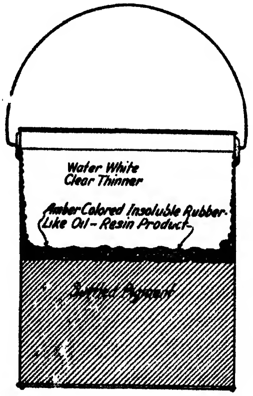

FIG. 15.

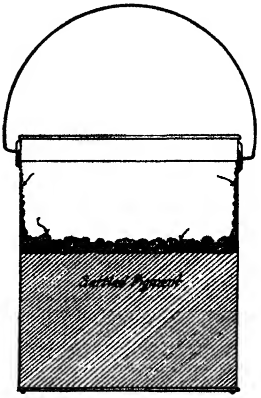

FIG. 16.

FIG. 15.—Phenomena that might be observed in a flat paint containing an excessive percentage of petroleum thinner of a type that is a poor solvent for the gum and oil. Upon long standing, the apparent solution is disturbed, the oil and resin being precipitated to an amber colored, insoluble, rubber-like form upon the top of the settled pigment, leaving the petroleum thinner above, water white and clear.

FIG. 16.—Exaggerated view of phenomena observed upon several years' standing of some paints. Small amounts of pigments are taken into solution as linoleates and resinates through the acidity of the oil or the influence of driers. Upon reaching concentration in the oil (about 2 per cent) in some cases, they are thrown out as metallic soaps, causing grittiness when the paint is applied.

These small particles may also be found scattered throughout the settled pigment portion of the paint. They gradually build up, serving as nuclei for the further development of other particles. They give to the paint a gritty appearance as though sawdust or other material was present. They generally consist of about 90 per cent organic matter and 10 per cent of metal, the lead and zinc pigments used in the paint having interacted with the acid portions of the liquids to form soaps that go into solution, or to form colloidal suspensions with some of the pigments. Generally not more than one per cent of these soaps will be held in solution by the oil in the paint. Beyond this point of saturation the soaps will precipitate out as finely divided particles, and thus build up into larger flakes. A period of three years may be required to build up any substantial amount of these granules in a mixed paint. In order to prevent the formation of granules, the use of a linseed oil with an acid value of not over five is usually advisable. Linseed oil containing "foots," which, of course, has moisture present, is sometimes responsible, in that the moisture may hydrolyze the oil and develop free fatty acids which promote soap formation. Refined linseed oil containing sulphonic acid groups may also act as linseed oil splitters to develop free fatty acids, and from this standpoint alkali refined oils, free from sulphonic acid groups, may be used to advantage. Moreover, the alkali refined oils have a relatively low acid value and do not react rapidly with basic pigments. When liquids contain even as low as one per cent of resinates or free resin, stimulation of soap formation may occur. Linoleate driers and soaps, therefore, are preferable as not stimulating this formation so readily. On the other hand, great quantities of free fatty acids or resin acids may prevent the formation of granules, in that they disperse them or hold them permanently in solution, thus preventing precipitation of the soaps. Turpentine, pine oil, and benzol are good solvents for metallic soaps, and their use in moderate amounts in thinners for paints sometimes prevents the precipitation of these soaps.

It is a curious fact that while small amounts of water in a paint may serve to stimulate the setting free of fatty acids that cause soap formation, the use of a large amount of water may act in the reverse way by forming emulsions or protective colloids so that no reactions can occur.

Brownian Movement.

The clear oil separated from prepared paints, which have stood for a considerable period of time, may show particles in Brownian movement on thinning with benzol. The clear liquid from a para-nitraniline red in oil, when mixed with benzol, will become very strongly red, showing suspensoids. One of the most interesting illustrations of this was found in a red lead paint that had been standing in the writer's laboratory for four years. Examination showed that the percentage of red lead present had dropped considerably. The linseed oil had become viscous but was still clear. Ashing the oil, which was fairly clear but viscous, showed the presence of 10 per cent of lead oxide. This was a greater amount than could have formed as lead linoleate through interaction with the oil in the cold and be maintained in real solution. Undoubtedly much of the lead was in colloidal suspension. Examination showed Brownian movement.

Emulsions.

It was at one time the practice to use water in certain exterior paints of the emulsion type, the water being introduced usually with dilute caustic salts. Non-aqueous protective colloids, such as palmitates and oleates, were sometimes added. If an oil is stirred up rapidly with a small amount of a soap solution, the particles of oil are broken up into the form of drops which are coated over with the soap solution and thus kept apart. As long as coalescence of the particles is prevented an emulsion will be maintained. This same principle applies to the use of water in emulsion paints.

In many grades of flat wall finishes on the market, there may be present as high as 2 per cent of water. This is not added as a cheapening agent but to get better suspension of the pigments. It may sometimes be added in a haphazard manner. The writer believes that if it was first emulsified with mineral spirits, it would accomplish its function in a better way. The use of a small percentage of tannin or of soap solution as a dispersing agent in such products might be experimented with.

Dispersion of Resins.

The first step in making a varnish is the melting of the resins. The temperature required is high. This heat apparently causes a depolymerization or breaking down of the highly complex molecules into simpler ones that may be readily dispersed to form an apparent solution. The smaller these molecules or groups of molecules become, the more readily they are dispersed in the oil or go into solution in solvents. When the resins have not been properly cooked or "run," the varnish may show rapid "throwing out" of particles and be of false body.

After the varnish resins have been run, the addition of oils, that have been previously heated, is made, and the mass heated for a considerable period. Oils that contain some driers, such as resinates or linoleates, probably have a greater dispersing action, and from this standpoint the addition of drier during the process of manufacture is considered by some students of the subject to be superior to the addition of a drier to the varnish, after manufacture.

After fusion of the oil and gums, the thinners, such as turpentine or mineral spirits, are added. Some thinners form colloidal solutions with the varnish base, the thinner being the dispersing agent. Certain other thinners may possibly form true solutions with a part of the varnish base, and the viscosity induced may be quite permanent. Thinners such as toluol and xylol are of this type. Other types of thinner, notably some of those obtained from petroleum, may form highly colloidal supensoid solutions with the base and the viscosity may later change slightly, due to coalescence of the particles. If an attempt is made to add too great an amount of the latter type of thinners to a varnish containing a hard resin of the fossil type, the suspensoids may agglomerate and throw out to the bottom of the kettle, or the varnishes may become cloudy. The portion precipitated may have been well dispersed by the varnish base but later agglomerated by the addition of too much thinner. Such thinners usually contain only a very small proportion of cyclic hydrocarbons.

Yield Value of Varnishes.

Properly made varnishes have only very small yield values. However, the plasticity of varnishes cannot well be explained on the hypothesis that it is due entirely to solid friction. Examination under a high power microscope reveals the presence of some solid particles in Brownian movement. Undoubtedly they contain a large proportion of the disperse phase in the emulsoid state. These emulsoid particles which consist of liquid globules or aggregates of solid particles held together by liquid films, may, if sufficiently numerous, form a continuous structure throughout the varnish, and in this way be similar to a paint or clay suspension. It has been found that certain varnishes upon ageing show greater yield values, due, undoubtedly, to the formation of aggregates of some of the particles that have previously been well dispersed. Other varnishes may show rapid decrease of body.

Most all varnishes are colloidal solutions, and as such may vary greatly in the nature of the disperse phase and the size of the particles. The necessity for ageing certain varnishes may be explained in this way. Through ageing, certain of the aggregates may be agglomerated and thrown out at the bottom of the tank, thus leaving the aged varnish of somewhat less colloidal viscosity but of better working and drying properties. There may, moreover, be some possible relation between the viscosity and durability of some types of varnishes. Accomplishment of ageing through some quick means would be greatly welcomed in the varnish industry.

Polymerization Phenomena.

Bodied linseed oil contains polymerized particles in colloidal suspension. In the polymerization of Chinese wood oil, probably a similar condition exists. The presence of fatty acids and other decomposition products delays solidification of tung oil by dispersing the polymerized particles as they are formed. Rosin has the same effect. Upon further and prolonged heating, the amount of polymers increases until saturation is reached and the polymerized products form a solid gel. The addition of substances like glycerin or sulfur has a very marked effect, even in small quantity, in preventing the coalescence of the polymer. One per cent of sulfur or five per cent of glycerin will usually prevent the solidification of Chinese wood oil even at 280° C.

Reduction of Viscosity.

It has been suggested above that varnish resins, when they are run and fused with oils, are simply dispersed throughout the oil liquids. Acceptance of this theory affords an explanation of why two very heavy bodied varnishes when mixed together may produce one that is very thin in body. This reduction in viscosity would be due to further dispersion of the particles of varnish resin, which would, of course, effect a reduction of the colloidal viscosity.

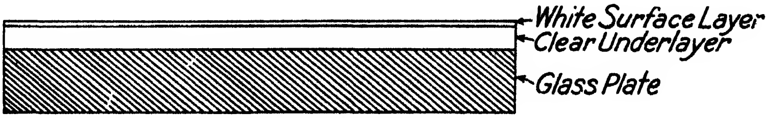

Fig. 17.—Diagram illustrating various phenomena. Some types of varnishes poured upon a clear glass plate may, upon immersion in boiling water or long time immersion in cold water, show a white film. This is generally a surface layer, due to water adsorption and its clouding effect. Below the surface skin there is generally an under layer of varnish that is perfectly clear. If an aluminum pigmented varnish or aluminum pigmented bituminous solution is brushed upon a glass plate, the aluminum immediately leafs to the surface to a continuous metallic film, leaving below a thick film of almost perfectly clear varnish or bituminous solution. By reversing the plate and looking at it from the under side, practically no aluminum powder is seen. When a paint containing zinc oxide is applied to a surface, and especially if bodied oil is present, the zinc oxide, being of extreme fineness, tends to float toward the surface. Analysis of the surface film will show a higher concentration of zinc oxide than in the paint as originally applied. The high gloss of zinc enamels is to some extent dependent upon this phenomenon.

Whitening Action of Water.

Substances such as metallic soaps of lime or of zinc, which of themselves in the dry condition show great resistance to water, may, when dissolved in liquids or fused with oil, show the reverse under actual exposure to water, fairly rapid emulsification being possible.

The whitening of a varnish layer when subjected to water probably is caused by an emulsion of the water with the coating. It does not mean that the water always goes through the coating but that it forms a surface emulsion giving a white effect. It is less observed with tung oil varnishes than with other types, although the latter may not always be more impermeable. The

(2) The second method is known as the "hot-dip" method. The metal is heated to 250° C. and while at that temperature is quickly plunged into the water-japan. The heat energy produces the same end result as the electric energy does in the electric dip method. The mechanism of this is not yet clear, but it seems to have to do either with the cohesion-temperature properties of the disperse phase and the dispersion medium, or with the adhesion-temperature properties of the emulsifying agent. The coated metal is then baked to "set" the japan base.

The hot-dip method is not easily applicable to metal less than 50 mils thick, due to the small heat capacity of thin metal.

The cost of preheating is largely offset by the saving due to not having to clean the metal by the usual processes. Cleaning by this method apparently removes all greases and oils ordinarily found on metal and leaves a good surface on which the japan can adhere. In addition, this preheat offers a very decided advantage from the metallurgical standpoint. Mr. T. S. Fuller of this Laboratory showed[3] that when iron or steel is pickled it absorbs atomic hydrogen which considerably lowers its fatigue value. If the metal is free from any considerable strains previous to pickling, then the fatigue value may be restored by heating. It appears that the ordinary preheating of 250° C. for twenty minutes is sufficient to attain this end.

Water-japan was developed at the Research Laboratory of the General Electric Co., Schenectady, N. Y. The use of this product has gradually increased until. at the time this is being written, the company is japanning about eleven tons of metal per day with water-japan. Tests made by other companies show that water-japan, properly baked, is as resistant to abrasion and weather as are other japans.

The practical advantages of water-japan may be summed up as follows: (1) Elimination of fire hazard due to inflammable solvents; (2) secondary drip reduced to a negligible amount; (3) low cost; (4) minimum of supervision required.

Water-japan is manufactured by the General Electric Co., Schenectady, N. Y., and by its licensees, under the following fundamental patents:

U. S. Pat. 923,228 to Willis R. Whitney on a colloidal suspension of gum in water.

U. S. Pat. 1,294,422 to Wheeler P. Davey, on an emulsion of japan forming materials with the aid of an alkali.

U. S. Pat. 1,357,688 to Harry Chislet, on the use of protective colloids in a water-japan.

It is used by the General Electric Co. and its licensees under the following fundamental patents:

U. S. Pat. 1,294,627, to Wheeler P. Davey, on the electric-dip method.

U. S. Pat. 1,266,335 to Buell Smith, on the hot-dip method.

EDITOR'S NOTE.

The principles involved in making emulsions of this and analogous types, are applicable to a wide variety of commercial products, among which may be mentioned cosmetic and polishing creams, shoe and leather dressings, pharmaceutical and culinary emulsions (e.g., of laxative mineral oil; mayonnaise). Reference may be made to the paper by Dr. Wm. Clayton in this volume, and also to his book "The Theory of Emulsions and Emulsification" (P. Blakiston's Son & Co., Philadelphia, Pa.).

The Colloids Committee of the British Association for the Advancement of Science have reprinted a selection of early papers bearing on colloid chemistry ("The Foundations of Colloid Chemistry," edited by E. Hatschek; published by Ernest Benn, Ltd., London). The first of these is a paper by Dr. Ferdinand M. Ascherson of Berlin, read before the Paris Academy of Sciences Nov. 12th, 1840, from which the following is epitomized:

"Starting from the assumption that it is never the facts which contradict one another, but that all disputes arise from their incomplete observation and varied interpretation," Ascherson envisaged the theory that emulsions of cell-like nature would result if, for some reason, a coagulable liquid like albumin would coagulate at the surface of contact between it and, e.g., a drop of oil. He made experiments and "with a pleasure which will be readily understood, I made the important discovery: *that coagulation in the form of a* *membrane occurs inevitably and instantaneously when albumin comes in contact with a liquid fat,* and that consequently an oil drop cannot be surrounded even for a moment by an albuminous liquid without a vesicular membrane or a cell forming round it. For the sake of brevity I shall call the property of forming membranes by contact *Hymenogony,* and the membranes thus formed Haptogen membranes. . . . For studying the properties of the haptogen membrane a few drops of oil are shaken with dilute white of egg or blood serum, and a small drop of this mixture is examined under the microscope. . . . For greater contrast a colored oil may be used. . . . The membrane formed by the contact of oil and albumin is surprisingly tough and elastic."

"This skin appears to be the only cause of the spherical shape and of the isolation exhibited by drops of fat in plants and animals according to my observations; likewise in milk, where Raspail had already conjectured the existence of a membrane on the globules, and in artificial milk." Oil shaken with distilled water showed that all drops which could conform to hydrostatic laws, became lenticular with thin transparent edges; but if coated by a haptogen membrane of mucus or albumin, they remained spherical with black margins, even in a large volume of water. By using very little albumin, both types of droplets. "It is then still possible to distinguish among the droplets, the diameter of which does not exceed 1/700 mm., those surrounded by a membrane, which increase in number with the albumin content of the liquid, from those which have remained free. The latter are best seen by focusing the microscope exactly on the surface of the liquid and illuminating from the side.* The formation of a few globules which do not become flattened again is perhaps the most delicate reagent for discovering in distilled water the slightest trace of an organic substance, and I must add that up to now I have not found any which has passed this test completely."

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[1] Langmuir, *Proc. Natl. Acad. Sci.* 3, 251-257 (1917).
[2] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," London, Macmillan and Co., Ltd., 1922, 6th ed.
[3] T. S. Fuller, *Trans. Am. Electrochem. Soc.* 1919.

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* This is, in essence, the principle of the ultramicroscope. If some very hot water be examined, especially against a dark background, by sidewise illumination, tiny droplets of condensing steam may be observed even with the unaided eye. J. A.

Synthetic Mother-of-Pearl.*

By L. Clément and C. Rivière, Pantin, France.

The investigations here described were directed toward the synthetic production of mother-of-pearl (of shells and pearls). The problem is beset with difficulties, but on the other hand its solution is desirable because of the industrial applications which it suggests. The results obtained seem interesting and encouraging; they throw light on the constitution of mother-of-pearl and indicate some possible though still distant applications.

What is mother-of-pearl?

Everyone knows the splendid appearance exhibited by certain shells; "pearliness" is a silkiness, sometimes metallic or silvery, presenting magnificent iridescent tints. It is the same as with fine pearl, but with a more pronounced play of color; the explanation will be given below. Chemically, there is no difference in composition between mother-of-pearl and pearl. The difference lies in the internal structures of the layers.

Mother-of-pearl is composed of calcium carbonate enclosed in albuminoid material, a scleroprotein resembling keratin and called conchyolin. This scleroprotein retains a certain quantity of water, which, though variable, plays a rôle in the preservation of the pearl and the mother-of-pearl, whose average composition is:

	Parts
Calcium carbonate	75
Water	25
Conchyolin	5

It must be remembered, however, that this is only an average composition, for Professor Dubois has found fine pearls (from pintadines) which contain only about 4 per cent of water.

Nature has, then, used only very simple materials to produce such beautiful substances; for from the standpoint of mere chemical analysis, mother-of-pearl resembles ordinary painters' calsomine—water, glue and whiting. But in mother-of-pearl the calcium carbonate is crystalline, and the crystals are arranged in lines, in layers, to which alone are due the admirable optical effects produced.

Professor Dubois, in a profound paper, concluded that the pearly effect could not be explained by any phenomena of birefringence possible with calcium carbonate and its arrangement in thin plates. Only a reticulated surface, capable of producing the phenomena of a net-work, would suffice to explain it. When calcium carbonate is precipitated in a colloidal medium, under certain conditions it automatically forms a net-work which exhibits all the optical phenomena of nets. The pearly effect appears in all its different color tones.

Structure of Pearl and of Mother-of-pearl.

Both of these substances contain a frame-work or skeleton of an albuminoid, conchyolin, within the voids of which are deposited the crystals or grains of calcium carbonate. This frame-work is alveolar, with partitions of conchyolin. It thus resembles a honeycomb whose compartments contain calcium carbonate. In the case of pearls the cells radiate from a center, the

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* Translated by Jerome Alexander.

partitions situated at the same level thus forming concentric spheres, giving the pearl an onion-like structure, and accounting for its cleavage.

How are pearl and mother-of-pearl formed?

Prof. Dubois says: "The animal's mantle secretes conchyolin, which takes the form above referred to. The filling of this skeleton or mold, as we may call it, is effected by calciferous migratory cells which, for defensive measures, transverse the epithelium by diapedesis." For the production of mother-of-pearl, as with pearls themselves, there are also required two different craftsmen: a carpenter and a mason. The animal forms calcium carbonate by excreting the essential materials into the sea-water.

The following experiments confirm these views. When calcium carbonate is formed by diffusion into a colloidal mass, it automatically forms itself into an alveolar net-work, which, optically, produces a pearly effect. Pearliness is not a specific property of calcium carbonate; in fact we can produce a more or less beautiful pearly effect with other salts—barium, lead, silver, copper. The superior beauty of calcium carbonate pearl is due to its fineness of grain.

This automatic net-work formation by various precipitates formed upon diffusion into a colloid medium, has, in our opinion, considerable importance. The chemical phenomena of life take place in colloid media; the formation of protective structures in animals, e.g. shell, mother-of-pearl, feathers, carapaces, scales, etc., made as they are of different materials, should exhibit a structure analogous to the one here dealt with. The brilliant colors of the casings of insects, of butterflies, of birds' feathers are to be explained only[*] by the optical phenomena of net-works. The scales on the wings of the butterfly *Morpho* show 1,400 striations per millimeter.

Precipitation of Calcium Carbonate by Diffusion in a Colloid Medium.

Our work reported here, which we have carried out rather extensively, represents simply a development of certain indications given by Prof. Stéphane Leduc[†] in his well-known book "Théorie Physicochimique de la Vie." As a colloid medium to support the calcium carbonate, we used gelatin, which takes the place of conchyolin. The calcium salt is dissolved in aqueous gelatin solution, its concentration being high so as to approach, as far as possible, the chemical composition of pearl. The following solution is typical:

	Grams
Water	80
Gelatin	10
Calcium acetate	10

The hot solution is filtered. Calcium salts of organic acids (lactate, glycocholate, etc.) are particularly suitable. The filtered solution is spread on a glass plate, and after it chills (about 3 to 5 minutes) the sheet is ready for further procedure.

A second solution is made with the following composition:

	Grams
Water	80
Sodium carbonate	10
Trisodium phosphate	2
Albumin	8

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[*] This statement is too broad, for in many cases the colors found are due, in part at least, to other than structural optical effects. Thus some birds have actually a segregation of copper in their brilliantly colored feathers. A certain tree-toad supplements a structural blue in his skin with a yellow oil deposited drop-wise there; so that the toad, which appears green in nature, turns blue when soaked in alcohol which dissolves out the oil. W. D. Bancroft has written extensively on these topics—see *J. Phys. Chem., circa*, 1920. Freshly fallen snow, especially in very cold weather, often preserves a net-like structure which makes it look decidedly blue, a fact well recognized by artists. J. A.

[†] See paper by Prof. Stéphane Leduc in Vol. II of this series. J. A.

This solution is carefully centrifuged or filtered, and allowed to flow slowly but uniformly (advancing 2 to 4 centimeters per minute) over the gelatinized plate, which is placed in a dish, the precipitating liquid being fed from a vessel having a stop-cock. Within a few minutes, upon examining the plate by transverse illumination, a pearly effect is observed. After half an hour (50 minutes at most) the supernatant liquid is carefully washed off, and the gelatin layer is treated with formaldehyde and dried with alcohol. It shows lively colors of pearly nature, which is quite intense by reflected light. The pearly effect may be intensified by deposition of several layers.

On microscopic examination the pearly layer appears to consist of a series of parallel rows of calcium carbonate, which are exceedingly close, as there can be counted 1,000 to 1,100 rows per millimeter. It is this optical network which is responsible for all the phenomena of "watering," iridescence, metallic glance, "silvering," etc., shown by pearl. A very close net-work (1,000 to 1,400 lines per millimeter) shows intense spectral colors; a looser one (800 to 1,000 lines per millimeter) gives the sheet a silvery appearance, without spectral colors. These differences may be controlled by variation in the concentration of the precipitating bath or by regulation of the rapidity of flow of the precipitating liquid.

If the water in the calcium or sodium solution materially exceeds 80 per cent, there is formed merely a continuous, opaque, white or porcelain-like precipitate. If the water is much below 80 per cent, the precipitate, curiously enough, is poorly formed, having much difficulty in getting started. There can thus be produced some of the aspects of natural pearl, from the white, slightly iridescent shell of the common oyster, to the highly iridescent shell of the "pearl-oyster."

If the support is spherical, it yields an iridescent ball resembling a pearl. It must be pointed out that this method cannot yield a precious pearl, for that is a ball of pearl whose pearly layers are disposed radially about a center. The "pearl" we produce necessarily consists of a series of parallel circles around a spherical object.

Heated for a long time in an oven at 50° C., the pearly sheets become chalky because of dehydration, a phenomenon identical with the "death" of pearl or of mother-of-pearl.

We have observed that the beauty of the pearly effect is markedly dependent upon the conductivity of the gelatin-calcium solution.

The gelatin we used gave the solution, normally, a pH of about 7, which gave rather nice iridescence. But if the solution is slightly acidified, for example with hydrochloric acid, or, better yet, with acetic acid, to pH 4.6, the iridescence is greatly increased. The reaction is also more rapid, occurring within 15 minutes at most. It must here be noted that we approach the isoelectric point of gelatin, where its osmotic pressure is at a minimum, an important fact because we are here dealing with a diffusion by osmosis.

Our pearly net-works of calcium carbonate have been examined by X-ray methods by Mr. Dauvillier, who, in his interesting work on "The Differentiation of Natural and Cultivated Pearls," states: "Under the conditions indicated by MM. Clément and Rivière, the gelatin seems to form a real spatial net-work in which is produced a precipitation of microcrystals of calcium carbonate."

An interesting experiment proves that the pearly appearance is not due to optical properties of calcium carbonate, but to its disposition in a net-work. If we pour a nitro- or acetyl-cellulose collodion on the surface of the network, we find that the pellicle stripped off after drying, exhibits a magnificent pearly appearance, sometimes exhibiting marked opacity. Obviously this pellicle contains no calcium carbonate; and furthermore, the original surface remains as pearly as ever, and will serve for other tests like this. There is simply a molding; the pellicle, in drying, has assumed the most detailed relief of the pearly surface, and has been molded upon its net-work.

These pellicles may be used for decorative purposes. If several of them are superimposed, the combined mass resembles a bit of mother-of-pearl.

Mechanism of Precipitation in a Colloid Medium.

Precipitation in a viscous colloid medium has already been described by various authors; it is the mechanism of periodic or rhythmic precipitation described by Liesegang and by Leduc.* Under these circumstances the products formed are not homogeneously and uniformly distributed, but are layered in zones. Thus, a drop of silver nitrate placed on a sheet of bichromated gelatin gives rise to concentric circles which sometimes extend quite far. There are "waves" of precipitation, or rather waves of diffusion, which may interfere with each other, be reflected, and even be refracted according to certain experiments of M. Leduc. The phenomenon should be closely studied. If a test tube of jelly be employed, the rings of precipitate are equidistant,† just as is the case with the precipitation of calcium carbonate in a colloid medium.

Leduc showed that when the gelatin contains traces of a calcium salt, a drop of sodium carbonate produces concentric iridescent circles. It is this experiment which served as the basis of our own, for we simply passed from traces to larger amounts; but there were numerous disappointments.

The explanation of these phenomena involves the study of semi-permeable membranes. Calcium carbonate forms such membranes, and through them the precipitating liquids work by osmosis. Biological phenomena involve reactions in colloid media. The great savant Lumière has said: "The colloidal state is life; flocculation is death." ‡ In fact in the midst of these multiple jellies of which organisms consist, occur all the chemical reactions whose ensemble constitute life.

Conclusions

Calcium salts, precipitated by diffusion in colloid media, form net-works which produce a pearly effect.

If several pearly layers, thus produced, are superimposed, we get a structure of the alveolar type of mother-of-pearl.

We believe that our experiments represent a true synthesis. To make it complete, there should be found an albuminoid analogous to conchyolin in which to produce the precipitation. The concentration of calcium salt must be increased somewhat, in order to match exactly the chemical composition of mother-of-pearl.

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* *See* papers by R. E. Liesegang in Vol. I and by S. Leduc in Vol. II of this series. J. A.

† This is not always so. *See* papers by H. N. Holmes and by S. C. Bradford in Vol. I of this series. J. A.

‡ *See* papers by Auguste Lumière, by S. Leduc, and by J. Alexander and C. B. Bridges in Vol. II of this series. The latter deals with life, mutation, and evolution. J. A.

Color Lakes.

By Prof. Harry B. Weiser,

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The adsorption of many dyes by wool, silk, and cotton is so weak that they are of value to the practical dyer only when used in connection with mordants. The term mordant (from mordre, to bite or to corrode) was first applied by the French to metallic salts which were supposed to act by biting or opening up a passage into the fibers of the cloth giving access to the color. Thus alum was believed to be effective in fixing certain dyes, owing to the solvent or corrosive action of the sulfuric acid. It is now known that the real mordant is the hydrous oxide and not the acid derived from the salt.

In general, a mordant may be defined as any substance that is taken up strongly by the fiber and in turn takes up the dye strongly. Two classes of mordants are generally recognized; acid, and basic or metallic. The acid mordants are the tannins, the fatty acids, albumin, hydrous silica, arsenic acid and phosphoric acid, while the basic mordants are the hydrous oxides of the heavy metals, the most important of which are the hydrous oxides of chromium, aluminum, iron, tin, and copper in the order named.

In dyeing a mordanted cloth it is, in most cases, the mordant rather than the fiber which takes up the dye. When a dye is taken up by a mordant in the absence of a fiber, the complex is called a color lake. The most common color lakes are those formed with dyes and the hydrous oxides. It is with the nature and mechanism of formation of such color lakes that this chapter chiefly deals.

For a long time it was believed that color lakes were definite chemical compounds between the dye and the mordant. This was based largely on the observation that acid dyes in which the anion is the colored radical are taken up only by basic mordants and *vice versa.* Thus alumina takes up the acid dye alizarin under certain conditions and it was taken for granted that a definite aluminum alizarate was formed. While certain color lakes may be definite Dalton compounds it seems more likely in the light of recent work that most lakes are adsorption complexes between the mordant and the dye, the composition of which is determined by the conditions of formation.

The general principles of the lake formation process will be taken up in connection with specific cases that have been investigated most thoroughly.

Alizarin Lakes.

Alizarin or dihydroxyanthraquinone is the most important mordant dye. It was formerly obtained from the roots of madder, a plant of Indian origin, which was cultivated largely in France and in Holland before synthesis of the dye from anthracene was accomplished in 1868. The chief mordants for the dye are alumina which yields a red lake, chrome which yields a reddish brown, tin which gives an orange, and iron which gives purple or black.* If the fiber is treated with the so-called sulfonated oils before mordanting with alumina, there results the brilliant Turkey-red, a color remarkable for its fastness to light and to the action of soap and water.

Since, in general, alizarin is not taken up by alumina in the absence of calcium, the lake is usually assumed to be a calcium aluminum alizarate.[1] It is claimed that strontium, barium, and magnesium may be substituted for calcium but are less satisfactory. Davison[2] found that hydrous alumina prepared from aluminum acetate takes up more alizarin in the absence of calcium salts than that prepared from the sulfate. Since the alumina mordant bath is aluminum sulfate, Bancroft[3] suggested that the function of the calcium is not to fix the alumina on the fiber or the dye to the mordant but to remove sulfate which cuts down the adsorption of alizarin. If this were true, soluble barium salt would be more satisfactory than calcium salt, and it is not.

Biltz[4] was the first to suggest that the alizarin lakes might not be definite chemical compounds. Thus with hydrous chromic oxide the amount of alizarin SW taken up increases continuously with increasing concentration of solution showing no indication whatsoever of the formation of chromium alizarate. On the other hand, with hydrous ferric oxide there was a rather marked increase in the amount of alizarin taken up with relatively small change in the equilibrium concentration, leading Biltz to conclude that iron and alizarin combine in the ratio of one molecule of Fe_2O_3 to three molecules of alizarin. But the amount of alizarin taken up by the iron oxide is far in excess of that necessary to form alizarate, hence one is confronted by the necessity of assuming either that alizarate adsorbs the excess of dye or that the whole phenomenon is a case of adsorption of the dye by the oxide. Recently the iron and aluminum lakes of alizarin have been investigated in Bancroft's laboratory[5] and the conclusion reached that the lakes are adsorption complexes of sodium alizarate and the hydrous oxides of the iron and aluminum, respectively. As we shall see, this view is inadequate to account for all the facts and does not afford a satisfactory mechanism of the lake-formation process.

Since the hydrogen-ion concentration is such an important factor in the fixing of dyes on fibers,[6] it would be expected to influence the taking up of dyes by mordants.[7] Moreover, observations on adsorption of ions from mixtures of electrolytes[8] would seem to indicate that the concentrations of ions present in a dye bath, including hydrogen and hydroxyl, might be quite as important in determining the composition of a color lake as the concentration of the dye itself. Furthermore, the nature, physical character, and purity of the mordant would be expected to influence the composition of the lake. The importance of these several factors is strikingly illustrated in the case of the alizarin lakes.

To throw light on the mechanism of the lake formation process some observations will be reported of the effect of varying the hydrogen-ion concentrations on the taking up of the inorganic anion sulfate and the organic anion oxalate both separately and simultaneously by highly purified hydroxides of known composition. This will be followed by a report of similar observations with some alizarin dyes. In all cases sols of the hydrous oxides were mixed quantitatively with the several solutions and the adsorption determined from the change in concentration of the supernatant solution. The hydrogen-ion concentrations were determined with the hydrogen electrode both in the super-

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* Since mere traces of iron seriously affect the brightness of alizarin reds, iron-free aluminum sulfate is used, and iron apparatus avoided. Similarly traces of iron dull the brightness of beers, especially Pilsner (light beers). J. A.

natant liquid and in a similar mixture in which water was substituted for the sol. In the tables, the former values are designated as "pH after adsorption" and the latter as "pH before adsorption."

The Adsorption of Sulfate.

Observation on the taking up of sulfate by hydrous chromic oxide typifies the behavior of salts of multivalent anions with hydrous oxides in general. In all the experiments, the initial sulfate concentration was maintained constant at 0.005 normal, while the pH value was varied through wide limits using suitable proportions of sulfuric acid, potassium sulfate, and potassium hydroxide. Obviously, this procedure introduces varying amounts of potassium ion as well as of hydrogen and hydroxyl ions. This effect may be considered as negligible, since it was found in some experiments, to be recorded in a later section, that very little or no alkali ion is adsorbed under similar conditions. If the alkali adsorption were appreciable it would serve to increase the adsorption of the negative ions. It should be pointed out that the same initial concentration of sulfate leads to a varying equilibrium concentration. Since the final concentration is smaller the greater the adsorption, it follows that the variations in the adsorption values would have been somewhat larger than those observed if the final concentration had been kept constant. However, the final concentration is sufficiently large in all cases to put the adsorption well on the flat of the isotherm.

The marked effect of the hydrogen and hydroxyl ions on the adsorption of sulfate is shown by the data recorded in Table I and shown graphically in Figure 1.

TABLE I. *Adsorption of Sulfate by Hydrous Chromic Oxide at Varying pH Values.*

Cc. of Soln. Mixed with 50 cc. of Sol Containing 0.125 Gram of Cr_2O_3 in a Total of 200 cc.			Adsorption Values, Milliequiv. per Gram Cr_2O_3	pH Values	
$N/50$ H_2SO_4	$N/50$ K_2SO_4	$N/50$ KOH		Before Adsorption	After Adsorption
50	0	0	4.66	2.42	2.87
40	10	0	4.60	2.49	2.97
30	20	0	4.52	2.59	3.15
20	30	0	4.28	2.73	3.64
10	40	0	3.48	3.09	5.15
0	50	0	1.90	8.68	8.29
0	50	5	1.28	10.61	8.73
0	50	10	0.48	10.95	8.96
0	50	20	0.08	11.28	9.39
0	50	30	0.10	11.41	9.87

It will be seen that raising the concentration of the hydrogen ion increases the positive charge on the particles, thereby increasing their capacity to adsorb sulfate. The adsorption of the sulfate falls off quite rapidly with increasing concentration of the hydroxyl ion, the carrying down of the sulfate being completely nullified at a pH value of about 9.2. It is obvious, however, that both sulfate and hydroxyl are adsorbed in the alkaline range from a pH of 7 to 9. In Loeb's investigations on the proteins[9] it seems probable that he overlooked the specific effect of cations other than hydrogen and of anions other than hydroxyl since he worked with relatively low concentrations of salts.

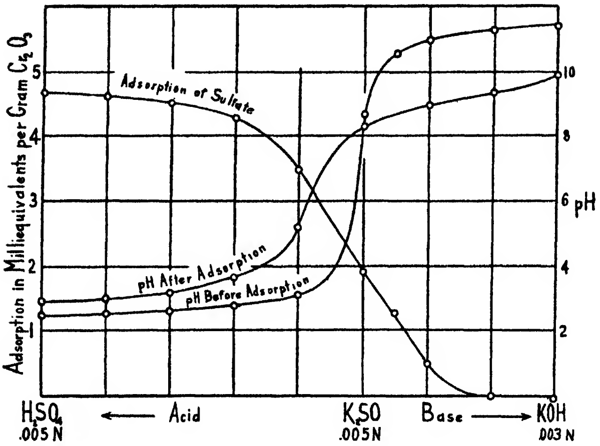

FIG. 1.

The pH-adsorption curve is smooth throughout showing no indication of the formation of a compound between the sulfate and the aged hydrous oxide even at pH values as low as 2.0.

Simultaneous Adsorption of Oxalate and Sulfate.

Miller[10] studied the simultaneous adsorption of oxalate and sulfate by alumina and arrived at the conclusion that the adsorption was a solid solution phenomenon since the concentration of oxalate (or sulfate) in the solution divided by its concentration in the adsorbent was a constant. This conclusion is not justified since the maximum value for the alleged constant was over a thousand times the minimum value. Moreover, even if these values had been constant, his data would not have justified the conclusion, since the hydrogen-ion concentration was allowed to vary through wide limits and this is the determining factor in the particular range of variation that Miller happened to get. It should be noted further, that as the ratio of total sulfate to oxalate falls off, the value for the sulfate constant increases, the increase being very rapid as equal concentrations of sulfate and oxalate are approached. Had Miller taken ratios of oxalate to sulfate greater than one, the so-called constant for sulfate would have been found to approach infinity very rapidly, for in a neutral solution the adsorption of sulfate becomes zero in the presence of an appreciable excess of oxalate. This is illustrated by some comparable observations on the simultaneous adsorption of sulfate and oxalate by hydrous chromic oxide, recorded in Table II.[11] In these observations the adsorption of 25 cc. of the $N/50$ solution corresponds to 1.77 milliequivalents per gram of chromic oxide.

Since the precipitation concentrations as well as the adsorptions of oxalate and sulfate are so nearly equal, one might be led to conclude that their adsorptions would be nearly equal when both are present in the same solution. This is not even approximately true if the solution is neutral or basic. In order to get any measurable quantity of sulfate adsorbed at a pH of 8 it is necessary to have a very low concentration of oxalate, and to get equivalent adsorptions at this pH value the final concentration of sulfate must be approximately 128 times that of oxalate. The conclusions to be drawn from these data are: First, under the same conditions the equivalent adsorption by the hydrous

TABLE II. *Adsorption by Hydrous Chromic Oxide from Mixtures of Oxalate and Sulfate.*

Cc. of Soln. Mixed with 50 cc. of Sol Containing 0.283 Gram of Cr_2O_3 in a Total of 150 cc.		Adsorption in Milliequiv. per Gram of Cr_2O_3			pH After Adsorption
$N/50$ $K_2C_2O_4$	$N/50$ K_2SO_4	Oxalate	Sulfate	Total	
50	0	2.13	0.0	2.13	8.30
60	0	2.17	0.0	2.17	8.37
50	25	2.09	—0.03	2.06	...
50	50	2.04	0.14	2.18	8.11
25	50	1.45	0.46	1.90	7.68
10	50	0.65	1.30	1.95	7.49
0	50	0.00	1.86	1.86	7.32
25	25	1.63	0.36	1.99	7.97

chromic oxide is approximately equal whether it be all sulfate, all oxalate, or some of each. Second, so long as there is an excess of oxalate in the bath it displaces the sulfate almost completely while an excess of sulfate has but little effect on the adsorption of oxalate. Third, it is necessary to limit the concentration of the oxalate in order to make a study of the simultaneous adsorptions of oxalate and sulfate in a neutral or basic solution.

To determine the effect of varying hydrogen-ion concentration in the simultaneous adsorption, a total quantity of oxalate plus sulfate corresponding to 16 milliequivalents per gram of oxide was used throughout the series of observations. In actual quantities of reagents this is represented by sufficient sol to contain 0.125 gram of oxide and 50 cc. of each of the $N/50$ solutions. The concentrations are sufficiently high so that at maximum adsorption, the bath will not be exhausted with respect to either sulfate or oxalate ion. The results are given in Table III and shown graphically in Figure 2. The form of the adsorption curves show: first, that the oxalate is displaced appreciably by the sulfate when the final solution is but faintly acid, and second, that the adsorptions approach equivalence in the strongly acid solution. This observed behavior is probably not due to a shift in the relative adsorbability of the bivalent oxalate and sulfate ions but is due to the relatively greater conversion of bivalent oxalate to the less strongly adsorbed bioxalate ion than of the

TABLE III. *Replacement of Oxalate by Sulfate at Low pH Values.*

Cc. of Soln. Mixed with 50 cc. of Sol Containing 0.125 Gram of Cr_2O_3 in a Total of 200 cc.						Adsorption in Milliequiv. per Gram of Cr_2O_3			pH of Mixture
0.037 N KOH	$N/50$ K_2SO_4	$N/50$ H_2SO_4	$N/50$ $K_2C_2O_4$	$N/50$ $H_2C_2O_4$	$N/25$ HCl	Oxalate	Sulfate	Total	
10	50	0	50	0	0	0.23	0.01	0.22	8.91
0	50	0	50	0	0	2.01	0.01	2.00	8.80
0	40	10	50	0	0	3.12	0.25	3.37	8.68
0	30	20	50	0	0	4.04	0.53	4.57	8.51
0	10	40	50	0	0	4.25	1.54	5.79	4.06
0	0	50	40	10	0	3.81	2.09	5.90	3.06
0	0	50	20	30	0	3.56	2.56	6.12	2.85
0	0	50	0	50	20	3.37	2.85	6.22	2.72
0	0	50	0	50	20	3.31	2.96	6.27	2.59

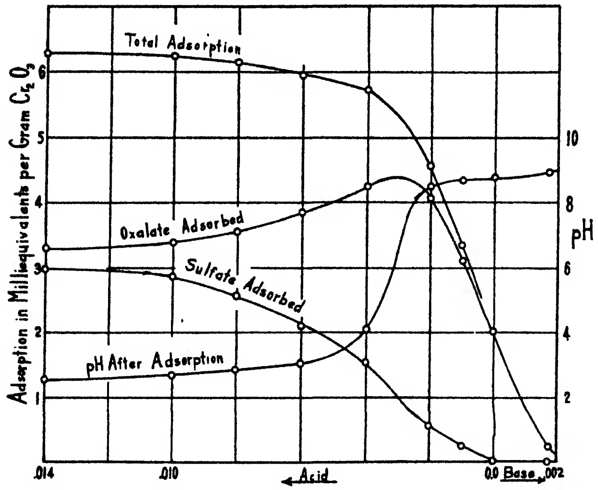

FIG. 2.

bivalent sulfate to bisulfate ion in the acid solution. In the next section it will be shown that the behavior of oxalate in this respect is typical of the acid dyes.

The Adsorption of Alizarin SW.[12]

The sodium salt of alizarin monosulfonate was used in the initial observations for several reasons: It is easy to determine quantitatively even in small amounts; it is not reduced at the hydrogen electrode in dilute solution; its acid is sufficiently soluble that no precipitation takes place throughout a wide pH range; and finally it is readily purified and weighed.

The adsorption of alizarin SW by hydrous chromic oxide at varying hydrogen-ion concentrations was determined by the same general method of procedure as was used in determining the adsorption of sulfate at varying pH values. The analysis of alizarin was accomplished by oxidation with potassium permanganate under carefully controlled conditions. The data are shown in Table IV and represented graphically in Figure 3. The pH curve for the acid and alkali alone in the same total quantity of water is also given. The length of a horizontal line drawn from any point on the curve for the pH of the mixture without the colloid to the acid-alkali curve gives the quantity of acid or base reacting with the dye. The adsorption curve is continuous giving no indication of the formation of a compound at any pH value. As would be expected, there is quite a buffer effect in the titration of the monosodium to the disodium salt. Moreover, there is a corresponding holding up of the adsorption-concentration curve in this region. This has two causes: the concentration of the hydroxyl ions is not increasing in proportion to the alkali added; and, at the same time, the concentration of the highly adsorbable dye ions is rapidly increasing. Just as was found in the case of sulfate and of oxalate, hydroxyl ion may completely displace the dye, the latter requiring a slightly higher hydroxyl-ion concentration than the former. This indicates that the dye is more strongly adsorbed than either sulfate or oxalate but is not so strongly adsorbed as hydroxyl.

TABLE IV. *Adsorption of Alizarin SW by Hydrous Chromic Oxide at Varying pH Values.*

Cc. of Soln. Mixed with 5 cc. of Sol Containing 0.0125 Gram of Cr_2O_3 in a Total of 20 cc.			Adsorption Value in Millimols Alizarin SW per Gram Cr_2O_3	pH Values		
0.04 *N* HCl	0.037 *N* KOH	0.01 *N* Dye		Without Dye or Colloid	Without Colloid	Total Mixture
2.5	0	5	2.46	2.86	.....	2.419
1.5	0	5	2.40	.....	2.400	2.717
1.0	0	5	2.32	.....	2.727	2.822
0.5	0	5	2.18	3.11	2.873	3.042
0	0	5	1.70	.....	4.173	4.478
0	0.57	5	1.41	10.62	5.490	6.170
0	1.13	5	1.15	.....	7.554	7.556
0	2.27	5	0.16	.....	10.529	9.283
0	3.39	5	0.09	11.17	10.634	10.445

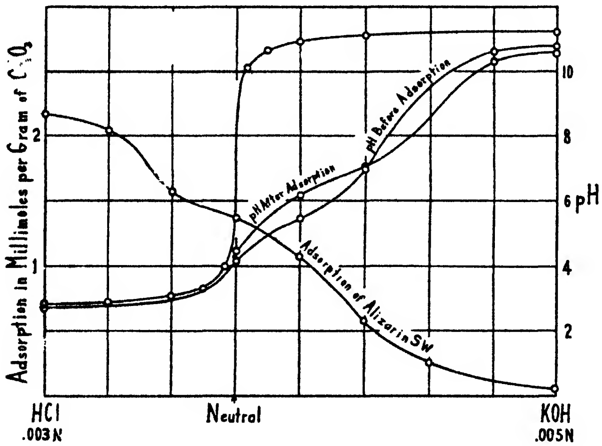

FIG. 3.

Simultaneous Adsorption of Alizarate and Other Ions.

Pelet-Jolivet [13] has demonstrated that readily adsorbed anions such as sulfate and phosphate cut down the adsorption of acid dyes (*e.g.*, crystal ponceau) and readily adsorbed cations such as magnesium increase the adsorption of acid dyes.[14] Davison [2] made some qualitative observations on the effect of sulfate ions and of calcium ions on the adsorption of dyes by fibers as well as by alumina. Thus he finds that 8 grams of Na_2SO_4 in 100 cc. of bath prevents the dyeing of wool by crocein violet. In lower concentrations, the dye is taken up in increasing amounts as the concentration of the sulfate is decreased. Alumina precipitated from aluminum acetate was found to adsorb certain acid dyes, including alizarin, more strongly than that from aluminum sulfate. Calcium acetate was found to increase the adsorption of the acid dye crocein orange but to decrease the adsorption of the acid dye acid green. There are other inconsistencies such as one might expect in qualitative observations.

The addition of sulfate to acid baths which give up their color too rapidly, has long been followed by the practical dyer. The sulfate by decreasing the adsorption and by retarding the rate of adsorption of the dye anion, tends to give a more even dyeing of the fabric. Sometimes, however, the presence of a very small amount of sulfate is objectionable. Bancroft[3] assumes that the purpose of adding calcium ion as calcium acetate to an alizarin bath is not to give a calcium aluminum alizarate or calcium chromium alizarate of some sort[1] on the mordanted cloth but to remove sulfate ion which cuts down the adsorption of alizarin ion. As will be seen in the next section calcium sulfate is too soluble to enable one to account for the action of calcium ion in this way.

The Effect of Sulfate on the Adsorption of Alizarin SW.

A series of observations was made to determine the effect of sulfate on the adsorption of alizarin SW by hydrous chromic oxide at varying pH values. The method of procedure was essentially the same as was used in determining the effect of sulfate on the adsorption of oxalate. The data are summarized in Figure 4a. Just as in the case of oxalate, it will be noted that the sulfate has little effect on the adsorption of alizarin SW anion in the neutral and basic solutions since, under these conditions, the presence of the much more strongly adsorbed hydroxyl ion masks the relatively small effect of the sulfate. In the acid range, however, the effect of sulfate is quite marked. Since the dye anion is adsorbed more strongly than sulfate from the same concentration, one might expect the latter to have little effect on the adsorption of the former. But the behavior of the dye is similar to that of the oxalate. In the acid solution the effective concentration of the dye becomes very small due to the suppression of the ionization; and the action of sulfate manifests itself. If the sulfate had been determined in the series of experiments the results would

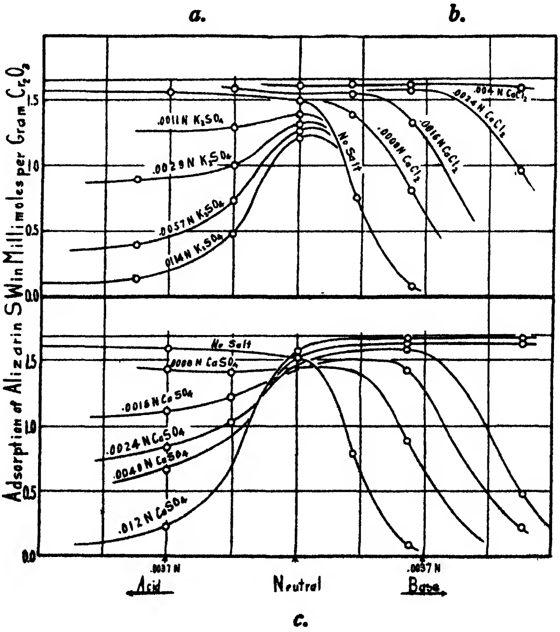

FIG. 4.

have been similar throughout to those obtained with sulfate and oxalate; *viz.*, sulfate adsorbed more from the acid bath and dye adsorbed more from the neutral and basic bath. Since acid baths are usually employed in dyeing acid dyes, the retarding effect of sulfate is explained even though the dye cation may be more strongly adsorbed than sulfate ion from the same concentration.

The Effect of Calcium Ion on the Adsorption of Alizarin SW.

The results of the observations on the adsorption of alizarin SW in the presence of varying amounts of calcium ion as well as varying hydrogen-ion concentrations are given in Figure 4b. Just as the effect of sulfate ion is small in the presence of the relatively highly adsorbed hydroxyl ion, so the effect of calcium is small in the presence of the relatively strongly adsorbed hydrogen ion.

The Effect of Calcium Sulfate on the Adsorption of Alizarin SW at Varying Hydrogen-Ion Concentrations.

Since the foregoing experiments show that the effect of the sulfate is large in the acid and negligible in the basic baths and that the effectiveness of the calcium increases with the hydroxyl-ion concentration, one is led to conclude that if calcium sulfate were present, the effect of the sulfate would predominate in the acid solutions and that the influence of the calcium will be unaffected by the sulfate in the basic baths. Direct experimental verification of this conclusion is given by the data plotted in Figure 4c. If the curves *a*, *b*, and *c*, Figure 4, are superimposed it will be seen that *a* and *c* are alike in the acid range while *b* and *c* are alike in the basic range. These data show that the effects of the calcium and sulfate ions in the bath are practically independent of each other and that each is dependent on the hydrogen-ion concentration.

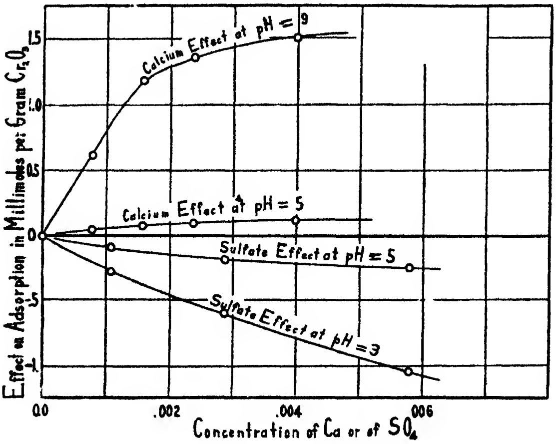

FIG. 5.

From the above data the effect of sulfate and of calcium on the adsorption of alizarin SW was calculated at different constant pH values with the results shown in Figure 5. It will be noted that the effectiveness of the calcium approaches zero as the pH value decreases while that of sulfate increases with decreasing pH value.

The Effect of Calcium Ion and Sulfate Ion on the Adsorption of Alizarin.

Observations on the effect of calcium and sulfate ions on the adsorption of alizarin from a sodium alizarate bath are given in Figure 6. Since the bath must be basic in order for the dye to remain in solution, one would expect the effect of sulfate to be slight, as the observations show. On the other hand, the effect of calcium is marked and increases with its concentration. Hence by the addition of a strongly adsorbed cation one may use a slightly basic bath in which the alizarin is soluble and at the same time avoid the displacement of the dye anion by the hydroxyl. This is the function of calcium ion in the formation of alizarin lakes on the fiber. That the effectiveness of calcium ion is not due to the direct precipitation of alizarin as calcium alizarate is evidenced by the fact that in curve *B*, Figure 6, the quantity of calcium is greater than that of alizarin and yet the dye bath is far from exhausted.

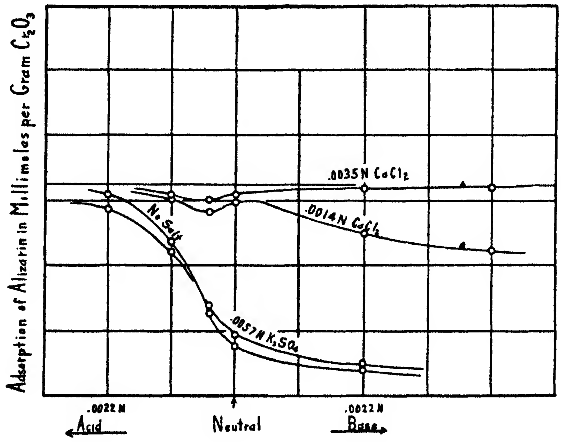

FIG. 6.

From these considerations the effect on the lake formation process of the addition of salts to the dye bath, may be generalized as follows:

(a) The presence of a strongly adsorbed cation in the dye bath increases the rate and quantity of adsorption of acid dyes and has an opposite effect on basic dyes, its effect increasing with the pH of the bath and with its own concentration.

(b) The presence of a strongly adsorbed anion in the dye bath decreases the rate and quantity of adsorption of acid dyes and increases the adsorption of basic dyes, its effectiveness increasing with the acidity of the solution and with its own concentration.

(c) If the dye bath is either acid or basic the effects of the cations and anions are practically independent of each other, the influence of the cation predominating in the basic bath and of the anion in the acid baths.

Mechanism of the Formation of Alizarin Lakes.

In the light of the experiments above described it seemed altogether probable that the alizarin lakes are formed by adsorption of the alizarin anion by the hydrous oxides. Bull and Adams, and Williamson[5] shook up a solution of sodium alizarate with the hydrous oxides and concluded that metallic alizarates were not formed since the hydroxide equivalent to the alizarate taken up was not set free as would happen if a double decomposition reaction took place. The absence of an appreciable amount of alkali in the bath led to the further conclusion that the lakes are adsorption complexes between the hydrous oxide and sodium alizarate. This mechanism appeared unsatisfactory since it had been found that when the hydrous oxides are brought in contact with highly ionized salts yielding a strongly adsorbed anion, it is the anion of the electrolyte and not the entire molecule which is adsorbed chiefly. To settle this point a $N/100$ solution of sodium alizarate was prepared; enough Cr_2O_8 sol was added to 100 cc. of the solution in order to completely decolorize it; and an aliquot part of the supernatant solution was analyzed for sodium as sodium sulfate. It was found that more than 85 per cent of the sodium remained in the bath. Similar observations were made with ferric oxide and alumina. The results of some experiments with an alumina sol prepared by the action of amalgamated aluminum on water [15] containing a small amount of hydrochloric acid are given in Table V.[16] As the data indicate the sodium in the solution after the lake formation, is associated with an equivalent amount of chloride displaced from the gel by the more strongly adsorbed alizarate and hydroxyl ion in the original dye bath. The lake formation process appears to consist in an exchange adsorption of the dye anion with less strongly adsorbed anions on the hydrous oxide rather than to direct adsorption of neutral sodium alizarate. Since the sols used in the original experiments were assumed to be positively charged owing to strong adsorption of hydrogen ion, the lakes formed were tacitly assumed to be hydrous oxide-alizarin acid adsorption complexes. Bancroft [17] questions the accuracy of this conclusion on the ground that the alumina-alizarin lake was always red and adsorption of the yellow orange alizarin acid would not be expected to give a red lake. It was shown, however, that red lakes are formed by mixing a suspension of alumina gel prepared by the action of amalgamated alumina in water and alizarin acid dissolved in alcohol.

TABLE V. *Adsorption of Sodium Alizarate by an Alumina Sol.*

Substances Mixed		Salt in 50 cc. Weighed as		NaCl		Na_2SO_4	
Sol	Sodium Alizarate $M/100$ cc.	NaCl	Na_2SO_4	Calculated	Observed	Calculated	Observed
90	25	0.0122	0.0153	0.0293	0.0281	0.0355	0.0352
		Salt in 75 cc. Weighed as					
		NaCl	Na_2SO_4				
80	28	0.0224	0.0291	0.0328	0.0322	0.0398	0.0419

While the lake formation is usually an exchange adsorption, a red alizarin lake results on adding sodium alizarate solution to a freshly prepared gel of alumina formed from amalgamated aluminum and, hence, free from exchangeable anions. Since the supernatant solution above the red lake is neutral, the lake is a hydrous oxide-sodium alizarate adsorption complex.

In this connection it is of interest to note that a gel free from adsorbed ions ages quite rapidly. Two samples of gel were prepared from amalgamated aluminum. In preparing the first special precautions were taken to avoid the presence of chloride while the second was formed in water containing a small amount of sodium chloride. The adsorption capacity, as indicated by the color of the lake formed with samples of the gel after different time intervals, is given in Table VI. It is evident that the chloride-free oxide loses its capacity to adsorb dye much more readily than the one containing chloride.

TABLE VI. *Adsorption Capacity in Relation to Color of Lake.*

Age of Alumina	Color of Lake	
	Chloride-free Alumina	Alumina Containing Adsorbed Chloride
10 minutes	Dark red	Dark red
16 hours	Light red	Bright red
1 day	Light red	Bright red
2 days	Pink	Bright red
7 days	Light pink	Bright red

Since Sorum has prepared a sol of hydrous ferric oxide free from chloride,* it was of interest to determine to what extent this preparation would adsorb alizarate ion. A 50 cc. sample of such a sol containing 4 grams of Fe_2O_3 per liter required but 0.45 cc. of $M/100$ sodium alizarate for coagulation. Further addition of dye solution caused peptization of the oxide as a negative sol.

Since dilute ferric chloride is completely hydrolyzed at high temperatures, a dilute sol was formed by adding quite dilute ferric chloride dropwise to boiling water and dialyzing at the boiling temperature short of removal of all the chloride. Such a procedure would be expected to yield a sol entirely free from ferric ion and stabilized by preferential adsorption of hydrogen ion. Actually, a sol containing 0.125 gram per liter gave no test for ferric ion with potassium ferrocyanide even after long standing. A 250 cc. portion of this sol was coagulated with 8 cc. of sodium alizarate solution. Two hundred and fifty cc. of the supernatant solution was evaporated and the residue of sodium chloride converted to sodium sulfate and weighed. The weight was 0.0118 gram, the theoretical amount in the 250 cc. being 0.0111 gram. Since the values are approximately equivalent it is evident that chloride ion was displaced by the alizarate while the stabilizing hydrogen ion was not displaced by sodium.

In conclusion one appears justified in saying: The formation of hydrous oxide-alizarin lakes is usually an exchange adsorption process in which the relatively strongly adsorbed dye anion displaces a more weakly adsorbed anion such as chloride from the hydrous oxide. If the adsorption capacity of the gel is satisfied with a strongly adsorbed anion such as hydroxyl, little exchange adsorption can take place and lake formation is prevented. Since a bath must be slightly basic in order for alizarin to remain in solution, the necessary adsorption of alizarate ion for suitable lake formation from such baths, takes place only in the presence of a relatively strongly adsorbed cation such as calcium.

Lakes are formed by the addition of sodium alizarate to positive hydrous oxide sols stabilized by preferential adsorption of hydrogen ion. If the accompanying anion is chloride, the amount of alizarate ion taken up by the coagulated oxide is equivalent to the amount of sodium chloride in the supernatant solution. The addition of an amount of sodium alizarate above the coagula-

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* Such sols doubtless contain a trace of some anion such as nitrate, sulfate, or carbonate.

tion concentration merely reverses the charge on the sol. Alizarin likewise is adsorbed by the colloidal particles giving a lake which remains in the sol state.

If the oxide gel is formed rapidly in the absence of an anion such as chloride, highly unsaturated atoms of aluminum on the surface will adsorb alizarate from aqueous sodium alizarate solutions or from alcoholic solutions of alizarin acid yielding red lakes. On standing, the highly unsaturated atoms of aluminum on the surface will adsorb alizarate from aqueous sodium alizarate solutions or from alcoholic solutions of alizarin acid yielding red lakes. On standing, the highly unsaturated atoms on the surface of the newly formed oxide become oriented into the normal lattice of crystalline alumina and the adsorption of alizarate decreases to such an extent that only a pale pink lake results. The rate and amount of this ageing is appreciably diminished by the adsorption of chloride, say, since a part at least of the abnormal unsaturation of surface atoms in the rapidly formed oxide is satisfied by the adsorption. An ion more strongly adsorbed than chloride would have a greater retarding action on the rate at which the atoms assume their position in the normal oxide lattice. But as we have seen, the presence of an ion more strongly adsorbed than chloride, will correspondingly decrease the adsorption of alizarate by exchange.

In the light of these observations it follows that, depending on the conditions, adsorption of alizarate may be either an exchange adsorption, direct adsorption, or both.

The red color of alumina-alizarin lakes is neither the dark purple to purplish black of the alkali and alkaline earth alizarates nor the orange of the alizarin acid but is a bright red suggestive of the color of the alizarate ion in aqueous solution. The color of the lake is doubtless due to adsorption of the alizarate ion oriented toward the aluminum atom of the oxide. The ion associated with the alizarate ion and oriented toward the oxygen atom of the oxide may be sodium, potassium, ammonium, hydrogen, or calcium without materially modifying the color of the lake except in so far as the extent of its adsorption influences the amount of adsorption of alizarate ion.

In accord with Bancroft's view, the sodium and alizarate ions under certain conditions may be adsorbed in equivalent amounts from sodium alizarate solution. This will be true only in case the oxide is free from adsorbed ions or in case the sodium and alizarate ions displace equivalent amounts of the corresponding ions adsorbed on the oxide during preparation. In any event, the sodium associated with the alizarate is without specific influence on the color of the lake since a similar color is obtained with alizarin acid.

The concept that the alumina-alizarin lake consists of alizarate adsorbed on aluminum atoms might be interpreted to mean that the color is due to a definite aluminum alizarate. This appears to be the point of view of Rheinboldt and Wedekind.[18] Such an interpretation would imply, however, that alizarate radicals are bound to aluminum atoms on the surface of the oxide by primary valence forces; in other words, that two aluminum atoms on the surface hold exactly three alizarate radicals. Followed to its logical conclusion this would mean that sodium, ammonium, or hydrogen alizarate adsorbed by aluminum oxide consists of aluminum alizarate plus sodium oxide, ammonium oxide, or water, as the case may be. There is no experimental evidence to justify this conclusion and it is probably incorrect.

CONGO RED LAKES.

Congo red, the disodium salt of diphenyl-diazo-bis-naphthalene-4-sulfonic acid is a red dye substantive to cotton. Aqueous solutions of the dye contain red colloidal ionic micelles (aggregate of simple ions) which are too small and hydrous to be visible in the ultramicroscope but which will not pass a membrane permeable to ions in true solution. Replacing the sodium in Congo red with hydrogen, gives a blue colloidal acid. The equations for the reaction may be represented as follows:

$$2\text{Na}^{\cdot} + R'' \text{ (red)} + 2\text{H}^{\cdot} + 2\text{Cl} \leftrightarrows \text{H}_2R \text{ (blue)} + 2\text{Na}^{\cdot} + 2\text{Cl}'$$

where R stands for the anion of the dye. This blue colloidal acid was recently shown [19] to be slightly soluble in water yielding the red anion. The solubility increases with rising temperature. Thus in the blue sol the following equilibria exist:

$$\text{nH}_2R \text{ (blue)} \rightleftarrows \text{nH}_2R \text{ in solution} \rightleftarrows 2\text{nH}^{\cdot} + \text{n}R'' \text{ (red)}.$$

These conclusions were based on observations in quartz containers since the alkali dissolved from ordinary glass at room temperatures is sufficient to change dilute Congo acid from blue to red.

The hydrous oxides of iron, chromium, and aluminum adsorb Congo red forming stable color lakes. From the standpoint of the theory of the lake formation process, the most interesting Congo red lakes are those obtained from the blue acid. Bayliss [20] found that hydrous alumina adsorbs the blue acid from its colloidal solution. If this adsorption complex is washed, suspended in water, and heated, the color changes from blue to red. Since Congo red salts are red, Bayliss attributed this change in color to the formation of an aluminum salt. The experiments were extended to the precipitates obtained by mixing the blue negative sol with the positive sols of the hydrous oxides of aluminum, zirconium, and thorium. The blue adsorption complex becomes red on heating in every case, provided the hydrous oxide sols are dialyzed until practically free from acid. A small amount of acid is sufficient to prevent the color change. Assuming that the color change is due to the formation of a Congo red salt of aluminum or zirconium, there is no obvious reason why a trace of acid should prevent the change provided there is an excess of hydrous oxide with which the Congo red acid can react.[21] Blucher and Farnau [22] attempted to get around this difficulty by assuming that the hydrous oxide adsorbs and stabilizes the free red Congo acid which they erroneously believed to be instable in aqueous solution.

Wedekind and Rheinboldt [23] confirmed Bayliss' observation and suggested, but did not prove, that aqueous sols of the blue acid contain more or less red acid which is changed to a blue isomer by acids. The red lake was believed to be a salt of indefinite composition formed by reaction of alumina with the red acid.

Color of Congo Red Alumina Lakes.

A sol of the blue Congo red acid was prepared by adding an excess of hydrochloric acid to a dilute solution of the sodium salt. The precipitate was washed thoroughly by the aid of the centrifuge until it was completely peptized and the sol dialyzed for two weeks. Samples of the sol containing 7 grams of dye acid per liter were mixed with a highly purified Al_2O_3 sol containing 1.7 grams of Al_2O_3 per liter. The several mixtures were poured into quartz test tubes which were placed in water at 100° C. for two hours. Thereafter, the tubes were allowed to stand for 12 hours and the observation noted in Table VII were made.[19] It will be seen that although there is present at all times a large excess of alumina, the lakes vary in color from red through purple to blue as the concentration of the dye sol is increased. It will be noted that, as usual, the range of complete mutual precipitation of oppositely charged sols, is narrow.

The effect of acid on the color of a given lake is shown in Table VIII. It will be seen that under the conditions of the experiment 0.00005 normal hydrochloric acid prevents the formation of a pure red lake. Heating in the presence of acid causes complete coagulation of the sols.

TABLE VII. *Color of Congo Red-Alumina Lakes.*

Sols Mixed (Total Volume 25 cc.)				Color after Heating	
In Ccs.		In Milliequivalents		Precipitate	Supernatant Liquid
Al_2O_3	Dye	Al_2O_3	Dye		
9	1	0.9	0.0022	Red	Pink
8	2	0.8	0.0043	Red	Pink
7	3	0.7	0.0065	Red	Colorless
6	4	0.6	0.0086	Red	Colorless
5	5	0.5	0.0108	Purple	Red
4	6	0.4	0.0130	Purple	Red
3	7	0.3	0.0151	Purple	Red
2	8	0.2	0.0173	Blue	Red
1	9	0.1	0.1940	Blue	Blue

TABLE VIII. *Effect of Acid on Color of Congo Red-Alumina Lakes.*

Ingredients Mixed in Ccs. (Total Volume 25 cc.)			Color			
Al_2O_3	Dye	HCl (0.025 *N*)	Without Heating after Two Days		After Heating	
			Precipitate	Liquid	Precipitate	Liquid
5	2	0.0	Red	Colorless	Red	Purple
5	2	0.5	Blue	Red	Purple	Colorless
5	2	1.0	Blue	Pale blue	Purple	Colorless
5	2	2.0	Blue	Light blue	Purple	Colorless
5	2	4.0	No Precipitate	Blue	Purple	Colorless
5	2	6.0		Blue	Blue	Colorless

Mechanism of the Lake Formation Process.

The mechanism of the formation of the Congo red lakes appears to be as follows: In the blue sol the following equilibria are sėt up:

$$\underset{\textbf{\textit{blue sol}}}{nH_2R} \rightleftharpoons nH_2R \rightleftharpoons \underset{\textbf{\textit{red solution}}}{2nH + nR''}$$

where R'' is the anion of Congo red.* Rise in temperature displaces the equilibria to the right. On mixing the hydrous oxide sol with the blue dye,

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* Experiments with benzopurpurin, a dye closely allied to Congo red, show that the color produced by precipitating sols of the dye with acid, may be largely changed by the presence of colloidal protectors, such as gelatin, gum arabic, etc. On following these color changes ultramicroscopically, it may be seen that, similar to the case of colloidal gold, the larger groups of ultramicrons verge toward the blue, while the smaller ones vary between claret-red and chocolate brown, those verging toward the red being the smallest. Comparing the effects of acid on benzopurpurin dyed on wool, silk and cotton, it was found that the two animal fibers gave a protective effect to the dye comparable with that of gelatin (a good protector), while cotton gave a protective effect comparable with that of starch (a poor protector). The shade of color lakes is obviously much influenced by the size of the adsorption aggregates. *See* J. Alexander, *7th Intern. Congress Applied Chem.* (London, 1910), Section II, p. 141; *Trans. Am. Inst. Chem. Eng.*, 2, 222; "The Nature of the Combination between Fibre and Dye," *J. Soc. Chem. Ind.*, 30, 517 (1911). J. A.

mutual coagulation of oppositely charged particles results in the formation of a blue lake. Following this process the alumina adsorbs the red colloidal ion, shifting the equilibrium gradually to the right. The color of the lake ultimately formed depends on the hydrogen-ion concentration and the amount of the blue dye. If the amount of dye is not in excess of the adsorption capacity of alumina for the red anion, the lake will be red. If there is an excess of the blue dye, the blue color blends with the red giving purple or if the excess of blue is sufficiently great the red color is masked completely. Rise in temperature increases the rate at which the adsorption equilibrium is set up. The addition of even a small amount of acid cuts down still further the low solubility of the acid as well as the degree of ionization of the acid, and blue lakes only are formed.

From these considerations it follows that if the excess of blue dye above the adsorption capacity of alumina for the red anion, were such that it would dissolve and become red on heating, the lake should be red when hot and purple to blue when cold. This proved to be the case: To 25 cc. of a blue sol containing 0.00067 gram of dye was added 1 cc. of the alumina sol. The blue lake was changed to red on heating but on standing for some time at room temperature, it became purplish blue.

The observations indicate that the red lake like the blue is an adsorption complex and not an aluminum salt. If the alumina sol is free from cations other than hydrogen, then the red lake consists ultimately of an adsorption complex of alumina and the red acid. To the extent that alkali or ammonium cations are present, the dye may be held as the red alkali or ammonium salt.[24]

METHYLENE BLUE LAKES.

Methylene blue is a typical basic dye, the cation being the colored radical. Pelet-Jolivet [25] showed that this dye is adsorbed by the acid mordant, silica, the amount taken up varying continuously with the concentration of the solution. He observed also that the extent of adsorption is determined by the age and the previous history of the mordant. Marker and Gordon [7] obtained a smooth curve for the amount of dye taken up by hydrous silica at varying pH-values; but a sharp break in the pH-adsorption curve was observed with the basic mordants, ferric oxide and alumina at a pH value near 11. Marker and Gordon imply that the lake formed in all cases is a chemical compound; but until someone shows that a very weak base like methylene blue will react with ferric oxide to give a stable salt under special conditions, there appears to be no ground for assuming that the iron-methylene blue lake as ordinarily formed is ever a definite chemical compound. The following experiments bear on this point.[26]

Since methylene blue is a basic dye it is not surprising to find that it is not appreciably adsorbed by the positive sols of the hydrous oxides of the iron group. In Table IX is shown the effect of adding alkali to the hydrous oxide sols of iron and chromium and the corresponding effects on the adsorption of methylene blue. The amount of oxide present was sufficient to make its concentration 0.1 normal. In the adsorption experiments 5 cc. of 0.5 per cent methylene blue was employed. The total volume in all cases was 20 cc. The adsorption data are accurate at all concentrations but pH determinations were not satisfactory in the basic solutions in the presence of a considerable quantity of methylene blue.

TABLE IX. *Adsorption of Methylene Blue from Basic Solutions by Hydrous Oxides.*

Cc. 0.037 *N* KOH	Effect of KOH Alone	Effect of KOH and 5 cc. 0.5 Per Cent Dye	Methylene Blue Adsorbed	
			Per Cent of Total	Millimols per Gram
	A. Hydrous Chromic Oxide			
0	Clear positive sol	Not precipitated	0	0
1	Not precipitated	Not precipitated	0	0
2	Precipitation complete	Precipitation incomplete	0	0
3	Little peptized negative	Precipitation incomplete	0	0
4	More peptized	Precipitation complete	4.4	0.08
5	Nearly all peptized negative	Precipitation complete	56.0	0.91
7	All peptized negative	Precipitation complete	81.0	1.43
10	All peptized negative	Precipitation complete	84.0	1.51
	B. Hydrous Ferric Oxide			
0	Clear positive sol	Not precipitated	0	0
1	Precipitation complete	Precipitation incomplete	0	0
2	Little peptized negative	Precipitation complete	0	0
3	More peptized negative	Precipitation complete	4.2	0.07
4	All peptized negative	Precipitation complete	30.0	0.52
5	All peptized negative	Precipitation complete	38.3	0.67
7	All peptized negative	Precipitation complete	40.1	0.70
10	All peptized negative	Precipitation complete	41.8	0.72

From the data recorded in Table IX and plotted in Figure 7, it will be seen that the adsorption of methylene blue by both ferric and chromic oxides begins sharply at the concentration of alkali which, in the absence of the dye, starts peptization of the hydrous oxides as negative sols. The breaks in Marker and Gordon's curves have this same significance. Above the pH values necessary to start lake formation, the amount of methylene blue adsorbed is a measure of the negative charge introduced by the adsorption of hydroxyl ion; hence it corresponds to the hydroxyl adsorption isotherm. In this connection it will be noted that the maximum adsorption of methylene blue is

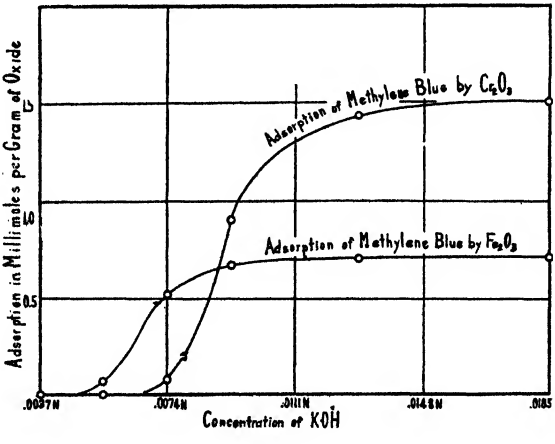

FIG. 7.

obtained in the presence of the same concentration of hydroxyl ion which, in the absence of the dye, gives complete peptization of the oxide as a negative sol. At still higher pH values the adsorption of methylene blue falls off. A similar effect on the adsorption of methylene blue by wool was observed by Briggs and Bull,[27] who assigned the effect to increase in the colloidality of the dye in the basic solution. The suppression of the dissociation of the weak base might also be an important factor.

THE QUESTION OF COMPOUND FORMATION.

The typical lakes considered so far appear to be adsorption complexes between the mordant and the dye rather than compounds of definite composition. That a definite chemical compound is sometimes formed under special conditions is well illustrated by the case of the acid dye orange II and alumina. Marker and Gordon [7] observed that little dye was taken up by an alumina gel until a pH value of approximately 3 was reached when the amount carried down increased enormously. The break in the pH-adsorption curve was attributed to the formation of a definite compound in accord with the following mechanism where $X =$ the dye radical

$$\mathrm{Na}X \overset{\mathrm{H}}{\rightleftarrows} \mathrm{H}X \overset{\mathrm{Al_2O_3}}{\rightleftarrows} \mathrm{Al}X_3.$$

Since metanil yellow shows a similar break in the so-called pH-adsorption curve, owing to precipitation of the dye, which is insoluble in acid, Weiser and Porter [26] attributed the break in the orange II-alumina curve to the precipitation of orange II acid which was assumed to be relatively weak and but slightly soluble. Actually, the acid is fairly strong and quite soluble.[28] Moreover, Weiser and Porter claimed that crystals formed by digesting orange II with alumina in the presence of mineral acid were crystals of orange II acid when as a matter of fact they were crystals of aluminum salt of orange II, as demonstrated conclusively by Reinmuth and Gordon.[29] There is thus no doubt that alumina and orange II will form a definite salt at a suitable pH value, such that aluminum ions are obtained. This does not necessarily mean that an alumina-orange II lake is always a definite aluminum salt. Recently Mr. Paquin in the author's laboratory placed amalgamated aluminum in solutions of purified orange II of varying concentrations. The freshly formed "grown" alumina [15] took up the dye strongly from the weakly basic solutions giving a lake. Little or no reduction of dye could be detected in the process. Some preliminary observations completed as this manuscript is being written are reported in Table X.

TABLE X. *Adsorption of Orange II by "Grown" Alumina.*

Original Concentration of Orange II Mols $\times 10^{-5}$ per 200 cc.	Time of Action of Al	Adsorption of Dye Mol $\times 10^{-5}$	Alumina Corrected[1] Mol $\times 10^{-5}$	Adsorption Mol NaX per Mol Al_2O_3
6.494	30	5.344	1.793	0.030
12.98	30	8.96	1.566	0.057
19.48	25	11.13	0.960	0.116
25.98	30	14.18	1.054	0.135
32.47	30	16.94	1.059	0.160
38.97	30	21.14	1.157	0.185

[1] Calculated amount of Na_2SO_4 formed by ignition of dye was subtracted from weight of ignited lake.

The above observations give no indication that the lake is a definite aluminum salt of orange II. The adsorption was practically irreversible since the color was not extracted from a lake formed in this way by as many as 20 washings by the aid of the centrifuge. Since the conditions of formations preclude the presence of aluminum ions and since the slightly soluble aluminum salt of the dye would be extracted by the repeated washing, it seems altogether probable that the lake is not an aluminum salt on the surface of the alumina particles but an alumina-orange II adsorption complex.

That it is not safe to assume a lake to be a true compound simply because the constituents in question can form a definite salt under special conditions is further emphasized by the work of Gilbert[30] on the copper lakes of eosin. Gilbert prepared a definite crystalline copper eosinate; but found it to be a different substance from the precipitate obtained by the interaction of copper sulfate and sodium eosinate. Although the precipitated lake has a fairly constant composition, it always contains an excess of copper when an excess of copper salt is employed. By shaking hydrous copper oxide with varying concentrations of an ether solution of eosin, a typical adsorption isotherm is obtained, showing no evidence of compound formation. The maximum amount of eosin adsorbed under these conditions is only about one-tenth of that necessary to form copper eosinate. Starting with colloidal hydrous copper oxide and colloidal eosin acid, lakes were obtained varying in composition between 2 molecules of copper to 1 of eosin and 2 molecules of eosin to 1 of copper. All the lakes behave like the one in which copper and eosin are in equivalent quantities, and all can be carried into colloidal solution. In the presence of ether, small amounts of certain salts decompose the lakes. This is because the adsorption of the anions of the salts by hydrous copper oxide is sufficiently great to displace the adsorbed eosin. The order of displacing power of the anions is the usual order of adsorption: $SO_4'' > Br' > Cl' > NO_3'$.

The taking up of crystal ponceau by wool mordanted with alum was shown by Pelet-Jolivet[25] to be a clear case of adsorption when the process is carried out at room temperature; but at 90° C. the amount taken up is practically independent of the concentration of the dye bath, when the latter contains more than 700 milligrams per liter, the lowest concentration employed. It is probable that, in this instance, a definite aluminum salt of crystal ponceau is formed. Pelet-Jolivet prepared such a salt in crystalline form.

Considering the acid mordant tannin, for a moment, we find Dreaper[31] stating that magenta and tannic acid form a definite salt; but no proof is offered for the statement, and the admission is made that 100 parts of the alleged salt will take up at least 160 parts of tannin when the latter is present in excess. Sanin[32] likewise states that basic dyes form definite salts with tannin when the dyes are in excess; but when tannin is in excess, the latter is adsorbed. In no case is any proof of compound formation presented except the fact that a formula for the product can be written.

In conclusion one seems justified in saying that the color lakes are usually adsorption complexes between dyes and the so-called lake bases. In certain cases definite salts may be formed but these constitute the exceptions to the general rule.

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Addition Agents in Electrodeposition.

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Early in the development of the art of electrodeposition of metals, it was learned that certain substances, chiefly those that are now known to be colloidal, exert marked effects upon the structure and properties of the deposits. To such substances the term "addition agents" has been generally applied, regardless of whether they are colloidal or crystalloidal. Their effects are so similar or closely related that it will be necessary to discuss addition agents in general in order to decide which applications specifically involve colloids.

During the past decade two reviews of this subject have been published,[1, 2] each of which contains numerous references to the literature and a discussion of the theories that have been proposed. These papers emphasize the inadequacy of the present theories to account for the specific action of colloids or other addition agents in electrodeposition. A review of the literature of the past few years indicates that while many new and interesting observations have been made upon the effects of colloids, we are still far from an understanding of the mechanisms involved. Such an understanding must await the development of more comprehensive and conclusive theories of the simple processes of electrodeposition and crystal growth when colloids are absent. Pending such developments, any critical analysis of the different views would be largely a repetition of previous articles.

As a basis for more exhaustive research and for the more intelligent application of existing knowledge, it seems desirable to summarize the present commercial applications of colloids and other addition agents in electrodeposition. Most of the data to be included are derived from published statements to which reference will be made. Some of the information, however, is based upon verbal reports, received directly or indirectly. Even though efforts have been made to verify such statements, they may not be as authentic or as quantitative as is desirable. They are included in order to give as nearly complete a picture as possible of the present status of such applications.

Following the discussion of applications, the generalizations that may be warranted will be considered, and the theories that have been advanced to explain or correlate our present knowledge will be presented. This order of treatment is parallel to the chronological development, as the applications of colloids are almost entirely empirical and have not awaited or to any large degree been influenced by theories or predictions of their effects.

APPLICATIONS

ELECTRODEPOSITION PROCESSES:

As the applications of colloids are largely specific, it is necessary to consider them in connection with the individual metals or solutions used in electrodeposition. Each metal or bath may, however, be employed for a number of purposes, which may have different requirements. The following processes will be considered, so far as appropriate, for each metal.

Electrorefining. The anodes consist principally of the metal to be refined. The purpose is to convert an impure into a pure metal. The process therefore involves the separation of metals by electrolysis. The structure and physical properties of the deposits are of minor importance, as the refined metal is usually melted before use. Marked roughness is objectionable because it may cause short circuits and thus reduce the cathode efficiency.

Electrowinning. Insoluble anodes are used in a solution derived by leaching ores or metallurgical products. The purpose is to recover a pure metal from a solution which usually also contains other metals. The physical requirements of the deposit are the same as for refining. *Electroanalysis* is in effect an application of electrowinning, in which all of the metal from the electrolyte is deposited as a pure metal, in a form suitable for quantitative weighing. Colloids are seldom if ever intentionally introduced in electroanalysis as they are likely to be included in the deposits and thus increase their weight.

Electroplating. Articles, usually of metal, are coated with a layer of another metal for the purpose of ornament or protection. Non-metallic articles such as wood and plaster are first coated with a conducting layer of graphite or copper powder. The physical form of the deposits is important because it determines the properties, such as luster, hardness and ductility.

Electroforming. In this process articles are produced or reproduced by electrodeposition. Common applications include the reproduction of printing plates as in electrotyping, and of phonograph matrices. In some cases metal sheets and tubes are produced by electrodeposition. In general the deposits are much thicker than those used in electroplating, and there is a greater tendency toward roughness.

Effects and Purposes of Addition Agents:

As every constituent of a solution may and usually does have some effect upon the character of the metal deposited from it, it is difficult to find an exclusive definition of an addition agent. Research has shown that the principal effects of the major constituents of the solution, usually salts, acids or bases, may be measured and expressed in terms of the conductivity, metal-ion concentration and hydrogen-ion concentration. Addition agents are usually present in relatively low concentrations and have little or no effect upon these three properties. They do, however, produce more marked changes upon the structure and properties of the deposits than are usually caused by relatively large cause roughness or even "trees." The decrease in crystal size is usually in the operating conditions such as temperature and current density. Pending a better understanding of the effects of addition agents it may be necessary to use the negative definition, viz., that they have a marked influence upon the character of the deposits without materially changing the physical properties of the solutions.

Addition agents are used principally for their effects upon the structure, appearance and other physical properties of the deposits. Satisfactory addition agents lead to the formation of smoother, brighter deposits at a given current density; or they permit deposits of a given smoothness to be produced at higher current densities. This smoothness is caused by a decrease in the size of the individual crystals and also of the crystal aggregates, which when large cause roughness or even "trees." The decrease in crystal size is usually accompanied by greater hardness and less ductility. This change in properties may be desirable or objectionable, according to the requirements of the product. Unsatisfactory addition agents, or excessive concentrations of satisfactory agents, usually produce spongy or "burnt" deposits, and in some cases actually increase the roughness. In general, the presence of an addition agent decreases the current density at which a "burnt" deposit first forms.

The addition agents or products derived from them may be included in the deposited metal, usually in traces, but occasionally in significant amounts. When the purpose is to separate metals as in refining, or to co-deposit them as in brass plating, the use of an addition agent may affect the ratio of metals in the deposit.

Usually the "throwing power," i.e., the ability to deposit metal in recesses, is improved by addition agents. The greater throwing power is due principally to an increase in cathode polarization. Most addition agents have little effect upon the true conductivity, and only small effects upon the true cathode efficiency. They may increase the apparent cathode efficiency by eliminating "trees" and short circuits.

Requirements of a Satisfactory Addition Agent:

The ideal addition agent should have the following properties. As no such substance exists, the actual choice depends upon the relative importance of these properties for a given process or product.

(1) It should produce a smooth or bright deposit at a higher current density than will yield smooth deposits without the addition.

(2) It should not materially reduce the current density at which burnt deposits form.

(3) It should be equally effective over a wide range of relative concentrations, such as 10: 1, so that its concentration need not be controlled within narrow limits. This is the more important because, in the small concentrations commonly used, some of the compounds can scarcely be detected, much less determined, by the customary analytical methods.

(4) It should be capable of at least approximate determination, either by chemical analysis or by means of some physical property of the solution.

(5) It should be stable and not be appreciably reduced in concentration by evaporation, precipitation, oxidation or reduction.

(6) If decomposed it should not produce any deleterious substances in the solution.

(7) It should not be included in the deposit to any large extent and hence require frequent replenishment.

(8) If included in the deposit it should not produce effects upon its composition or properties which unfit the product for its intended use.

(9) The increased voltage required to produce a given current density should not be so great as to represent a large economic loss in operations such as refining. Through the use of addition agents at the same or higher current density than is otherwise employed, some increase in voltage is always involved. As there is usually no increase in cathode efficiency (apart from the elimination of short circuits) the cost of electrical energy for a given weight of metal is always increased by addition agents. This added cost must be justified by an improvement in the product, by a saving of time, or by a decreased investment.

(10) It should be cheap enough to justify its use for a given purpose.

Specific Applications:

The actual uses of addition agents in metal deposition will be discussed in connection with each metal that is now deposited commercially. The metals will be considered in the order of their arrangement in the periodic system.

Copper:

Acid Sulfate Baths. Addition agents have been more extensively studied and applied in connection with copper than with all other metals combined. One reason is the very large scale upon which copper refining and winning are conducted. The ease with which small scale experiments in copper deposition from sulfate solutions can be made, and with which the copper deposits can be polished, etched, and photographed, no doubt accounts for much of the research on this metal. Literally hundreds of addition agents have been tried in copper solutions though comparatively few have found commercial application. Many of the effects and limitations observed in copper solutions may be applicable to other metals. On the other hand the mechanism of copper deposition from sulfate solutions involves the existence of both cuprous and cupric ions, and may be less typical than is commonly supposed.

Refining and Winning. These operations are usually carried out on a very large scale, and the cost and consumption of the addition agent and the added cost of electrical energy may become significant factors. All operations are under technical control, so that simplicity of operation is not so important as in small plating or electrotyping plants. The chief purpose of using an addition agent is to produce smoother deposits and to prevent the formation of trees. Because of the close spacing of electrodes in copper refining, such projections are likely to cause short circuits and thus reduce the current efficiency. For a long time glue was the only agent used in these industries, and it is still used universally, either alone or together with another agent. The favorable concentration of glue is from 2 to 5 mg./l, or 2 to 5 parts per million.

It was early known that the presence of glue causes an increase in the tank voltage, which in some cases was erroneously attributed to an effect of the glue upon the conductivity of the solution. It was shown by S. Skowronski and E. A. Reinoso[3] that as much as 1 g./l. of glue, which is about 300 times as much as is used in copper refining, changes the conductivity of acid copper solutions less than one part in one thousand, if at all.

Even after it was recognized that glue increases the polarization, some time elapsed before measurements of the anode and cathode polarizations were made and published. Data of H. E. Haring and W. Blum,[4] H. E. Haring,[5] E. W. Rouse and P. K. Aubel,[6] C. G. Fink and C. A. Phillips,[7] and E. F. Kern and R. W. Rowen,[8] all show that in the concentrations used, glue produces only a slight increase in anode polarization but an appreciable increase in cathode polarization. This latter increase is roughly proportional to the glue content if the latter is from 1 to 10 mg./l. Haring therefore suggested that simple polarization measurements could be used to determine and control the effective glue content of the solution. This method has proved helpful, as no analytical methods are available for determining such small concentrations of glue. In the absence of such methods, the additions of glue have usually been regulated by the appearance of the deposits and by the consumption of glue observed over long periods. The latter is approximately one-half ounce per ton of refined copper. If, as is not probable, all of this glue entered the copper, it would represent only 0.0015 per cent by weight. It is not detrimental, as it is destroyed during the melting and casting of the refined copper.

During recent years a by-product of the sulfite pulp industry, known as gulac (or goulac), has been employed as an addition agent in copper refining. It probably contains ligninsulfonates as well as other substances, some of which may be colloidal. The work of Kern and Rowen[8] shows that while gulac improves the deposit it does not increase the cathode polarization. Best results were obtained by adding both glue and gulac to the copper baths.

Plating. Until recent years addition agents were not generally applied in acid copper plating baths, in fact such baths were not used extensively. Now, especially in connection with the automobile industry, acid copper baths are largely employed. Relatively thick deposits of copper are applied between an initial layer of "cyanide copper" or of nickel upon the steel, and a final coat of nickel (upon which a thin external layer of chromium is now plated). It is desirable to produce this intermediate copper layer as rapidly as possible and still have it relatively smooth. The practice in this field is not yet standardized but in some cases at least additions of glue, dextrin, urea, phenol or aluminum sulfate have been employed successfully. Another application in which addition agents may prove useful is in the production of a thin, bright copper deposit on brass, to be followed by nickel and chromium.

In the copper plating of ornaments and art objects made either of antimonial lead or of plaster, relatively thick deposits are applied, and addition agents such as the above are frequently used in order to make them smoother than they would be otherwise.

Forming. In electrotyping, which is the oldest and most extensive application of electroforming, copper is deposited either upon a graphited wax mold or upon a lead mold. In many cases an initial layer of nickel is applied, with a thickness of about 0.025 mm., followed by about 0.15 mm. of copper. In either case the copper is deposited from acid sulfate solutions, which are agitated with air. A current density of from 5 to 10 amp./dm.^{2} is commonly employed in solutions that contain no addition agent. Under these conditions it requires from 2.5 to 1.25 hours to deposit the required thickness of copper.

The recent interest in addition agents in copper electrotyping solutions is the result of a desire to deposit the copper more rapidly, and also to produce harder "shells" than those formed in plain solutions. The greater smoothness, while desirable, is not so important as in plating or refining, because in electrotyping it is the layer of metal first deposited that governs largely the quality of the finished printing plate. (In plating, the structure of the metal last deposited determines the finish.)

While many addition agents, including proprietary or secret preparations, have been long used in electrotyping, there has been a lack of knowledge regarding their effects, optimum concentrations and methods of analysis or control. Consequently erratic results were frequently obtained, especially in small plants where the volume of work varied greatly from day to day or week to week, and where neither the solution composition, temperature nor current density was under close control. Obviously no addition agent can be a substitute for intelligent operation or a panacea for all the ills of deposition. It is equally obvious, however, that any addition agent that is to be used must not require too exact control of operating conditions.

A brief study of this subject was recently conducted at the Bureau of Standards by R. O. Hull, Research Associate of the International Association of Electrotypers. The results, recently published,[8a] showed that of the substances that have been used or suggested for this purpose, including glue, dextrin, urea and phenol, the last is most suitable for this industry.

When phenol is added directly to such a solution it at first produces softer and coarser grained deposits than are obtained from plain solutions at that temperature and current density. After electrolysis for one or two days, this effect disappears and the deposits are relatively hard and fine-grained. The difference is no doubt due to the gradual combination of the phenol with the free sulfuric acid to form phenolsulfonic acid. On this assumption, the latter compound was prepared by heating equal volumes of phenol and sulfuric acid to 100° C. for one hour. When the product was added to a copper solution, hard smooth deposits were produced at once. It was found that concentrations of phenol (added as the sulfonic acid) from 0.5 to 5 g./l. produced equally good results. Baths containing initially 1.0 g./l. of phenol (as sulfonic acid) still yielded improved deposits after several months operations, by which time the equivalent phenol content, determined analytically, had fallen to 0.1 g./l. These facts point strongly to the conclusion that it is not the phenol or phenolsulfonic acid that is effective, but some product derived from it, perhaps by oxidation. Hydroquinone and quinone, which are products of the oxidation of phenol, were tried and found in small scale tests to act similarly to phenol.

Cyanide Solutions: Copper Plating. The operation of cyanide copper plating solutions, which are strongly alkaline, seldom involves the direct addition of colloids. Small concentrations of substances such as sodium thiosulfate or sodium plumbate have however been added as "brighteners." So far as known, no detailed studies of their effects have been made; and it is not known with certainty whether any sulfur from the thiosulfate, or lead from the plumbate, is included in the deposits. It is not improbable that such substances give rise to the formation of colloids, especially in the cathode film, the composition of which largely determines the character of the deposits.

Brass Plating. Brass is deposited upon steel and iron hardware from solutions containing sodium cyanide, copper cyanide, zinc cyanide, and sodium carbonate. In general the purpose is to produce deposits of a certain color rather than a definite composition. The composition is usually not the same as that of cast or rolled brass with the same color. The color may be changed by varying almost any one of the operating conditions. Addition agents have been used to produce smoother and brighter brass deposits and also to regulate the color. Among those commonly employed are arsenic (as arsenite), lead (as plumbate) and phenol. The latter probably forms some phenolate, as the solutions are relatively alkaline (the pH is usually from 11 to 12). The use of all these substances is empirical, and it is not known whether colloids are present, and if so, how they produce the observed effects.

Silver:

Nitrate Solutions: Refining. It is well known that silver nitrate solutions are very susceptible to the effects of colloids.

No addition agents are used in the silver refining baths, however, as the purpose is to produce coarsely crystalline deposits which can be readily detached from the cathodes.

Cyanide Solutions: Plating. Although carbon bisulfide was one of the first addition agents used in plating, and it is still employed as a brightener in silver plating, almost nothing is known regarding the mechanism of its effects. The concentration is very low, probably about 1 mg./l. or one part per million of solution. It has been reported that traces of sulfur are present in the silver deposits from such baths. The optimum concentration produces fine-grained bright deposits; while an excess causes dark deposits, which probably contain sulfur. That the carbon disulfide is not combined in any stable compound, is evident from the fact that it evaporates from the solution, especially if the latter is warmed or agitated. It is at least probable that it is present as a true solution, as the customary concentration is much less than the solubility of carbon disulfide in water.

Gold:

Chloride Solutions: Refining. No colloids are intentionally added to the solutions used in gold refining. As these solutions are strongly acid, there is less probability of colloidal inorganic hydroxides being formed during electrolysis than in neutral or alkaline baths.

Cyanide Solutions: Plating. Addition agents are not commonly employed in gold plating, probably because the deposits produced under normal conditions are very fine-grained. Some of the constituents of gold baths, such as phosphates and ferrocyanides, may give rise to the formation of colloids, especially in the cathode film.

Zinc:

Sulfate Solutions: Refining and Winning. When zinc is deposited from acid solutions there is a marked tendency to produce coarsely crystalline deposits which, especially at low current densities, may consist of isolated crystals. This behavior is characteristic of processes of electrodeposition in which the cathode polarization is low.[9] The common use of addition agents in acid zinc baths in order to produce dense deposits depends largely upon their effect on the cathode polarization for zinc deposition. In addition they usually increase the polarization (overvoltage) for hydrogen discharge and thus increase the cathode efficiency. To some extent they thereby overcome the deleterious effects of even minute traces of nickel, cobalt and other objectionable metals. When used,[10] the additions of glue represent about 1 to 1.5 oz. per ton of deposited zinc, i.e., about 0.003 per cent. It is believed by some authorities, however,[11] that the use of glue or other addition agents in zinc baths is a "makeshift," and that with proper purification of the solutions their presence is unnecessary.

Plating. In zinc plating from acid solutions there is a real need for substances that will improve the brightness or smoothness of the deposits. Such deposits not only have a desirable appearance but they probably also exert better protection against corrosion than coarse deposits, which is the chief function of zinc coatings.

Almost every type of addition agent, both inorganic and organic, has been used in zinc plating. Among the former, aluminum salts are most common. Observations by M. R. Thompson[9] indicate that no aluminum is deposited with the zinc, and that the chief function of the aluminum salt is to serve as a buffer, and to prevent the pH from getting much above 4. This action depends upon the fact that in the concentrations used, aluminum salts hydrolyze at a pH of about 4, with the formation of aluminum hydroxide. The latter is likely to be colloidal and to increase the cathode polarization and thus produce brighter deposits. There is some evidence that the aluminum hydroxide also retards chemical solution of the zinc anodes, the dissolving of which is objectionable as it causes an increase in the zinc content and a decrease in the acidity.

Among the organic additions to zinc baths[12, 13] are dextrose and dextrin (both of which are present in the commercial glucose sometimes added), glycerol, gum tragacanth, licorice (which contains glucosides and gums), glue and other proteins, and β-naphthol. It is obvious that even though the effects of substances of such widely different chemical composition are similar, the mechanism of these effects may be quite different.

Cyanide Solutions: Plating. The alkaline zinc plating baths contain both the double zinc cyanide, $Na_2Zn(CN)_4$, and the zincate, Na_2ZnO_2 or possibly $NaHZnO_2$. In addition, it is not unlikely that some zinc hydroxide is present in a colloidal condition. If so, this might account in part for the fine-grained deposits from such baths, the formation of which is usually explained on the basis of the low zinc-ion concentration present in the complex cyanides.

A common inorganic addition agent is mercury, introduced either from zinc anodes containing mercury or as mercuric oxide or cyanide. The mercury, which is deposited with the zinc, produces brighter and denser deposits, especially on cast iron. This effect is probably due to a change in the hydrogen overvoltage caused by the presence of mercury in the deposit. Organic addition agents include gums and reducing sugars,[14] and gulac [15] ("lignol").

Cadmium:

Sulfate Solutions: Refining and Winning. In the electrolytic refining of cadmium,[16] no addition agents are used, although there is a marked tendency toward roughness and treeing unless the metal is deposited on revolving cathodes. F. C. Mathers and H. M. Marble [17] did not find any additions satisfactory in cadmium sulfate baths.

Cyanide Solutions: Plating. The solutions used for cadmium plating are similar to the zinc cyanide baths, except for the fact that cadmium does not form any salt with the excess of sodium hydroxide which is present. Addition agents are almost invariably used. The presence of a very small amount of nickel causes the formation of brighter deposits.[18] It is difficult to explain such an effect, or to determine whether it involves the formation of colloids. Very little if any nickel enters into the cadmium deposit.

Among the organic additions are casein, gulac, turkon oil [18] and peptone.[19] All of these contain colloids and other substances of unknown composition or properties.

Tin:

Acid Solutions: Refining.[20, 21, 22] In both the fluosilicate and sulfate baths, addition agents are employed to produce smoother deposits. The most common are glue, aloin, and cresolsulfonic acid. Often two of these substances are used in the same solution.

Alkaline Solutions: Plating. Most of the baths used for tin plating are alkaline and contain sodium stannite and stannate, and in some cases sodium cyanide. One addition agent frequently used is rosin,[23] which in the alkaline solutions no doubt forms rosin soaps which are colloidal. It is at least probable that some colloidal stannous or stannic hydroxide is also present in such solutions.

Lead:

Acid Solutions: Refining. In the fluosilicate solutions for refining lead,[24] glue is almost invariably used as an addition agent; in fact without it the deposits are coarse and spongy. The concentration of glue is materially greater than that used in copper refining, being generally about 0.1 g./l. In addition, molasses is often added. This contains reducing sugars, and usually also dextrin and other colloids.

Plating. Glue is also used as an addition agent in plating lead from either fluosilicate or fluoborate solutions. In perchlorate baths [25] clove oil and peptone are common additions.

Chromium:

Chromic Acid Solutions: Plating. Practically all chromium plating is now done with baths in which chromic acid is the principal constituent. A small amount of some other ion, usually sulfate, is present. During operation some trivalent chromium is always formed. This is generally assumed to be present as "chromium chromate," to which however no definite formula can be attached. That this compound is present at least partly in the colloidal condition is indicated by the very dark color it produces. It causes an increase in the resistivity of the solution. The latter change may be most simply explained on the assumption that the formation of the chromium chromate reduces the concentration of free chromic acid. This would occur whether the chromium chromate is colloidal, or whether, as concluded by E. A. Ollard,[26] it is in true solution but only slightly ionized. That it is at least partly colloidal, especially near the cathode, is indicated by the observations of F. Adcock,[27] who found both oxygen and hydrogen in the deposited chromium, which may therefore have contained chromium chromate or hydroxide.

Practically, it has been found[28] that trivalent chromium is not advantageous as it decreases the conductivity and narrows the range within which bright chromium deposits are produced. In high concentrations it produces a slight increase in throwing power.[29]

When chromium baths are kept in steel tanks or operated with steel anodes they may contain an appreciable amount of iron. This is no doubt present as ferric chromate, the properties and effects of which are similar to those of chromium chromate. Alter and Mathers[30] found that the addition of silica-gel to chromium baths produces no beneficial effect on the throwing power or the cathode efficiency.

Iron:

Acid Solutions: Refining, Winning, Plating and Forming. Organic addition agents are not usually employed in the various processes that have been used or proposed[31] for producing pure electrolytic iron in marketable forms, such as sheet and tubes, or for building up articles with iron. In fact most organic compounds when present in such baths in even small concentrations are likely to contaminate and embrittle the deposits. Some of the difficulties in iron deposition are due to the formation in the baths of basic ferric salts, which may be in colloidal suspension and become included in the deposits.

Alkaline Solutions: Winning. A very interesting application of colloids is the Estelle process for the electrolysis of sodium hydroxide containing hydrated ferric oxide, which is largely in colloidal suspension.[32] The oxide migrates to the cathode where it is reduced to metallic iron.

Nickel and Cobalt:

Sulfate Solutions: Refining. In nickel refining it is generally recognized that colloids, either organic or inorganic, are detrimental, and their presence is avoided. Here also colloidal nickel or iron compounds may be formed, especially in the cathode film. A few preliminary experiments at the Bureau of Standards indicate that dense nickel deposits may contain not only hydrogen, but also small amounts of oxygen. If confirmed, this may be explained by the presence of inclusions of nickel hydroxide. These would be less likely to form in solutions of low pH, in which bright deposits are usually produced.

Plating. In general, organic substances are excluded from nickel baths; in fact the brittleness and pitting of nickel deposits is often attributed to the presence of organic matter.[33] In some cases, however, gums such as tragacanth have been used successfully as brighteners. Solutions containing glycerol or ethylsulfuric acid have also been used abroad to produce brighter nickel deposits. It is not known whether colloids are formed in such baths.

Cobalt solutions are so similar in behavior to nickel that colloids probably have about the same effects in them as in nickel baths.

MECHANISM OF THE EFFECTS.

From the necessarily incomplete survey of the present applications it is evident that the actual use of colloids or other addition agents in electrodeposition is almost entirely empirical. It is not possible with existing knowledge to predict with certainty the effect of any given addition to a bath in which it has not been previously used or tried. Even when a given addition has been found advantageous, it is usually difficult to predict even approximately the optimum concentration or the effect of an excess. The methods of control depend almost entirely on visual observation of the deposits. When two or more addition agents are used simultaneously in a bath, it becomes still more difficult to so control their concentrations as to produce a uniform product.

The most general and most characteristic effect of addition agents, especially colloids, on the electrochemical properties of solutions is the increase which they produce in the cathode polarization. Such an increase from any cause usually results [34] in (a) a decrease in crystal size, (b) the formation of a "broken" or random structure as distinguished from a fibrous, columnar or conical structure produced in most simple salt solutions, (c) a reduction in roughness or "treeing," and (d) an increase in throwing power. All of these effects are observed to some extent with most addition agents, and in many cases are the reasons for their use.

Various explanations have been offered for the effect of colloids on the cathode polarization. Any increase in viscosity of the solution is certain to increase the polarization, as it hinders the processes of convection and diffusion, by which the metal-ion concentration in the cathode film is largely maintained. (The rate of migration of the metal ions is usually not nearly sufficient to maintain their concentration at the cathode when relatively high current densities are used.) In the concentrations commonly employed the colloids do not greatly increase the viscosity of the body of the solution. However, if they migrate toward the cathode, the colloids may there reach a higher concentration and produce a greater viscosity, and thus increase the polarization.

It is generally assumed that in order to affect the polarization and the crystal structure, the colloids must migrate toward the cathode. Whether a given colloid does so depends in part on the pH of the bath. Frölich [35] has shown that with a low pH in the bath a colloid may migrate toward the cathode but will not actually reach it if the pH of the cathode film is higher than that of the body solution. This explanation accounts for the fact that while deposits of copper from a solution to which gelatin has been added, contain organic matter, deposits of zinc from a similar zinc solution have no organic matter in them.

M. C. Marie and M. L. Caudel [36] found that the excess weight of copper deposited from solutions containing gelatin was a maximum at a pH of about 3.2, and decreased as the isoelectric point (4.6) was approached. This result is in conformity with the observation of Frölich.

A striking example of the inclusion of colloids in an electrodeposit is that reported by C. G. Fink and J. D. Prince.[37] They found that as much as 16 per cent of graphite can be co-deposited with copper from a solution in which the colloidal suspension of graphite is stabilized with gelatin.

It is difficult to reconcile the use of certain colloids in both acid and alkaline solutions, in which we might expect the direction of migration to be reversed. It is of course possible that the concentration throughout may be sufficient to affect the electrode potentials at both electrodes, regardless of the direction of migration. Thus it is known that glue in acid copper baths increases slightly the anode polarization, although it migrates toward the cathode where it produces a greater effect on the polarization than at the anode.

As indicated in the first part of this chapter, many of the commonly used addition agents are not colloidal. Such substances may give rise to the formation of colloids, organic or inorganic, as a result of hydrolysis, oxidation or reduction. Fuseya [38, 39] and his students found that crystalloidal addition agents that produce effects on the crystal structure of copper and silver form complex cations with the metal present. When these migrate to and are discharged upon the cathode, the organic constituents may be included in the deposit. More recently Fuseya[40, 41] found that in lead and zinc solutions, glycocoll forms complex cations but produces no effect on the crystal size or weight of the deposits. This illustrates the difficulty of making generalizations.

Recently B. Clark and E. O. Jones[42] found that in acid copper solutions crystalloidal substances such as dimethylaniline, lactic acid and dextrose produced changes in polarization and crystal structure of the same magnitude as those produced by colloids such as gelatin and starch. These authors observed certain anomalous "breaks" in the polarization curves with some of these additions, but offered no explanation for them. It is surprising that they found the conductivity of the solution was decreased by 10 to 15 per cent by these additions, including glue, though previous investigators[8] have found that such changes are negligible with even large amounts of glue.

Clark and Jones confirmed approximately the prediction of Blum and Rawdon[34] that the grain size is a function of the polarization. It is not necessary, therefore, to assume that the addition agent (or its products) must be included in or adsorbed by the deposit. The fact that it is usually included may account for some of the more specific effects of certain additions in producing deposits with a characteristic form or structure. Among such effects is that of *m*-cresolsulfonic acid in stannous sulfate baths. F. Foerster and J. Fischer[43] found that this addition agent fosters the growth in the deposit of coarse "flower" crystals present in the sheet tin used as the cathode. It is possible that this effect may be due to a retardation of the hydrolysis of the tin salt, which if it occurs is likely to cause the mat deposit that is most readily produced in the absence of the addition agent.

Until more is known about the mechanism of crystal formation in metal deposition, it would be useless to attempt to explain the effects of complex compounds on that mechanism. All that can be safely said is that the presence of any substance foreign to the lattice of the metal crystal must hinder the growth of that crystal and hence foster the formation of new and necessarily smaller crystals.

S. Wernick[44] found that the "silver numbers" of various colloids (except dextrin), i.e., the weights of colloids required to prevent the coagulation of a silver sol by a salt, are approximately proportional to the effects of these colloids in reducing the crystal size of silver deposited from silver nitrate. This relation indicates that the colloids may be effective through their protective action against the growth of metal crystals. F. C. Mathers and A. B. Leible[45] found an approximate relation between the adsorption of certain essential oils on metal surfaces and the effectiveness of these oils as addition agents. No such evidence is at hand regarding similar effects of other colloids.

CONCLUSIONS.

Any complete theory or explanation of the effects of colloids or other addition agents in electrodeposition must take into account and if need be harmonize at least two major effects. First, they cause an increase in the cathode polarization, which increase usually produces finer-grained deposits regardless of whether it is caused by addition agents or by any other factor. Second, the addition agents or products derived from them are likely to be included in the deposited metals. Such inclusions will necessarily interfere with the normal crystal growth and foster the production of a larger number of smaller crystals with random orientation. The latter effect is to be expected regardless of whether the inclusion is caused by (a) direct migration of the colloid or

(b) migration of a complex cation containing the addition agent; or whether the colloid is (a) entrapped mechanically in the space lattice, (b) adsorbed on the surfaces of the crystals, or (c) present in the deposit as an actual compound with the metal. Probably in different processes or under different conditions, certain of these mechanisms may predominate. It is possible, however, that in a given operation all of them may come into play. To segregate them, it will be necessary to make extensive critical experiments, in which the structure and constitution of the crystalloidal or colloidal agents are more definite and more constant than in most of the rather qualitative experiments thus far conducted in this field.

Such a study is desirable, as it may throw light on the constitution of colloids and on the mechanism of metal deposition. From a purely industrial standpoint, however, it is doubtful whether voluminous studies of addition agents have been or will be warranted. A small number of such substances have found technical applications, and some are almost indispensable. Even in such cases, however, the results obtained are not so revolutionary as to warrant the all too prevalent belief that addition agents furnish a panacea for the ills of metal deposition. In many processes, research would be more productive in defining conditions under which addition agents are unnecessary than in multiplying their applications and incidentally the problems of plant control.

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Colloidal Aspects of Baking Chemistry.*

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The purpose of this article is to point out a number of factors of importance in connection with fermentation and baking of bread. The excellent text books by Bailey,[12] the work of Alsberg,[1] Jago,[121] and also Whymper have so thoroughly covered certain phases of the subject, that a further discussion will necessarily be limited.

The modern technology of bread making necessitates accurately controlled conditions and measurement of flour quality. Hence, a more comprehensive analytical study of the factors concerned has been initiated, because a synthetic study is limited by the inherent difficulties resulting from the complexity of the system (dough-bread), and the limitations of experimental methods. However, we should not forget that to the baker, the end product (the baked bread) is always the final criterion of the quality of any flour, for the many factors involved in bread making are integrated into the finished loaf. Thus colloid-chemical investigation of flour has not yet developed a satisfactory method for determining its quality. Unfortunately no single precise method exists for conducting baking tests; no universal yard-stick is known for measuring the effect of the numerous factors involved.

Bread making is a very ancient industry, the successful results of each generation having been incorporated into the general knowledge of the art. The methods of manufacturing flour have also been greatly improved during the last 50 years; and although many still desire the whole wheat loaf, the modern demand is mainly for white bread from flour of highest purity, whiteness and uniformity. The modern baking industry was not possible until the manufacture of a stable yeast enabled the baker to enlarge his equipment, to install machines, and to place the art on an industrial basis.

The chemist was called upon to assist with the new problems. The highly established state of the art has circumscribed his activities. However, the chemist has introduced numberless improvements, e.g., standardization of flour, and has developed a great body of information regarding the composition

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of flour, the dough colloids, the action of enzymes, the effect of pH and of various salts on doughs, the action of oxidizing and bleaching agents, the nature and action in doughs of yeast, and many other factors. The exigencies of commerce, the pressure of competition, and the greater discrimination of the consumer have demanded the urgent attention of the engineer and the chemist.

A knowledge of the colloid chemistry of bakery products such as bread, cake, cookies, doughnuts, etc., and of their ingredients, has helped to solve many perplexing problems. Bread in its simplest form is a very complex system prepared from flour, water, salt, sugar and yeast; for variety and betterment other ingredients are added, such as milk, fat, diastatic and nondiastatic malt syrup (each ingredient of which exerts a specific influence), yeast foods, and various chemical improvers. Cakes and cookies are made from flour, water, baking powder, starch, eggs, milk, fat, sucrose and various flavoring agents, and may require in addition, invert sugar, invertase, dextrose, water and salt.

In spite of the enormous difficulties encountered, some noteworthy progress has been made in improving dough properties. The combination of salts developed at the Mellon Institute is one of the outstanding contributions of chemistry to the industry. The schools of Swanson and of Bailey should be given due credit. Recent advances in colloid technique; the ultracentrifuge, X-rays, study of mechanical properties, and surface tension of colloids, augur the successful elucidation of many problems of the constitution and colloidal properties of gluten, starch, and other baking ingredients, and may lead to more reliable and simpler methods for determining flour quality, greatly facilitating the labor of the baking technologist.

FLOUR.

Definition.—Flour, according to the United States Department of Agriculture, is the fine, clean, sound product made by bolting wheat meal, containing not less than 7.1 per cent protein, and not more than 15 per cent of moisture, 1 per cent of ash or 0.5 per cent of fiber. It is a fine powder containing characteristic starch granules of sizes varying from 20 μ to 200 μ and apparently amorphous clumps of protein material. The chief constituents of flour are the gluten, starch, dextrin, mineral salts, enzymes, fats, lipoidal substances, pigments, pentosans, pectins, and fiber. Other important substances which have not been so thoroughly investigated are possibly present.

The wheat kernel contains at least five proteins; according to Osborne,[200] gliadin, glutenin, albumin, globulin, and proteose. Hoffman and Gortner[117a] found a prolamin, gliadin; a glutelin, glutenin; an albumin, leucosin; but no proteose in wheat flour.

Composition.—The following tables summarize the composition of flour:

TABLE 1.—*Proximate Composition of Patent Flour (per cent).*

H_2O	Ash	P_2O_5	Oil or Fat	Carbohydrates	Fiber	Pentoses	Total Sugar	Total N	Protein	Wet Gluten	Dry Gluten	Authority
11.52	0.403	0.216	0.99	....	0.16	2.94	1.32	1.82	....	30.64	11.64	Jacobs. *See* Bailey[12]
11.48	0.39	0.18	1.45	73.55	0.18	...	...	...	12.95	36.14	10.85	Jago[121]

TABLE 2.—*Protein Content of Wheat.* (Osborne and Voorhees.[203])

N × 5.68 = protein

	Spring Wheat N	Spring Wheat Protein	Winter Wheat N	Winter Wheat Protein
	Per Cent			
Glutenin	0.8245	4.683	0.7346	4.175
Gliadin	0.6977	3.963	0.6884	3.910
Globulin	0.1148	0.624	0.1148	0.624
Albumin	0.0657	0.391	0.0603	0.359
Coagulum	0.0453	0.269	0.0379	0.223
Proteose	0.0341	0.213	0.0791	0.432
Water Washings from Gluten	0.2259	1.272	0.1552	0.881
Total	2.0050	11.415	1.8703	10.603
In meal	2.10	11.93	1.94	10.98

The composition of the ash according to Snyder[245] is given in Table 3.

TABLE 3.—*Composition of the Ash of Wheat Flour.*

	Per Cent		Per Cent
Total Ash	0.46 (of Flour)	CaO	3.10 (of Ash)
K_2O	30.10 (of Ash)	P_2O_5	50.10
MgO	12.75	SiO_2	0.30

Glutenin is insoluble in water, salt solutions, and dilute alcohol, but soluble in dilute acids and alkalis, from which it is precipitated by neutralizing. Sharp and Gortner[238] state that glutenin is changed by drying and by treatment with alcohol. Coagulation of glutenin takes place very slowly at 70° C. Table 4 gives the products of acid (HCl) hydrolysis which were obtained by Osborne.[200]

TABLE 4.—*Amino Acid Content of Gluten Proteins.*

	Glutenin	Gliadin		Glutenin	Gliadin
	Per Cent			Per Cent	
Glycocoll	0.89	...	Serine	0.74	0.13
Alanine	4.65	2.00	Tyrosine	4.25	1.20
Amino Valerinic acid	0.21	0.21	Cystine	0.02	0.45
Leucine	5.95	5.61	Lysine	1.92	...
α-Proline	4.23	7.06	Histidine	1.76	0.58
Phenylalanine	1.97	2.35	Arginine	4.72	3.16
Aspartic acid	0.91	0.58	Ammonia	4.01	5.11
Glutamic acid	23.42	37.33	Tryptophane	Present	Present
			Total	59.65	65.77

Gliadin, a protamine, is soluble in distilled water, forming an opalescent solution. It is precipitated by NaCl Wood and Hardy[288] state that its solubility is due to the presence of CO_2. It is insoluble in absolute alcohol, but is peptized in 60 to 70 per cent alcohol, from which it is precipitated by the addition of water or absolute alcohol. Blish[85] states that gliadin is the only flour protein which may be considered a chemical individual, its ratio to the total protein being fairly constant. Gliadin contains more glutamic acid, ammonia, and proline than any other flour protein.

Leucosin, an albumin, is soluble in pure water and in salt solutions and is comparatively insoluble in alcohol solutions. It is precipitated by concentrated solutions of NaCl and $MgSO_4$.[200]

The *globulins* are defined as simple proteins, heat-coagulable, insoluble in H_2O but soluble in dilute salt solutions. Wheat globulin is precipitated by saturation with magnesium sulphate. Sodium chloride does not precipitate globulin, nor does heating readily affect its coagulation.[200]

Wheat (tritico-) nucleic acid, was shown by Osborne and Harris[202] to exhibit colloidal properties in solution. The free acid is relatively insoluble in cold water, and forms a sticky mass in hot water, but does not pass into solution to any extent. Boiling changes the character of the acid. Alkali metal salts of nucleic acid are soluble and very stable.

Sucrose exists in flour to the extent of 1 to 1.5 per cent. Maltose is also present in flour, and is formed by diastatic action during fermentation of the dough. While 5 per cent of sugar has very little effect on gluten, 10 per cent slightly toughens and 20 per cent gives approximately the same degree of toughening as a 5 per cent NaCl solution.

Dextrins are present in flour in small amounts and are formed by the diastatic enzymes of flour or malt. The use of highly diastatic flours, or flours to which diastatic enzymes have been added, improves the texture, volume and water retaining capacity of bread. This is partially a result of the greater absorption capacity of the dextrins.

Starch in the form of fine granules constitutes 65 to 70 per cent of flour. Lippman[171] stated that the gelatinization temperature of wheat starch is 62.5° to 64° C. The density of starch is approximately 1.50.[218] Starch will absorb 31.6 per cent water at 0° C. The maximum heat of wetting has been determined to be about 28.8 calories per gram. The specific heat of starch is 0.44 cal./gm.[281] These figures are of importance in commercial mixing of dough ingredients. Wheat starch also contains a small amount of ash.

The *fat* content of flours increases as the grade decreases. Although the components have not been completely identified it is known that palmitic, stearic and oleic are present to the extent of 11, 20.7 and 52.24 per cent, respectively.

Analysis of a high grade spring wheat flour at the Fleischmann Laboratories gave a total ether and benzene extract of 1.49 per cent of which two-thirds consisted of unsaponifiable material, sterols, lecithin, etc. Jacobs and Rask[120] found the bran, germ and inner endosperm, to contain 5.6, 12.5 and 0.75 per cent fat respectively. Rittenhausen[217] isolated from gluten fat and leafy crystals which he concluded were cholesterol. Frankforter and Harding[86] found 1.96 and 2.03 per cent lecithin and paracholesterol, and 7.3 per cent glycerol in germ oil.

Lipoids and phosphatides are present in larger quantities in gluten from low grade flours than from high grade. Schulze and Steiger[225] concluded from the P analysis that wheat fat contained 6.51 to 7.24 per cent lecithin, although not all of it could be extracted with ether.

Two *sterols* were obtained by Burian[43] which he named "sitosterol" and "parasitosterol," while Ritter[216] obtained but one. Kosutany[154] states that wheat lecithin is a disteryl ester rather than a dioleyl ester. Schulze[224] found sitosterol in wheat kernel fat. Ellis[71] found the m.p. of Ritter's sterol to be 137.5° C. Anderson and Nabenhauer,[5] however, found "sitosterol" and "dihydroxysitosterol" in the endosperm. Ball[26] determined the chemical and physical constants of wheat germ oil and of oil extracted from patent flour. Wheat embryo oil kept from exposure to air increased in acidity only slightly, and developed only a trace of "oxidative" rancidity* during three years.

The pH of flour varies, but the higher grades usually have a pH of 5.8 to 6. Bailey and Johnson[15, 16] give a pH of 5.78 to 5.92 for patent and 6.03 to 6.38 for straight and clear flours. This difference is quite general.[7, 228] On aging a patent flour having a pH of 5.92 fell to 5.74 in 7 months, and a straight flour from 6.03 to 5.83.[15] Flours treated with chlorine and nitrogen peroxide are more acid than the untreated flours.

Molds and *bacteria* capable of excreting powerful proteolytic and liquefying enzymes are found in practically all flours.[149] These organisms may induce marked changes in the colloidal properties of the dough. Cohn, Cathcart and Henderson[51] showed that *Bacillus mesentericus*† as well as many other organisms do not develop readily in bread having a pH of 5, while Frey and Hoffman (unpublished results) found the limit to be nearer to a pH of 5.3. Hoffman and Schweitzer (unpublished results) later found that if the spore content of flour is over 10 per gram, there is considerable danger of an outbreak of rope.

Flour Enzymes. Since flour is prepared from the seeds of a plant it would be expected to contain all the enzymes required for its metabolism; proteolytic, lipolytic, catalytic, cytolytic, etc. Many investigators have shown the presence of these enzymes in flour.[9, 25, 73, 85, 168, 170, 258]

The *protease* content of normal flour was found by Sharp and Elmer[230] to be relatively small, but if given sufficient time to act, could still be recognized. It was greater

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* "Oxidative" rancidity as measured by the coloration given by treatment with concentrated HCl followed by a 1 per cent ethereal solution of phloroglucine: "the Kreis Test."

† This organism is responsible for the bread disease called "rope."

in immature than in fully ripened wheat. Flour made from sprouted wheats possesses a very high proteolytic activity and lower grade flours, that is, those containing larger portions of the coarser products of the wheat have greater proteolytic activity than the higher grades. A moist harvest is also likely to produce more protease than if the wheat is ripened in dry weather.

Flour *diastase,* in view of the importance of sugar in dough fermentation, has been extensively studied. Rumsey[219] placed the determination of diastatic activity upon a logical basis, and first showed that if the relative quantity and quality of the gluten is the same, the baking value is closely related to the diastatic activity. The diastatic value of flour depends upon the conditions under which the wheat is ripened. Immature or frosted wheat possesses greater diastatic activity than fully ripened wheat.[130] Wheat ripened under excessively dry conditions possesses a relatively low diastase content. If during storage the wheat becomes moist its diastase content is apt to increase, while if sprouted, a very large increase occurs.[196, 257] These variations are perfectly logical when we consider that the wheat seed is a living organism, which in the dry ripened state has relapsed into a temporary period of dormancy. The diastatic activity of flour apparently increases with the degree of fineness to which it is ground.[127] This effect may be due either to setting free a larger proportion of diastase or to injury of the starch granules, thereby rendering them more subject to enzyme action.

The *catalase* of flour, being of relatively small importance in fermentation has been but little studied. White flour is relatively poor in catalase, the activity increasing with the per cent of extraction.[170, 182] The determination of catalytic activity is thus sometimes used in determining flour grades. While Lindet[170] states that catalase is found principally in the peripheral parts of the grain, large amounts seem also to be present in the germ.[189]

Cytase exists in the aleurone layer.[102] During sprouting or malting of grains the cytotlytic activity at first diminishes slightly, then increases to a maximum of about 2 times the original value.[176] Addition of flour from sprouted wheat to normal flour would thus raise its cytase content. This is of considerable importance, for cytolytic activity is probably closely related to diastatic activity in the dough (*vide infra*).

Vitamins. Vitamins A and B have been reported in wheat and rye, but in the process of milling they are largely removed.[223] Nutrition experiments show that flour alone is incapable of supplying a sufficient quantity of accessory food factors; bread, however, if prepared with yeast and not with baking powder,[29, 63, 113] appears to contain considerable vitamin B. Bread is a particularly suitable carrier of certain vitamins, and accessory materials containing them may be readily incorporated.[267]

PHYSICO-CHEMICAL STUDIES RELATING TO FLOUR AND DOUGH.

Measurement of Flour Quality. Many attempts have been made to find a substitute for the baking test in the determination of flour quality:

(1) *Chemical analyses* of flour for ash, protein, wet and dry gluten, while not at all times expressing the real baking quality, serve as very useful criteria. Balland[9] found that gluten and protein content are not always correlated. Shutt[240] concluded that baking strength was related to protein content and Larmour[162] has shown that the baking quality of a single type of wheat (hard red spring) may be predicted with considerable accuracy from the protein content.

(2) *Viscosity determinations* have been extensively studied in the hope of finding a relation to flour quality.[114, 177, 231] The methods have shown some promise and seemed to indicate that viscosity measurements give an index of flour quality. However, more recent investigators have found that no satisfactory correlation could be established.[80, 68, 128, 160]

(3) *pH and buffer capacity* are closely correlated with ash content; i.e. with flour grade,[20] and have been suggested as valuable means of determining flour quality.[274]

(4) The ability to withstand *oxidizing agents* has been proposed as a guide.[163, 278]

(5) The *swelling* or *imbibition* of discs of gluten immersed in dilute solutions of electrolytes has been studied[269, 283] and Gortner and Doherty[97] concluded that weak flours had a lower rate and lower capacity for hydration than strong flours. Sharp and Gortner[288] found this difference in rate held in various concentrations of HCl, lactic acid, KOH, $Ca(OH)_2$, NaOH and NH_4OH.

(6) A certain degree of *diastatic activity* has been regarded as essential in high quality flours (*vide infra*).[28, 55]

(7) The percentage of water *soluble protein* present in flour has been suggested as an index of quality.[25, 85, 219, 282] The importance of the peptization value of flours has been pointed out.[98, 111, 112]

(8) The *ratio* of *gliadin* to *glutenin* should be 3 to 1 for a strong flour according to Fleurent.[83, 84] Others have also concluded that the gliadin-glutenin ratio was a factor in determining quality of flour.[103, 153, 248] Practically the value seldom varies enough to be of importance. Blish[35] states that the ratio of gliadin to the total protein seems to be fairly constant, the ratio of non-gluten to gluten protein being the chief variable factor.

(9) *Loss of* CO_2 from dough per unit increase in volume, provides a useful measure of gas-holding capacity of doughs under controlled conditions, and, as well as the factors (diastase, sugar, etc.) which control the rate of production of CO_2, may serve as a valuable index to quality.

(10) The number of *instruments* devised to measure the *mechanical properties* of gluten or dough is probably unknown. Among them the historic aleurometer,[39, 146] the Chopin extensimeter,[49] the Harrell penetrometer[109] and the Brabender mixer[40] are probably of greatest interest.

(11) The *specific conductivity* of flour extracts has been shown to be correlated with flour grade.[10]

(12) The *Pekar color test* is frequently of assistance in interpreting flour quality.[121]

(13) Last but not least the *source* and *variety* of a wheat, whether a hard red spring from Manitoba or a Persian Karachi, is one of the most important factors in influencing a final decision regarding the quality of its resulting flour.[131]

An attempt at classification of these methods is given in Table 6. None of them gives an adequate measure of the quality of the flour, the final criterion of which is the baking test. Although ordinarily regarded as a very simple determination, this is far from being the case. It may be regarded as a *synthetic* test and involves the consideration of many variables.

Action of Bleaching Agents on Flour. Avery[8] found that *sulfur dioxide* bleached flour very slowly and left a pronounced odor. Sulfur dioxide, when present in extremely small amounts, has a very marked effect on the colloidal properties of gluten.*

Nitrosyl chloride as a flour bleaching agent was patented in 1907.[279] *Nitrogen peroxide* bleaching was introduced from England to the United States in 1904.† Ladd and Stallings,[161] using the Foster Gluten Tester, reported that gluten from unbleached flour was superior to that from flour bleached with nitrogen peroxide, while Snyder[244] found no modification of the gluten. Mann[182] stated that the physical properties of gluten were slightly altered when flour was bleached, and Moore and Wilson[193] and Folin[84a] confirmed this opinion. However, Harcourt[107] reported that bleaching improved the volume and texture of the final loaves.

Brahm (Brahm, C., Mitt. Versuchsanst. Verein d. Müller, Berlin, 1904) found that NO_2 bleached flours increased in acidity over unbleached, but he may have used excessive quantities. A. I. Winton and A. W. Hanson (U. S. Dept. Agri. Bull. 152 [1912]) found no increase. A. C. Peterson (Thesis, U. of Minnesota, 1922) could find no change in acidity. However, Weaver[278] reported a slight increase in NO_2 bleached flour.

Baker[24] states that *nitrogen trichloride* apparently improves the gluten of flour and increases the viscosity of the water suspensions without altering the acidity, resulting in an increase in loaf volume. Weaver,[272] however, found no actual increase in volume after the treatment, but the crumb texture and color were improved.

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* It is well known in the paper and the corn products industries that SO_2 exerts marked swelling and disintegrative action on protein-carbohydrate complexes. J. A.

† "Alsop Process."

Table 6.—*Analytical Properties of Flour Found to Be Correlated with Loaf Volume.*

Analytical Property	Method	Correlation Found	Mathematical Expression	Author
Protein content	Chemical analysis	Roughly proportional for one type of wheat	L. V. (loaf volume) = $[r \pm c] \times$ per cent P.	Shutt,[240] and later Larmour [162]
Glutenin-Gliadin ratio	Fractionation by solvents	Not significant for small variations from 3:1 ratio	—	Blish,[35] Fleurent,[84] Snyder [243]
Hydration capacity of protein	Swelling of gluten discs	Roughly proportional	—	Wood and Hardy [283] Upson and Calvin [269] Gortner and Doherty [97] Sharp and Gortner [233] Ostwald [204] Luers and Ostwald [178] Denham, *et al.*[59] Blish and Sandstedt [36]
	Viscosity of suspensions	Proportional for one class of flour	L. V. = $K \times$ per cent P. $\times$ visc.	
Solubility of protein or peptizability	Extraction with salts	Roughly inversely proportional to protein extracted	—	Gortner, *et al.*[99] Geddes and Goulden [90] Wood [282] Baker and Hulton [25] Ford and Guthrie [85] Rumsey [219] Biechy, *et al.*[30]
	Viscosity of alkaline extract	Proportional for 80 per cent of cases studied	L. V. = $K \times$ Ferm. Power $\times$ visc.	
Mechanical strength of gluten or dough	Extensimeter	Roughly proportional to extensibility	—	Chopin [49] Harrell[109] Brabender [40] Kedzie,[146] Boland [39] James and Huber [122] Bailey [13]
	Penetratometer			
	Power recording mixer			
	Farinometer			
	Loss of CO_2 from dough			
Sugar content	—	Not significant for some formulas	—	—
Lipoid content	—	L. V. varies inversely with lipoid content	—	Working [285, 286]
Diastatic content		L. V. varies with diastatic content	—	Bailey and Sherwood [23] Collatz and Racke [55]
Fineness	—	L. V. reaches a maximum with increasing fineness		Alsberg and Griffing [2] Shollenberger and Coleman [239]
Development by oxidizing agents	—	Bromate differential test	—	Larmour and McLeod [163]
pH of suspension	—	Not significant for small variations from 5.0	—	Weaver and Goldtrap [274] Fisher and Halton [80]
Buffer capacity	—	Inversely proportional to strength	—	Bailey and Peterson [20]

In a further study Weaver[278] states that the H-ion concentration of NCl_3 treated flours is not altered. S. J. Lawellin (Natl. Miller, 29, 53, 86 [1924]) observed that the viscosity of flours treated with NCl_3 was increased.

Chlorine, a widely used agent, increases the buffer capacity and the H-ion concentration,[270] the effect being proportional to the dosage,[15] and more marked with high-grade (low buffer capacity) than with low-grade flours.[273] Avery[8] found effective bleaching occurred at 25° C., causing a marked change in gluten quality which paralleled the change in pH. Dunlap[64] observed that bleached flour and untreated flour after 116 days' storage gave approximately equal loaf volumes; thus bleaching is often termed "artificial ageing." Bailey and Sherwood[22] stated that an increase in volume and crumb color resulted from chlorine treatment, while Arpin[6] found no beneficial effects. Weaver[272] reported that a reduced fermentation period could be used due to improvement in quality.

*Benzoyl peroxide,** Stork says, increases the water absorption of flour by 1 per cent and improves the colloidal condition of the gluten.[254] It has been suggested that this is due to a modification of the relatively labile phosphatides.[286]

Weaver[278] found that benzoyl peroxide did not alter the H-ion concentration of the flour and Bailey[15] found no appreciable change in flour due to the use of this reagent.

pH and Buffer Action. Since the pioneer work of Jaques Loeb[173] the important rôle which H-ion concentration plays in determining the properties of proteins has been well recognized.† While at one time it was thought that the pH of dough was a most important factor in bread manufacture,[123, 166, 246, 274] subsequent work has definitely shown that H-ion concentration is not of great significance. Considering the pH range between 4.2 and 7.8; at the greater acid concentration a slight increase in toughness and some effect on taste is produced; but becomes pronounced only with a relatively large increase in acidity.[80] Only when doughs are brought to a pH in the neighborhood of 3 or 11 is the baking quality destroyed.[283]

However, the "intensity" of H-ion concentration or buffer capacity seems to be of more significance. Thus it has been known for some time that the buffer capacity decreases with the higher grade flours,[19, 104] a fact of considerable significance for dough fermentation.

Buffer Capacity of Wheat Flour. The water extract of practically all types of flour shows maximum buffer capacity in the same pH range, *viz.,* 6.5 to 7.0, while in the suspension it occurs within the range 5.75 to 6.25. The average maximum buffer capacity of the water extracts varies from 38 per cent (high grade) to 62 per cent (low grade) of that of the suspensions. Buffer capacity is proportional to the ash content, i.e., to the amount of branny material present, only for one grade of flour.[20, 118, 265] Halton and Fisher[105] pointed out that the pH and buffer capacity of doughs cannot be correlated with those of the aqueous extracts, the buffer capacity of the former, for example, being from 1.5 to 3.5 times that of the latter. While the pH of aqueous extracts remains fairly constant, the buffer capacity increases considerably with the time and temperature of digestion.[259] Dixon[61] substantiated the now generally recognized fact that pH cannot be used to predict flour quality.

The source of the acidity in flour is not definitely known. Thompson[265]

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* "Novadelox."

† Many papers in Vols. I and II of this series deal with various aspects of this problem, e.g. papers by Jacques Loeb, Wolfgang Pauli, Leonor Michaelis, T. Brailsford Robertson, Martin H. Fischer. J. A.

concludes that it is due to acetic or lactic acid only in the case of unsound flours. It is probably due mainly to the acids formed by decomposition of fats, phosphatides and proteins.

It has been proposed[108] to regulate flour pH by blending, but Weaver,[273] from observations extending over a period of years, concludes that it is not feasible. Treatment with chemicals has also been proposed as a correction for excessive acidity.[213]

Effect of Milling and Storage. The pH and buffer values of flour are governed to some extent by the milling treatment which the wheat receives, and frequently bear little relation to the values found for laboratory samples.[61] However, the tempering process, unless extended over a period of 36 hours or more, has little or no effect on the pH of the resulting flour. Geddes[89] reports that the buffer value is definitely increased by heat treatment, while the pH is but slightly affected. The pH increases with the fineness of grinding.[87] The effect of bleaching has been previously discussed.

The pH of flour decreases during storage, the effect being accelerated by high humidity and temperature.[76] This is undoubtedly due partly to the effect of enzymes and microörganisms.[165] It has been proposed to correct this condition by pre-treatment with alkaline materials.[167] The pH of lower grades decreases at a much greater rate than that of the higher grades,[77] following closely the ash content,[186] in spite of their greater buffer capacity. Patent, first clear and second clear required, respectively, more than 5 months, less than 150 days, and 40 days, to exceed the official limit of 0.15 per cent acidity. While bleaching with chlorine causes an initial decrease in pH, the subsequent rate of decrease during storage is lessened.[17] The acidity of the extract from unsound wheat may reach extremely high values,[53] while flours extracted with petroleum ether are not subject to pH change upon storage.[129] Johnson and Greene[129] conclude that it is the higher fatty acids which are responsible for the increase in acidity.

pH and Dough. Although it has been frequently stated that the optimum pH for the production of dough is in the neighborhood of 5,[56, 123, 246] it has been found possible to prepare excellent breads from doughs in which the pH varied from 4 to 7.[80, 101, 274] * Variations in pH have little or no effect upon the qualities of the flour constituents, but are of considerable significance for the enzymes of dough (*vide infra*). Greene and Bailey,[101] in baking their alkaline doughs, compensated for the decrease in activity of zymase and diastase by the addition of extra quantities of the enzymes. On the other hand proteolytic and bacterial (rope) activity also increase with decrease in acidity.[41, 50, 51, 79] In actual baking practice these factors must be balanced against each other for satisfactory bread production.

During fermentation the pH of the dough increases. While acid phosphates produced by the hydrolysis of phytin and organic acids from the metabolism of yeast probably account for some of this change, Johnson[124] concludes that the carbon dioxide is the major factor. Bailey and Sherwood[21] observe that since the pH rises upon baking, the acids must be volatile. Between 70 and 90 per cent of the total organic acid in dough is probably lactic.[124]

This change in H-ion concentration during fermentation is intimately connected with the buffer capacity of the flour, high-grade flours changing more rapidly than the low-grade.[21, 274] It has frequently been proposed to correct undesirable H-ion concentration by the addition of materials with a buffer action such as lime water, sodium bi-carbonate,[185] tartaric or other

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* **Fleischmann Laboratories, unpublished results.**

acids,[21, 47, 109, 123] or milk powder.[222] In general the higher the pH or buffer capacity, the longer is the fermentation period required to produce a satisfactory dough.[67, 274] Bailey and Johnson[17] warn, however, that this process should not be carried to the point of loss of CO_2.

The addition of buffers may be carried to a point at which the properties of the gluten are markedly affected. Since at a pH of 3 or 9 to 12 gluten quality is seriously reduced,[285] flours brought to these values by special treatment acquire "short" properties[65, 66] which are considered desirable in the production of crackers and cookies. The pH of the finished loaf is generally greater than that of the proofed dough. Fellenberg[75] states that the taste of bread and the degree of acidity are definitely correlated. Table 7 indicates a tendency in recent years toward the production of a more alkaline dough.

TABLE 7.—*pH of Bread.*

No. of Samples	pH	Date	Market	Authority
54	5.01–5.7 *	1918	Boston	Cohn, Cathcart and Henderson[51]
12	4.90–5.2	1922	New York and Pittsburgh	C. N. Frey (unpublished)
1	5.45	1922	New York and Pittsburgh	C. N. Frey (unpublished)
11	5.40–5.6	1927	New York and Pittsburgh	C. N. Frey (unpublished)
8	5.45–5.7	1929	New York and Pittsburgh	C. N. Frey (unpublished)

* Four samples only were above 5.5.

Flour Proteins.—Gluten. Osborne's[200] pioneer work on the fractionation of wheat proteins led to the belief that several fairly well-characterized proteins were present. Subsequent investigation, however, has thrown considerable doubt upon their individuality. Blish[35] has concluded that the individuality of gliadin only has been established with any degree of certainty. The term "gluten" is somewhat generally applied either to all the flour proteins or only to the hydrated combination of glutenin and gliadin. One school maintains that this combination "gluten" exists preformed in the flour.[264] Considerable evidence favors this idea and glutenin and gliadin may be fractions of the more complex preëxisting gluten. We will here apply the term *only to the coherent hydrated protein* present in dough or obtained by the method of "gluten washing."

The properties and structure of gluten apparently differ little from those of similar proteins from other sources.* No characteristic grouping or amino acid has yet been found to account for its peculiar properties (Table 4), although Nakashima[194] has isolated a tetrapeptid containing 3 molecules of glutamic acid and one of tyrosine. Of significance here is the recent production of synthetic highly polymerized compounds,[46] "linear condensation superpolymers," from linear dibasic acids and amines. These results indicate that the dibasic glutamic acid may play an important part in determining the properties of gluten. Speakman and Hirst[248] have concluded from studies of the elasticity of wool fibers, that this property is related to the presence of dicarboxylic acids and diamino acids in the keratin molecule; specifically to glutamic and aspartic acids, and to arginine and lysine. Elasticity is conferred upon the material by the reversible dissociation of some of the —$COO—NH_3$— links of the dibasic-diamino peptide unit. These studies are promising, but it still seems a prodigious distance to our final goal, *viz.* the explanation and prediction of physical behavior on the basis of chemical structure.

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* *See* any modern standard text on Biochemistry for a résumé of protein properties and structure.

The more important *colloidal properties,* viscosity, hydration, isoelectric point, etc., are treated under these specific topics. The commonly measured properties, osmotic pressure, degree of dispersion, cataphoretic behavior, etc., which have been so intensively studied in some cases, have been almost entirely neglected in the case of wheat proteins. The irresistible urge apparently has been for chemists to apply their efforts to the complex mixture of flour itself in the hope of finding the elusive correlation between some measurable factor and loaf quality. It is even possible that so many uncontrolled, perhaps unknown, factors enter into studies of this nature, that some of the work done in the last fifteen years may be found of questionable value. Analytical studies of the properties of individual proteins as compared with the synthetic study of the complex, it is true, may or may not be of greater value.* For example compare the complexity of the analytical correlations which have been worked out by W. H. Redfield[214] for the determination of the quality of eggs.

To be sure, a step has been made in this direction. Solubility or peptization studies have been very extensive (*vide infra*). In addition, diastatic activity has been given much attention, and proteolysis somewhat less. Blish[85] has investigated the fractionation and separation of wheat proteins and de Jong and Klaar,[133] have begun a study of the degree of hydration of gliadin. Svedberg[253] has shown that gliadin, glutenin and leucosin, each form polydisperse systems in dilute solutions. Tillman's and Hirsch's[266] "I curves" indicate that the molecular weight is very large or the chain very long in gliadin.

Washed Gluten. The importance of the gluten complex has stimulated considerable interest. This complex apparently exists only in systems with a comparatively narrow range of water content. Gluten washing has been a common procedure for many years, and Dill and Alsberg[60] have found that at least ten factors have a bearing on the characteristics of the product (Table 8).

TABLE 8.—*Factors Affecting Properties of Washed Gluten.*

Factor	Effect on Strength	Effect on Degree of Hydration
Length of dough time......	Increases	Increases to a maximum in about 8 hours
Length of gluten time......	No effect up to 24 hours	Decreases after 8 to 16 hours
Temperature	Increases slightly up to 50° C., then decreases rapidly	Increases up to 50° C.
Length of washing period..	Decreases	Decreases slightly
Amount of mechanical manipulation	Increases to an ill-defined maximum	—
Salt content of wash water or flour	Variable increase to an ill-defined maximum at about 0.1 per cent	—
pH of wash water or flour..	Reaches an ill-defined maximum in neighborhood of pH 5 to 7	—
Gluten quantity and inherent quality	Proportional to quantity and inherent quality	—

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* The explanation of many proven but elusive facts must be sought in the super-molecular, but ultramicroscopic ranges. Whether we call this "chemistry" is purely a matter of man-made definitions which nature disregards. Molecules, when once formed, aggregate under the urge of residual electronic forces, often forming queer groups. *See,* e.g. the first papers in Vols. I and II, this series; also the ultracentrifuge research on proteins by The Svedberg. J. A.

The washed gluten has acquired two or three additional properties, extensibility, elasticity and cohesion, which are found only in comparatively rare cases, such as in collagen.* The terms "strong" or "weak" as applied to gluten and "stiff" and "slack" to the dough reflect the changes in these properties. For their measurement many mechanical devices have been developed. The Chopin Extensimeter probably simulates dough conditions most accurately, measuring both the extensibility and its limit. A correlation is found between loaf volume and the "coefficient of extension" and the "specific energy of deformation."[49] The Harrell Penetrometer is a ballastic device, measuring the degree of penetration of a falling plummet into dough. This value is a measure of the stiffness, while the slope of the penetration-absorption curve gives the resistance of the dough toward slacking with increased absorption.[110] James and Huber[122] devised a machine to measure directly the extensibility and breaking strength of gluten and found that oxidizing agents greatly increased the limit. The gluten curves did not parallel at all closely the loaf volume curves, thus they conclude that while a high limit is necessary for good baking strength, failure of the gluten may occur through other causes.

Modification of these *properties* of extensibility and cohesion inherent in all glutens is produced by many agents; pH, salts, heat treatment, etc. At a temperature of 60° to 70° C. Alsberg and Griffing[3] found that the swelling power in acid becomes less and denaturation takes place over the whole range from 50° to 80° C. While extensibility is lost, the cohesion remains, thus providing a structure for the loaf. Treatment with alcohol, or even dehydration in vacuum at 30° C., reduces the extensibility.[233] Excessive mechanical treatment of the "pack-squeeze-pull-tear" type described by Swanson and Working[260] may so modify the gluten as to break down its structure entirely. At the end of seven minutes mixing at 120 r.p.m. it is seldom possible to obtain any gluten whatsoever from dough.

TABLE 9.—*Effect of Various Factors on Gluten Strength in Dough.*

Factor	Effect
Neutral Salts	Generally strengthening
Oxidizing agents	Strengthening in moderate concentrations
Heat treatment—mild	Strengthening
Heat treatment—severe	Weakening
Alkalis and acids	Weakening
Fermentation	Slight weakening if prolonged
Proteolytic enzymes	Weakening
Mechanical treatment	Strengthening up to a critical point

Many *structural interpretations* of these peculiar properties have been given. Solubility is probably responsible for the concept of particles of gliadin surrounded by glutenin sheaths.[174] The particles upon hydration may draw together, forming larger aggregates, the process being assisted by allowing the dough to stand for a time before washing is begun.[260] The final structure is that of an emulsified gel with inter-lacing fibers similar to a "mesh network" or a "brush heap."

The application of the micellar theory (Nägeli) to X-ray data lends strength to this view. It is well known that rubber when stretched, develops a typical crystallite or fiber structure, associated with parallel oriented micelles, and Katz and Gerngross[145] have shown that stretched gelatin also develops

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* It must be remembered that the behavior of mixtures is not necessarily the arithmetical mean of the behavior of its constituents. Thus "half and half" solder melts way below either tin or lead; and Sydney Young lists many curious "constant boiling" or azeotropic mixtures (*see* "Distillation Methods and Processes," Macmillan, 1922). J. A.

a regular structure similar to collagen. It is highly probable that the same phenomenon could be demonstrated in stretched gluten. The viscosity of flour suspensions (*vide infra*) indicates that the structure is probably not that of long threadlike molecules similar to the polystyrenes.[250] The relative insolubility of the gluten complex indicates the possibility of temporary two-dimensional chains, similar perhaps to the polymerized cyclopentadiene of Staudinger and Brusen,[251] which may be bound together by secondary or coördination valence. For this concept glutamic acid and dissociation of certain $-COOH-NH_3$ link, (*vide supra*) may be significant. Both water and protein phases may be continuous.

Assuming that the stretching of gluten is accompanied by micellar orientation with possible deformation of a lyophilic-particle, there are at least two concepts of the forces involved: (1) the intermolecular or secondary (van der Waals') forces, and (2) surface tension of the aqueous film. H. Mark[184] concludes from calculations based upon dissociation energy, that a thread of chains linked together with the oxygen primary valence would have a strength of 800 kg. per sq. mm. Calculations of the secondary or intermolecular forces[236] lead to a value of about 200 kg. per sq. mm. for a completely oriented chain. The tensile strengths of steel, linen, and cotton are in the neighborhood of 275, 100 and 30 kg. per sq. mm. respectively.*

TABLE 10.—*Tensile Strengths.*

Material	Max. Tensile Strength kg./sq. mm.	Theoretical Limit from Valence Force kg./sq. mm.	Type of Force
Steel Wire	245–300	>800	Primary
Flax	100	200	Secondary, oriented
Cotton	30	70	Secondary, unoriented
Gluten	.01–.05	0.2–2.0	Aqueous surface tension; oriented micelles.

While the strength of metals may be due to primary valence forces, Sheppard[236] concludes that the vegetable fibers owe their strength to the forces between secondary linkages. The maximum tensile strength of gluten is from 0.01 to 0.05 kg. per sq. mm. Assuming that a strand consists of oriented micelles of diameter from 10 to 100 mμ surrounded by a hydration film, it is calculated that if stretching is produced against the surface tension of this film, the tensile strength should be in the neighborhood of 0.2 to 2.0 kg. per sq. mm. This value is approximately of the same order of magnitude as that actually observed in a gluten strand and since the secondary valence is associated with a much larger tensile strength, lends credence to the second hypothesis (Fig. 1).

Starch.† In milling the starch granules are separated from the closely packed form in which they exist in the grain, and a certain number are frequently cracked or broken. However, this does not alter the essential details of molecular structure. While the glucose unit of the starch in the granule may exist as a five- or a six-membered lactone ring (furanose or pyranose structure), the existence of the ring seems to be generally accepted. X-ray studies have also practically established the fact that these lie in a series of parallel planes, the hydrogen and hydroxyl groups "protruding" on each side of the plane, and are probably linked together in each plane by primary forces. The planes are linked together by either primary or coördinate (secondary) linkages or perhaps both.‡ Study of the degradation products

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* *See also* paper by McBain and Alexander in Vol. III, this series, dealing with "Cohesion and Adhesion." J. A.

† *See* paper on "Starch" by M. Samec in this Volume. J. A.

‡ *See* "The Mesomorphic States of Matter" by G. Friedel in Vol. I, this series. A resemblance to the smectic state is here indicated. J. A.

produced by various means shows that certain comparatively simple structures are repeated throughout the granule. Thus the di-saccharides, maltose and gentiobiose, containing alpha and beta glucose linkages respectively, occur in the structure, as well as an "amylose" unit, consisting of 6 to 10 glucose units.

There are, in addition, certain accessory units whose precise position and function are but vaguely known. Phosphoric acid, probably esterified with one of the hydroxyl groups, occurs, usually associated with the alpha linked amylose. Long chain fatty acids occur to the extent of 0.4 per cent in wheat starch and seem to be associated with the beta linked amylose or amylopectin. These accessory constituents probably have an important effect upon the solubility of the starch and the viscosity of its solutions (*cf.* Samec in this volume). A starch solution probably contains a heterogeneous assortment of particles of different sizes containing a varying number of these units with various degrees of hydration.

Calculations from X-ray data by different authors are not in agreement as to the size of the elementary starch micelle; probably several micelles of different dimensions occur. According to some, the elementary micelle corresponds to one glucose unit, while others find it to contain 6 to 8 glucose units. However, for the present discussion, the important fact is that the structure is one of definitely arranged micelles.

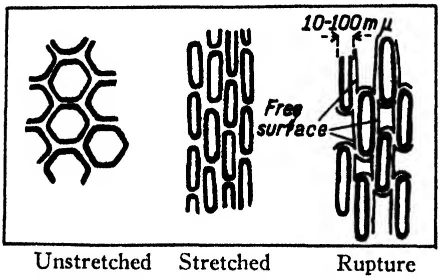

Fig. 1.—Diagrammatic representation of gluten micelles.

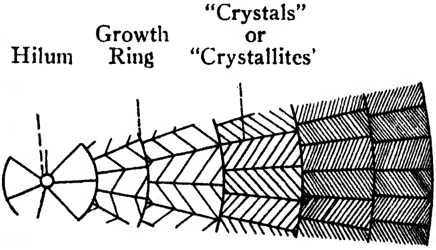

Fig. 2.—Diagrammatic representation of the fine structure of the starch granule.

In the starch *granule* this micellar structure is probably built up into small, crystal-like aggregates in the form of truncated needles oriented radially from a small opening near the center of the granule, termed the hilum (Fig. 2). According to an earlier or "apposition" theory, the macroscopic growth of the granules is assumed to take place outward from this point. Later evidence tends to support the "intussusception" theory; the outer layers of the granules being deposited first.* Deposition of subsequent layers apparently establishes a strain or tension within the granule giving rise to bi-refringence. It has been definitely established that the outer envelope is not cellulosic in nature. Some evidence seems to point, however, to the presence therein of many beta linkings, as in cellulose and gentiobiose, as well as to the presence of fatty acid residues.

Solubility Behavior. The "solution" of starch granules is an exceedingly complex phenomenon, involving finally a scission of numerous linkages to give submicroscopic particles; a colloidal solution of amylose or perhaps amylophosphoric acid. Temperature, viscosity, and swelling are intimately related

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* The structure of starch grains is also considered in a paper by H. Schade on "Concretions" in Vol. II, this series. *See also* discussion of intussusception by Alexander and Bridges in the first paper in Vol. II. J. A.

in the process. Let us consider a suspension of starch granules in from 1 to 10 times as much water. At any temperature between 65° and 100° C., depending on the starch characteristics, there is a definite relationship between the temperature, the viscosity of the mixture and the swelling of the granule. The viscosity and swelling rise to a maximum somewhat before or about the boiling point, then the viscosity suddenly drops, and the microscope shows disintegration of the granules. Upon prolonged boiling an insoluble portion separates and the viscosity of the supernatant liquid approaches that of water. The viscosity appears to depend upon the characteristics of the envelope, or of the lattice structure, or both; for upon thorough grinding of the granule, peptization takes place unaccompanied by any large increase in viscosity.[48, 263]

X-ray studies of gelatinization by Katz[144] have developed a remarkable picture of this process as the temperature is raised, water is taken up by the starch lattice as inter-micellar water, producing a large increase in the inter-micellar dimensions (swelling) without destroying the lattice. At any temperature below disintegration, there is a definite amount of imbibition and swelling. At the higher temperatures, the X-ray spectrum approaches that of an amorphous material. The final disruption of the lattice is accompanied by hydrolytic scission of various linkages and the bursting of the granule. Coincidentally, the system changes qualitatively from one of "water in amylose" (viscous starch paste) to one of "amylose in water" (soluble starch) and the viscosity collapses. Accompanying intermicellar imbibition, a release of the strain and tension within the granule destroys the bi-refringence.

Upon cooling, the lattice resumes a structure similar to that of the native granule, expelling intermicellar water. Compared to the original starch, the X-ray spectrum is now much more like that of a crystalline material. For this phenomenon, Katz[144] proposes the term "retrogradation." It has not yet been proved to be the same as the "reversion" occurring in starch pastes or autoclaved starch solutions.

Electrolytes in water greatly hasten the process of solution. Thus it is possible, even at low temperatures, slowly to bring the interior of the granule into solution by certain salts, such as potassium thiocyanate, or acids like hydrochloric acid.

Fats and Lipoids. The baker calls a product *short* when it breaks with a relatively brittle fracture upon the application of slight strain. The baked product which requires the least load to measure its breaking strength is the shortest; that requiring the heaviest load is the least short.[57] The same concept of "shortness" is applied to the "stretchibility" of dough. Except where the amount of fat used is sufficient to produce "flakiness," the effect is due principally to a modification of the gluten.

Action of Fat on Gluten. This action of fats and lipoids is probably one of lubrication, enabling the gluten strands or fibrils to slide more easily over one another.[286] While the exact mechanism is not well understood[100] it is quite possibly due to a reduction of surface tension, particularly in the case of lipoids,[289] in harmony with one of our hypotheses regarding the source of gluten extensibility. Gluten washed from flour by the usual procedure contains the major portion of the flour lipoids, and its color is due to carotin in the fat adsorbed by the gluten-forming protein.[192, 255] This fat is in a highly dispersed condition and seems necessary for gluten formation. Confirming this concept Bennion[28] states that the addition of an oil emulsion increased the apparent gluten content. Fermentation was slightly retarded, but the dough rose higher, indicating a greater extensibility, and crumb color and pile were improved. Working[286] explains the action of oxidizing agents on flour as a liberation of phosphatides, which in turn react favorably upon the gluten. Accompanying this liberation may occur an actual decomposition of the labile phosphatide, the decomposition products affecting the state of the gluten.

According to this explanation, extraction with fat solvents should result in a serious decrease of strength. As a matter of fact acetone and alcohol produce just this effect, but it is generally regarded as a denaturation of the proteins. On the other hand Salamon [220] and Johnson [126] report that improvement in color, texture and volume was produced by ether extraction, the gluten extensibility of the ether-extracted flours being slightly decreased. Contrary to this observation, and in confirmation of Stockham's [253] results, it has been found at The Fleischmann Laboratories that extraction with ether and benzene markedly decreases the quality, while addition of the extract to the extracted flour completely restores the original properties. This instance is but another indication of our ignorance of the phenomena concerned, inviting further experimental work.

Shortening Power. The capacity to produce the shortening effect varies for the different fats,[57] apparently being associated with the content of unsaturated glycerides.[208] Thus solid fats should have less shortening power than oils. Since small amounts of lecithin produce marked shortening effects, it appears that shortening power depends upon the "degree of polarity" or the number of active groups; a natural explanation if the action is due to surface activity. On the other hand, Davis [57] states that hydrogenation definitely increases shortening power, so that factors besides unsaturation may be involved.

Flakiness and Leavening Action. Fats are responsible for two other desirable characteristics. The tender flakiness, for example, of a pie crust, is due to the peculiar structure of alternate layers of fat and extremely short dough. The baked dough layers not being interconnected, break into a series of flakes and these impart a pleasing quality.

The consistency of fat is such that a considerable amount of air may be incorporated by beating and this capacity for foam production is partially responsible for the leavening action in certain types of cakes.

Enzymes. For a discussion of the nature of enzyme action the reader is referred to Vol. II of this series (R. K. Cannan, p. 349; R. Willstätter, p. 361; A. Fodor, p. 367). We shall discuss here only the application of enzymes to baking.

Proteolysis. Proteolytic enzymes may occur in flour to such an extent that gluten quality is seriously impaired.[275] This may be a desirable factor in certain cases, e.g., in cracker flours. There are several H-ion concentrations at which proteolysis reaches a maximum, indicating several such enzymes,[275] although the exact pH at which maximum activities occur, is not well defined. At the normal pH of flour, gliadin alone is appreciably attacked, while the glutenin fraction appears to suffer no change.[230] This change in the gliadin-glutenin ratio may be related to the lower hydration capacity of proteolyzed gluten. In general proteolysis in doughs from highly refined flours from sound wheat is very small.[45] Low-grade flours containing branny and germ particles, in which most of the enzymes reside, may cause considerable proteolysis. Addition of no more than 3 per cent of flour from sprouted wheat to normal flours increases proteolysis to an inappreciable extent.[45, 238] The separation of proteolytic from diastatic enzymes by use of safranine has been very recently accomplished by C. H. Bailey and his collaborators (unpublished results).

Diastatic Activity. Rumsey's[219] classical method for diastatic activity has been frequently modified and extended. Kent-Jones and Saxby[150] define the "maltose number," as the amount of maltose which is found to be present after one hour's autolysis at 27° C. A minimum maltose number of 1.5 per cent is considered sufficient for satisfactory fermentation. The addition of diastatic malt extract to deficient flours is used to improve the baking characteristics. The optimum pH for most plant diastases is from 4.6 to 4.85, and the optimum temperature from 49° to 58° C.[142] Variations in salt concentrations have a marked effect on the determination of diastatic activity.[85, 186] Flours if extracted at a pH of 5.9 may give a diastatic solution of more than twice the activity of an extract made at pH 6.6.[69] These figures may have considerable significance in the dough fermentation.

"Activators" and "Inhibitors." Diastase particularly, as well as the other enzymes, is subject to various inhibiting agents; thus adsorbent materials such as kieselguhr, cellulose and bone black produce almost complete inactivation. If, however, certain other materials, e.g., gelatin or saponin, are present the inhibition is markedly reduced.[226] Sufficient protein material is present in the dough to give this protective action.

Observations at The Fleischmann Laboratories in 1927 showed that the baking quality of dry milk powders could be greatly improved by the addition of diastatic malt. Certain dough conditioners also showed improvement giving a well-developed loaf. This is explained by the work of Skovholt and Bailey,[241] who reported that dry milks depress saccharogenesis in flour suspensions. The reason for this effect does not yet seem to be apparent.

Inorganic salts are known to have a marked effect upon the activity of enzymes. Proteolytic activity, e.g., is depressed by the action of bromate or of oxidizing agents in general.* This is of great significance in improvement of gluten by flour bleaching. The action of bromate on zymase and diastase has been investigated, but the results were indefinite.

Cytase is probably of considerable importance in fermentation, particularly since the introduction of malt extract, because diastatic activity in the dough seems limited or conditioned to a certain extent by cytolysis. The temperature of milling may account for the low cytolytic activity of flour. Malt diastase (from sprouted grain) can convert the usual quantity of wheat starch, whether freshly gelatinized (as in bread with not over 60 per cent absorption) or retrograded, while the action of flour diastase diminishes as retrogradation proceeds.[227] Cytolytic activity is undoubtedly involved in this phenomenon. The optimum pH and temperature of barley cytase are 5.0 and 40.5° C. respectively, and it is rapidly destroyed at 60° C.[179]

It is *zymase* which produces the gas for leavening dough and hence it is of fundamental importance. An intracellular enzyme closely related to yeast metabolism, it probably consists of at least two or more enzymes with "activators" or cozymase. Its properties have not yet been fully determined, but it is known to be very labile. Its optimum pH is between 4.5 and 5.5[72a] and it is apparently destroyed at 65° C. The fact that this is near the optimum temperature of diastase is of great significance in the baking process. Ethylene and acetylene produce increased zymatic activity in dough fermentation, partially explainable as an increase in cell permeability and diffusion rate of substrate and end products.

The action of *rope* (*B. mesentericus*) in bread has at times been considered to be enzymic in nature, breaking down the protein structure of the bread. According to Hibbert's[117] work it is probably due to a conversion of starch

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* Fleischmann Laboratories, unpublished results.

into another polysaccharide. The stringy characteristics of "ropy" bread are probably in part due to the properties of this polysaccharide.

Viscosity. This property is considered a direct measure of the "internal friction" of a liquid, and must be distinguished from plasticity in that no initial stress or deformation is required to produce flow. Methods for measurement, calculations and theoretical aspects are taken up in more detail in other portions of this work. (T. B. Robertson, Vol. II, p. 289; E. Hatschek, Vol. I, p. 727.)

Application to Measurement of Flour Quality. Concentrated flour suspensions are essentially plastic in character, plasticity being a factor in concentrations as low as 9 per cent.[229] Whymper in 1918 made some preliminary studies of the viscosity of flour suspensions. The first definite attempt to make a correlation between viscosity and baking strength was in 1919 when Ostwald [204] noted qualitatively that such existed. Many viscosity measurements on heated and unheated dough suspensions were made, and although inconclusive they served to stimulate more research on this problem. Numerous variations of the procedure have been used, involving lactic acid,[231] oxalic acid,[160] sodium hydroxide,[80] neutral salts,[23] hydrogen peroxide,[68] and gelatinization,[4, 180] with or without a preliminary leaching.[36, 242] Other factors such as protein content, glutenin content [36] and diastatic activity,[80] have been introduced in the attempt to obtain the elusive correlation.

Sharp and Gortner [231] made a comprehensive investigation of viscosity and concentration relationships, concluding that loaf volume was directly proportional to the product of a viscosity factor and gluten content. The slope of the logarithmic viscosity-concentration curve is apparently characteristic of the *quality* of the gluten.[94] An increase of mobility becomes evident as a suspension stands.[221, 231] This method was further developed and found equally reliable using the Ostwald Viscometer with large bore capillaries, if calibrated in viscosity units.[59] The decrease in viscosity on standing, if extrapolated to zero time is constant for any one flour, and partially correlated with strength. This "fall back" in viscosity may be due to a syneresis, to a continued peptization, or to the gradual assumption of a more globular shape upon further hydration.

But variations in temperature, degree of hydration and manipulation make the duplication of results difficult.[125] Moreover the carbon dioxide content of the water used causes discrepancies, a maximum viscosity being obtained at a pH of 5.0.[128] The grade and degree of grind is important, fine grinding producing a decrease in viscosity.[160]

Thus it is not surprising that none of these methods gives satisfactory correlation with flour strength in all cases. The opinion is gradually becoming prevalent [86, 164, 180, 242] that this tool, which showed so much early promise, is not an "open sesame" to estimation of quality, although a recently described method, using NaOH and diastatic activity is said to be applicable in 80 per cent of the cases.[80] The problem of a fully reliable physico-chemical test of flour quality still seems to await solution. The numberless factors entering into the development of gluten properties seem to indicate that the results of many individual determinations, more than the two or three which have heretofore been made, must be welded, we hope by mathematical means, into an expression which will give us one definite index of flour quality. Until then the baking test must remain the final criterion.

Theoretical Significance for Structure. That the viscosity of colloidal solutions is closely related to the structure of the dispersed phase, has recently become apparent and the concept has been extensively applied in this connection. For an ideal suspension of uniform spheres in which the radius of the particles is small compared to the distance between them, and the size of a capillary viscometer in which measurements may be made, the viscosity η of the suspension would be given by the equation:

$$\eta/\eta_0 = 1 + 2.9\,\phi = 1 + 2.9\,cv$$

where ϕ is the fraction of the volume occupied by the dispersed spheres, c the concentration in grams per cubic centimeter and v the partial specific volume of the dispersed phase.[*] In practice but a small number of colloidal solutions accurately obey this law, and it is thought that the observed discrepancies are due to variations in the shape and structure of the particles involved. The coefficient 2.9 represents a shape factor.[242a] It is probably 2.5 for perfect spheres and many times 2.5 for long rod-shaped particles. E. O. Kraemer,[154a] however, indicates that the equation may be used for comparative purposes and calls ϕ the "equivalent hydrodynamic volume" and the ratio ϕ/c the "specific hydrodynamic volume." The ratio of this quantity to the true specific volume v, is the figure which is of significance in interpreting structure. At present four factors have been distinguished which influence the structure of the dispersed phase, (1) the shape may vary from that of spheres to long thread-like aggregates (5 Å × 1000 Å).[250] (2) If considerably removed from the isoelectric point (hetropolar molecules) the particles carry a charge and the normal coefficient of the equation is increased by a factor due to an "electroviscous" effect. (3) The degree of hydration or solvation may also increase the normal size of the particles, and finally (4) they may clump together to form a porous aggregate enclosing relatively large amounts of solvent, thus removing the latter from the shearing stresses within the medium.

For comparative purposes the ratios of specific hydrodynamic volume and true specific volume of certain substances are given in Table 11.

TABLE 11.—*Ratios of Specific Hydrodynamic Volume to True Specific Volume.*

Substance	$\frac{\phi}{cv}$
Sucrose in water	1.6 [a]
Egg albumen in water	0.9 [a]
Diluted rubber latex	1.0 [a]
Clay in water	9 [a]
Starch in water	20 [a]
Gum arabic in water	50 [a]
Iso-electric in gelatin in water 20° C.	30 [a]
Gluten in flour suspensions—5%	10–12 [b]
10%	20–30 [b]
15%	30–45 [b]
20%	60–80 [b]
Agar in water, 50° C.	220 [a]
Cellulose acetate in acetone	200 [a]
Polyvinyl acetate in benzene	200–900 [a]
Polystyrene in benzene	4–1000 [a]
Gluten in flour suspensions—25%	150–200 [b]
33⅓%	220–280 [b]

[a] Kraemer.[262] [b] Denham, Blair and Watts.[59]

Roughly three general types may be distinguished (1) those in which the ratio ϕ/cv is approximately one, representing a nearly ideal suspension, (2) those in which the ratio is comparatively large (6 to 100), and (3) those in which the ratio increases to very large values (200 to 1000). Sols of the second group are generally considered to be the result of any or all of the four factors mentioned above. The third group, however, is still the subject of considerable discussion. It seems probable that the effect may be due to incipient gel particles; swollen, sponge-like structures, enclosing relatively large amounts of the medium.[†]

From the data of Denham, Blair and Watts,[59] this ratio has been calculated for several concentrations of gluten, assuming that the contribution of starch in the flour suspension to the viscosity is small compared with that of the gluten. It seems probable that at

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[*] E. O. Kraemer, Taylor's "Treatise on Physical Chemistry," p. 1614 (1931).

[†] Many of these factors were discussed by Jerome Alexander in a paper entitled "The Zone of Maximum Colloidality: Its Relation to Viscosity in Hydrophile Colloids, Especially Karaya Gum and Gelatin," *J. Am. Chem. Soc.*, 43, 434 (1921). Increase in viscosity accompanied the imbibition and swelling of discrete particles of gum and of gelatin. J. A.

concentrations below that equivalent to 25 per cent flour, this system falls into the second class, while above this concentration the relatively large value of the ratio places it in class 3. If extrapolated to dilute solutions (1 per cent) it would appear to belong in class 1. It is quite possible, of course, that at these concentrations the ideal condition, in which the radii of the particles is small compared to the distance between them, is not fulfilled and that the effect is still explainable in terms of the four factors previously mentioned. The significant point here, however, is that even in these solutions the particles are probably not far removed from an approximately spherical shape and do not possess a long thread-like structure. It is possible, of course, that in more concentrated suspensions much inter-micellar hindrance may occur, but the picture, particularly when gluten is stretched, is probably that of deformed particles which were originally more or less globular in shape. (Fig. 1.)

Isoelectric Point. The data available at present on the isoelectric points relating to flour are given in Table 12. Small concentrations of salts may affect the isoelectric point,[151, 158] thus considering the variation in methods employed, some deviation is to be expected. The possibility of disaggregation into lower class protein particles should not be overlooked,[90] resulting in the formation of what may be in effect a different protein. The temperature is also important, the isoelectric point of gluten being shifted toward the alkaline side by an increase.[128] It appears that no correlation exists between the isoelectric range and flour grade although correlations have been attempted.[26] Presumably satisfactory results may be obtained at any point within the range, but it cannot yet be definitely concluded that the isoelectric point is not a critical factor in baking.

TABLE 12.—*Isoelectric Points.*

Substance	Isoelectric Point	Method	Authority
Gliadin	6.5	"Transference" *	Tague [261]
	6.6	——	Eto [72]
	6.41–6.59	——	Kondo and Hayaski [152]
Glutenin	6.8	——	Sharp and Gortner [233]
	6.8–7.0	"Transference" Buffer action	Tague [261]
	5.15–5.39	——	Kondo and Hayaski [151]
	5.19–5.58	——	Kondo and Hayaski [152]
Leucosin	4.6	(Av. of five methods)	Lüers and Landauer [175]
Flour:			
Patent	5.88	"Transference"	Tague [261]
Clear	5.57	"Transference"	Tague [261]
Low grade	5.80	"Transference"	Tague [261]
Whole wheat	6.12	"Transference"	Tague [261]
Bran	6.35	"Transference"	Tague [261]
Patent	6.2–6.5	Precipitation	Johnson and Harrington [128]
1st clear	6.2–6.5	Precipitation	Johnson and Harrington [128]
2nd clear	5.5–6.0	Precipitation	Johnson and Harrington [128]
Durum	6.2–6.5	Precipitation	Johnson and Harrington [128]
Water extract	6.5–7.0	Buffer intensity	Holm and Grewe [118]
Suspension	5.75–6.25	Buffer intensity	Holm and Grewe [118]

* Transference: Action of protein on buffer series.

Heat Treatment of Flour. The development of heat treatment of flour * was conducted chiefly by Kent-Jones in England and Fisher and Jones in the United States. Addition of less than one per cent of flour heated to a temperature of 180° F. for 10 or 12 hours produced an increased absorption and

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* Heat treatment of Karaya gum markedly affects the viscosity of its solutions. *See* J. Alexander, *J. Am. Chem. Soc.*, 43, 434 (1921). J. A.

loaf volume, and an improvement in color and texture.[115, 147] Flour heated for not more than 3 hours in the presence of a current of air having a temperature of approximately 140° F., and a relative humidity of not less than 60 per cent gives similar results.[80a, 115] These heat treatments also bring about an increase in dough stability. Heat treatment is detrimental to gluten quality unless germ is present.[89] It produces at first a marked change in the imbibitional and physical properties of the proteins; a progressive decrease in viscosity, but if overheated the flour shows an increase.[115] However, this increase does not occur if bacterial action has been inhibited. Heat treatment of wheat at a given moisture content produces less deleterious action than similar treatment of flour.[88] The value of heat-treated flours as improvers at first increases, but as the heating is continued, the effectiveness is finally destroyed.[115]

Apparently modification of the proteins increases the imbibitional power and strength of the gluten fibrils of the dough. There is also greater resistance toward proteolytic action as the result of change in particle size. The first stage of heating affects denaturation while the second probably produces flocculation. In some cases the denaturation and flocculation occur in the flours but in others the protein is denatured by heating and the flocculation is brought about by the acids of fermentation.[148] This change is a structural alteration in the protein molecule and should not be regarded as denaturation,[172] which is generally accompanied by a complete loss of swelling power. It is, therefore, doubtful if the changes involved are strictly denaturation, in the usual sense, but there is evidence to indicate that a physical alteration has taken place which has increased the imbibitional power.

Emulsions. A list of some of the more important emulsifying agents and their uses as employed in the baking industry is given in Table 13. The preparation of commercial emulsions is sometimes quite difficult because the liquid to be dispersed must first be broken into small globules before the emulsifying agent can form a protective film.* The liquid to be dispersed is generally added slowly with constant agitation to the dispersing medium carrying the emulsifying agent. The particle size depends upon the rate of addition, the intensity of agitation, the nature of the liquids and the emulsifying agent. Under accurately controlled conditions a "mono-disperse" system is attained in which the particle size does not vary. The stability of an emulsion varies inversely as the particle size and the interfacial tension and usually directly with the viscosity of the medium and the amount of emulsifying agent. The nature of the emulsifying agent is a most important factor, generally determining the electric charge carried by the particle. Certain auxiliary agents, e.g., lecithin, greatly increase the stability of water in oil emulsions.[206]

The breaking of an emulsion involves the removal or destruction of the protective film and the neutralization of any electric charge. This is often very difficult, and a knowledge of the nature of the emulsifying agent and its chemical properties is of great assistance. The emulsifying agents generally used in baking are very sensitive to pH and temperature, and this sometimes offers a clue to a means of breaking a stubborn emulsion.

Gels. The formation of gels according to recently developed theories of micellar and macromolecular structure lead to the following pictures:

A. *Aggregation.* Upon cooling, the particles of dilute colloidal solutions gradually clump together, forming a fibrillar or inter-lacing structure enclosing large amounts of

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* Dr. F. M. Ascherson (*Arch. Anatomie Phys.*, 1840, p. 44; reprinted in "The Foundations of Colloid Chemistry," Hatschek, 1925) was perhaps the first to refer to the formation of what he termed *haptogen* membranes about globules in emulsions, the membrane-forming property being termed *hymenogeny*. Reference to Ascherson's work will be found elsewhere in this series. J. A.

solvent. This fibrillar growth has actually been observed by optical and ultramicroscopic methods.[82] The Tyndall beam becomes relatively intense upon cooling even before the gel has set, while if the process is reversed, the solution does not become optically void until a temperature of nearly 90° C. is reached. When the gel is stretched the interlacing fibrils or micelles are strongly oriented in the direction of stretch.[237]

B. *Infiltration.* While the structure of starch gels is probably quite similar, consisting of a greatly extended molecular system, the mode of formation is quite different. The enclosing of large amounts of water by an aggregation of micelles is here replaced by "infiltration" of water into an already elaborate, probably two or three dimensional micellar system (*vide supra*).

Gel formation is accelerated by chlorides, acetates, citrates, tartrates and sulfates in the order mentioned, while bromates, nitrates and iodides cause a retardation.[271] Gelatin gels containing lecithin swell much more than normal gels. Lecithin shifts the iso-electric point of a gelatin gel towards the acid side and increases the swelling power.[44] Bary [27] states that gels swollen by immersion in a liquid possess a greater vapor pressure than that of the liquid, because the dehydration at that stage is exothermic, and the temperature within the gel is slightly above that of its surroundings. This is of great significance in syneresis and staling.

The phenomenon of *syneresis* is apparently a continued aggregation, a micellar or fibrillar growth after gel formation with resultant expulsion of the previously enclosed solvent. De Jong and Kruyt [134] have introduced the term "coazervation" to describe the separation of a lyophile system into two liquid phases, and state that it is intimately related to coagulation. The essential factor is a change in the solvent layer from the wide, diffuse boundary to a sharp, oriented boundary between the particles and the medium. Undoubtedly a process of this nature is involved in syneresis. It also occurs in starch gels which have been cooled below the gelatinization point. Acetates, sulfates, oxalates, and citrates hasten the syneresis of such gels, while most other salts retard it, the effect of thiocyanates and calcium nitrate being particularly marked.[48]

TABLE 13.—*Common Emulsifying Agents Used in Baking.*

Emulsifying Agent	Used in Making
Gelatin	Icings
Egg albumen	Cakes, frostings
Egg yolk	Cakes, custards
Indian tragacanth (Karaya)	Icings
Stearines and oxidized vegetable oils	Caramels
Lecithin	Cream fillings

Peptization. A solid protein may be peptized (dissolved) by a solvent to form a mono- or poly-disperse colloidal solution. It has been mentioned that Svedberg [256] found the flour proteins to form poly-disperse solutions. This indicates that in the process of dispersion the proteins are broken up into "particles" of varying sizes, involving a fractionation. Methods of classification are based upon solvent action.

Salt Action. There is abundant evidence for the existence of a Hofmeister series in the peptization of flour proteins. Cereal proteins are increasingly peptized by (are soluble in) solutions of the alkali salts of the anions F, SO_4, Cl, Tartrate, BrO_3, I, in the order mentioned.[99, 249] While the oxidizing action of bromate is probably of little consequence in dilute suspension, in dough it is added to the lyotropic action. Sulfate does not react as a member of lyotropic series, behaving as a bivalent ion, hence its inclusion is not strictly correct.[182] The effect of sulfites on flour suspensions does not seem to have been reported, but extremely small amounts of SO_2 in the dough will entirely destroy its cohesive properties and cause liquefaction (*vide supra* for footnote). Cations have an increased lyotropic effect in the order Na, K, Li, Ba, Sr, Mg, Ca. The actual amount of protein extracted by solutions of these numerous salts varies from negligible quantity to 60 per cent or more. The theoretical aspects of peptization by salt solution are described in other portions of this series (Vol. II, N. R. Dhar and D. N. Chakravarti, p. 105, and T. B. Robertson, p. 255).

Relation to Flour Quality. Many attempts have been made to relate the differential solvent action of salt solutions to flour quality. While correlations have been found in certain cases, they do not seem to be generally applicable. Gortner[95] found that the peptizable protein varied inversely with loaf volume. MacLeod[181] found a negative correlation coefficient between the amount peptizable by certain salts, and flour quality. A significant relationship seems to exist between loaf volume, total protein, and protein non-extractable with magnesium sulfate. Other extensive investigations of the peptizing action of magnesium sulfate, potassium bromide, and potassium iodide in relation to loaf volume shows this tool to be of little practical significance in giving a reliable index of flour quality.[89, 90]

Action in the Dough. It has been mentioned that this is one field in which the chemist has been able to contribute to the baking art. Largely by shrewd trial and error, various flour improvers were developed before extensive studies of salt peptization had been made. The actual mechanism of the action of salts upon doughs is still unknown, and will probably remain so until a structure for the gluten micelle can be formulated.

In dough and fermentation (*vide infra*), salt action modifies not only the gluten, but influences enzyme action and yeast metabolism, and these effects interact upon each other in a complex manner. Thus the metabolic activities of the yeast in changing ammonia of ammonium chloride to a weaker base of protein character lowers the pH, which in turn affects enzyme activity and gluten properties. It is frequently difficult to determine which dough constituent is most affected. Thus it has long been known that $CaSO_4$ has a beneficial action on the dough. Cohn and Henderson[52] ascribed the effect to an increase in the extensibility. Bailey and LeVesconte,[18] however detected no such increase by direct measurements with the Chopin extensimeter. The salt seems to have a specific stimulating action on the fermentation and gas production.

Hydration. Adsorption is a general characteristic of proteins and in a dispersion this water is termed by Hardy[100] the "bound water," * and defined as that which is held more strongly by the dispersed particles than by any other phase present, or as water held by the colloid which is unavailable for the solution of an inert substance.[198]

According to Kruyt[156] the particles are surrounded by a layer of solvent in which two zones may be distinguished—(a)—a "compact" zone, probably one or two molecules thick with strong orientation, and (b) a diffuse zone where the orientation is indefinite. The latter zone may be removed at the isoelectric point by dessicating agents such as alcohol or acetone. For gliadin this probably occurs at concentrations of 48 per cent alcohol or 44 per cent acetone;[188] no change in viscosity occurring below these values. The fall in viscosity at higher concentrations is due to the gradual removal of the outer layer. Hydration may be conditioned by the electrostatic attraction of the ionized polar groups, the viscosity being greatest at the point of greatest electric charge.[205] However, the high degree of charge active in the iso-electric "twin ions" state of Bjerrum seems to indicate that hydration is probably not entirely conditioned by protein ionization.[276]

* Cf. "Hydration Space" of Weber and Versmold.[277]

Syneresis may be considered essentially the reversal of hydration, and according to Kuhn[159] is analogous to a crystallization caused by a decrease in absorption. This phenomenon is of great importance in baking, for within the dough or loaf we have at least two colloidal systems in equilibrium: gluten—water—starch. There is insufficient water present in dough or bread to hydrate completely both constituents. The relative humidity within the dough is perhaps slightly less than 100 per cent while within the loaf it is 93 to 94 per cent. The aqueous vapor tension from a hydrated substance is generally considered to be a measure of the tenacity with which the water is held. The vapor pressure-degree of hydration curves of coagulated gluten and stale gelatinized starch (Fig. 10) give information which is of value in studying this equilibrium.

In flour suspensions in dilute lactic acid starch is hydrated to the extent of 30 per cent while the figure for the unmodified gluten is 100 per cent for unwashed and 200 per cent for washed suspensions. It is about 85 per cent for the prepared proteins.[197] The presence of salts in the dough may exert a marked effect upon this equilibrium. Gortner's school[97, 231] found that Upson and Calvin's[269] conclusion that strong and weak glutens are the result of salt effect is incorrect. Gluten strength is a property inherent in the gluten itself, being roughly proportional to the rates of imbibition in acids and alkalis.

Fine Grinding. The degree of granulation of a flour affects its properties, the larger granulations possessing a higher absorption,[239] unless so finely ground that disintegration of starch granules occurs, causing an actual increase in the absorption.[2] In the average flour the medium granulation produces slightly better loaf quality, the fine granulation giving a faster fermentation, due to the increased attackability of the broken granules.[155] While a general opinion exists that overgrinding seriously reduces the quality, probably as a result of gluten injury,[2] Karacsonyi and Bailey found that only the apparent diastatic activity was modified, no appreciable effect being produced upon fermentation capacity. Moreover, the washed gluten of overground flour which had been ground with a cool roller is unchanged.[122] Apparently further investigation is necessary to reach a definite conclusion regarding this effect.

Mechanical Operations. Gluten "development" is a rather indefinite term used to describe a certain quality familiar to all bakers but difficult to define. It is associated with an increase in the limit of extensibility of the gluten, a certain "silkiness" of texture and usually a decrease in the ultimate tensile strength. This leads to an easier, more rapid fermentation.

Mixing and over-mixing. There are two important aspects to dough mixing: (1) Incorporation of the ingredients and (2) incipient development. Modification of the colloidal properties of the gluten by mechanical treatment may be due to an increased degree of dispersion.[204] This effect becomes pronounced in the later stages of dough mixing, the development reaching a maximum, beyond which the effect on quality is decidedly deleterious.[260] Dough taken at this optimum mixing time may produce excellent loaves by a short pan fermentation only. Swanson[260] presents a theory of dough modification by mechanical means, involving progressive attenuation of the gluten strands to form an ever finer fibrous network. At the optimum point the attenuated strands are just weak enough to allow easy expansion during fermentation, and yet strong enough to retain the gas.* Further modification produces a still finer network and finally destroys the capacity for gas retention.

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* This might correspond to a zone of optimum dispersion or colloidality, referred to throughout the various volumes of this series. J. A.

These results have been independently corroborated at the Fleischmann Laboratories. It is believed that this modification is associated with and aided by the process of working the starch grains to the surface of the strand, producing one stronger and more coherent (Fig. 9).

Action of Molders and Rounders. While separating the individual loaves from the main dough mass, a further mechanical modification is produced, one much less violent, but which, at the fully developed stage reached by the end of fermentation, may nevertheless produce marked effect upon loaf quality. If the dough is not gently handled the effects of over-mixing may be obtained, resulting in loss of gas-retaining ability. At the Fleischmann Laboratories, portions of dough, after passing through the rounder, were passed through two molders with various adjustments. When the molder was set too tightly, the loaf obtained was dark colored, coarse textured and of small volume, whereas the control had excellent volume and crumb color.

Baking Test. In reviewing the properties of flour and dough we have found only certain rough relationships; thus we have seen that for any one class of wheat, loaf volume is correlated with protein content and with viscosity, and that under certain circumstances diastatic activity may seriously limit loaf volume. Diastatic activity is also sometimes related to crust color. The whole system is so complex and interrelated that it is difficult to find any generally applicable correspondence between a single factor and the loaf quality. Hence we are forced to rely upon the baking test, which integrates the various factors.

Interpretation. What should the baking test show? Blish [32] has emphasized that a standard experimental baking test should not be attempted until there is a general agreement regarding the exact nature of the information to be deduced. Presumably we require information concerning the "flour quality" or the "baking strength." Various definitions, such as "ability to make large well piled loaves," [119] or "ability to make a loaf of good texture" [268] have been offered for these terms. Obviously such vague descriptions do not convey equivalent meanings to bakers of varying experience. Since the character of the loaf produced becomes the "scale" upon which we read the degree of "baking value," it must be capable of precise and accurate analysis. The details of such analysis have been tentatively suggested by Blish.[34]

But the baking test should in addition tell how we should treat a flour; the accessory ingredients, if any, which we should add, and the type of fermentation which we should use. By the size, type, structure and development * of the loaf, we may eventually be able to deduce correctly the individual characteristics of the flour and be in a position to tell what modifications of the commercial baking procedure are necessary in order to utilize fully the flour's capacity.

Baking Factors. Even with our present relatively limited knowledge, certain loaf variables can be traced back to specific flour qualities. Table 14 is an attempt to classify such relationships. At present the only means of evaluating these relationships is by varying the conditions listed in the "dough" column, that is by making a sufficient number of tests to cover the range of the qualities to be investigated.

Variation in Baking Tests. It is impossible to say how many different kinds of baking tests have been developed, but forty-five variations were in common use when the A. A. C. C. "Standard Experimental Baking Test" [88] was adopted

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* As defined by Blish [34] the loaf "development" refers to that portion which rises above the rim of the pan. It refers to a static condition, not a dynamic change; as is implied in *gluten* "development."

TABLE 14.—*Relationship of Principle—Bread Baking Factors.*

In Wheat or Flour	In Flour or Dough	In Bread	Determined by
Gluten:			
Hydration capacity	Absorp. to constant plasticity	Yield and Loaf Vol.	Absorption or Loaf Volume
Extensible Qualities or "Strength"	Dough "Stiffness" or plasticity Fermentation Time Mixing Time	Loaf Volume Loaf Shape Crust Structure Crumb Texture	Loaf Volume with excess sugar and var. in Fermentation time
Degree of "Development"	Age	Response to Bromate	"Differential" Test
	Bleaching and Oxidation	Response to Bromate	
	"Mechanical Modification"	Response to Mixing	Mixing
"Stability"	Fermentation Tolerance Reaction to Salts Reaction to acidity or pH Reaction to proteolytic activity	Loaf vol. : Crumb Texture	Loaf vol. with var. in Fermentation time, Salts, and with excess sugar
Diastase	Fermentation time	Loaf vol., crust color	Loaf vol. with no sugar Crust color
	Leavening, yeast action	Loaf vol. crumb texture	Punching
Starch	Little effect other than source of sugar Depends on character of granules	Crumb texture staling rate	Microscopic Search for ruptured granules or diastase test

in 1928. The supplementary procedures of this test were apparently designed to evaluate the relationships listed in Table 14. Although fairly encouraging preliminary results [85, 116, 191] were obtained, it was soon found that accurate replication of the test was difficult or impossible even by the same individual using the same ingredients.[78, 110, 268] Oven temperatures, mixing time, individual differences in molding and panning technique, "molding personality," and the yeast were blamed.[14] However, a 10 deg. variation in oven temperature has little or no effect if humidity is controlled.[190] Mixing beyond a certain limit, one minute for the modified Hobart-Swanson mixer [190] may account for considerable variability, since at this point mechanical development of the gluten begins. Extensive experiments [78, 90] have shown that machine molding cannot eliminate completely the individual "molding personality." [268]

If reasonable precautions are taken to procure fresh yeast of the same brand and strain there is no reason to expect variation from this cause. Table 15 indicates the reliability over a period of time to be expected from a popular brand of yeast, even from widely separated sources.

Separation of Baking Factors. Analyzing the Standard Baking Test with reference to the separation of the factors listed in Table 14, we note that a fermentation time of nearly three hours with 3 per cent yeast and 2.5 per cent

TABLE 15.—*Yeast Reliability.*

(Average Values During Months Listed of Fermentation Strength of a Popular Brand of Yeast.)

Fermentation time in minutes with 1 per cent yeast—3⅛ per cent sugar: Same flour; storage and testing conditions identical.*

	East	Mid-West	Far-West
July-Sept.	151	148	153
Oct.-Dec.	150	149	152

* Each figure is an average of at least 40 samples.

sugar at 58 per cent absorption is specified. Supplementary test A: variation in absorption can be expected to measure the gluten hydration capacity. Supplementary test B: varying fermentation time involves at least three factors—gluten, extensibility, stability, and in some cases diastatic content. Supplementary test C: potassium bromate is a direct measure of the degree of or capacity for gluten development, whether due to age or previous bleaching. Supplementary test D: variation of mixing time is in part a measure of gluten extensibility and in part of the capacity for mechanical development. It appears that two of these supplementary procedures offer direct determination of certain important flour qualities: hydration capacity and degree of development. The other procedures, even the basic test itself, are concerned with several distinct properties. An illustration of this was pointed out in no uncertain terms by Jorgensen,[185] who gives data to show that only in the case of relatively highly diastatic flours is the basic test a true measure of the extensible properties. More sugar in the formula or the addition of 3 per cent of flour made from sprouted wheat to supply additional diastase would eliminate this uncertain factor.[186] * The need can also be conveniently met by the use of diastatic malt extracts. Finally the point to be emphasized is the importance of *separating*, by *controlled variations* in the baking test, those factors which we can recognize among the complex which we designate as flour quality, for it is only by the distinct separation of such factors that logical variations in commercial baking technique may be made.

BREAD MAKING.

Briefly the process of bread making may be outlined as follows:

1. Formula: evolved from baking test.
2. Mixing with power mixers or high speed mixers.
3. Fermentation.
   (a) Sponge type.
   (b) Straight dough type.
      (1) Short fermentation with high per cent yeast.
      (2) Long fermentation with low per cent yeast.
4. Punching—may or may not be omitted.
5. Dividing, rounding, preliminary proof, molding and panning.
6. Final proofing.
7. Baking.
8. Cooling.
9. Slicing and wrapping.
10. Staling.

The Formula. For many years, the trial and error method has established rule of thumb procedures which have developed into an empirical formula for making satisfactory bread. Considering the variability of the large number

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* Fleischmann Laboratories, unpublished results.

of factors involved, one cannot help but admire and pay tribute to those masters of antiquity who are responsible for the art. Following the application of science, reasons for some of the empirical methods used were developed and formula variation put upon a more logical basis. The formula to be used involves the following considerations.

1. *Type of Flour.*—The quality and fermentation characteristics are determined from the baking test, which should give specific information regarding (a) the absorption of the flour, that is, the amount of water to be added to produce the optimum plasticity, (b) diastase content, i.e., sugar producing capacity, (c) susceptibility to improvement by oxidizing agents. The baking test should also indicate the type of fermentation to be employed for the best volume, crumb color, texture, etc., and corresponding changes in the formula are made, which may call for the addition of malt extracts, sugar, fats, lipoids, or yeast foods, etc.
2. The type of fermentation adopted: The two general types of fermentation require slightly different formulas: (a) sponge types, which may be long or moderately short fermentations, (b) the straight dough types which may be very short or long fermentations. In the "sponge type" the yeast is mixed with a portion of the flour and allowed to work slowly for a variable period. The sugar, salts, and the remainder of the flour are then added and fermentation proceeds as in the straight dough method.
3. The type of bread to be produced: Hearth breads, such as the Vienna loaf or rolls require variations in the formula. Breads prepared from a mixture of flour with other cereals, rye, corn, etc., are frequently produced.

Mixing. There is a dual purpose in mixing [*vide supra*]; [1] incorporation of ingredients and [2] development of gluten. In the commercial dough mixer the heat of hydration of the large dough mass is sufficient to produce an appreciable temperature rise which must be considered in standardized production. High speed mixing is responsible for the incorporation of some air into the dough mass. This leads at times to the presence of small amounts of gases which may produce unfavorable effects.

Fermentation. The colloidal complex which we call dough has been described as a poly-dispersoid, water being the dispersion medium in which protein particles are held in a gel like structure containing crystalloidal and microscopic particles, salts, sugar, alcohol, yeast cells, starch grains and gas bubbles. The consistency is essentially plastic. Dough production is nothing more nor less than the making of a coarse foam, involving the dispersion of a gas in a plastic hydro gel of the flour proteins. It means the production of thin films of material wherein the mechanical factors of film elasticity or *extensibility* * and elastic limit or *limit* of *extensibility* become of paramount importance.[207] The concept of bubble size or "grain" is of significance in this connection.

Rate of *gas production* by yeast in doughs reaches a broad maximum from a pH of 4 to 6, falling rapidly on either side of this range. Under certain circumstances an appreciable production of gas at 0° C. occurs, the rate increasing to a maximum between 30° and 40° C., then decreasing to 0 from 40° to 50° C. as the yeast is killed. Acclimatization of a yeast to the sugar which it is to ferment may be of considerable importance [*b.*, Fig. 1]. Concentration of sugar above a certain limit, usually 5 to 8 per cent, exerts a definite inhibition. Five to 10 per cent of flour, itself, in the absence of salt, can almost entirely suppress fermentation in sugar solutions. The products of metabolism may retard activity as they reach a certain concentration. The percentage inhibition due to alcohol is a linear function of the alcoholic concentration up to the value of 8 to 10 per cent.[218] In practical bread production, however, this figure is never approached. Salts, such as NaCl, retard fermentation in amounts above a few per cent. On the other hand certain salts show specific

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* The baker's term for a concept which is similar to the reciprocal of the modulus of elasticity.

activation, of which calcium sulfate and ammonium phosphate are probably the best known. This is likely a nutrient effect on the yeast, stimulating enzyme production. Calcium sulfate also tends to lower the solubility of CO_2 in the H_2O and thereby inhibits toxic action due to its accumulation.

Doughs, however, are usually produced under fairly carefully controlled conditions of temperature, pH and humidity. The yeast used is usually reasonably uniform, modern baking technique being impossible without uniformity in yeast. Under these conditions the rate of gas evolution may be taken as essentially constant *as long as the supply of sugar is maintained.* The rate remains approximately constant throughout ordinary fermentation periods. With lightly buffered flours the pH may change sufficiently to cause a slight falling in the rate during excessively long fermentations. Finally the concentration of yeast, itself, determines the rate, but in doughs this relationship is not strictly linear.

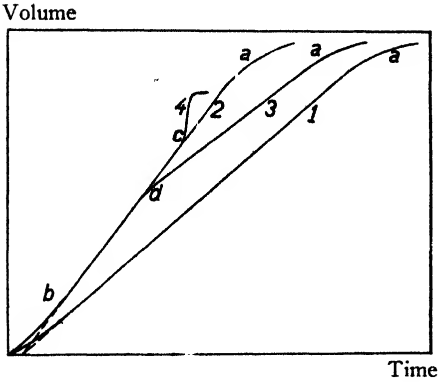

FIG. 3.—Generalized diagrammatic representation of yeast fermentation rates in doughs.

(1) Gas curve with 1 per cent yeast. (2) Gas curve with 2 per cent yeast. (3) Gas curve with limited amount of sucrose and a small amount of diastase. Break at *d* due to exhaustion of pre-existing or added sugar. (4) Gas curve when placed in oven at point *c*.

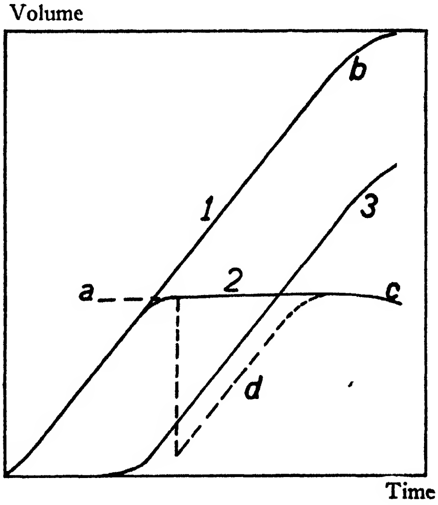

FIG. 4.—Loss of gas from fermenting doughs (after Karacsonyi and Bailey[141]).

(1) Fermentation rate. (2) Dough volume. (3) Gas lost from dough. (a) Maximum extensibility or maximum dough volume. (b) Falling off in fermentation rate due to lack of sugar. (c) Loss in maximum dough volume due to decreased fermentation rate.

Under certain conditions, particularly with low diastatic flours, the sugar becomes exhausted before the fermentation is finished. Curve 3, Figure 3 indicates what happens when this occurs. The fermentation rate is reduced and becomes limited to the rate of sugar production. Obviously, it is poor economy to limit the capacity of the yeast by insufficient diastase. The rate is greatly increased when the dough is placed in the oven until five to eight minutes elapse, when the thermal death point of the yeast is reached. [Curve 4, Fig. 3]. This increase in activity is one of the important features in oven spring.

In consequence of the extensibility of the gluten strands which comprise the dough, gas evolution by uniformly distributed yeast cells gives rise to the *foam structure.* It is intimately associated with many factors:—hydration, "development," salts in the water film, and finally inherent properties of which we know nothing at present. This extensible property confers upon the dough one which we call "stiffness" and in overcoming this resistance to expansion considerable pressure is generated within the cellular structure. The height to which the dough rises in a given time at a constant fermentation rate depends, of course, upon the degree of stiffness, other conditions being equal. Any modification of gluten extensibility will have a corresponding effect upon the rate of rise. For example, gluten development shows a progressive change during fermentation. This change may be due to products of yeast metabolism, proteolytic activity, hydration changes, or a number of, as yet, little understood causes. Upon severe punching or breaking, the gluten becomes "mechanically" developed. The starch granules are worked to the exterior of the strands, which by their coherence gain in extensibility [Fig. 9]. The foam structure is modified, the gaseous phase becoming more highly dispersed and the gluten films thinner and more homogeneous. It is probable that the action of dough breaks upon the foam, when the dough is put through a number of times, is not unlike that of a colloid mill or homogenizer upon oil emulsions. The effect is apparent in finer texture and whiter color.

Elastic Limit or *"Limit of Extensibility."* It is obvious from a mechanical standpoint that the dough cannot continue to rise indefinitely; the limit of extensibility of the gluten strands is finally reached. Rupture of the vesicles takes place, releasing the entrapped gas; broken films coalesce and re-form, producing a new crop of bubbles. At this point the escape of gas finally becomes equal to its rate of formation and the dough ceases to rise; it has reached its point of maximum extension. Karacsonyi and Bailey [141] have made an excellent study of this phenomenon (Fig. 4). We notice the constant fermentation rate, curve 1, the maximum dough volume (a), the rate of loss of gas from the dough, curve 3, and finally the drop in maximum dough volume (c), caused by exhaustion of sugar (b). The dotted curve (d) indicates what would happen if the dough were punched back to its original volume.

Let us consider the inter-dependence of maximum dough volume, limit of extensibility, and loaf volume. It is obvious that the *loaf volume* cannot exceed the *theoretical maximum dough volume* at the temperature of coagulation. Although no exact measurements have been made of the variation of maximum dough volume with temperature, the theoretical value at coagulation temperature probably does not differ greatly from the actual value at fermentation temperatures. The volume of dough must be so controlled that when it is placed in the oven the resulting expansion will not exceed the maximum dough volume. In other words, for a good loaf the dough must be taken from the proof at such a volume that when placed in the oven, the resulting expansion of the gases in the dough which takes place will not produce a total volume greater than the maximum dough volume. If a greater expansion occurs, it means that the limit of extensibility is exceeded and holes,[207] coarse texture, and ragged loaf development result.

Punching. At intervals during fermentation, the dough is mechanically beaten or "punched," the gluten strands are forcibly ruptured and the gas expelled. The punching may vary greatly in severity. This process is generally conceded to produce various desirable changes; (a) it continues the mixing process and expels CO_2, redistributing the sugar and metabolic products of the yeast, (b) it increases the degree of dispersion of the foam,

(c) it causes mechanical development of the gluten. These changes usually result in improved texture and sometimes increased volume. It has been mentioned that mechanical development has a marked effect on extensibility. The curves of Karacsonyi and Bailey[141] show this effect to a slight extent. Thus in Figure 5 (idealized) the maximum dough volume is indicated at (a, Curve 2) for a certain flour. If the dough is severely punched as at (b) and if mechanical modification should increase the limit of extensibility of the gluten, the maximum volume in the next rise would be at (c), and after subsequent punching a strong flour might give gradually increasing maximum dough volume (d). The work of Swanson and Working[260] on over-mixing indicates that a point is reached after which the maximum dough volume progressively decreases. For certain soft flours, successive punches cause a diminution in the maximum dough volume, i.e., the maximum degree of development is reached during, or soon after the initial rise of the dough. *See* (e) and (f) in Figure 5. This type of mechanical modification reaches its extreme in the use of dough breaks. Even doughs made from strong flours after being subjected to sufficient treatment with dough breaks lose in maximum volume.

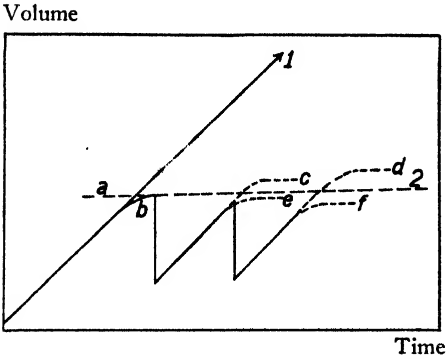

FIG. 5.—Generalized diagrammatic representation of "punching."

(1) Fermentation rate. (2) Dough volume. (a) Maximum dough volume—no punch. (b) 1st punch. (c, d) Increase in maximum dough volume of "strong" flour due to mechanical modification and gluten development, following 1st and 2nd punches. (e, f) Decrease in maximum dough volume of "weak" flour due to mechanical modification following 1st and 2nd punches.

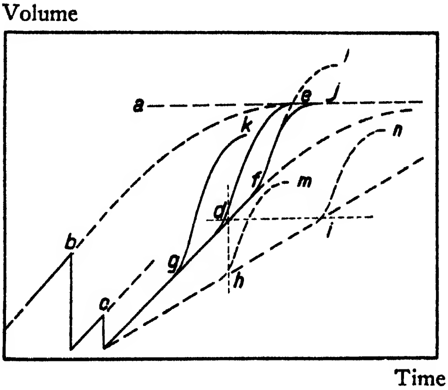

FIG. 6.—Enlarged diagram of proof and oven spring.

(a) Maximum dough volume. (b) Dividing and rounding. (b-c) "Bench" proof. (c) Moulding. (c-d) Pan proof. (d) Oven point. (d-j) Oven spring (normal). (g-k) Oven spring (proof taken early). (f-l) Oven spring (proof taken late). (j-l) Gas lost due to late proof. (h-i) Fermentation rate with diminished sugar. (h-m) Oven spring with diminished sugar and normal proof time. (i-n) Oven spring with diminished sugar and extended proof time.

When gluten development is complete and foam structure satisfactory, the dough is divided, rounded and molded into loaves (b. Fig. 6). During this process some of the gas is again expelled, and time must be allowed for recovery. The rounded dough mass is allowed to gain a little in volume (the "bench proof"), (b) and (c) Fig. 6, in order to facilitate handling. After molding and panning a further interval is allowed for the dough to reach a state which will give the maximum loaf volume without sacrifice of texture.

Of course, a distinct interval is not allowed for *each individual* dough *mass* in modern practice, although the time may be varied from batch to batch. This interval is termed the "pan" or final proof. The loaf is then placed in the oven.

Oven spring. The significance involved in the ancient term "proof," applied to the period immediately preceding the introduction of the loaf into the oven, hinges upon the potentialities inherent in this moment. We have seen that the loaf volume cannot exceed the maximum dough volume, consequently the expansion which takes place upon the introduction of the loaf into the oven must not be greater than this value. On the other hand, in certain markets where large volumes are desired it is necessary to approach this maximum volume as closely as possible. The expansion which takes place during the first 10 to 15 minutes in the oven is termed *oven spring. See* (d) and (e) in Figure 6. At least three factors are involved: (a) the thermal expansion of the gases already present or generated, including the increase in vapor tension of water, (b) dissolution of the carbon dioxide held in the dough moisture, and (c) increase in the rate of fermentation. It is obvious that the point at which the proofed dough is taken should be *not more* than the difference between the maximum dough volume and the sum of the volume increases due to these factors. *See* (d) in Figure 6. If for example the proofed dough be taken at (f), the increase in volume during oven spring will be more than that required to reach the maximum dough volume, i.e., the limit of extensibility of the gluten films will be exceeded and the excess gas will escape. This will have an unfavorable effect upon the texture. On the other hand, if the proofed dough be taken at (g) the expansion in the oven will be insufficient to produce the maximum dough volume and a smaller loaf will result. The texture of such a loaf is ordinarily quite satisfactory. In this discussion it is of course assumed that gluten development is essentially the same for any one set of conditions.

Some Popular Fallacies. The fact that sugar concentration, diastatic activity and fermentation rate are closely related to each other, but altogether distinct and separate from gluten quality or flour strength, has been but rarely recognized. Fortunately, through the efforts of Jorgensen[185] and Bailey's school,[186, 187] this truth is becoming apparent. Flours which fail during the last stages of fermentation were formerly classed as "weak," whereas the addition of a small amount of diastatic malt extract or sugar produced excellent results.* This same failure has also frequently been ascribed to the yeast. We have noted the effect of sugar shortage upon fermentation rate (Curve 3, Fig. 3). If a shortage occurs during proof time the volume of the proofed dough will be decreased (h., Fig. 6), and hence the amount of gas available for expansion will also be smaller. This decrease might be compensated by increase in proof time to point (i); however the decreased rate of fermentation caused by the limited sugar would be unable to supply the usual amount of gas produced during the normal oven spring. This would inevitably result in a decreased loaf volume (Fig. 6). In modern baking it is absolutely necessary to distinguish between *sugar deficiency* and *gluten strength* as influenced by inherent properties, development, proteolytic action, etc.

Baking. The colloidal changes occurring in the dough when placed in the oven are deep seated and profound. The gluten strands are coagulated and lose their extensibility, becoming set, while the entrapped gas and some water vapor escape. (With reference to the heat coagulation of proteins the reader is referred to Mona Spiegel-Adolph, this series, Vol. II, p. 303.) The starch is partly gelatinized, its susceptibility to diastatic attack increased. The outer surface of the loaf dries out and carbohydrates and N compounds are pyrolyzed in the formation of crust color. Differences in rates of heating of outer and inner portions of the loaf produce marked effects upon its shape and ex-

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* **Fleischmann Laboratories, unpublished results.**

ternal characteristics.[84] After the action of the oven heat is satisfactorily completed, the loaf is removed for cooling and wrapping. There is a modern tendency toward slicing of loaves before wrapping; this requires very careful control of micro-organisms, as bread is an excellent medium for the growth of many bacteria and molds.

Fermentation Tolerance. Let us take a perspective of the complete process. While there may be variations in time of fermentation, in methods of incorporating yeast (sponge), or in mechanical modification, the general process may be illustrated by the diagram in Figure 7. We shall definitely rule out the factor of sugar shortage, by the use of a highly diastatic flour or addition of malt extract. Our fermentation then proceeds at a nearly constant rate, as indicated by the curve ending at a (Fig. 7). When the dough has risen to the level indicated at (b) it is punched and allowed to rise to (c). This process may or may not be repeated, but the dividing, molding and proofing processes generally give the picture indicated by (d) to (j). The oven spring under controlled conditions of yeast nutrition is generally not highly variable. We speak of "taking" the dough at the point (d); this is referred to as the completion of fermentation. Since flavor and texture are usually improved by longer fermentation and greater mechanical modification, the question arises as to the amount of such manipulation which a particular flour will withstand. We may "take" the dough at the point d_1 or d_2, c_1 or c_2, b_1 or b_2, we may treat it gently and omit the punches; we may also punch it severely, and finally modify the structure by drastic treatment on the dough breaks. What will be the effect of these variations on the final loaf volume?

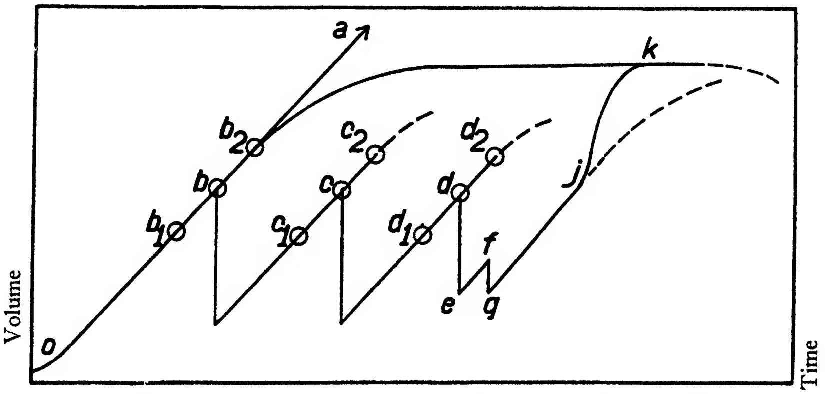

FIG. 7.—Generalized diagrammatic representation of the complete baking process (straight dough or after mixing in the sponge).

(o-a) Fermentation rate. (b) 1st punch. (c) 2nd punch. (d-e) Dividing and rounding. (e-f) "Bench" proof. (f-g) Molding and panning. (g-i) Final or "pan" proof. (j-k) Oven spring.

When an experiment of this kind is performed, taking strict precautions to insure a plentiful sugar supply throughout all stages, curves similar to those given in Fig. 8 are obtained. The proof procedure is identical in all cases. We find two general types of curves. That which we shall designate as a "strong" flour gives a curve similar to 1. (Fig. 8.) The maximum loaf volume is maintained over a long period of time, and only after three to four hours or more do the effects of fermentation or mechanical modification begin to tell upon the limit of extensibility. The gluten of "soft" flours, however, rapidly reaches its maximum development, Curve 3 (Fig. 8). Its limit of extensibility then declines. This lower limit of extensibility, however, may in some cases be compensated for by the use of a more rapid fermentation rate, enabling a greater dough volume to be obtained before the unfavorable effects of prolonged fermentation upon the gluten become manifest (Curve 2). We define this reaction of the gluten towards the abuse which it receives during fermentation, as "Fermentation Tolerance." Flour with a "good" fermentation tolerance is easier to work, but under very accurately controlled conditions, satisfactory results may be obtained from flours with relatively poor fermentation tolerance.

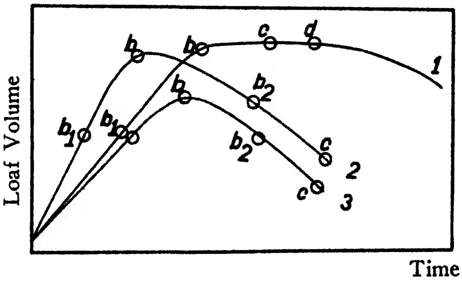

FIG. 8.—Fermentation tolerance with *excess diastase.*

(1) "Hard" flour. (2) "Soft" flour. (3) "Soft" flour with high yeast; short fermentation.

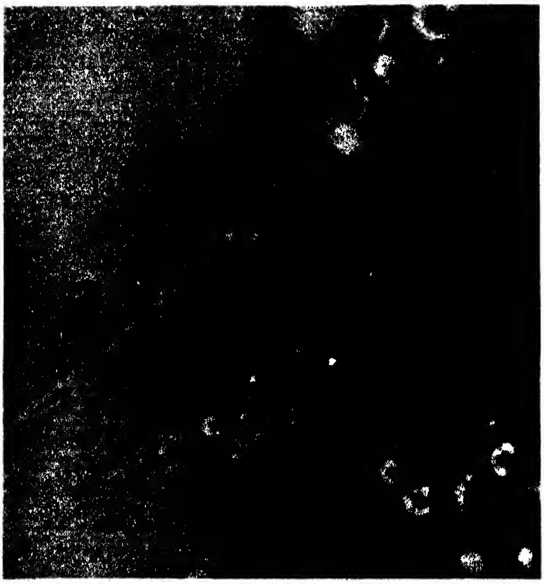

FIG. 9.—The condition of starch and gluten in the dough.

(a) Homogeneous gluten strand.
(b) Starch grains clinging to exterior of gluten strand.

Staling. At any temperature an equilibrium (*vide supra*) exists between starch granules and water. In the oven the interior of the loaf reaches a temperature of 95° to 99° C., and the equilibrium is shifted in favor of swollen granules, the starch approaching a colloidal system with the amylose lattice as the external phase. While the limited amount of water precludes any large degree of swelling or rupture, a "first degree gelatinization" [144] and characteristic changes in properties occur. Unfortunately, we have no quantitative data on the distribution of water between the now coagulated gluten strands and the starch granules at that temperature. (Fig. 9.)

Upon cooling and ageing, the equilibrium is shifted back, water is probably expelled from the starch lattice structure, the granules shrink or "retrograde" and the character of the crumb changes accordingly, becoming harsh, brittle, crumbly and stiff. This staling has been investigated from the following points of view:

(1) "Absorption Coefficient"; the ratio of the densities of the bread starch to that of normal dry starch. (Lindet.[169])
(2) Determination of "Soluble amylose" of the crumb. (Katz.[143])
(3) "Swelling power" of the crumb. (Katz.[143])
(4) "Compressibility" or "Hardness" of the crumb. (W. Platt.[209])
(5) "Viscosity" of the crumb. (Karacsonyi.[188])
(6) Change in pH of the crumb. (C. N. Frey, unpublished; Karacsonyi.[139])
(7) Change in X-ray spectrum of the starch. (Katz.[144])
(8) Susceptibility of the starch to diastatic attack. (Schultz and Landis.[227])

All these methods show that a rapid change occurs during the first 8 to 20 hours after removal from the oven. With the exception of (4) and (6), they are essentially methods of determining the degree of turgidity of the starch.

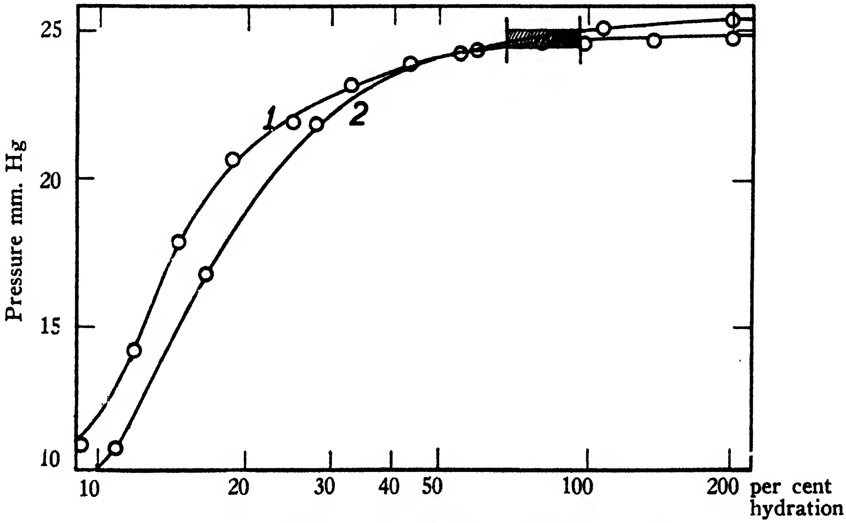

FIG. 10.—Typical vapor pressure—hydration curve.

(1) Coagulated gluten. (2) Gelatinized starch. Temp. 20° C. ± 0.2°. Shaded area represents that in which bread normally exists.

Recalling the changes taking place upon cooling gelatinized starch, we conclude that the ageing of bread is accompanied by these changes, the phenomenon being termed "staling." Reheating the stale loaf causes a reversal of the equilibrium, and the loaf regains its original freshness. Where does the water go during staling? According to Alsberg[1] it is taken up by a re-hydration of the gluten. Karacsonyi[140] however, maintains that it is not transferred to the now coagulated gluten, but simply remains as superficial or as capillary water.

Recent investigations on the vapor pressure of coagulated gluten and stale gelatinized starch, however, appear to confirm the explanation of Alsberg. (The Fleischmann Laboratories, unpublished results.) In Figure 10 the possible range of starch hydration occurring in bread crumb is delineated in the shaded area. Under these conditions the starch has a slightly higher vapor pressure than the gluten, and hence to reach thermodynamic equilibrium water must pass from starch to gluten. Figure 11 also indicates that starch loses water more readily than gluten. In this connection, the antagonistic swelling between connective tissue proteins and cell proteins may be mentioned. Here it is pH rather than temperature changes which causes one component to swell or contract at the expense of the other (Spiegel-Adolph, Vol. II).

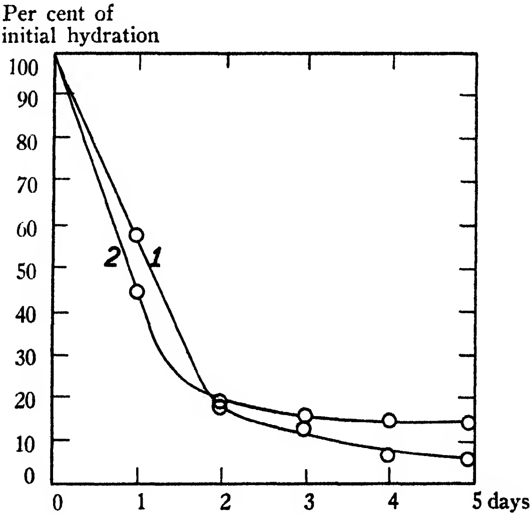

FIG. 11.—Comparative rates of loss of water.

(1) Coagulated gluten. (2) Gelatinized starch. Initial hydration of gluten, 180 per cent; of starch, 90 per cent. Relative humidity, 90 per cent. Temp. 30-32° C.

It should be emphasized that loss of water on drying is not to be associated with this type of staling.* True, if dried beyond a certain point, reheating fails to restore the freshness, but that is simply because the swelling of the granule is impossible without sufficient water. If the dried loaf or slice be restored to its normal moisture content of 38 per cent the freshness will be regained.

There is a definite relation between the degree of *staling* and the *temperature* of *storage*. At temperatures above 55° to 60° C. as Katz[143] first showed, there is little or no staling during the course of a week. The maximum amount of staling, according to the criteria listed above, occurs in the neighborhood

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* W. Platt[209] defines ordinary staling and inherent staling as drying and retrogradation respectively. Flavor and aroma are partially lost, and are not completely regained upon reheating.

of 0° C. (Fig. 12). At lower temperatures the loaf becomes frozen and staling is again retarded. In this connection it may be noted that the addition of small amounts of highly diastatic malt appears to decrease the extent of staling at the lower temperatures as measured by the diastatic method.[227] The addition of aldehydes,[148, 140] particularly if water soluble, has been found to retard staling.

Crust Starch. It seems possible to distinguish two zones in the crust: (1) the outer, or caramelized zone, which gives the X-ray pattern of an amorphous substance, containing pyrofaction dextrins as a result of the thermal decomposition of the starch; (2) the interior zone, containing gelatinized starch and a varying number of granules of native or ungelatinized starch. This is a logical consequence of the drying out of the outer layers when first placed in the oven. Insufficient water remains in them to gelatinize the starch. Naturally these zones are ill defined and merge gradually into each other and into the interior or crumb portions of the loaf. The rate of retrogradation is relatively slower in this second layer than in the crumb, a consequence of the lack of moisture.

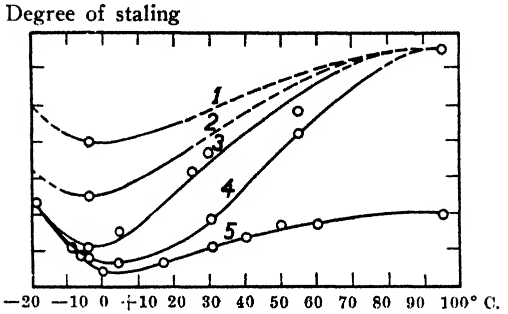

Fig. 12.—Staling (after Schultz and Landis[227]).

Staling as measured by degree of action of bread starch by flour diastase. Bread aged: (1) 4 hours. (2) 8 hours. (3) 16 hours. (4) 88 hours. (5) Staling as measured by swelling power. Curve plotted from the results of J. R. Katz.[143]

Cakes and Cookies

In the foregoing discussion we have indicated in a general way the principal factors of importance in bread making. These same considerations apply to the manufacture of cakes and cookies, but the picture is almost hopelessly complicated by the interaction of other factors which are impressed upon the system by the addition of other ingredients. The specific processes involved in the manufacture of baked goods other than bread have been so little studied from the scientific point of view, that little can be said regarding them.

Among the added ingredients are eggs—white and yolk, fat in widely varying quantities, baking powder, with its resultant effect on the pH of the dough, and comparatively large concentrations of sugar and spices. The colloidal aspects of these ingredients in relation to cake baking involves not only the nature of the substances themselves, but also their effect upon each other and upon the flour proteins.

Investigations have been made upon the development of a synthetic test for the coordination of these factors. Under the chairmanship of M. M. Brooks[42] a group of specialists in the field is engaged in an extensive study of the effect of variations in formula and conditions on cake quality. These efforts may be expected to result in valuable contributions to our knowledge of general baking chemistry as well as to cake baking.

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Butter and Margarine from the Standpoint of Colloid Chemistry.

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Butter and margarine being solidified emulsions, and involving in their production the special treatment of milk (itself a complex colloid system), present many interesting problems in colloid chemistry and physics. Most of the phenomena involved are concerned with the effects of surface tension (air/liquid) and interfacial tension (fat/milk serum). Although this discussion is not specially devoted to the colloid chemistry of milk,[1] certain very fundamental details must be considered in order clearly to understand the main facts connected with butter and margarine. Thus we must consider such questions as the foaming of milk, homogenization of milk, and cream separation, in order to explain the practice of butter formation.

Milk

The average composition of cow's milk is as follows:

	Per Cent
Water	87.27
Fat	3.64
Lactose	4.88
Casein	3.02
Albumin	0.53
Ash	0.71

The specific gravity of cow's milk is 1.0316, that of the milk-fat being 0.92. The fat is present in the milk as fine globules, so that milk is an emulsion of the oil-in-water type. The diameters of the fat globules vary between 0.01 mm. and 0.0016 mm. The size and number of the globules depend on such factors as the breed and the age of the cows, and on the period of lactation.[2]

Cream is formed by the rising to the surface of the fat globules through the denser milk serum. Thick cream contains about 56 per cent of fat and 39 per cent of water, whilst thin cream contains about 29 per cent of fat and 64 per cent of water. The fat content varies between wide limits, and the percentage of fat is in inverse ratio to the density of the cream.

The true colloids in milk, the proteins, have been the subject of many investigations,[3] but much remains to be done, especially with regard to the existence of a third protein in addition to casein and lactalbumin.

Milk Froth

New milk readily froths, e.g. after just drawing, on stirring, and on passage through a cream separator. Milk foam is a technical nuisance, and foam-destroyers are frequently employed in dairies. One excellent method is to run the milk into a detention tank, drawing the milk continually from the bottom. Thus a round tank 16 inches in diameter and 36 inches high, permitting one foot head of froth, has been found to eliminate the froth from violently-agitated milk, at the rate of 400 gallons per hour, the time of detention being approximately 3¼ minutes.[4]

The phenomenon of frothing is well-known in colloid systems and is a consequence of the accumulation of colloid substances at the air/liquid surface. Thermodynamically it can be deduced that whenever a substance is dissolved in a liquid, so that the surface tension of the solvent is altered, concentration changes occur in the boundary layer between the liquid and air. If the surface tension be diminished owing to the presence of the solute, the latter must concentrate at the air/liquid surface. This accords with the "principle of mobile equilibrium," since the most stable arrangement accompanying interfaces in general is that the surface energy be a minimum. This particular case of the principle is usually referred to as the Gibbs-Thomson theorem,[5] and the phenomenon of interfacial concentration-change is termed *adsorption.*

When milk is agitated in such a way that the boundary, air/liquid, is considerably extended, adsorption of the milk-colloids at this boundary is intensified. Frother or foam represents an enormous film-like area of liquid supported in a gas (usually air). The air-bubbles persist for some time owing to the presence of the milk-colloids in a solid condition—the *Ramsden phenomenon.* Ramsden [6] with a variety of colloid solutions and emulsions showed that in certain cases the adsorbed colloid may become concentrated to such a degree as to be "precipitated" in solid or semi-solid lamellae or membranes.[7] * Particularly striking were his experiments with aqueous solutions of albumin, which on agitation or pouring from one vessel to another gave a most persistent foam stabilized by solid albumin, irreversibly "precipitated" from the solution. He further proved that in a solution of two or more colloids, each of which independently would accumulate at the interface, there was a preferential accumulation of one colloid to the more or less complete exclusion of the others. The colloid preferentially adsorbed is, of course, the one effecting the most marked reduction in surface tension.[7]

In the case of milk-froth, quantitative proof of the Ramsden phenomenon has been given by Siedel and Hesse.[8] Examining the froth on skim-milk after cream separation by centrifuging, they found an increase in the protein content, but no change in the inorganic content. The following table of their results is quoted by Rahn: [9]

Analysis of Dry Solids.

	Strongly Frothing Milk		Ordinary Milk	
	Protein	Ash	Protein	Ash
	Per Cent	Per Cent	Per Cent	Per Cent
Froth	38.87	8.63	36.39	8.52
Milk	35.60	8.58	34.72	8.57
Excess in froth	+3.27	+0.05	+1.67	—0.05

Froth allowed to remain undisturbed on milk gradually collapses, and eventually, wrinkles of delicate, membrano-solid character lie on the surface. Brouwer claims to have proved the existence in milk of peculiarly shaped small bodies which were membranes originally formed by adsorption of protein on gas bubbles and remaining in the milk after the bubbles had collapsed. Rahn [10] showed that the addition of 0.5 per cent of peptone to the milk

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* *See also* paper by R. E. Wilson in Vol. I of this series, on "Surface Films as Plastic Solids." *J. A.*

altered the character of the froth, bubbles forming which burst in upon one another, gradually uniting to larger and larger bubbles. This is due to the change in character of the bubble-walls, which are solid in the air phase, but redissolve in the liquid phase. Addition of gelatin to the peptone-milk causes still further change owing to the displacement of the peptone by the gelatin. The outer walls of the bubbles are now only semi-solid, and slow collapse of the bubbles follows the occurrence of rents in the walls.

Siedel[11] found that churning milk at a low temperature for about 45 minutes inhibited froth formation later when passed through a cream separator. Cooling the milk without churning did not affect froth formation. Also separated milk, cooled and churned, and then mixed with cream, frothed as usual when passed through a separator. Two facts emerge from these experiments: (1) churning fat-poor milk renders the foam-colloid inactive; (2) the greater portion of the foam-colloid is in the cream. Both facts are explicable on the Gibbs-Thomson theorem. Churning skim-milk causes frothing with the consequent irreversible coagulation of the milk colloids; thus the cause of frothing being removed, later agitation has no effect.[12] Cream is rich in milk colloids owing to the marked adsorption occurring at the enormous fat/water interface. That the proteins of milk do concentrate round the fat globules has been proved quantitatively by Rahn[13] by analytical tests on skim milk, cream and butter.*

It is most probable that the skin which forms on heated milk[14] is also due to the colloids concerned in milk-foam, the thin delicate skin being already present on the surface of cold milk, and becoming concentrated on evaporation.[15] †

Whipped cream is a special case of milk-foam. The remarkable stability and the great viscosity of whipped cream are due to the cell-like structure imparted by the air bubbles whose walls are stiffened not only by the coagulated protein ‡ but by the solidified milk-fat. The latter factor vanishes on heating, and the whipped cream more or less collapses, but some foam-structure persists owing to the protein being now insoluble.

Rahn raises the question of the chemical nature of the substance responsible for foaming in milk and cream. He points out that it is not identical with lactalbumin, because this coagulates on heating the milk sufficiently and yet the milk is still capable of foaming. He doubts, too, whether casein is responsible, since acidified milk or cream in which the casein is flocculated, can froth. He believes a third protein exists in milk; the isolation of this has been claimed by Storch,[16] and by Voeltz.[17] Some workers[18] believe in the existence in milk of another protein, lactoglobulin, present to the extent of 0.15 per cent. Further research work on the protein content of milk is urgently needed.

Homogenized Milk

Milk is an unstable emulsion, as witness cream-rising. By sufficiently subdividing the fat globules in milk, a new emulsion is obtained of very great stability. The process of reducing the fat-globules of an emulsion to an approximately equal (small) diameter is termed homogenization. The methods employed in technical dairy practice to hemogenize milk and cream

* Investigations of the U. S. Dept. of Agriculture have shown that the bacterial content of cream is generally much greater than that of the whole milk from which the cream is won. Apparently bacteria also concentrate at the fat-serum interface, and may well be a factor to be reckoned with in stability considerations. J. A.

† In this connection *see* paper by du Noüy in Vol. II of this series. J. A.

‡ Gelatin is very commonly added to cream before whipping, and by tending to concentrate at the air bubble interface, would aid in stabilizing the foam. J. A.

have been described by the present writer elsewhere.[19] The process of homogenization reduces the diameters of the fat particles in milk or cream to about one-hundredth of their original value. Such emulsions may even defy separation when centrifuged. The stability of homogenized milk with respect to the separation of the butter-fat has been studied by Sobbe,[20] who found that there was very little creaming in homogenized milk, whilst untreated milk creamed rapidly. Homogenized milk cannot be churned into butter, and hemogenized cream cannot be whipped; the addition of a colloid such as gum tragacanth is necessary if a permanent foam is desired. The Brownian movement is very marked, and there is a measurable decrease in the surface tension.

The cause of these remarkable changes is the increased adsorption of casein on the fat globules. Since the number of fat globules is increased about a thousand times, the adsorbing surface created is enormous. The adsorption of casein is at once manifested by the large increase in viscosity, homogenized milk and cream being much thicker than the original liquids. Wiegner [21] reduced the average diameter of the fat globules in milk from 2.9 μ. to about 0.27 μ. and from viscosity measurements calculated that, of the casein in milk, 2.27 per cent was adsorbed in the ordinary sample, and 25.5 per cent in the homogenized milk. (This is based on the assumption that only casein is adsorbed, and that the mean thickness of the adsorbed layer is 6.8 mμ.). Skim milk cannot be homogenized since it is practically fat-free.

Wiegner examined two samples of homogenized milk and found that the number of fat globules had increased 1,188 times and 1,258 times respectively. The surface area of the fat globules had been increased 112 and 117 times respectively. The viscosities of the raw and hemogenized milks were in the ratio (a) 1 : 1.12 and (b) 1 : 1.15.

Homogenized milk and cream are more easily digested than the ordinary products, owing to the fine subdivision of the fat globules,[22] and thus are valuable in infant feeding.[23]

Cream Separation

In large dairies cream is separated from milk by means of centrifugal separators,[24] and though many interesting facts are connected therewith, especially from the standpoint of the breaking of emulsions,[25] centrifugal separation has no immediate bearing on the colloid theme discussed in this report. In order to lead up to a rational explanation of butter-formation, the creaming of milk by the older methods of undisturbed gravity influences must be considered.

The usual view of the creaming of milk will be gathered from the following quotations from leading text-books: "This separation of fat in the form of cream is possible, because of the difference in the S.G. between the fat globules and the other constituents of the milk. If the milk is allowed to stand undisturbed, the fat particles will slowly rise to the surface and can then be skimmed off in the form of cream, the rapidity and completeness with which the fat globules rise to the surface depending on the difference in S.G. between the fat globules and other elements in the milk, and on the viscosity of the milk serum. Anything which affects either of these factors will affect the creaming process. The conditions which most commonly affect the creaming process are: the size of the fat globules, the percentage of solids-not-fat, and the viscosity of the serum" (Stocking).[26] "The principal agent retarding or preventing the upward passage of the fat globules is the viscosity of the milk which is largely due to its . . . constituents of a colloid nature inherent in milk and cream, and to the milk sugar. If the viscosity of milk were no greater than that of water, the fat globules would rise to the surface instantaneously in a similar manner as oil poured into water rises to the surface" (Hunziker).[27]

Recent work by Rahn[28] has shown the usual view of creaming, as given above, to be incomplete, and, as regards the viscosity factor alone, quite untenable. Thus, Hunziker's last sentence in the above quotation is entirely wrong.

Ordinary gravity—creaming of milk may be carried out in three ways:

I. Standing the milk in shallow pans to a depth of two to four inches for 24 to 36 hours. The cream is removed by a skimmer, but from 0.5 to 1.0 per cent of the cream is left in the skim milk.
II. Standing the milk in deep pans (about 20 inches) set in cold water. The skim milk is withdrawn from the bottom and the amount of fat retained in the skim milk is only about 0.2 per cent. Regarding this method, Bancroft[29] has pertinently remarked: "The dairymen have noticed that, contrary to what one would expect, cream rises more rapidly and more completely in a deep vessel than in a shallow pan.[30] The finer particles of butterfat are caught by the coarser ones and swept upwards because the concentration of the coarser particles per unit of cross-section soon becomes high enough to have a filtering effect. . . . Nobody has made any experiments as to any possible relation between the concentration at which the filtration becomes effective and the concentration for zero fluidity."
III. The water dilution method: to the new milk is added hot or cold water to the amount of one-quarter to one-third by volume. The idea involved is that lowering the viscosity of the milk serum will expedite the rising of the fat globules. The results, however, are not very good,[31] and about 0.7 per cent of butterfat is lost in the skim milk.

Rahn[32] has shown that the viscosity of milk can be increased, yet instead of the creaming being slowed down it is accelerated. Moreover, the increase in viscosity is attained by adding water-soluble colloids, e.g. gelatin. Using warm milk at 40° C. containing gelatin, Rahn reports: "The addition of gelatin caused a quicker creaming, a thicker cream layer, a looser cream of smaller fat content, a much more complete separation of fat as cream, and also a skim milk of lower fat content, in spite of the fact that the viscosity much exceeded the highest limit for normal milk which lies about 2.4. These experiments have been repeated with other substances, and even where the viscosity was 5.61, there was a considerably better yield of cream than with untreated milk."

Other colloids such as gum tragacanth, gum arabic, peptone and albumin, in small quantities accelerated creaming. Increasing the viscosity of the milk by adding non-colloids like sugar, delayed creaming. Obviously these results demand a new interpretation for the phenomenon of creaming.

Rahn further showed that the inhibited creaming of heated milk (formerly explained as due to the loading of the fat globules with coagulated protein) could be changed to a normal value by adding gelatin or other accelerating colloid after heating. By measuring the velocity of ascent of fat globules in milk under various conditions Rahn concluded;—"that the fat globules in raw milk do not rise singly, but clot together, the clumps possessing a greater buoyancy." In raw milk are numerous such clumps, seldom apparent in heated milk, and herein lies the essential difference in the mode of creaming. Heating was found to destroy clumping of the fat globules; the addition of albumin, gum arabic, and gelatin enhanced clumping due to the formation of an adsorbed glutinous envelope "which makes possible the sticking-together of the globules as they collide owing to their molecular movements." Analytical proof is given of this concentration around the fat particles in the case of gelatin, since nitrogen determinations were carried out in the cream and skim milk. "The assumption of clotting and of a colloidal envelope, was supported by the observation that increasing addition of the colloid made the cream looser (more spongy) and of less fat content." Thus:—

FAT CONTENT OF CREAM.

Gelatin added (%)	nil	0.35	0.70	1.05	1.40
Fat Content (%)	33	30	27	25	23
Gum Arabic added (%)	nil	1.18	2.35		
Fat Content (%)	27	26	25		

Heating reduces the adhesiveness of the envelope-colloid and the fat globules rise singly giving a thicker cream layer.

The Churning of Cream

Older views accounting for the phenomenon of churning have been to the effect that the globules of milk fat are in a superfused condition and become solidified by churning (Fleischmann). Soxhlet believed a solid membrane around the fat globules became broken by churning, thus permitting the coalescence of the fat particles. Although there is a membrane present, his idea of it is not in accord with the modern theory of colloidal adsorbed films. Storch[33] believed that the fat-globules were surrounded by a protein envelope (slim-membrane) of thickness about one-tenth the radius of the fat globules, and of composition 92.5 per cent water, 1 per cent ash, and 6.5 per cent lacto-mucin. Churning gradually rubbed this protecting envelope away, exposing fat.

The present view is that the fat-globules in milk have an adsorbed protein covering. During churning or aeration the protein becomes re-adsorbed at the enormous liquid-air interface. Thus, Rahn[34] holds that during churning, the protein envelopes, coagulated by exposure to air, are subsequently broken by the churning movement, frothing ceases, and the fat globules coalesce to form the small grape-like masses of butter. He later[35] showed that butter can be produced so long as the liquid froths, even if the fat is liquid in the cream particles, but under these conditions the agglomerates of liquid fat break again owing to the agitation, and the yield of butter is small. The time necessary for the formation of butter decreases as the temperature rises, and at 5° C. practically no butter forms.

Hittcher[36] found that the initial churning temperature of the cream and the fat content have hardly any influence on the size of the agglomerates of butter formed. He made the interesting observation that freezing the cream prior to churning at usual temperatures greatly hastened churning. Probably this is due to some change in the physical characteristics of the protein envelope (cf. changes on thawing frozen meat).

Besides churning milk or cream, other methods have been proposed for the separation of the butterfat. Thus Clavel[36a] claims that by converting milk into a froth by streaming gases through it, the cream may now be obtained by pouring through a fine sieve which will retain the fat. This is an instance of the Ramsden phenomenon in adsorption, and the method has been used for breaking emulsions in other technical operations.[36b] North[36c] proposes to whip cream in the cold (13° C.) and then dilute with 1 to 4 volumes of hot water to melt the fat, subsequently passing the lot through a whey separator and finally through a centrifugal oil dehydrator.

Methods depending on altering the state of the casein have been patented by Alexander[36d] and by Stevenson.[36e] The former heats milk under pressure so as to dissolve the casein and thus facilitate separation of the fat. The latter method is to add hydrochloric acid until the pH of the milk serum is 3.0, the precipitated casein being thus re-dissolved.

Margarine

Margarine is a substitute for butter, the milk-fat of the latter being replaced by a mixture of animal and/or vegetable fats and vegetable oils. The oil-mixture is usually emulsified with milk (artificially "soured" if required, for flavoring purposes) or water, depending on the quality of margarine demanded. The technology of margarine has been fully described by the present writer elsewhere.[37]

The margarine industry offers an attractive field of research in applied colloid chemistry and physics,[38] the main problems being connected with the subject of emulsions. The modern * conception of emulsions may be briefly summarized as follows: [39]—A stable emulsion consists of one liquid dispersed as drops in another liquid which forms a continuous phase. Stability depends on the presence of an adsorbed protecting "envelope" around the dispersed globules, the adsorbed material being soap, gelatine, gums, milk colloids, etc., and, in some cases, solid particles such as carbon, silica, metallic oxides, etc. For two liquids A and B, two sets of emulsions may be prepared, viz:—A in B, and B in A, of any concentration up to 99 per cent of the dispersed phase. Which liquid remains continuous surrounding the other as globules, depends on the relative wetting powers of the liquids for the emulsifying (protecting) agent, this being quantitatively connected with the angle of contact of the liquid interface with the adsorbed emulsifier.[40]

On the market are margarines in which the emulsion type is either water-in-oil or oil-in-water. A ready means of distinguishing between them is to test their electrical conductivity.[41] The emulsion type depends essentially on the procedure of manufacture. The use of milk in a margarine emulsion naturally promotes the formation of the oil-in-water type, in accordance with the observed rule that water-soluble colloids promote the oil-in-water type and oil-soluble colloids the water-in-oil type of emulsion. Since the volume ratio of the oil phase to the aqueous phase is about 5 : 1, margarine technologists have usually operated so that the aqueous phase (milk and water) becomes dispersed in the oil. By slowly running the aqueous portion into the whole bulk of the oil with constant stirring, an emulsion is formed, which, though inherently unstable at working temperatures (25° C. to 50° C.) is rendered stable by instantaneous freezing.

Little scientific work has been published on margarine practice, though the present writer has outlined physico-chemical investigations of much interest.[42] The patent literature reveals some interesting features in colloid chemistry. Thus Blichfeldt [43] was granted a patent for the idea that a stable margarine emulsion of the oil-in-water type resulted when the oil phase is slowly run into the aqueous phase with constant agitation. This is fundamentally sound. Various water-soluble colloids have been used in making margarine emulsions of the oil-in-water type, e.g. gelatin, egg-yolk, lecithin, casein.[44] On the other

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* The following quotation from Dr. Wm. M. Ord's book, "The Influence of Colloids on Crystalline Form and Cohesion," published in London in 1879, but dealing with work done before then, will show that sometimes views considered "modern" are quite old. Referring to a paper of Ascherson (Muller's Archiv for 1840, p. 44), Ord says: "The paper shows that when oil and albumen are brought together, a membrane consisting apparently of coagulated albumen is formed wherever there is contact between the two substances. When oil and albumen are shaken together, an emulsion is formed which is permanent, because every globule of oil is instantly invested by a pellicle. The forms thus produced correspond with the condition in which fat is found in milk, in the fat-masses of animals, in eggs, and in plants." Ord's book is full of valuable information which was not appreciated at the time of its publication. J. A.

hand patents have been granted for the use of emulsifying agents which would promote the water-in-oil type.

Schou[45] proposes to oxidize a refined vegetable oil, e.g. soya-bean oil, at 250° C., until gelatinization sets in. The product is cooled to 100° C. and mixed with twice its volume of cold soya-bean oil. This "gelatinated oil" is an excellent agent for preparing water-in-oil emulsions. About 1.0 per cent added to fresh oils allows the emulsification of about 70 per cent by volume of water (or milk). Apparently Schou's oil has been oxidized so as to result in the molecular structure developing polar groups which would make the oil automatically capable of dispersing water.

Ayres[46] has patented the use of coconut oil stearine as an oil-soluble solid colloid capable of promoting the dispersion of water in oil. In this case the amount of stearin added, and the temperature of emulsification, are so adjusted that the stearin is present as a solid suspension, and it is, of course, much more easily wetted by oil than by water. The idea is excellent.

The actual margarine emulsion in technical practice is exceedingly complex. When the oils and fats are emulsified with milk which has been soured by the use of lactic acid bacteria, account must be taken of the influence on the emulsion of lactic acid, lactose, milk colloids, and solid flocks of casein.*

The type of emulsion represented in a margarine should be further investigated in relation to: (a) spreading capacity on bread, (b) taste, e.g. the water-in-oil type may be preferred; (c) deterioration in storage (rancidity); (d) solution and diffusion of materials added in blending, e.g. salt and preservatives; (e) the exudation of moisture, especially in paper-wrapped lots.

Another problem of interest to margarine technologists is the action of shortenings in cooking bread, cakes, biscuits, etc. Margarines are made of special composition for use in slab-cakes and pastry,[47] but their effects are noticeably different to those of butter or lard. Recently Platt and Fleming[48] have discussed the action of shortening in the light of the newer theories of interfacial tension and oil films, including the Harkins-Langmuir views of molecular orientation at interfaces.† This interesting paper should be read as introducing a new field of investigation of practical utility.

Plasticity of Butter and Margarine

It is well known that although butter is capable of being spread on bread, over a fairly wide temperature range, margarine is constantly subject to formula alterations depending on the seasons.[49] The plasticity[50] or spreading-capacity of margarine soon alters with temperature. Oleomargarines containing beef-fats and lard more nearly approach butter in physical behavior. The so-called vegetable margarines soon lose their spreading-capacity below quite definite temperatures depending on composition.

Undoubtedly the problem is bound up with the actual differences in chemical constitution, i.e. in the nature of the mixed glycerides.[51] In this connection reference should be made to the increasing use in margarines of the very plastic fat—refined palm oil. At the same time it is quite likely that an investigation of butter and margarines from the plasticometric standpoint would yield useful information and possibly help to define certain definite physico-chemical factors in a margarine for enhancing its plasticity. The nature and volume of the external phase, and the size of the dispersed globules, in the chilled emulsion will probably affect the plasticity.

No attempts appear to have been made to investigate this problem of colloid physics, though several workers have studied the viscosity of butter fat

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* And perhaps even of the bacteria themselves. J. A.

† *See* papers by Frey et al. in this volume. J. A.

and margarine *fats* with a view to detecting adulteration of butter or distinguishing it from margarine.[52]

One or two slight complications would have to be considered in such a research. Firstly, the effect of occluded air beaten into the final product during blending is important. Little data is available on the gas content of butter and margarine. Thus Rahn and Storm [53] have given a table showing the air content of butter; the highest value was 7.2 cc. per 100 grams of butter, and the lowest was 0.97 cc. per 100 grams. They found that butter made in winter has a lower air content than that made in summer. Similarly Rogers [54] found that fresh butter furnishes 10 per cent by volume of gas, analyzing 20 per cent oxygen, 33 per cent nitrogen, and 47 per cent carbon dioxide. As a rule margarines undergo more blending than butter, and it is well known that overblending makes the product too soft. No work appears to have been published on the gas content of margarine in relation to blending, to plasticity, and to keeping qualities.

Another complication is the water content of the products.[55] Assume 16 per cent of water is present. Now butter is usually considered as a solidified water-in-oil emulsion; a margarine may be had of either emulsion type. It is quite clear, however, though but little attention seems to be paid to this point, that some of the water in butter is not truly emulsified, but is mechanically occluded as a result of the churning process. How much of the water is in fine emulsion globules and how much is occluded, relatively large drops, has not been determined.

With margarine, conditions are possible whereby *all* the water can be truly emulsified, or some can be thus dispersed and a definite percentage added mechanically by blending. The influence of these factors on plasticity, dealing with a standard margarine (or a margarine made by using melted butterfat) would make an interesting study.

Finally, the effect of homogenizing margarine emulsions of opposite types should be investigated in relation to plasticity, bearing in mind the enhanced thickness of homogenized milk or cream.

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Colloidal Chemistry and the Art of Beer Brewing.*

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Until the beginning of this century, the technical science of beer brewing was based on purely chemical considerations. It was mainly the problem of chemistry to examine the raw materials and the finished product. The opinions formed on this basis and the mere chemical elucidation of the various operations in the production of malt as well as of beer were by no means satisfactory, until F. Emslander made the first effort to study the processes and analyses in brewing technic from the colloid chemical standpoint, thirty years ago.

The first step was thus made into the realm of colloids. However preconceived opinions and prejudice could not be very readily abolished. Even the term "colloid" had a somewhat strange effect and not until Dr. H. Freundlich became interested in the subject, was this new science approved and accepted by wider circles.

The art of brewing has, as its object, the preparation of a beverage from malt and hops which combines in its properties the highest degree of taste, flavor, wholesomeness and beneficial action upon the digestive processes. The manufacture of beer can be traced back to remote antiquity and it will be the successful task of unbiased medical science to demonstrate the reason why beer has remained the drink of the masses in spite of much enmity and prejudice. Beer, as a colloidal solution, acts as an emulsifying agent upon other foods, thereby promoting digestion. This characteristic quality is highly important, particularly in Germany, where everything depends upon attaining the highest degree of food efficiency at the expense of the lowest possible degree of energy.

Scientific Aspects.

In beer brewing the chemistry of interfaces is all important. We must distinguish between the surface tension of the entire system and the interfacial tensions of the existing phases. The gross surface tension plays a somewhat inferior part. However the interfacial forces control the action of enzymes, the clarification and formation of break (coagulation), and particularly the taste flavor, palatability, and foam-keeping quality of beer.

F. Emslander and H. Freundlich [1] had observed that the colloids of beer migrate in the electrical current to the negative pole, and that they are therefore charged positively against the aqueous phase. During this experiment dark flakes developed in as short a time as ten minutes at the cathode (negative pole) and after one-half hour, thick flaky masses had coagulated there while the anode remained perfectly bright, even after an electrolysis of five hours. The flaky masses were deeply colored and after one-half hour, they observed a decided clarification at the anode and a considerable increase of color at the

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* Translated by Dr. Emil Schlichting, N. Y. City.

cathode. The foam at the cathode was yellowish, very viscous and permanent; at the anode pure white and transient; a further proof of the migration of colloids to the cathode. The result of these experiments shows that the colloids present in beer travel in the electrical current to the cathode, that beer is a solution of positive colloids, and that acidity plays a very important part in beer as well as in the brewing process.

These observations led to the possible solution of the second question—what kind of electrical charges take part in the brewing process, and what relation do they bear to the degree of acidity? The solution of this question was difficult, because costly and suitable apparatus had to be constructed for the necessary experiments. However the generosity of the well-known brewer, Julius Liebmann, of Brooklyn, N. Y., made it possible to bring the experiments initiated to a successful conclusion. Acknowledgment and sincere thanks are due to Mr. Liebmann for his valuable co-operation.

The conductivity method promised to give the most direct insight into the internal conditions in wort and beer. However, many other ions interfered with the acid ions it was desired to measure, so that unequivocal results could not be obtained. The colloids in particular interfered; they acted more or less as retardants in the path of the ions, rendering this method unreliable. If, however, titration with barium hydrate was combined with the measurement of the concommitant conductivity factors,—curves of characteristic type were produced. It could be at once established whether carbonate or gypseous water was employed in the brewing process. It was possible from the cusps or inflections of the curves to determine the more or less profound decomposition, as well as the amount of colloids present. It was easily possible to determine the various important beer types. This quantitative method is therefor indispensable for the colloid chemist, as is also proven by the interesting research work of H. Lüers.[2]

Bugarsky and Liebermann have demonstrated by the potentiometric method that acids are fixed by proteins. F. Emslander[3] succeeded (1913) in making this quantitative method available for zymotechnic research. He also tried to establish a definite relationship between the solubility and stability ratios of albuminoids in the brewing process as well as in beer, and the hydrogen-ion concentration (pH). H. Lüers and in particular W. Windisch and his co-workers (*Wochschr. Brauerei* 1919-20-21-22) have continued this research with great promise of success. The influence of the hydrogen-ion concentration upon the enzymic decomposition of carbohydrates and proteins as well as upon the palatability and foam-maintenance of beer, has been materially clarified. Many practical results shown by the employment of the potentiometric method will be mentioned later. It may here be mentioned that Gibbs' law was confirmed. (Gibbs found that all substances which lower the surface tension of a liquid concentrate at the interface. The interface may be solid, liquid, or gaseous.) F. Emslander[4] found that with the potentiometric procedure of L. Michaelis, higher acid values were always found than with the method of the bubbling hydrogen electrode. According to Michaelis, the platinum electrode is brought only to the surface of the liquid to be measured. As in wort and beer surface-active substances must have a more acid character, it is evident that the above results confirm Gibbs' law. These results are especially useful in explaining the palatability and foam-keeping qualities of a good beer, which are solely dependent upon its surface-active constituents. Their stability is favored by the nature of the surface of the Bavarian "stein" (Masskrug).

These studies furthered particularly the knowledge of enzymic degradation, and the stabilizing power of colloids in brewing. Ultra-filtration, used by W.

Windisch, W. Dietrich, and P. Kolbach[5] in a thorough and detailed research concerning the nature of the influential colloids, resulted in very sweeping conclusions. I shall refer briefly to these results later, in considering the several steps in the brewing process.

The process of brewing is divided into four main steps—malting, brewing proper, fermention, and storage or lagering.

MALTING.

Malt is the soul of beer. During the malting process, we meet with the first colloid chemical reactions which continue through the entire brewing process, and the fermentation phenomena, until the beer is matured. The barley is steeped in water over a period up to 90 hours, varying according to its temperature, and the chemical composition of the water is the decisive factor for the type of the finished beer. Although our knowledge is comparatively limited in this matter, it may be safely assumed that the mineral salts present in the steeping water—the anions or cations—in the sense of the Hofmeister series, are chiefly responsible for the formation of the diastatic and proteolytic enzymes in the barley kernel. The greatest influence is exerted in this case, as in the entire brewing process, by the hydrogen ion concentration. A laboratory experiment of F. Emslander[3] has fully proven this: An electric current was passed through barley contained in two dishes. It was observed that a much more rapid growth occurred at the cathode than at the anode. The measurements of H^+ at the negative pole showed: $pH = 3.83$. At the positive pole $pH = 9.61$. It was thus proven that the swelling and growth of the barley is very particularly influenced by the hydrogen-ion concentration. This experiment is significant for agriculture or farming, as up to the present, the reaction of the soil has been given only minor consideration.* Artificial fertilizers are frequently used without thought or purpose, whereby in many cases the soil becomes acid to such a degree that its productivity and the quality of the grain suffer materially. To utilize the results and achievements of colloid chemistry along this line will be a pubic service of highest grade.

It is not known at what point the soluble mineral salts of the water penetrate into the barley kernel, for the husk is considered a semi-permeable membrane. I believe that the mineral salts enter at the tip of the embryo, where they are separated by dialysis and adsorbed by neighboring colloids so that they may again become activated during the germinating process. It is certain and proven by my own experiments that, either in or directly on the husk, are stored those albuminoids which are so difficult of solution (gluten). I have found that worts and beers made from the pure malt kernel only, do not show gluten-turbidity; whereas this disagreeable phenomenon appears whenever husks are also employed as an adjunct.

Notwithstanding the practical fact that the chemical composition of the steep water exerts a decided influence upon the quality of the malt, I have made steeping experiments with various modified waters ($pH = 4.5$ to 7.0) with the result that the steep waters become darker colored as they approach neutrality. Varying with the H^+ of the steep water, there arise different diffusion-potentials. In the case of an alkaline reaction (addition of slaked lime), substances are extracted which are undesirable in the brewing process. The nature of these products of diffusion is not known, but it is certain that they are more or less represented by colloids such as proteins and tannins.

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* There already exists quite a literature regarding the hydrogen-ion concentration of soils and its effect on the soils and the growth of plants. See e.g. Edgar T. Wherry, O. Arrhenius. J. A.

In this connection, attention must be drawn to the fact that water is also an important factor in the hop-extraction process. Brewing waters which have been softened require much more hops than hard waters (temporary hardness due to carbonates). Laboratory experiments with waters of varying hydrogen-ion concentration show that the diffusion-potential plays an important rôle which has hitherto not been sufficiently considered. Beers produced from softened waters possess a finer hop-aroma than beers with carbonate waters; in the first instance only the more delicate, fine aromatic constituents are into solution by diffusion; the hop resins are saponified. With soft water, on the other hand, the hop resins form an emulsion.

It is for this reason that our ancestors did not exhaust the malt with water, and even to-day there exists a popular belief that beers made in olden times were much better than they are to-day.

In the malting process the developing barley germ breaks down the albumin. If the internal reaction is neutral (to methyl orange), the peptic enzymes are favored; if alkaline, the tryptic enzymes. A temperature of over 18° C. in the barley corn evokes lactic acid formation to such an extent that the H-ions hinder tryptic action. Since the tryptic ferments dissolve the proteins more completely than the proteolytic ferments, lower temperatures are preferable even if a longer time is needed for malting. The optimum reactions for the malt peptase and tryptase are pH 3.2 and pH 6.4 respectively. Excessive heat in the malt pile is like a fever, it leads to marked loss of carbohydrate.

It is well known that the amylolytic and proteolytic enzymes are formed on the malting floor at low temperatures up to 18° C. during a germinating period of 7 to 9 days. The dissolution or modification process, especially of the proteins, commences in the kiln at higher temperatures up to 80° C. over a kilning period of 48 hours; and during kilning-off at temperatures from 80° to 100° C., coloring matter, caramelized and aromatic substances are formed, particularly for the darker beers. The coloring and aromatic substances possess a purely colloidal character. The aromatic substances are compounds of sugar with amino-acids, according to J. C. Lintner's investigations.*

The grinding process, which follows, is fraught with the danger of a dust explosion. A reasonable colloid-chemical explanation of this infrequent but potent phenomenon, long obscure, has been given by P. Beyersdorfer: The tiny malt particles adsorb and condense oxygen at their free surfaces, forming a high explosive with the strength of dynamite, somewhat like a mixture of carbon with liquid air. The shattering of particles develops an electric charge on the fragments, and sufficient tension produces a spark which sets off the explosive. The finest colloidal dust is the most dangerous. Colloid-chemical explanation also fits best the explosions which sometimes occur on spraying pitch into casks or tuns.

BREWHOUSE OPERATIONS.

During operations in the brewhouse, the proteins and particularly the carbohydrates, undergo a further degradation and are finally brought into solution. The most influential factors during these processes are time, temperature, and hydrogen-ion concentration (H^+). The optimum H^+ for the degradation of the carbohydrates and proteins lies at $pH = 4.5$ to 5. W. Windisch, W. Dietrich, and P. Kolbach, later Adler and the Americans, Sherman, Thomas, and Baldwin[6] have each found a different optimum for the H^+ as well as a somewhat different course in the activity of the diastase. The H^+ of the

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* **Thomas Graham included many interesting experiments on caramel in his pioneer researches. J. A.**

medium is, therefore, not the sole criterion; the interfacial potential of the reacting substances is also a factor, as may also be differences in acid anions. F. Emslander [7] has proven this by making experimental mashes with pale malt in the usual manner, and also using a covering of mineral oil. In the first case, the ratio of maltose to non-maltose was 1:0.39—in the second case 1:0.69. Even the experienced, practical brewer knows empirically the influence of surface tension upon the mashing process; if the mashes "bump" during boiling, they are difficult of fermentation; if, however, the mashes simmer or foam, it is fair to figure on an easy conversion or saccharification. In the first case, we have a low surface-tension; in the second case a high surface-tension against the pan wall.

These considerations lead us to the nature of enzymic processes, and I should like to state my views concerning them. I had previously proven [*Z. ges. Brauwesen* **42**, 135 (1919)] that it is not correct to say, the optimum activity of an enzyme *always* lies at a certain H^+. It is more correct to say that the optimum activity of enzymes occurs at a specific surface-tension of the substrate. Enzymes appear to form these constants by influencing the formation of acidity in such a manner that thereby an H^+ is produced which determines the surface tension (interfacial tension) most favorable for the reaction. Enzyme action may be assumed to proceed in such a manner that it continues until such an H^+—and incidentally such a low interfacial tension, is reached that the enzymic reaction suffers.

The mineral salts of the water also play an important part in the brewhouse, as well as in the steeping process. They influence, in my opinion, not so much the H^+ but rather the manner of extraction of the malt constituents. I have found that digestion-worts give beers with a much lower degree of stability (gluten-turbidity) than worts produced by extraction for only a short period. In the digestion-worts, proteins are extracted, but they contain either no enzymes for their degradation, or the enzymes present have very little enzymic power. The practical brewer also knows that beers produced with gypseous waters show less stability than those with carbonate waters, a colloid-chemical problem which has not yet been thoroughly explained. However, this appears to be the reason why, having brewing waters of different composition, every brewery produces a differently tasting beer. The composition of the brewing water appears to be a decisive factor for the type of beer to be produced. This is the reason why, for instance, the character of beer differs so fundamentally in Munich, Pilsen, Burton-on-Trent, Dortmund, etc.

After the extraction of the malt, the wort is boiled with hops. The extracted hop resins act as protective colloids on the proteins; they increase the keeping qualities of the beer as they are protective agents against infection and particularly against Sarcina. They increase the foam-keeping qualities and palatability of the beer, as they are surface-active; they also impart to the beer the desired bitter flavor. The tannin of the hops acts as a precipitant on the proteins; it is responsible for the fact that the lability of the proteins disappears by gradual precipitation. An important part during these precipitating processes is played by the H^+. An intensive and long-continued boiling of the hops increases the dispersion of the hop resins, thereby promoting their protective action, and their effect upon the gustatory nerves. Windisch and his pupils [7a] by ultrafiltration experiments found that hop tanins aggregate as well as precipitate albumins.

At the end of the hop-boiling process, the malt-hop-wort is cooled; and the proteins coagulated by heat during boiling are agglutinated and precipitated.

During cooling, the wort is in a constant rolling motion. This motion causes the finer coagulated particles to come into mutual contact; they aggregate and agglutinate, thus hastening their precipitation and sedimentation. The manner of cooling is therefore very important for the subsequent fermentation process. The clearer the worts, the better the fermentation. It is for this reason that the coagulated albuminoids or so-called dregs are separated by filtration. The course of filtration shows how the solution has progressed during brewing; the better this solution in the brewhouse and the coarser the protein precipitation, the clearer and more rapid the filtration. These are established facts well known to the empirical worker, which however can only be explained by the colloid chemist.

Fermentation.

The action of yeast upon wort (its maltose, dextrines, proteins, hop resins, etc.) gives rise to manifold colloid chemical reactions. There is particularly a decided formation of acidity so that the hydrogen-ion concentration within a few hours reaches $pH = 4.5$ an optimum for yeast in worts from carbonate waters; and $pH = 4.2$ in worts from gypseous waters. F. Emslander[8] has found that this automatic optimum reaction of yeast serves to transform the surface tensions of the worts, which are entirely different in the beginning, into the surface tension best suited to the yeast enzymes, so as to secure the most favorable fermentation. During this phase, there occur in the yeast cell most peculiar transformations of electric charge. For instance, H. Lüers and K. Geys[9] found that resting yeast when wet shows a positive charge in worts; however, after a few hours when increased cellular activity begins, the yeast appears to show a distinctly negative charge, changing on the fifth day again to a positive charge.

At the beginning of fermentation, the yeast is positively charged: as Emslander showed it produces in sugar solutions, the optimum hydrogen-ion concentration and simultaneously becomes negatively charged as H. Lüers and Geys found. The charge, and with it the stability of the yeast, reach an optimum; the surface tension according to Emslander's measurements, a minimum. At the end of fermentation the yeast becomes again positive towards the fermentable medium, or in other words, isoelectric with the beer colloids, and the interfacial tension reaches a minimum. The chief requirements for the agglutination of the yeast are thus provided. The practical brewer says "the break appears" indicating to him the end of the main fermentation process.

The surface tension exerts, according to Emslander and Freundlich[1] a powerful influence upon the fermentation process in practice. The lower the wetting capacity for the walls of the fermenting vessels, the higher is the surface tension of the fermenting wort; and the result is a comparatively higher degree of fermentation of the beer. From a series of experiments may be mentioned the following: the degree of fermentation in a glass vat was 52.9 per cent, in a varnished fermenting vat 57.4 per cent, in a pitched fermenting vat 68.4 per cent; while in a wooden fermenting vat, not previously moistened before fermentation, the fermentation degree was 72.8 per cent. If the wooden fermenting vat is scalded before filling it with wort, the air imbibed in the wood pores disappears and the wort adheres better to the wooden walls, the surface tension of the wort is thus diminished, as is also the degree of fermentation. This phenomenon has long been well known to the practical brewer.

In modern breweries the tendency is toward large fermentation tanks of aluminum, enamelled iron or cement, the latter coated with a protective layer of asphalt, paraffin or the like. Enamelled tanks give a quiet, satisfactory fermentation which favors the body and bead of the beer; but cement tanks give a so-called "boiling" fermentation, which presents analogies to cooking in the mashing process. For when, on cooking, the mash "plops," it indicates a low surface tension. Low surface tension of the wort, indicated by boiling fermentation, leads to high fermentation, which is detrimental to body and bead. Too little consideration has heretofore been given to these factors on the fermentation and storage of beer, which often arise from the influence of the container walls. F. Emslander[9a] has recently referred to this matter; but the industry took it amiss, although they should pay the closest attention to colloid-chemical developments.

It is not possible to measure directly the influence of the walls on the surface tension; however, the latter can be calculated by the determination of the boiling points prevailing in the various vessels. The boiling point as determined in the before-mentioned vessels with *previously well-boiled water,* using an electric heater, showed glass > varnish > pitch > wood. It is possible to examine in the same manner the vessels used at the present time, consisting of enamel, glazed clay, aluminum, slate, paraffin, etc.

It has already been mentioned before that the formation of the break of the yeast during fermentation, depends upon surface tension. The coagulable albuminoids are also a function of surface tension. Emslander and Freundlich found that the degree of fermentation parallels the degree of clarification. Beer fermented in paraffin vessels was clear even after five days, in wooden vessels after six days, in pitched vessels after seven days, while the beer fermented in glass vessels was still very turbid after eight days. This observation coincides with the fact established by R. Klinger[10] concerning the coagulation of blood, which coagulates very much quicker on glass walls than in vessels coated with paraffin, only here charge conditions are reversed.

The influence of container walls on the intensity of fermentation, on clarification, and on formation of "break" has been discussed for decades. Only recently has F. Emslander advanced a satisfactory explanation. Glass or enamel walls, having a positive electrostatic charge, repel the similarly charged bubbles of CO_2 resulting from fermentation. The negatively charged paraffin walls attract and hold the bubbles, which rise only when their tendency to float overcomes the electrostatic attraction.* Clarification is similarly affected, the positively charged beer colloids being repelled by positively charged walls, but attracted by negatively charged walls.

A recently observed factor should be mentioned here.[10a] Copper cooling worms are used in the modern type tanks (aluminum, enamelled iron, non-rusting steel, etc.), and beer functions as an electrolyte between the copper and the less "noble" metal. A galvanic current results, and the earthing of pipes and tanks means completion of the circuit. The current causes corrosion and electrodeposition of valuable beer constituents as "bierstein" (beer-stone). Acid as well as oxygen arises at the + pole (Al), while alkali is formed with hydrogen at the — pole. Since bacteria and wild yeasts are favored by more alkaline media (rather than brewers' yeast), we have here a factor favoring infection.

The theory advanced by others concerning the formation of break as a

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*** Probably the formation of these *larger* bubbles at paraffin walls causes the bumpy fermentation; for they would unite and burst the surface in "blobs." J. A.**

function of the hydrogen-ion concentration may point to the fact that the apparent contradictions can be explained from the fact shown by H. Helmholtz,[11] that each and every change of electrical energy $(= H^+)$ corresponds to an equal change of surface energy: If the surface tension of the substrate has reached a minimum, the charge of the colloidal particles is the greatest and *vice versa.* The minimum charge, or the maximum surface tension, is however the isoelectric point and in this condition the proteins are coagulated.

Storage of Beer.

The subsequent storage of the beer and its treatment during the maturing process form the keystone in the whole process of beer manufacture.

In the storage cellar all errors become evident to the extent they have occurred during the manufacturing process, and it is this field in which colloidal chemistry has attained its greatest triumph. Palatability, foam-keeping quality, and stability of beer are particularly influenced by operations in the storage cellar. It is not possible to prescribe methods in this respect. The observations of colloid chemistry must coöperate with practical experience in order to put a good product on the market. It therefore remains to explain what is understood by stability, palatability, and foam keeping quality of beer from the colloid chemical standpoint.

Stability.

The biological stability of beer, as far as it is influenced by the presence of wild yeasts or bacteria, depends, in addition to lack of cleanliness, chiefly upon the reaction of the wort; infection becomes prevalent so much more quickly and easily, the more alkaline the reaction, or the lower the hydrogen-ion concentration. We may apply here the maxim of Emslander: "reaction produces sick beers." This much-disputed theory has only recently been confirmed by an interesting research work of M. H. Van Laer.[12] This investigator concludes as follows: The acidity of worts and beers, that is the actual amount * of acidity present, is a principal factor controlling their stability. The most serious infection is without any consequence, if a wort is sufficiently acid in reaction. As beers during fermentation generally reach a pH of about 4.5, they are at that moment resistant against bacterial infection, provided this has not previously developed.

Under the term "stability" we may also understand the property of beer to hold the albumin in as stable a condition as possible.

It seems an almost unrealizable demand to impart to beer this valuable stability factor by *normal* manufacturing processes, so that, for instance, it may withstand long ocean trips or profound chilling on ice before consumption. Pastuerized beers in particular become cloudy and uninviting more or less rapidly after long storage in the bottle, and particularly if strongly chilled. This cloudiness is often erroneously called "gluten turbidity."[14] Gluten is analogous to animal gelatin. The real gluten does not occur in brewing. This is readily proven by the fact that the so-called beer-gluten cannot be acted upon by the proteolytic enzyme of yeast—endotryptase—while animal gelatin can be easily liquefied by means of endotryptase at a temperature of 2° C.

The so-called beer gluten is an albuminous substance which is transformed by heating in the presence of tannin into a more complex body; it coagulates. The coagulation may be prevented, if by the addition of a proteolytic enzyme,

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* The *active* or *effective* acidity (as expressed by C^{H^+} or pH) is the controlling factor, rather than the *total* acidity. See e.g. J. Alexander, "Colloid Chemistry," 3rd ed., 1929. J. A.

such as pepsin, bromelin, papayotin, at pasteurizing temperatures, this protein body is modified—peptonized. This advantageous colloid chemical reaction forms the basis of various patents granted to L. Wallerstein by the U. S. Patent office.

The coagulation of gluten requires the presence of tannin in addition to heat. The gluten turbidity differs in its first stage from other turbidities in that the cloudiness is not caused by suspended coagulated albuminous particles, but spherical particles, floating in the chilled beer, diffract the penetrating light and thus produce the undesirable and uninviting appearance of such beers. These beers are lacking in palatability; they are "empty" and hard to the palate. By heating the beer these spherical particles burst and there appears under the microscope finely coagulated albumen.

In order to understand this reaction, it must be mentioned that beer is a very complex compound. Beer is not a pure solution of various constituents, but an emulsion consisting of completely water-soluble substances, of colloidal albuminous bodies, hop resins, carbohydrates, and carbonic acid gas. If beer is cooled to 0° C. or below, the colloidal albuminous bodies cohere to oleaginous droplets and produce structures known by the name "gluten particles." There are also in beer very finely divided and coagulated albuminoids in suspension which have a tendency to lower the surface tension. Since, according to Gibbs, substances which lower the surface tension concentrate at the surface, it is not surprising that the colloidal albuminous bodies, after having been transformed through cooling from true solution into finely divided oleaginous droplets, thus form interfaces against the aqueous solution and are surrounded by a membrane of coagulated albumen. The gluten particle is therefore a structure in which the nucleus consists of colloidal, and the wall of suspendable albumen. If this gluten body is heated, the colloidal albumen expands, the leather-like wall bursts, and the albumen is again distributed in the beer; the wall appears under the microscope as coagulated tannalbumen.

H. Lüers [18] was successful in explaining the nature of these haze-producing albuminous bodies. He established the fact that beer during storage increases in its content of coagulable proteins. He then proved by the classical method of anaphylaxis that a series of proteins are responsible for the turbidities of pasteurized beer, and that a considerable portion of these is derived from yeast.

The method of anaphylaxis is based upon the following: A solution of albumen is injected into the experimental animal, for instance a guinea-pig, subcutaneously or, better yet, intravenously or intraperitoneally. This injection is repeated with the same albumen solution after a period of 12 days. Peculiar abnormal symptoms then appearing are defined as hypersensitiveness or anaphylaxis. These symptoms appear suddenly and violently in proportion to this second dose and to various circumstances; a few minutes after the re-injection, death may occur accompanied by violent convulsions and sudden lowering of temperature. This is commonly called "anaphylactic shock." * A considerable number of guinea-pigs were injected with a solution of albuminous matter, coagulated by pasteurization, and 14 days later an aqueous extract of plasmolysed yeast was again injected. The typical symptoms of anaphylaxis with lowering of temperature down to 4° C. immediately appeared. We have thus unmistakable proof that the turbidity in pasteurized beers also includes yeast albumen. This would warrant the conclusion that all means for the

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* Immunological tests of this kind may detect quantities of specific proteins as small as 0.00005 of a milligram. See, e.g. "Chemical Aspects of Immunity," by H. Gideon Wells (New York, Chemical Catalog Co., Inc., 2nd ed. 1929). J. A.

prevention of haziness in pasteurized beers are comparatively valueless, if they are employed before the end of the main fermentation. The only successful remedy is the above-mentioned addition of proteolytic enzymes or of precipitating agents. It still remains to be solved to what degree the proteins or the tannins of the husk are responsible in this problem, especially because gypseous waters are inclined to produce beers which have a tendency towards "gluten turbidity."

The results of Lüer's observations are also worthy of mention, that 100 liters of beer contain only about 1 gram of precipitate due to pasteurization, producing such marked turbidity. This also shows the enormously fine subdivision of this small quantity of albuminous matter capable of producing such strong diffraction of light in such a large proportion of beer. This is a beautiful example of the colloidal state.

PALATABILITY.[14]

A very important quality of a good beer is its palatability or "smoothness" (Vollmundigkeit), a property that makes a beer appear to be apparently more full-bodied than it is in reality.

The public speaks of a "smooth" beer: "the beer goes down like oil." The connoisseur ascribes to such a beer a characteristic quality similar to oil. It is known that oil has a very low surface tension, a high degree of viscosity and generally a marked spreading capacity. It is, however, impossible to measure directly the spreading capacity of a liquid against another interface.

For the purpose of explaining palatability, we must necessarily resort to the spreading capacity. This characteristic property is peculiar to all colloidal albuminoids and hop resins. It is proven by the fact that an excessively cold beer generally always has an empty and raw taste. By the excessive chilling, the colloidal albuminoids and hop resins are changed from a soluble state into a condition of oleaginous division; whereby membranes are formed surrounding the albuminous bodies, so that they are not allowed to come into direct contact with the gustatory nerves. The albuminoids and hop resins have lost the property of spreading out over the mouth cavities; the sense of taste in this direction is excluded—the beer tastes empty.

If drastically filtered beers are also empty in taste, this must be ascribed to the fact that the colloidal bodies—the factors of palatability—have been removed by filtration. Determinations of extract before and after filtration easily prove the loss of some of the most valuable constituents of a good beer. W. Windisch and V. Beermann[15] have been able to identify these substances by ultrafiltration.

FOAM-KEEPING QUALITIES.[14]

We must distinguish between production of foam and foam-holding capacity. Every liquid with a low surface tension is capable of producing foam. As mostly all beers show a low surface tension, nearly all of them also foam well, provided they contain a sufficient quantity of carbonic acid gas. The foam consists of a fine dispersion of carbonic acid gas in the beer—really a gaseous emulsion. The dispersion of carbonic acid gas in beer—foam—is only permanent if so-called emulsifying agents are present. Such agents were assumed to consist of substances which possess high viscosity. This assumption is erroneous; as for instance, the highly viscous substance, glycerin—does not increase the foam holding capacity of beer in any degree. However, the addition of mere traces of egg albumen produces an extremely lasting foam. This is again a hydrophile colloid. A substance of high surface activity or a hydrophile colloid, or certain oils, hop resins, etc., is therefore responsible for good foam-holding capacity, a stable gaseous emulsion.*

As the practical brewer knows that "smooth" beers always possess good foam-keeping qualities, it is sufficient to refer to the statements made under the heading—palatability. The causes of palatability and foam-holding capacity are identical. It is the spreading capacity of the colloidal albuminoids as well as of the soft hop resins, which produce an excessively thin, but strong membrane around the gas bubble, thus imparting great resistance to the bursting of the latter.

A contributory factor in the foam-holding capacity is the presence of a solid, very finely divided substance, coagulated or suspension albumen. When the carbonic-acid-gas-bubble rises through the beer, both kinds of albumen above-mentioned enter the surface of the gas bubble according to the laws of surface tension (Gibbs), and envelop the bubble. The dextrins increase the tenacity of the gaseous membrane and the solid particles form so-called anchors or fixing points for the albumen-colloid present, in the same way that the solid particles (silica) in a concrete mixture together with cement form a sustaining arch, whereas the individual constituents by themselves would form unstable structures.[19]

What small quantities are required here, is shown by H. Freundlich who says that 3×10^{-7} grams peptone is sufficient for a surface measuring 1 square centimeter, in order to form a solid membrane and simultaneously produce a solid foam. Such membranes have a thickness of 3 $m\mu$.

Nutritive Value of Beer.

The food or nutritive value of beer has been based upon its content of calories, as with other foods. This is an erroneous theory; as J. Alexander[16, 17] justly says: "We do not live on what we eat, but on what we digest." It is, for instance, well known that pure cow's milk is digested with difficulty by children, because as soon as the milk comes into contact with the gastric juice (hydrochloric acid), it at once coagulates and forms curd. With the addition of protective colloids, such as gelatin, Iceland moss, or barley water, the casein is either entirely prevented from coagulating or, if it does coagulate, the curd consists of such finely divided flakes that they are easily dissolved during the digestion process. Just such conditions are the case with mother's milk, which is always wholesome for children. In mother's milk, albumen—a reversible colloid—acts as a protective agent. Beer also contains such protective substances in large quantity. These protective colloids are present particularly in the extract of caramel malt, and dark malt; they can be isolated from all beers by alcohol precipitation. If the precipitate is dissolved in water, and added to milk, only a very finely divided suspension is observed after the addition of acid, which disappears entirely by heating to 37° C. to such an extent that no more coagulation is apparent to the naked eye.[18]

Practical experience has long foreseen this observation. Physicians advise nursing mothers to consume in addition to milk, full malt beers (nursing mother's beer). It is also well known that black bread and cheese, together with beer have a highly nutritive value. The beer in this case aids emulsification and thereby provides large surfaces of attack for the digestive enzymes. From this viewpoint, beer acts in addition to its own nutritive value, as a stimulant to digestion, enabling other foods to be completely utilized.

This theory is also sustained by practical facts. The poorer people are

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* Only polyphasic systems give stable foams with CO_2 (or air), especially in vessels to whose walls beer adheres strongly, whereby small bubbles are formed.

partial to the consumption of dark, "smooth" beers, whereas the richer classes like pale and dry beers. The poorer man seems to recognize instinctively that the larger amount of protective colloids contained in dark beer permits a better digestion of this somewhat scanty food, while the richer classes consider the pale beer more of a condiment. The rôle played by the dark beer for the poor man in the nutrition process is the "mayonnaise" or emulsifying material of the rich.

Beer as Diagnostic Agent and Medicine.[18]

Beer has sometimes been used as an aid in diagnosis. It can be observed that with some people the beer foam immediately disappears and falls flat as soon as they drink it. Such persons are generally assumed to be very sick * (diabetes, kidney disease, tuberculosis) or they are carriers of incipient disease. This phenomenon, often observed, may be explained by the fact that in such cases beer comes into contact with substances which increase the surface tension whereby the foam-holding capacity is destroyed. Diabetics often exhale acetone, diacetic acid, etc. Such powerfully surface-active substances overmaster the relatively weaker foam stabilizers in beer. Similarly surface tension determinations must not be made in rooms where there are traces of ether vapor, etc.

The main principles of colloid research, which have already brought many advantages to the brewing industry have thus been presented to our view in a short résumé. If the heights of scientific research and truths have not been reached, it must be accounted for by the fact that this new sphere of science has not as yet become popular among fermentologists. Let us hope that the preceding discussion will help to attain the desired goal.

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* Hyperacidity of the skin secretions due to passing or pathological acidosis, probably lies at the basis of such popular ideas. Some people, especially some women at certain times, cannot successfully bake bread, transplant seedlings, handle flowers, or do certain kinds of ceramic work; for yeast, plants and even clay, are highly sensitive to slight changes in hydrogen-ion concentration. In many cases, popular observation outruns scientific explanation. J. A.

The Pectic Substances.

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A little over a century ago there appeared the first accounts of the isolation of the peculiarly interesting substance called pectin to which the extracts of certain fruits owe their jelly-forming properties. The field of investigation opened by Payen[53] and Braconnot[5] has attracted the attention of many workers, and chemists as well as botanists, through their various researches, have greatly extended our knowledge of the pectic substances.

Certain aspects of the subject, such as the occurrence of these compounds in different plants, methods of extraction and estimation, and the rôle of pectin in jelly making, have been extensively investigated. In the last decade also, there have been a number of reports of studies of the constitution of the pectic compounds and of the natural changes which they undergo during plant growth and senescence. It is surprising to find, however, that the literature contains few accounts of detailed study of the colloidal properties of these substances, even though Frémy as early as 1840 called attention to these significant characteristics. In the light of our present knowledge of the influence of degree of dispersion on the activities of certain substances, it is not unreasonable to believe that some of the discrepancies in the behavior of the pectic compounds reported by various workers may be attributed to differences in the state of aggregation resulting from the particular method of preparation used. This phase of the subject needs to be studied thoroughly, for even if the chemical constitution of the pectic compounds should be definitely established, exact knowledge of the colloidal systems which they represent would still be fundamental to an understanding of their behavior.

No attempt will be made in this chapter to give the historical development of the subject. The early work was ably reviewed by Sucharipa in 1925[64] and Branfoot[6] has just published a valuable critical and historical study of the pectic substances of plants to which the reader is referred for detailed information. Only those contributions will be discussed here which may have a direct bearing on some of the practical problems involved.

It has been difficult, at times, to evaluate properly the results of some researches, because products described as definite entities have since been shown to be mixtures; and the arbitrarily chosen nomenclature has been confusing. In her monograph, Branfoot[6] has brought the early work into harmony with our present knowledge, using the nomenclature which she considers to be in use by the majority of workers. Her system agrees, in the main, with that adopted by the Committee on Nomenclature of the American Chemical Society,[49] which is as follows:

Pectic Substances.—A group designation for those complex carbohydrate derivatives which occur in plants, or are prepared from plants and which are characterized by the presence of galacturonic acid units. In the naturally occurring pectic substances, the galacturonic acid units apparently exist in an acid-reacting complex associated with arabinose and galactose units. This acid complex may occur as a free acid or as a metallic salt, but usually occurs as a methyl ester.

Protopectin.—The term applied to the water-insoluble, unhydrolyzed pectin substances in the state in which they occur in plant tissues. *Protopectins* are rendered soluble by treatment with enzymes, acids or certain other reagents, whether by peptization or hydrolysis not being known. The substances thus rendered soluble are designated collectively as *pectin;* it is not known whether or not the *pectins* are different chemical individuals from *protopectins.*

Pectin.—The term applied to the water-soluble, methylated pectin substances occurring in plant tissues or to the methylated pectic substances obtained by restricted treatment of *protopectin* with *protopectinase,* acids or other reagents, the treatment being so regulated as to produce maximum solution of pectic substances with a minimum cleavage of methyl ester groups. The product may be a mixture of substances of varying methyl ester content; the term *pectin* or *pectins* is accordingly a group designation for all intermediate pectic substances between *protopectin* and *pectic* acid. It is proper, however, to refer to an individual of the group as a *pectin.*

Pectic Acid.—The term applied to the pectic substances obtained by the hydrolysis of *pectin* with the complete elimination of the methyl ester groups. Pectic acid may be variable in composition according to the type of hydrolysis employed; accordingly there may be a number of *pectic acids,* all of which are ester-free.

Branfoot[6] retains the name *pectose* for the protopectin of the American Chemical Society and recognizes a group of primary hydrolytic products of pectin with varying methyoxy content, called *pectinic* acid and a final stable product of hydrolytic decomposition of pectic acid called *meta-pectic* acid, thought to be identical with the d-galactose-galacturonic acid described by Ehrlich[17] in 1917.

Occurrence of the Pectic Substances.

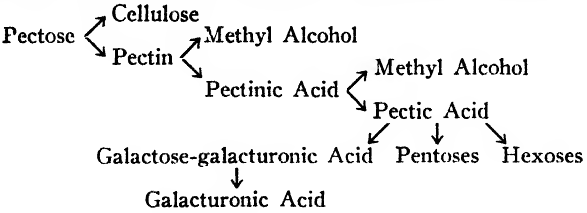
The pectic substances occur in varying amounts in the roots, stems, and fruit of most plants and play an important rôle in their life history. The pectic layer is the first one laid down in cell division and as growth proceeds, the definitive walls of adjoining cells are constructed by the addition of successive layers of cellulose-like substances on each side of the thin partition of protopectin, the final layers consisting chiefly of cellulose. Some of the pectic material forms a continuous layer, the middle lamella or primary wall which envelops the cells; but there are also pectic substances intimately associated with the secondary and tertiary cell walls.

The existence of the insoluble pectic constituents of plant tissue was first observed by Frémy,[26] who followed the course of its formation in unripe currants microscopically. His results were confirmed by Mangin,[38] who was one of the first to develop a technique for studying the cell membrane by the use of stains such as ruthenium red.

Evidence in support of the idea that the insoluble protopectin of the cell wall is a pectin-cellulose complex is to be found in the recent work of Sucharipa.[58] After removal of all the soluble pectic substances from the albedo of lemon by successive extraction with cold water, hot water under pressure, 50 per cent sugar solution and 0.5 per cent ammonium oxalate, and the removal of free cellulose by treatment with Schweitzer's reagent, there remained a substance containing neither free pectin nor free cellulose, which Sucharipa believed was pure protopectin. Further hydrolysis of the material, with hot 0.5 per cent ammonium oxalate, split off soluble pectin, and the cellulose nature of the remaining residue was shown by its almost complete solubility in Schweitzer's reagent. Carré [8] corroborates Sucharipa's results in her extensive studies of the physiology of apples. Norman,[50] however, thinks that the evidence so far produced is not sufficient to justify the assumption of any cellulose linkage.

The changes which the pectic substances undergo during growth and senescence have been the subject of much careful study by Carré,[7] Carré and Haynes,[9] and Carré and Horne.[10] It seems to be quite a well established fact, as shown by chemical and microscopic studies of apples and other fruits, especially pears, that insoluble protopectin gradually decreases in amount and soluble pectin increases as maturity is reached. At the same time some pectinic acid may be formed. Subsequent hydrolysis of pectin *in situ* produces pectinic acids by partial de-esterification, the final completely de-esterified product being pectic acid. Apparently the total amount of pectic material remains constant. As a result of the chemical and histological studies of Carré and her associates and the earlier studies of Ehrlich, Fellenberg and others, Carré says that the metamorphoses of the pectic substances may be provisionally represented as follows:

Diagram Representing the Pectic Changes in Apples.



In the case of the fruit studied by Carré [8] it was shown that advanced stages of maturity were marked by a thinning of the cell wall and that softness and over-ripeness occurred as the middle lamella pectic substances disappeared with consequent separation of the cells. The technique worked out by Carré should prove of value in determining the state of maturity of stored fruit.

Extraction and Purification of Pectin.

The extent to which the nature of the resulting pectin is influenced by its method of extraction has probably received too little attention. The usual custom is to digest the plant material with boiling water to which acids or salts, such as ammonium oxalate, are sometimes added. This procedure not only dissolves out soluble pectin but also effects the hydrolysis of a certain amount of protopectin, so that the resulting product is a mixture of variable composition depending upon the temperature, pressure, length of time of heating, and the composition of the extracting medium. Nanji and Norman [46] suggest differential extraction with water to remove free pectin, extraction of a fresh sample with 0.5 per cent oxalic acid to remove pectin in combination with metallic ions and the third extraction of another portion with 0.5 per cent ammonium oxalate to remove pectin in combination with metallic ions together with pectic acid both free and combined.

Hardy [30] found that under similar time conditions, the total quantity of pectin extracted from the inner white rind of the fruit of the lime seemed to vary directly with the concentration of the hydrogen ion when the extraction is carried out at temperatures below the boiling point, and directly with the temperature when the final acidity of the extract is less than pH 2.0. The conditions of extraction determine not only the quantity of pectin obtained but also its quality. Johnstin and Denton[35] found considerable difference in the jellying-power of citrus pectin extracts prepared with water and with dilute acids at atmospheric pressure and at higher pressures and temperatures attained in an autoclave. While the pressure extracts contained a large amount of pectin, as measured by the quantity of alcohol precipitate, the viscosity and jellying-power of these solutions was markedly less than when lower temperatures and pressures were employed. Similar results were obtained by Sucharipa,[62] who attributed the decrease in viscosity and jellying-power to loss of methyl alcohol since the methoxyl content of the pectin was found to decrease as the extraction was carried out at higher pressures and for longer heating periods. This agreed also with the earlier observations of von Fellenberg[28] as to the variation of viscosity with methoxyl content, and with those of Fellers[24] that long extraction periods yielded apple pectin with impaired jellying-power.

For the ordinary purposes of jelly making, pectin extracts are not usually subjected to any great amount of purification. Some of the commercial pectins on the market are scarcely more than concentrated water extracts of apple or citrus fruit residues containing most of the water soluble constituents of the original material. These solutions are sometimes clarified and then freed from starch and other undesirable materials by enzyme action (Daughters[14]). Citrus pectin is sometimes marketed in the form of a dry powder consisting of the entire white peel which has been dried and comminuted. In other cases, after filtering the water extract, it is treated with alcohol; and pectin, together with other alcohol insoluble substances, is thrown out of solution. It is estimated that three quarters of a million gallons of alcohol are used annually in the United States for this purpose. The gelatinous precipitate thus obtained is freed from water by centrifuging and dried in a current of air at as low temperature as possible, after which it is pulverized. The solutions may also be evaporated by the spray method and the pectin left in powdered form (Poore[56]).

Any method of extraction which involves the use of raw plant material without first removing such organic compounds as terpenes, resins, tannins, etc., by treatment with ether or alcohol as recommended by Bourquelot and Hérissey,[4] will yield a very impure product. Many of these organic impurities as well as their oxidation products are colloidal, and when once precipitated along with pectin their subsequent removal is almost impossible. A much purer product is obtained by preliminary digestion of the material with several portions of alcohol and finally with ether. The dry residue can be ground very fine, extracted as above and the pectin then precipitated from the filtrate with alcohol. Further purification is frequently accomplished by dissolving the pectin in water and reprecipitating with alcohol.

The degree of success in the removal of impurities attained by repeated precipitation with alcohol is determined largely by the way in which the operation is carried on. In accordance with the well-known principles of precipitation, if excessive adsorption is to be avoided, alcohol must be added drop-wise to the dilute, constantly stirred pectin solution and not pectin solution to alcohol. Furthermore, a flocculent precipitate is produced if a small amount of acid, such as hydrochloric, is added to the alcohol; in this condition, the pectin is much more easily filtered and washed free from salts. Pectin solutions free from acid give very gelatinous precipitates or sometimes real gels on the addition of even a large excess of alcohol, especially if the solution is kept warm. The authors[28] have found that the filtration of such solutions is greatly facilitated by first breaking up the gel by thorough stirring and then adding more alcohol. A still more satisfactory method is to pass an electric current (110 volt. D. C.) through the mixture for about two hours, using spiral platinum electrodes. In a short time the whole anode region becomes filled with flocculent pectin which filters easily. If the filtered pectin after a thorough washing with ninety per cent alcohol is spread out on glass plates to dry, it forms hard horny transparent sheets resembling gelatin.

The ash content of the purified product depends upon the source from which the pectin was originally obtained, and the methods of extraction and purification. A small amount of hydrochloric acid in the alcohol used for precipitation has been found effective in reducing the ash, since some mineral constituents are thus held in solution as soluble chlorides; also the addition of oxalic acid or soluble oxalates to the water solution before filtration precipitates a considerable portion of the calcium. Probably the most effective means of removing soluble inorganic compounds is by electrodialysis (Emmett [21]) or by dialysis.

The authors [84] have prepared highly purified pectin by the following method. Lemon albedo was extracted with alcohol and ether and dried at 60° C. The pectic material was removed from this by three extractions with 0.01 *M* hydrochloric acid, and was then precipitated with alcohol. The precipitate was dissolved in calcium-free distilled water and the solution dialyzed with constant stirring in parchment paper bags against 0.01 *M* hydrochloric acid, until the dialyzate showed no calcium when tested with ammonium oxalate. Distilled water was then substituted for the acid and the dialysis continued until the water was chlorine-free when tested with silver nitrate. Once in every twenty-four hours during the dialyzing process the dialyzate was changed and the sol heated to 90° C. to prevent bacterial action. When the process was complete, the solution was evaporated in large crystallizing dishes at 60° C., which left the pectin in thin transparent colorless sheets. If sufficient care is taken, the ash content of this final product is as low as 0.01 per cent. This pectin was easily soluble in water and had high jellying-power. Its hydrosols were acid in reaction, a 0.10 per cent sol having a pH value of 3.26 in water whose pH value was 6.6. The specific rotation of purified lemon pectin was found by Poore [56] and by the authors [28] to be +230.

ESTIMATION OF PECTIN.

The quantitative determination of the exact amount of pectin in any solution has afforded considerable difficulty. The alcohol precipitation method of Wichmann and Chernoff [72] does apparently give the total weight of pectic substances except when other insoluble materials are present, but the amount of alcohol precipitate is not a satisfactory measure of the jellying-power of the solution since this is also dependent upon the kind or condition of the pectin present.

The only substances of constant composition which can be determined definitely are the products of hydrolysis of pectin, i.e. methyl alcohol and pectic acid, or compounds of these. Von Fellenberg [23] devised means of determining methyl alcohol by both the Zeisel and Deniges methods and estimated the quantity of soluble pectin from the amount of alcohol split off during hydrolysis. Since the presence of methoxyl groups in the pectin molecule differentiates it from related substances and also appears to be responsible for those properties of pectin which are desirable from a practical standpoint, a method for estimation of pectin based on the quantity of methoxyl would seem to be most valuable. Nanji and Norman [46] estimated the methyl alcohol formed on hydrolysis, by oxidation to carbon dioxide with alkaline permanganate solution. Wichmann[72] worked out a method for the determination of pectic acid—the product formed when hydrochloric acid is added to a pectin solution after saponification with sodium hydroxide. A volumetric method for estimating pectin has been devised by Ahmann and Hooker,[1] who measured the acidity developed on saponification of the pectin, by the amount of sodium hydroxide neutralized during the saponification. Nanji, Paton and Ling[47] have described a method based on the definite yield of carbon dioxide from the uronic acids of pectin. The gas is absorbed in standard barium hydroxide solution and the excess of hydroxide titrated. The per cent of carbon dioxide multiplied by 5.66 gives the percentage of pectic material, existing both as pectin and pectic acid. This figure was based on the fact that pectic acid was found to contain 17.64 per cent of CO_2. Dickson, Otterson and Link[15a] add as important details of this method, the use of exactly 12 per cent hydrochloric acid, and decarboxylation at a temperature of 135° to 140° C. for at least four hours, preferably five. The work of Conrad[12a] on decarboxylation of pectins and calcium pectates shows the necessity for this accurate control of condition. However, it must be noted that Norman and Martin[50a] state very definitely that the carbon dioxide yield cannot be taken as a measure of the decarboxylation of pectin since other hydrolytic products formed at the same time may also give off carbon dioxide.

Carré and Haynes[9] and later Emmett and Carré[22] devised a method which is widely employed and which seems to be considered by many as a standard method. The pectin, which is first precipitated with a large excess of acidified alcohol, is filtered, redissolved in water and saponified with sodium hydroxide. The solution is then acidified with acetic acid and pectic acid precipitated with calcium chloride. This yields a compound, calcium pectate, of constant composition having the formula $C_{17}H_{22}O_{16}Ca$. The petin content of the original solution is expressed as weight or per cent of calcium pectate. While it is convenient to work with an easily filtrable pectic compound and one of definite chemical composition, still when interpreting these results, it must be remembered that the total weight of the calcium pectate obtained gives no indication of the proportions of the several pectic components of the original mixture.

Other methods which emphasize the quality of the pectin as well as the quantity, have been suggested by several workers, notably Wendelmuth,[71] Mehlitz,[41] and Lüers and Lochmüller,[37] who have determined respectively the viscosity of solutions, the pectin number, and the tearing strength of jellies formed. Fellers and Griffiths[25] found the Bloom gelometer of value in grading commercial pectins, while Wilson[76] combined viscosity measurements and standard test jellies for this purpose.

CONSTITUTION OF PECTIC SUBSTANCES.

The chemical constitution of the pectic substances has been the subject of much discussion. Their carbohydrate nature was recognized by a number of the early investigators, some believing them to be related to the gums while others linked them more closely to the plant mucilages.

In 1888 Weisberg[70] obtained from beet marc a gelatinous substance resembling pectin which on hydrolysis with sulfuric acid gave a furfural-yielding sugar. This sugar was later identified as arabinose by Herzfeld,[33] who concluded that the pectins are complexes of araban and galactan since on oxidation with nitric acid they yield mucic acid. Additional proof of the presence of such sugar residues was furnished by Tromp de Haas and Tollens,[69] who hydrolyzed pectins from many sources. Tollens[68] further assumed the presence of one or more carboxyl groups which might be either dehydrated or esterified and he was inclined to regard pectin as closely related to plant mucilage, possibly as oxy-mucilage.

In 1909 Wilhelmi[78] obtained arabinose by the action of molds on the pectin of sugar beet chips. He regarded this as a matter of considerable importance to the sugar beet industry because in those years when the beets are moldy the arabinose thus produced might affect the estimation of sucrose in the juice.

The next important contribution to the knowledge of the constitution of pectin was made by Ehrlich[17] in 1917. From the hydrolytic products of the raw pectin of beet marc, Ehrlich succeeded in isolating galactose whose presence previously had only been assumed; and in addition he discovered an acid, *d*-galacturonic acid, an isomer of glucuronic acid. Since its presence in the pectic acid of sugar beet pectin was established, *d*-galacturonic acid has been obtained from a variety of fruits and vegetables and Ehrlich's assumption that this acid plays an important part in plant metabolism seems to be justified. Ehrlich regarded the neutral pectin obtained by hydrolysis of protopectin with hot water as the calcium-magnesium salt of anhydro-arabino-galactose-methoxy-tetragalacturonic acid, in which the arabinose groups were easily split off, the remainder of the complex being a fairly stable substance.

The existence of a calcium-magnesium-pectin compound of definite chemical composition was held to be untenable by von Fellenberg[23] because he was unable to establish any quantitative relation between calcium and the pectin residue. Nanji, Paton and Ling,[47] however, seem to favor the idea of a definite combination of metallic radicals when they say that insoluble pectin may be a compound of pectin and iron. Later, Nanji and Norman[46] suggest that the insoluble form is produced by polymerization of completely esterified tetramethyl pectic acid and partially de-esterified pectic acid, the latter linked to metallic ions. The constant occurrence of calcium and iron in all the forms of pectic compounds which they have isolated, has been noted by Johnstin and Griggs.

Ehrlich's conception of the nature of the pectin complex, however, agreed very well with the results obtained by von Fellenberg in his exhaustive studies of the soluble pectins of plant tissues. Von Fellenberg prepared pectins from currants, quinces, apples, beet chips and orange peel and found in all cases that, during acid hydrolysis, methyl alcohol was split off, which could be determined quantitatively and used as a measure of the amount of pectin present. By carefully regulating the conditions of hydrolysis of orange pectin he was able to eliminate methyl alcohol in successive stages and to produce thereby pectins of decreasing methoxyl content. Since these pectins at the same time show increasing acid characteristics, loss of methoxyl results in the formation of free carboxyl as in the usual hydrolysis of an ester. Von Fellenberg concluded therefore that pectin is an ester acid, neutral pectin being one in which all the carboxyl groups are esterified. Some of the reported discrepancies in solubility and degree of acidity may be ascribed to differences in degree of esterification of the pectin, since neutral or fully methoxylated pectin is soluble while pectic acid is difficultly soluble in water. Furthermore, according to Sucharipa,[62] jellying-power is closely related to methoxyl content, this property decreasing as the number of free carboxyl groups increases until pectic acid is reached, where the ability to form sugar-acid gels is entirely lost.

In more recent work, Ehrlich and Sommerfeld[20] and Ehrlich and Schubert[19] showed that the pectic portion of the material extracted from unripe flax seeds, on hydrolysis with hydrochloric acid gave di-galacturonic acid, acetic acid, *l*-arabinose, *l*-xylose, di-galactose and methyl alcohol. Ehrlich and Kosmahly[18] studied the pectic substances of orange peel, currants and strawberries and they maintain that the pectin obtained from these sources was composed of exactly the same units as their beet pectin and consisted of four molecules of galacturonic acid, two molecules of methyl alcohol, two molecules of acetic acid and one molecule each of arabinose and galactose. Mild hydrolysis of the pectic acid gave the same three tetra-galacturonic acids as that of the sugar beet. Ehrlich's repeated reports of the existence of acetic acid as one of the hydrolytic products of pectic acid is of interest in view of the fact that Nelson[48] was able to detect only slight traces of acetyl groups in the citrus and apple pectin which he studied in 1926.

In addition to the work of Ehrlich and von Fellenberg in 1917-1918, other significant contributions to the study of the constitution of the pectic substances are those of Clayson, Norris and Schryver,[12] Carré and Haynes,[9] Norris and Schryver,[52] Sucharipa,[68] Nanji, Paton and Ling,[47] Nanji and Norman,[46] Henderson,[32] and Norris.[51] While there seems to be some disagreement in the various formulas proposed by these workers, the encouraging thing is the uniformity in the number and kind of basic groups which have been found in all the different complexes studied. A critical study of this work leads to the belief that there is sufficient evidence to justify the conclusion that insoluble protopectin is a compound of pectin and cellulose and is of the nature of a glucoside. Soluble pectin is esterified pectic acid of constant methyl alcohol content (11.76 per cent) and upon complete de-esterification gives pectic acid. When subjected to strong acid hydrolysis, pectic acid is resolved into *d*-galacturonic acids (α and β), galactose and arabinose, and as mentioned before according to Ehrlich, there is also acetic acid and sometimes xylose. Norris and Henderson, however, think that the existence of xylose is doubtful. Branfoot[6] believes that the formula $C_{39}H_{58}O_{33}$ for pectin can be accepted provisionally and the basal molecule of pectic acid is a compound of such definite composition, $C_{35}H_{50}O_{33}$ that its calcium salt can be depended upon as a measure of the relative quantity of pectic material present.

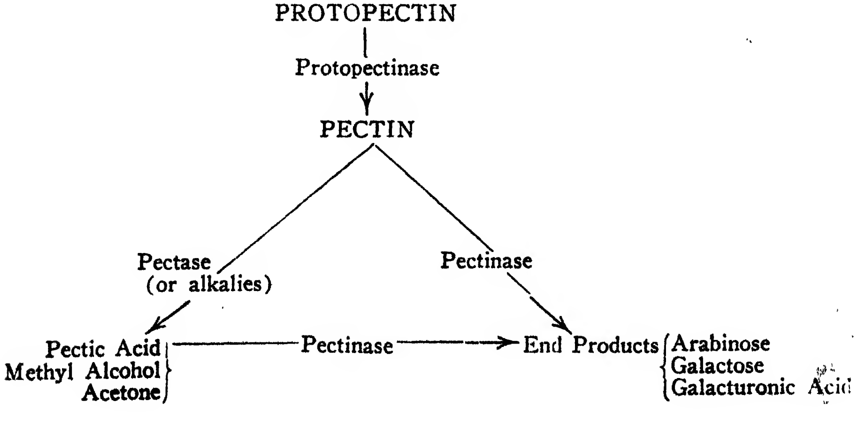
As to the way in which these units are linked together to form a stable molecule of pectic acid there is some doubt. In 1925, Nanji, Paton and Ling[47] proposed a ring formula showing four free carboxyl groups of the four galacturonic acids, with the galactose and arabinose joined by linkages other than 1 : 6, which has been very generally accepted. In view of the fact that there is still so much uncertainty in regard to the actual presence of some of the basic units thus represented, as evidenced by the work of Henderson,[32] McKinnis,[39] Norman,[50] and Ehrlich and Schubert,[19a] we believe that the chemistry of the pectic substances will not be furthered by too ready acceptance of such a formula. It does seem, however, that a very profound change, which may indicate the rupturing of a ring, is effected by the action of dilute alkalies and less dilute acids. Norman and Martin[50a] recently attempted to follow the course of this change by measuring the calcium pectate, furfural and carbon dioxide yields at various stages. At the concentration of alkali which they used (0.5% and 0.2%) there was rapid hydrolysis, presumably with simultaneous rupturing of the ring, within the first five minutes. This work has been repeated in the author's laboratory, and in addition to the calcium pectate and furfural yields, we have made spectrographic studies of each hydrolyzate. Our results agree fairly well with those of Norman and Martin. The spectrum curve of the first hydrolyzate shows the maximum characteristic of the carbonyl group which indicates a marked change in the original material within the first few minutes after treatment with alkali. This method of study seems to offer great possibilities, provided the rate of change can be sufficiently retarded.

The Pectic Enzymes and Their Action.

Several workers including Willaman, Davison, Pitman and Cruess have called attention to the need of more thorough study of the enzymatic changes in pectic substances because of their importance in such practical problems as the retting of flax, the keeping qualities of fruits and vegetables in storage and the resistance of plants to certain diseases.

The natural changes, *in situ,* whereby insoluble protopectin is converted into soluble pectin and eventually into pectic acid, have been attributed to the action of plant enzymes since the early days of Frémy [26] and rotting has long been thought to be caused by enzymes secreted by bacteria and fungi. Bertrand and Mallèvre [3] showed that the coagulation caused by the enzyme pectase was possible only in the presence of certain electrolytes such as salts of calcium, barium or strontium with the formation of the corresponding pectates. Ball [2] also studied the action of pectase but he concluded that the coagulating effect of calcium was that of a di-valent electrolyte and that there was no evidence of the formation of calcium pectate. Kopaczewski [36] studied the coagulation of pectin and found that the effect of calcium was not specific but that other ions, such as barium, strontium, magnesium copper and iron, also had coagulating effects but in varying degree.

The more recent work of Willaman and his associates [74] on the cause of rotting has brought to light some valuable information in regard to enzyme activity. In 1920, Willaman studied the effect of the fungus, *Scelerotina cinera* (the brown rot organism of stone fruits), on pectin prepared from prunes and peaches. He found that the invading fungus followed the line of the middle lamella and gradually dissolved it, this action being effected by the enzyme pectosinase. The soluble pectin of the juice was coagulated to a gel of calcium pectate, by secretion of the enzyme pectase, which helps to preserve the firmness of the rotted fruit. In a later paper of Davison and Willaman [15] they produce what they claim to be proof beyond reasonable doubt that three distinct pectic enzymes exist—protopectinase (pectosinase) which hydrolyzes or dissolves protopectin, forming pectin with separation or masceration of the plant cells; pectase which converts soluble pectin to pectic acid; and pectinase which breaks down pectin and pectic acid to cleavage products such as arabinose, galactose and galacturonic acid, as follows:



Pitman and Cruess[55] studied the pectinase effect of a number of different microörganisms occurring on fruits. Two molds, *Penicillium glaucum* and a Pythium species, exerted marked hydrolytic effect. In one instance the effect of the organism was to change the character of the pectin, rather than the quantity, so that the jellying-power was greatly reduced. A comprehensive review of the subject is given by Willaman in a University of Minnesota Bulletin.[75]

THE COLLOIDAL NATURE OF PECTIN.

Pectin sols are clear in transmitted light and opalescent in reflected light, exhibiting the typical Tyndall effect. In the ultramicroscope the Brownian movement can be seen; the movement ceases, however, on the addition of alcohol, and then the solution appears to contain thread-like particles consisting of cohering submicrons (von Fellenberg[23]). The curves constructed by plotting the pH of a pectin sol against the added volume of acid and against the added volume of base show no isoelectric point but rather indicate that pectin has strong acidic properties and no basic properties—in other words it is not amphoteric (Myers and Baker[45]).

Pectin is a lyophilic colloid which in a water system carries a negative charge. The addition of alcohol to the hydrosol evidently increases the polarity, the pectin then collecting in large quantities around the anode either as flakes or as a clear hard gel depending on whether or not the solution is stirred. According to von Fellenberg, when ferric chloride is added to a pectin sol and then ammonium hydroxide, the sol remains clear and no ferric hydroxide is precipitated, due, no doubt, to the action of pectin as a protective colloid.

Pectin is a reversible colloid and is coagulated by a number of metallic salts but not by the salts of the alkalies. Von Fellenberg believed that this action was due either to electrolytic precipitation or to the formation of metallic salts of pectin which was first partially demethoxylated by the weak base of the hydrolyzed precipitant. He made an extensive study of these reactions but his results do not agree in all instances with those of other workers, including the authors. This lack of agreement may be due to a difference in the pectins used or to the varying concentration of hydrogen ions. Precipitation of pectin with electrolytes should not be confused with those reactions in which the pectin is hydrolyzed by alkalies, forming pectates such as were studied by Haynes.[31] It is incorrect to speak of this hydrolytic product as "gelatinized pectin."

Pectin is not dialyzable to any extent either from a hydrosol or from a gel containing sugar and acid. The solid gels permit the diffusion of electrolytes and Liesegang rings can be prepared very easily with them. The alcohol-pectin gels have been prepared quite as successfully as the sugar-acid-pectin gels and they allow the formation of Liesegang rings of both silver chromate and ferric ferrocyanide.[28]

When dry pectin is treated with water there is a very noticeable swelling, similar to the behavior of gelatin in water, but apparently, in this case, the swelling is less when excess acid is present. Wendelmuth[71] studied the swelling of powdered pectin in sugar solution and finds the maximum effect occurs when the concentration of sugar is about fifty per cent. When tartaric acid is added to the sugar solution the swelling is increased but sodium hydroxide has the opposite effect. The degree of swelling of pectin in this sugar-acid mixture is a very interesting point in connection with the preparation of fruit jellies.

The viscosity of pectin solutions seems to be very much greater than the viscosity of gelatin solutions of equal concentration. This property of pectin solutions was studied in some detail by Myers and Baker,[45] whose results show that the relative viscosity increases slightly to a maximum and then decreases greatly as the pH increases. Here again no indication of an isoelectric point of pectin is obtained. Ohn [52a] found that citric acid decreased the viscosity of unheated pectin sols and that of pectin-sugar sols.

The degree of dispersion of the pectic substances in an apple pectin sol has been established by Mehlitz,[43] by the fractional membrane filtration method. One-third of the particles were greater than 0.6 μ, nearly two-thirds were of the size between 0.2 μ and 0.6 μ, and less than 10 per cent have a dispersion value of less than 0.2 μ. As the size of the pores of the membrane filter decreased, the resulting filtrate showed a decrease in the total acidity, the concentration of hydrogen ion, the viscosity, the starch reactions, jellying-power and methoxyl content.

The Donnan method of studying equilibrium conditions across semi-permeable membranes has been applied to pectin-calcium chloride systems by Johnstin.[34] The results show that when a dilute pectin sol is separated from a solution of an electrolyte such as calcium chloride by a membrane which permits the free diffusion of the salt, but is impermeable to pectin, there is unequal distribution of the ionic constituents. In a general way the concentration of the salt on the opposite sides of the membrane at equilibrium is in agreement with the theory of membrane equilibrium proposed by Donnan.

FORMATION OF PECTIN GELS.

Before proceeding to a review of the work on the well-known sugar-acid-pectin gels, attention should be called to the gels formed by the addition of alcohol to pectin sols. These can be obtained through a wide range of alcohol concentrations, provided the solution is kept warm and well stirred during the addition of the alcohol and provided also that the concentration of electrolytes, especially acids, is kept low. On the other hand, when the concentration of alcohol is small a very solid gel may be formed by the addition of hydrogen or calcium ions. It is of interest to note that many substances which are commonly thought of as precipitants of pectin can be used to form stable gels if the conditions of mixing are carefully adjusted.

The familiar pectin gels, containing water, sugar, and acid, present a very complicated problem because of the several constituents and of the varying conditions under which gelation may occur. For this type of gel all four components are essential although the proportions may vary greatly as evidenced by the results of many different workers.

As regards the pectin content, Tarr [65] and Tarr and Baker,[67] in their study of the rôles of acid and sugar, used a concentration of about 1.1 per cent to 1.5 per cent, while Halliday and Bailey [29] made satisfactory jellies containing 0.424 to 0.70 per cent pectin. Sucharipa [62] used 1.0 per cent pectin, but he also stated that gel strength was increased by the increasing methoxyl content of the pectin. The authors have prepared very soft gels with as little as 0.15 per cent pectin. Singh [61] reported that the per cent of sugar could be greatly decreased if the concentration of pectin was considerably increased; thus 0.9 per cent pectin required 65 per cent sugar, while with 5.5 per cent pectin the sugar was reduced to 43 per cent. Johnstin and Denton [35] found that the quantity of pectin necessary to produce satisfactory gels varied greatly with the source and method of extraction of the pectin.

From the standpoint of the practical jelly-maker the *proportion of sugar* required for good gelation is a matter of greatest economic importance; consequently this factor has been widely studied. Sucharipa as well as Halliday and Bailey used 50 per cent sugar in their experimental jellies. Singh[61] emphasized the importance of sugar as against the importance of acid because he was able to prepare jelly from a mixture "quite deficient in acid," although not entirely acid free. It may be noted in passing that while the percentage of sugar in fruit jellies can be reduced considerably by increasing the amount of pectin and acid as recommended by Singh, it is doubtful whether such procedure should be advocated, since fruit jellies of low sugar, high acid and pectin ratios do not have the best texture and flavor.

Goldthwaite[27] found that with most fruit juices too little sugar made a tough jelly, while too much sugar produced a very soft jelly or syrup. Cruess and McNair[18] advocated boiling down the mixture of sugar with fruit juice to a boiling point of 104° to 105° C. which was equivalent to a concentration of dissolved solids equal to 65 to 70 per cent. Tarr and Baker[67] in their very complete study of the rôle of sugar in fruit jellies showed that the per cent of sugar in the finished gel was a constant. They found also that with a constant quantity of pectin, the quantity of sugar that may be added to produce a satisfactory gel varies with the hydrogen-ion concentration as follows:

pH	Cane Sugar Grams
3.37	125–130
3.23	145
3.10	180

It should be noted that these measurements were made on the mixture before heating, and not upon the finished product. For any hydrogen-ion concentration, however, the per cent of sugar in the finished gel is at least 64.1 per cent and it is usually as much as 69 per cent. This would appear to mean that the gel is a super-saturated solution of sugar, but they explained that part of this sugar was inverted by boiling with acid and since sucrose is more soluble in the presence of invert sugar, the condition which exists at the gelation point is practically that of a saturated solution.

The quantity of acid required for satisfactory gelation also shows wide variation. Halliday and Bailey[29] used 1 per cent citric acid in a standard jelly mixture while Sucharipa[62] employed 0.5 per cent of the same acid and Singh,[61] by varying the sugar content, obtained gels with acid ranging from 0.5 per cent to 4.05 per cent in the finished product. Cruess and McNair[18] considered the limits of acidity of the original fruit juice to be 0.5 per cent and 1.5 per cent calculated as citric acid. With the aid of a newly devised jelly strength tester, Tarr[65, 66] has made the most complete scientific study of this constituent of jellies with the very interesting conclusion that gelation is not a function of total acidity but of the concentration of hydrogen ion. However, the hydrogen-ion concentration at which the *optimum* jelly forms varies with the acid employed, as does the strength of these optimum jellies. The optimum pH for the acids tested varied from 3.05 to 3.30. Mehlitz,[42] as well as Lüers and Lochmüller,[37] give the optimum pH as between 2.9 and 3.1, while Wendelmuth[71] considered that the optimum condition corresponded to a lower concentration of hydrogen ion, i.e. pH = 4.1. These results are scarcely comparable since the workers were not using the same kinds of pectin nor the same concentrations of other constituents. Of the acids commonly present in fruit juices, Tarr,[66] as well as Goldthwaite,[27] found that tartaric acid was most efficient for jelly making, then malic acid and lastly citric acid.

Tarr also stated that there was a stoichiometrical relation existing between pectin and the combining power of the acids, but this was not conclusively proven. Spencer's [61c] work substantiated this point and showed further that pectin does not have a buffer action on acid solutions, tending to suppress acid ionization.

Sucharipa [62] emphasizes the importance of evaporation during gelation, but in the experience of the authors this seems a negligible quantity since the loss due to evaporation is so slight. Johnstin and Griggs believe that the time factor in the setting of pectin gels is as important as concentration, for they obtained gels with very low concentrations of lemon pectin after the mixture stood a week or more, although there was no appreciable loss in weight. A practical illustration of the effect of time on gelation is to be found in fruit jellies which acquire a much stiffer and tougher structure as they grow old, provided, of course, that they are kept well sealed and there is no decomposition due to spoilage.

While it is customary, in preparing pectin gels, to heat the mixture to a certain temperature and then allow it to cool, this process is not really necessary since solid gels can be formed easily in the cold by mixing the constituents in the proper proportions and allowing sufficient time for the gel structure to form. Neither is the long stirring advocated by some cook books necessary, although gelation is favored by stirring up to a certain critical point. Overcooking or over-stirring may destroy the gel structure.

The effect of salts on gel strength has been studied in detail by Halliday and Bailey,[29] who show that calcium chloride can be substituted in part for any one of the three components of a sugar-pectin-acid gel. In a standard jelly mixture consisting of 1 per cent pectin, 1 per cent citric acid and 50 per cent sugar, the pectin could be reduced 50 per cent, the acid 70 per cent, and the sugar 8 per cent by the addition of 0.5 to 1.0 per cent calcium chloride. They suggest that this favoring action of calcium chloride may be due either to the formation of a calcium salt of pectin which has greater tendency to gelatinize than the original pectin or the calcium chloride may increase the hydrogen-ion concentration by lowering the buffer action of the pectin. Tarr [65] showed this buffer effect experimentally, but states that the presence of salts probably reduces the concentration of hydrogen ion at which the jelly forms. Myers and Baker [44] using Tarr's jelly strength tester demonstrated the usual buffer action of salts, but showed that the optimum jelly strength occurred with but slight variations and at a lower pH in the presence of a salt. Von Fellenberg [23] found that the addition of salts of organic acids to pectin-sugar sols caused the formation of a gel, while mineral salts caused pectin to coagulate, while Spencer [61b] says that a given amount of salt will aid in the sugar precipitation of a given pectin sol if it lowers the sugar jelly boundary curve of that particular system. If it raises the boundary curve, it will hinder jelly formation, or at least retard it.

THEORIES OF GELATION OF PECTIN-SUGAR-ACID-WATER GELS.

No attempt will be made to discuss the general theories of gel structure for that subject is amply covered by the chapters in Volume I of this series by D. J. Lloyd and S. C. Bradford. Only such theories will be presented here as have been used in the not too successful attempts to explain the formation of pectin-sugar-acid-water gels.

Two points are commonly emphasized by theorizers in this field: first, the function of sugar as a dehydrating agent, and second, the rôle of pectin in providing a framework for the gel. According to Wendelmuth,[71] in the formation of fruit jellies, sugar acts both as a dehydrating and as an emulsifying agent. Through competition for the water of hydration, two phases, hydrated pectin-hydrated sugar are formed, which are dispersed into one another in a colloidal condition resembling an emulsion. The part played by the acid is not well understood but it probably influences the swelling or shrinking of pectin or it may even effect some sort of chemical change.

McNair[40] also believed that sugar acts as a dehydrating agent and in addition it increases the viscosity of the solution. He observed that pectin, acid, and sugar, each increases the viscosity of water but that when they are combined there is a greater increment than can be accounted for by the summation of the viscosities of each component separately. This increase in viscosity may be attributed to the effect of hydrogen ion on the dispersion of the pectin.

Spencer[61a] postulates that pectin jelly-formation is a precipitation phenomenon. The pectin sol is stabilized by adsorbed water and anions but soluble organic compounds, such as sugar and alcohol, which lower the vapor pressure of the dispersion medium and neutralize the acquired negative charge, have just the opposite effect. Excess of hydrogen or hydroxyl ions on either side of the critical precipitation point decreases the amount of adsorbed water and thus less precipitating agent is required.

Sucharipa,[62] on the other hand, thought gelation might be due to coagulation of pectin in the liquid sucrose-acid medium since pectin is difficultly soluble in sucrose-acid solutions of certain concentrations. When the limit of solubility is reached, owing to loss of water as the solution is boiled, the gel forms as a result of the coagulation or gradual crystallization of pectin which, remaining uniformly distributed throughout the liquid, forms the framework of the gel. This idea of gelation is substantiated by the fact that the liquid which oozes out of "the net work of the coagulum" when syneresis occurs, does not contain appreciable amounts of pectin. "If the meshes or honeycomb-like cells are small and dense, capillary forces will retain the mother liquor within; if the net work is coarse, the liquid will ooze out." Syneresis or "weeping" evidently depends upon the pectin concentration. Sucharipa believed that gelation is not caused by chemical reaction because it was possible to wash out most of the sugar and acid from a gel with 75 per cent alcohol, leaving the pectin with too little sugar or acid to indicate a chemical compound. This result was confirmed by the authors,[28] who were able to dialyze out from a gel so much sugar that the residue was tasteless, and so much acid that a gel could not be made from the residue without the addition of acid as well as sugar. This does not agree with Tarr,[65] who suggested that the buffer effect of pectin on acids indicated the possible formation of actual pectin-acid compounds, nor with Chernoff,[11] who believed that gelation might be due to esterification of the few free-acid groups of the pectin by some of the alcohol groups of the sugar, or by the displacement of the methyl alcohol groups of the pectin by sugar.

Peters and Stratford[64] thought that the character of the gel depends upon the hydrolysis of both the sugar and the pectin and also that the relation of the cane sugar to the invert sugar is a controlling factor in determining jelly strength. Tarr and Baker[67] believed that the function of the sugar may be that of a dehydrating agent, especially since jelly formation is conceived of as a precipitation of pectin in the presence of a saturated or approximately saturated solution of sugar. This precipitation of the pectin appears to be controlled by the hydrogen-ion concentration.

None of the theories of gelation yet proposed seems entirely adequate.

Both the fact that von Fellenberg[28] was able to substitute certain salts of organic acids such as calcium or aluminium malate for the acid in these gels and Tarr's work on the influence of hydrogen ion, emphasize the importance of the positive ion in effecting the gelation of pectin. The favoring action of sugar may be attributed to the fact that maximum swelling of pectin in sugar solutions occurs at about the concentration which gives the most satisfactory gels. In the opinion of the authors the degree of dispersion of the pectin in the hydrosol determines the ease with which gelation occurs when sugar and acid are added. The skeletal structure of the gel must consist largely of pectin, since sugar and acid can both be removed by dialysis and since the time required for building up the gel structure increases as the percentage of pectin decreases. A study of the structure of simpler pectin gels ought to lead to a better understanding of these more complicated ones.

The investigation of colloidally dispersed pectin offers an attractive field for research. There are needed standardized methods of preparation which will give products of uniform composition, whose physical and chemical constants are so stated that the results of different workers can be compared and their work properly evaluated.

Uses of Pectin.

Rooker,[57] in an interesting article on uses of pectin, mentioned its value as an emulsifying agent together with gum tragacanth for such substances as castor, mineral, and other oils, as well as for tree spray emulsions and mayonnaise dressing. As an adhesive a 3 to 6 per cent solution is employed with the addition of a preservative. The jam and jelly centers of confections, the crushed fruits for sundaes, etc., and whip and meringue powders, all frequently contain pectin. While pectin gives a smooth texture to ice-cream, it has not been used extensively for this purpose. It has, however, been found satisfactory in "candy doctors" which are used to prevent crystallization of finished candies. Rooker also notes that pectin added to fresh milk increases the viscosity and digestibility and that it has been a successful agglutinant in the few cases where it has been tried. Semichon[60] suggests that the hydrolysis of pectose may favor the production of a delightful aroma in wines.

Up to the present time the largest single industry in which pectin has been employed has been the jam and jelly industry in the factory and in the home. While this has already attained considerable importance, there is no likelihood that it will ever develop to such an extent that it can use all the prepared pectin available. In fact, Wilson[76] says that "as near as can be determined, less than half the citrus pectin produced to date has been used in jam or jelly and the proportion so used is decreasing as the other uses are developed." According to Dore[16] in 1924, 30,000 tons of *pectin* were available annually as a by-product from the cider, citric acid, and beet sugar factories, while Wilson estimated in 1928 that probably there were available annually in California alone 40,000 tons of *citrus fruits* for conversion to other products. With such an abundance of material available and such a constantly increasing variety of applications, the pectin industry should rapidly assume greater and greater importance.

The patents on pectin are well-reviewed by M. R. Daughters in Rooker's recent book "Fruit Pectin"[59] and a résumé of the various government standards for preserves has been made by Rooker.[58]

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"Solidified" Alcohol.

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The discovery of solidified spirit is said to be the outcome of an attempt on the part of an unscrupulous person to hoodwink the Paris Customs officials. He mixed with the alcohol a white grated soap, producing an homogeneous solution which, when set to a solid, was cut into small cakes. These passed the Customs without difficulty, and all that remained was for the alcohol to be distilled from the solid. The scheme was discovered and the inventor found his ingenuity rewarded by a term of imprisonment at Fresnes. While there may be no reason to doubt the truth of this story, it certainly was not the first occasion upon which solidified alcohol was mentioned. Work upon this subject began in Germany in 1887, which was at least twenty years before the attempted fraud on the Paris Customs. An article by R. Hirsch and Otto N. Witt[3] gives an excellent résumé of the researches which led up to the first attempts to produce a solidified methylated spirit. The present authors propose to start from the work of Hirsch, and to trace the development of the work up to the present time. A chronological sequence has been mostly observed, but, occasionally, for the sake of clarity, it has been necessary to depart from that order.

Preparations using alcohol in the solidified or hardened form may be grouped into two classes, according to the use for which they are intended. Many of the early patentees had as their object the making of a solid fuel, and employed soaps as the hardening agents. By varying the amount of soap, products were obtained which could equally well serve as detergent agents. In consequence of this, the first class has been further subdivided into a group comprising fuels, which could be used as soaps by varying the amount of hardening material, and into a group of fuels proper. The second class, comprising more recent patents, includes soaps, and medicinal and toilet preparations.

Since the War of 1914-1918, there have been but few patents for solid alcohol fuel, as improvements in the methods of transporting liquid fuel, together with the ease with which the latter may be utilized in internal combustion engines, have rendered the solid fuel of limited practical value. Solid fuels consisting of hardened liquids have been used for curling tong heaters, laundry irons, portable spirit stoves and firelighters, but, on the larger scale, coal briquettes, prepared from small coal or coal dust and suitable binding compositions, have completely displaced solidified spirit.

On the other hand, medicinal and toilet preparations having alcohol as their basis, are being used to an increasing extent owing to their superior cleansing and astringent properties. The early transparent soaps were usually made by shredding and drying the soap, and dissolving it in alcohol or methylated spirit. The bulk of the spirit was distilled off and so recovered, the resultant mass being dried in the air to enable the residual spirit to evaporate at normal temperature. As the soap was kept it became more and more transparent. The reason for this transparency was supposed to be the separation of the soap from the solution as a "true colloid." Recent investigations tend to the view that soap exists as a simple unpolymerized electrolyte in true solution in alcohol.[1, 2]

This is especially so with the oleates, and there is little doubt that they are very much simpler in alcoholic solution than other soaps, a fact which accounts for the indifferent value of oleates as solidifying agents in comparison with stearates and palmitates. Potassium oleate is a typical simple electrolyte moderately dissociated, whereas oleic acid, although a normal electrolyte, is very little ionized. The sodium salt is so strongly ionized, especially near the boiling point of the solution, that it obeys neither the Ostwald nor the Rudolphi Dilution Law. The amount of theoretical work done upon this subject is very small, but it shows that, although it is possible to obtain gels by "salting out" sodium oleate solutions in water by the addition of alcohol, those gels are not very stable and are of little commercial value. This fact seems to have been known to the earliest workers in this field, principally as a result of experimental work undertaken without any theoretical background, for every attempt to solidify alcohol with soap employed the harder soaps rather than the oleate, which tends to soften the final product.

FUELS.

Soap as the Solidifying Agent.

The earliest attempts to prepare a solid fuel from alcohol were due to R. Hirsch, who, in conjunction with Otto N. Witt, pointed out[3] that a transparent soap containing small quantities of spirit did not differ essentially from mixtures containing larger quantities. They were all solid solutions. He succeeded in preparing a solid solution containing 99.5 per cent spirit and 0.5 per cent soap. The results of his research were embodied in two patents, the one[4] taken out by himself and the other[5] by A. Wolff. The latter patent reveals the influence of the nature of the soap upon the melting point of the solidified alcohol. Small proportions of water-free sodium soap were dissolved in water-free alcohol. The mass solidified when cool, and had a melting point near the boiling point of the alcohol. By adding water greater amounts of soap were dissolved, but with increasing amounts of water the product became softer and softer and finally did not set. Moreover the amount of soap which could be dissolved, and the hardness of the end product depended upon the fat in the soap. Fats with a high saponification value, such as coconut fat, gave hard products. The most stable products and those with the highest melting points were given by stearic acid soaps, which were also very suitable for the preparation of alcohol soaps for toilet purposes.

Hirsch's patent describes the preparation of a solid alcohol using pure sodium stearate. If the commercial soap is used, an inferior product is obtained, owing to the presence of oleic acid in the soap. Soaps containing the latter acid yield mixtures with alcohol which do not set solid as do those containing stearic acid. Moreover mixtures of sodium stearate and oleate are as little suited to the building of hard solutions as the oleate alone. The addition of sodium oleate to an alcoholic solution of sodium stearate lowers the melting point of the product in much the same way as the addition of water.

The solid was prepared in the following way: 100 parts of 96 to 98% alcohol were heated to 60° C., then 1 part of stearic acid was added, and then, with constant stirring, 0.5 part of 30% caustic soda solution was added so that phenolphthalein indicator just turned red. The solution set to a solid mass on cooling. Alternatively, 1.25 parts of stearin could be added to the stearic acid, and as much caustic soda as was necessary for saponification.

Substances other than stearin have been frequently used to supplement the action of the soap. J. Rosenthal[6] employed shellac together with an acid soap. The addition of shellac enabled the patentee to produce a solid with the minimum addition of soap. To the warmed spirit 18 per cent by weight of curd soap was added. After prolonged heating over a small flame, a further addition of 2 per cent of shellac was made. The liquid mass solidified on cooling. Moderate heat converted it into a liquid again, so that it might be used in a spirit lamp, or, indeed, any small lamp or stove. When the flame was extinguished, the mass soon solidified again. Rosenthal has also patented[7] a small heating apparatus, which was designed to use his solid fuel. Its chief merit was its compactness and ease of transport, rendering it very suitable for field work. In an additional patent[8] Rosenthal further perfected his process, and it is interesting to note that he reverted to stearin and discontinued the use of shellac, as he found that commercial shellac varied considerably in composition, and hence the amount needed for solidification was indeterminate. Stearin was more easily obtained in constant composition, was cheaper, and, moreover, was a more efficient hardening agent than shellac. To 100 parts of 98% alcohol, 6 parts of sodium stearate in a pulverized form were added, followed by 1 to 2 parts of stearin.

In 1898, H. Hempel attempted to put the production of solidified spirit upon a commercial basis. In several patents, he described methods of making it from ordinary animal fats, which were cheap and easily obtained. He further designed a piece of apparatus, whereby the product could be obtained conveniently and economically on a commercial scale.

According to the earliest of these patents[9] Hempel employed saponified animal tallows, obtained from sheep and deer especially, and stearic acid. 100 parts of this tallow were warmed with 12.5 parts of stearic acid until molten. The mass was then thoroughly mixed by stirring. On cooling, it was saponified with sodium hydroxide and the cold mass pulverized. 1 part of the pulverized mass was dissolved by warming in about 25 parts of 80% spirit. On cooling, a solid alcohol was obtained. On account of the small proportion of solidifying material used, this fuel burnt with very little residue. The hardening material may also be prepared by the following method:[10] 400 grams of mutton fat was added to a solution of 45 grams of caustic soda in 600 grams of water. The mixture was boiled for some time, after which 40 grams of caustic soda in 300 grams of water was added. After further boiling, 85 grams of sodium chloride and 50 grams of scraped stearic acid were added, and on cooling a solid was produced. This was used to produce the solid alcohol in the proportions indicated above. The solid fuel was sold as a granular product in closed receptacles or by weight.

To prevent losses due to evaporation of the alcohol during the heating processes, and to enable the finished product to be drawn off in the liquid condition from the still in which it was prepared, Hempel invented a combined still and condenser, which is the subject of a further patent.[11]

The apparatus consisted of a still in which the solidified spirit was prepared, and a vessel in which the alcohol was heated before being admitted to the still. Within the preheating vessel was a condenser, which served to trap the vapor from the still, with which it was connected by a pipe. The lower half of the still was steam jacketed, an extension being provided around the outlet pipe so that the mass could be drawn off in the molten state. The condenser, which was semi-circular in shape, was fitted with an overflow pipe which returned the condensed spirit to the preheating vessel. The condenser as well as the preheater was in direct connection with the still, so that spirit could be introduced easily and conveniently into the still. At the top of the preheater was an air condenser sufficiently long to trap any vapor, which would return as liquid to the condenser. The pulverized mass, prepared by the formula given above, was introduced into the still, and at the same time, spirit was allowed to flow into the condenser, and overflow into the preheating vessel. When the mass was thoroughly heated in the still, the spirit was allowed to enter the still, and the mass dissolved with constant stirring. The product was drawn off while still kept liquid by the steam, and in the course of a few minutes set to a solid mass.

Another hardening material prepared in a similar manner to that of Hempel, utilizes coconut oil and sodium laurate.[12] The soap became, to a certain extent, spongy in appearance, and absorbed the alcohol into its pores, the resulting product having fairly good lasting properties when placed in air-tight containers. According to this formula, 20 parts of coconut oil were heated to 75° C., and 11 parts of sodium laurate solution of 38° Bé. were added with 10 parts of alcohol or denatured spirit. After saponification was complete, and when the mass had assumed a uniform consistency, another 80 parts of spirit were added and the whole warmed. The soap completely dissolved. The liquid was poured into molds and left to congeal.

E. Skriwan modified this method by employing with his soap-producing substances, certain inorganic materials and wood pulp,[13] whilst H. Mayer[14] employed paraffin wax and resin. Mayer dissolved in 2 l. parts of water, 1 kg. of tallow or palm oil soap, and cooled the hot solution to 60° C. At the same time he melted together in a 16 to 20 liter vessel, 0.5 kg. of paraffin wax and a little resin. The temperature of the melt was allowed to fall to 60° C., the same temperature as the soap solution, which was poured into the paraffin wax, when the whole set to a homogeneous mass, which was subsequently dissolved in 6 kg. of denatured spirit. The solution was left to cool for two days, at the end of which time it had set to a solid mass, which was cut into cubes of 1 cc. in size. By adding red or green coloring matter to the liquid, the solid mass was given a distinctive appearance. Citronellol and other essences were also incorporated.

Instead of the wax and resin, gums have been used.[15] To 1 liter of spirit, warmed to 75° C. on a water bath, was added 30 grams of grated soap, and 2 grams of gum. On stirring, the soap and the gum completely dissolved, and set to a solid mass when cold. It was marketed in little tins, suitable for use in spirit lamps. The flame was easily extinguished by covering the tin with a lid, or another tin box. The contents of the tin could be preserved for some time, the effect of the gum being to prevent rapid evaporation of the alcohol.

If the soap is produced in the alcohol whilst warm, the solution sets on cooling. R. Fallnieht[16] employed this reaction. Whilst 100 kg. of spirit was being heated to 65° C., 3 kg. of a solution of caustic soda, containing 1 kg. of solid in 2 liters of water, was prepared, and to this solution 5 kg. of the warm spirit was added. If the solution was too hot or had stood too long, it turned brown. This had to be avoided. In an iron vessel of 15 liters capacity, 5 kg. of stearic acid was melted, and 8 kg. of the solution of caustic soda in spirit was poured in with continued stirring. This new solution was added to the rest of the spirit, and, on cooling, the whole set.

More recently, Morpurgo[17] used the same reaction by a much simpler method. He prepared separately, alcoholic solutions of sodium hydroxide and stearic acid. These he mixed cold, so that sodium stearate was formed on mixing. The liquid very soon thickened, and acquired a gelatinous appearance, finally setting to a homogeneous product.

One great disadvantage of the solid fuels described above was that in burning they produced a large amount of soot and left a bulky residue behind them. Strobl found that the sooty flame was due to the ethyl alcohol in the denatured spirit (90% ethyl alcohol, 10% methyl alcohol with a trace of benzine). Consequently he used[18] methyl alcohol, either alone or mixed with the denatured spirit. The greater the proportion of methyl alcohol used, the less the amount of soot formed during combustion of the fuel. He used the same solidifying agents. As an example of his method of preparation, he suggested the addition of 2 to 3 grams of stearic acid to 100 grams of methyl alcohol, followed by sufficient alkali to saponify the fatty acid, and convert the mixture to a solid mass. In actual practice, the amount of caustic soda was insufficient to neutralize the fatty acid completely. It was preferable to heat the fatty acid to 60° to 70° C. to facilitate the solution of the acid. When the caustic soda was added, the mass set on cooling. As an alternative 40 parts of methyl alcohol were added to 60 parts of the denatured spirit. Sodium stearate was dissolved in denatured spirit, in which it is more soluble than in methyl alcohol, and into this hot solution methyl alcohol was poured. It was found preferable to have an excess of unneutralized stearic acid present. After burning, the sodium stearate left a porous bulky mass filling the whole of the container, whereas free stearic acid melted with the sodium stearate, and formed a thin layer at the bottom of the can. This was the object of a further patent.[19] In order to ensure that there was the required excess of stearic acid, Strobl added sufficient soda just to neutralize the acid, and then added a little more acid.

This idea was still further exploited by H. L. Fisher.[20] He employed a mixture of ethyl and methyl alcohols in the proportion of 3 to 1 containing about 4 per cent of water, which improved the product. To the mixture at about 70° C. was added the reaction product of caustic soda and stearic acid free from oleic and palmitic acids, together with a small amount of free stearic acid. One object was to produce a fuel which would, on being extinguished, automatically seal itself from the air, and so prevent evaporation of the alcohol. The stearic acid caused the soap left on the surface of the material to melt at a relatively low temperature so that the fuel could be easily relit. The fuel was marketed in a special container provided with a flange at the rim, so that in the event of its being overturned, there was no risk of fire, as the molten fuel would be trapped under the flange. Moreover a lid fitting closely into the flange facilitated the extinction of the flame. The advantage of these fittings was that the one container could be used again and again, till the fuel was all consumed, and it was no longer necessary to burn all the fuel in any one container at one lighting. When the flame was extinguished, a thin layer of the soap-stearic acid mixture set, and closed over the top of the fuel and the sides of the vessel. To relight, the crust had to be broken by means of a match. As the burning proceeded, the soap melted, and, owing to surface tension, assumed the globular shape, exposing a fresh surface of the fuel to the flame. On extinguishing, a new film formed as before. This continued until all the fuel was consumed. Whilst the burning was proceeding, the film was porous, and allowed fuel to pass through it to feed the flame. The product was poured molten into the container in which it was to be used. More than 4 per cent of water, and traces of oleic acid cause softening of the gel.

A recent patent of H. S. Mork and G. J. Esselen[21] sought to embody in one fuel the various improvements outlined by previous patentees. The objects of the patent were to prepare a fuel which would burn quietly, and not liquefy during the process. This latter had not been realized by any of the foregoing patents. The fuel was to be readily ignited, and to leave but small residue. Special attention was given to economical manufacture, evaporation losses being reduced to a minimum. The fuel, being non-explosive, presented no outstanding transport difficulties. It comprised three substances: a saponaceous base, a combustible alcohol solvent, and a volatile combustible liquid or mixture of liquids, the major portion of which was non-alcoholic in character and function. Stearic or any other saturated non-volatile fatty acid was dissolved in alcohol, and the solution heated to a temperature just below the boiling point of alcohol. A non-volatile alkali was added in sufficient quantity to neutralize the acid. A slight excess of alkali was not detrimental. The third substance, a non-solvent for the soap was added, and any soap which may have been thrown out of solution during the addition of this substance, was redissolved by heating the mixture. It was then poured into cans, in which it congealed on cooling. The following example will give an idea of the proportions used: 8.4 grams of triple pressed stearic acid was dissolved in 90.7 grams of denatured alcohol (188 to 190 proof), and to this solution 32.8 grams of wood spirit was added. The solution was heated to 60° C., and 1.14 grams of caustic soda dissolved in denatured alcohol added, with continual stirring to facilitate the solution of the soap. At a temperature of 70° C. 65.6 grams of acetone was added, the mixture being agitated to redissolve the soap, which was thrown out of solution. The mixture solidified at 50° C. It was cut into cubes and wrapped in tinfoil or paraffined paper to keep it from the air. Since the acetone was a non-solvent for the soap, it helped to retain it in the solid form during burning, and moreover, modified the surface crust, making it less dense. Owing to the vapor pressure being higher than that of either alcohol, acetone facilitated the relighting of the fuel. Either alcohol might be used instead of both, and a little water was permissible. Liquids other than acetone, having the effect of reducing the solubility of the soap and raising the gelatinizing temperature could be used, e.g. commercial acetone, or methyl acetate. Palmitic acid may replace the stearic, whilst the soap could be used instead of its being prepared in the alcohol. Potassium hydroxide might be used as an alternative neutralizing agent.

Other Solidifying Agents.

Solidified spirit, prepared by means of soap, had the disadvantage that, owing to the porosity of the soap, the alcohol tended to separate from the solidifying agent and sink to the bottom of the container. Owing to this the flame might spread quickly over the fuel, with every possibility of explosion. This disadvantage was mitigated by the introduction of wool into the fuel. This absorbed the liquid as it separated. Unfortunately, such fuels left residues which made the containers very dirty. To overcome this, the following fixing materials have been used in conjunction with the hardening material having soap as a basis. The success of some of these substances has emboldened patentees to use them by themselves without the soap, so that the majority of the recent patents dispense with soap altogether.

Organic materials which leave no residue on burning have been generally, although not exclusively, employed. Compounds which contain oxygen are especially useful in so far that they provide the oxygen necessary for burning, and hence promote rapid and uniform combustion. There are many patents making use of cellulose derivatives of which nitrocellulose in various forms and cellulose acetate are the most favored, the former more than the latter owing to its superior oxygen content, and the consequent more complete gasification of the fuel.

Gibson and McCall[22] have measured the viscosity of solutions of nitrocellulose in mixtures of ether and alcohol, and have determined the range within which gels can be formed in the absence of any other hardening agent. They employed ether of specific gravity 0.72 and alcohol of specific gravity 0.817 measured at 15° C./15° C. This corresponded to 92% alcohol. Within certain ranges a solution of 4 grams of nitrocellulose in 100 grams of solvent set to a gel, the setting being determined by the proportion of ether to alcohol in the mixed solvents. Thus beginning with a solvent rich in either component, and gradually decreasing the amount of that solvent present, the viscosity decreased in proportion. Solvents containing ether and alcohol in the proportions 80:20 and 30:70 gave gels, but the viscosity curve showed a minimum at 55:45 as the proportion of the solvents. Furthermore, the solution rich in alcohol actually showed a viscosity less than that shown by a solution rich in ether, but as the solution aged, the increase in viscosity of that rich in alcohol was very much more than that of the solution rich in ether, which increased but little.

The property of nitrocellulose of giving gels in alcohol-ether solutions has been utilized for the manufacture of a solid fuel for many years. In his book "Industrial Alcohol" published in 1907, Brachvogel described a solid fuel, which uses alcohol containing a little ether, and gun cotton. This fuel is said to keep for upwards of a twelvemonth in closed vessels, although the alcohol evaporates on exposure to air. It is further claimed that it can be used in any container which will not itself burn, and, since it was marketed in cubes about one-third of an inch in size, could be used wherever ordinary alcohol had been used before. It burned quietly, leaving no residue. Brachvogel also described a number of stoves burning alcohol as well as spirit lamp kettles, coffee percolaters, spirit cookers, alcohol-heated flat irons, and water heaters. For all these the little cubes of solid fuel could replace the liquid spirit. The fuel was marketed under the name of "Smaragdin."

Another disadvantage in the use of soap for the production of fuels is that the calorific value of the fuel is considerably reduced by the addition of soap. V. Perelzveich and G. Rosenbusch[23] sought to overcome these difficulties by the use of a neutral fat instead of the soap, in the presence of sodium sebate. They used synthetic tristearin as being free from admixture with other fats, which have a deleterious effect upon the solidity of the fuel. Glycerin and stearic acid were heated together at a high temperature, when, at first, monostearin, and finally, tristearin were produced. To the denatured alcohol was added 3 per cent of the tristearin and 5 per cent sodium sebate. The mixture was heated together, when the fat and the sodium sebate dissolved. An alcohol-ether solution of the tetranitrate of cellulose was added. The strength of the solution was such that the amount of the cellulose compound did not exceed 1 per cent of the total fuel. Soon after this dissolved, the mass solidified. This fuel was said to have the advantage that it gave a flame of intense heat, with no danger of explosion. At the same time, it melted very slowly, and quickly resolidified on extinguishing the flame, and, when burnt through, left no residue.

By a patent granted a year or two after the one just described the Aktiengesellschaft für Spiritus Beleuchtung und Heizung[24] protected a process, which sought to avoid the disadvantages associated with solidified alcohols containing soap, and to prepare a solidifying mass from which the alcohol does not separate and which does not leave a solid residue. The liquid was absorbed by a fine network of nitrocellulose, in such proportions that the amount of carbon present in the fuel could be completely burnt in the oxygen in the fuel without leaving a residue. Either collodion was poured into alcohol or nitrocellulose was dissolved in an alcohol-ether mixture. The liquid was evaporated, and a residue resembling a transparent gel, the consistency of which depended upon the extent to which evaporation had been carried, remained behind. Traces of suitable essences were added to the gel, which was cut into any desired shape. The product inflamed easily, burning quite regularly, whilst retaining its shape throughout combustion. Burning a specimen upon tin foil, showed that the fuel left only the slightest trace of residue. It was stored in vessels of glass or tin or paraffined paper.

An earlier patent [25] taken out by F. Bayer & Co. used cellulose triacetate, which gave a very stable product, having the advantage of burning quite regularly, although it melted as it burnt. When alcohol was introduced into a solution of cellulose acetate, a voluminous precipitate resulted, which entrapped most of the alcohol, which was not given up easily when the solid was exposed to air. This reaction was made the basis of the process. 100 grams of cellulose acetate was dissolved in 500 grams of glacial acetic acid, and to this solution 2 liters of spirit was added, when the acetate separated in thick gristly masses, which were freed from excess of alcohol and acid by pressure. The resultant product dried quickly in the air. In closed vessels it could be kept for an indefinite period. Moreover, it was claimed that the product was safe to handle, and was therefore eminently suitable for transport. Although other acetates of cellulose were used, it was found that the triacetate gave the most stable product.

E. Raynaud [26] made use of sodium silicate as a fixing material to be used in conjunction with soap. It is interesting that this was the first time that a purely inorganic material was used for the preparation of solid fuel. Use was made of the gelatinous properties of the silicate, and it is not surprising to find that the hardening mixture was principally sodium silicate. The larger the proportion of the silicate, the smaller the amount of mixture that had to be used for solidifying a definite weight of alcohol. Such a mixture was used for hardening other hydrocarbons especially petroleum products.

A complete departure in the method of hardening fuels was attempted by C. Baskerville,[27] who used a quasi-inorganic substance as his hardening agent. To the alcohol, he added about 10 per cent of a saturated aqueous solution of calcium acetate, with a trace of stearic acid. The purpose of the acid was not to harden the alcohol, but to neutralize the alkali produced during combustion. When calcium acetate is burnt calcium carbonate and acetone are produced. The acetone is consumed, but, provided the temperature is high enough, the carbonate decomposes to lime and carbon dioxide. The lime reacts with the water present producing an alkali.

The presence of any ionized substance causes the breaking up of the gel, and to obviate this during burning, stearic acid was introduced to neutralize the lime, producing a slightly ionized calcium stearate.

A detailed investigation of this reaction was undertaken by the authors of this article.[28] On the addition of the calcium acetate solution to the alcohol, the gels form very readily, the more so the drier the alcohol. Excess of calcium acetate solution failed to produce gels, the limits within which gels could be formed depending upon the amount of water mixed with the alcohol. Unfortunately the gels do not remain stable for very long. Nodules soon begin to form, and within about two days the gel has either completely or partially broken up. These nodules are more or less crystalline according to the amount of water present in the gel, and the whole reaction seems to be one of delayed crystallization due to the adsorption of the alcohol by the minute crystals of calcium acetate, and the gels are more of the nature of those described by P. P. von Weimarn [29] than of the type produced by soaps, cellulose compounds or indeed, any gelating agents previously described. The authors have found that the addition of dehydrating agents, notably acetone and pyridine have the effect of increasing remarkably the stability of the gel by delaying the process of crystallization. Acetone especially seemed to give rise to a mass more of the nature of a gelatinous precipitate than a true gel. The change in the structure of the gels due to the addition of the dehydrating agents will be evident from the microphotographs. (Figs. 1 & 2.) Figure 1 shows a gel, which contained 8% water, two hours after preparation. It will be seen to possess a very fine structure of the honeycomb type, and does not show any marked opalescence. The development of the crystals will be clearly seen, together with the clearing of the gel in the neighborhood of the crystals.

Fig. 1.

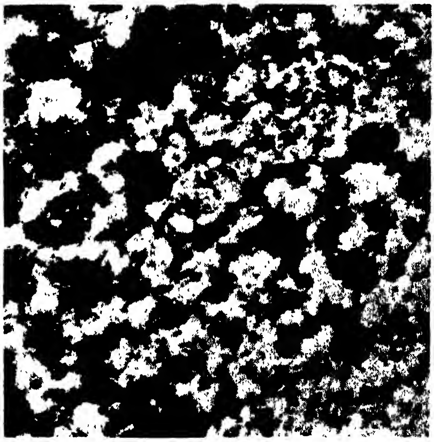

Fig. 2.

It will be noted that the crystals appear within two hours after preparation. This was always so with gels containing a relatively large amount of water. Figure 2 shows another gel prepared from a sol containing too much water for gelation, by the addition of a dehydrating agent, in the example, acetone. The photograph was taken immediately after preparation. In less than an hour after preparation the structure had completely broken up, leaving a gelatinous deposit. The much coarser structure, giving rise to a distinct opalescence, will be apparent, and already there is a tendency to form gelatinous masses.

The addition of small quantities of soaps with the acetate also increased the stability, and delayed the crystallization. Some gels containing potassium oleate and iron oleate remained stable for over a year, and then broke up to very large crystals indicative of a very lengthy crystallizing process. In preparing these gels care was taken not to add so much soap that the solubility of calcium oleate in alcohol was exceeded. If, however, calcium stearate and palmitate were precipitated in the alcohol in the presence of calcium acetate, the addition of either acetone or of pyridine gave rise to a very stable gel. It was found that the presence of the acetate was necessary for the production of the gel. Neutral substances failed to give a gel, so that gel formation in which calcium acetate was employed was evidently due to dehydration.

Sufficient has been written upon the methods of solidifying alcohol to show the agents employed are drawn from almost every class of substance. Many of them depend upon their natural gelatinous properties, whilst others cause solidification because of their insolubility in alcohol. This is especially the cause of the behavior of calcium acetate, which is not alone in thus promoting gel formation in alcohol. E. Hatschek [30] observed that when camphorylphenyl thiosemicarbazide was dissolved to the extent of 5 per cent in hot alcohol, and the solution allowed to cool slowly crystals were obtained, whereas if cooled very rapidly a glass-clear gel was obtained. This gel possessed the blue sheen characteristic of many other gels and sols, notably silica gel, and due to the presence of particles of colloidal dimensions. Gels having this bluish color have also been formed by the use of calcium acetate provided an alcohol containing 8 to 10 per cent water was used. Hatschek's gel required very careful temperature regulation for its formation, otherwise crystallization, either complete or partial, ensued. On standing for twelve hours, the formerly clear gel contained crystals, a change which also took place in the calcium acetate gels (*Cf.* Fig. 1). Evidently in both gels heavy alcoholation of the solid particles occurred, delaying the crystal formation. This is preceded in the calcium acetate gels by the replacement of the water around the molecules by an alcohol-water mixture with the agglomeration of the molecules to particles of colloidal dimensions. This change took time, as is shown by the clouding of the gel as it sets. Gels in which dehydration had occurred to the greatest extent were the most opalescent, whilst those in which the amount of water was relatively high were comparatively clear. A comparison of the microphotographs (Figs. 1 & 2) will confirm this.

Some years after the patent of C. Baskerville, J. E. Crane [31] was granted a patent to manufacture a solidified spirit in which basic lead acetate was used in conjunction with nitrocellulose. Celluloid scrap was the source of the nitrocellulose, and was present to the extent of 5 per cent of the whole. The basic lead acetate increased the viscosity of the nitrocellulose, and caused it to set to a stiff paste or jelly so that, should the container be overturned, there would be no danger of fire. The spirit consisted of 90 per cent denatured ethyl alcohol and 10 per cent methyl alcohol, the latter tending to reduce the soot. Instead of the acetate, aluminium hydroxide could be used with the nitrocellulose.

J. M. Kessler [32] modified this method by the use of copper or bronze powder to stiffen the nitrocellulose.

Two methods using nitrocellulose as the subsidiary rather than the principal gelatinizing agent have been suggested by C. L. Wagner and H. Kranich respectively. The first of these [33] is interesting in that it reverts, in principle, to the method of Skriwan.[13] Instead of using wood pulp as the absorbent for the alcohol, Wagner makes use of the pith of the sugar cane, which is known in the West Indies as "Bagascello." If pyroxylin is used, the burning of the fuel is accompanied by spluttering, and sparks fly out from the burning mass, often to a considerable distance. The object of the patent was to produce a fuel, in which these rather dangerous features were absent. Two solutions were prepared, the one of dehydrated cotton in a 1:4 ether-alcohol mixture (188 proof denatured, pyridine-free alcohol used) and the other of ammonium nitrate in a similar alcohol. Bagascello was added to the ammonium nitrate solution, and stirred until the bulk of the alcohol was absorbed. This mixture was then added to the cotton solution, and air blown through to remove the ether, causing the partial precipitation of the cotton which assumes a fibrous structure and binds together the bagascello. Water in the form of a very fine spray was then introduced into the mixture, which was stirred the whole time, until it set. Either the aeration or the spraying of water may be dispensed with, and the remaining process carried on long enough to complete the precipitation of the cotton. The preparation consists essentially of absorbing the alcohol on the fibers of the bagascello, and, hence, it is important that the bagascello be added to the ammonium nitrate-alcohol solution before the alcoholic cotton solution, as otherwise the latter will absorb the whole of the alcohol. In order to reduce sooting, the alcohol used was mixed with methyl alcohol. Bagascello burns very quietly, leaving about 2 per cent ash. It is claimed for this fuel, that, besides burning quietly, it gives a flame of intense heat, and that it is safe to handle and transport, and cheap to manufacture.

The second patent, due to H. Kranich,[34] uses a special solution of cotton as the absorbent for the alcohol. This, known as "Sericose," is prepared by dissolving cotton in acetic acid and anhydride containing a little sulfuric acid. On cooling this sets to a thick gel. Before setting it was dissolved to the extent of 1 per cent in alcohol, and this solution used as the gelatinizing agent. 17 per cent by weight of an acetone-soluble nitrocellulose was dissolved in 83 per cent by weight of mixed alcohols containing 20 per cent of methyl alcohol. 1 per cent of acetone was added, when there resulted a heavy viscid solution. A 5 per cent ammonium nitrate solution in alcohol was prepared. The water in the alcohol was taken up by the ammonium nitrate, which existed in aqueous solution within the alcohol-water mixture. This solution, when at the temperature of 60° C. dissolved the pyroxylin solution giving a thin limpid liquid, which was gelatinized in the container in which the fuel was to be marketed, by the addition of the 1 per cent sericose solution, in such quantity that the total amount of sericose present represented about 20 per cent of the whole. The coagulant diffuses into the nitrocellulose solution, and precipitates it as a coagulum, which is caused to swell by the ammonium nitrate. As it swells it absorbs alcohol, which reduces the amount of solvent for the sericose, causing it to gelatinize, so that the entire mass sets.

One of the most remarkable methods of hardening alcohol was that described by K. Rast in United States[35] and the I. G. Farbenindustrie Aktiengesellschaft in Great Britain.[36] The chief hardening agent was magnesium alcoholate, prepared by dissolving 1 part of magnesium in 30 parts of alcohol. This solution was added to 120 parts of alcohol, which could be either ethyl or methyl, containing 0.5 to 1.0 per cent of water. The mere dissolving of the metal in the alcohol was not sufficient to produce the alcoholate. It was necessary apparently to set going a reaction between the metal and the solvent. Such a reaction was promoted by traces of bromine or a previously prepared magnesium alcoholate. If the temperature rose too high, the compound began to decompose. The method of solidifying the alcohol may be varied by mixing 10 parts of castor oil, 1 to 2 parts of the alcoholate and 0.1 part of water in a little alcohol. A jelly was produced very readily by this method. The consistency of engine oil may be increased similarly. Among other substances solidified by this method was liquid cyanic acid, epichlorohydrin, chloroform, benzene, xylene and alcoholic ammonia, showing that magnesium alcoholate has a wide application as a hardening agent. The alcohol fuels produced by this method has the advantage of burning without melting, and the amount of residue was very small. If a fuel solidified by soap, and therefore melting on heating, was mixed with a little of the alcoholate, prepared as detailed above, a fuel resulted which burnt without melting.

There is on the British and Continental markets a solid fuel, sold under the name of "Meta," which in appearance and behavior closely resembles the fuel described in the foregoing patents. This is actually metaldehyde. It is a white solid, bearing a close resemblance, except that it lacks the odor, to a peppermint lozenge. It burns quietly with a slightly luminous flame, without melting, and leaves no residue. It can be burnt in any suitable container, since it is in small tablets, and appears to keep indefinitely. It has a considerable vogue, not merely for children's toys in which it can be used with safety, but for many domestic purposes, and appears to be a very suitable portable fuel for use in small stoves.

Apart from absorbents, the majority of the substances used in the preparation of solid alcohol fuels have possessed a definite, and comparatively simple structure, there being few patents which use anything more complex than tristearin. There are, however, just two, which are worthy of mention. The first due to Drapier and Dubois [37] prepared a coagulum from gelose obtained from Ceylon moss (*Gracilaria lichenoides*), a form of seaweed found in the Indian Ocean, and the second due to J. A. Dos Santos [38] employed waxes.

Drapier and Dubois suggested that 1.5 to 2 parts of gelose should be dissolved in 100 parts of water. On cooling this mixture set to a gel, which could be cut or molded. By steeping in alcohol, the water was displaced, producing a fuel which burnt without residue. The replacement of the water by alcohol was said to be due to diffusion or to osmotic action, or both, but there is little doubt that the strong dehydrating action of the alcohol played a very definite part, for the alcohol had to be almost water free. The fuel could be colored by such dyes as methyl violet, and perfumes could be added to it.

Dos Santos added to 100 parts of alcohol 12.5 parts of cerine, an ether from ceryl alcohol $C_{26}H_{53}OH$ and the same proportion by weight of myricin or myricyl palmitate, $C_{15}H_{31}CO.OC_{30}H_{31}$. If less than 25 per cent by weight of the combined ether and wax were added the resulting compound was semiliquid.

An entirely new and very valuable departure in the methods of making solid alcohol has been recently patented by H. Ohle and J. Othmar-Neuschiller.[39] Although some may not have been definitely toxic, all the hardening agents previously used have been non-edible, so that if the alcohol was ever wanted for any purpose other than as a fuel or soap, especially for the preparation of foods, the hardening having been done to facilitate transport, distillation of the alcohol from the solid material became necessary, and the inconvenience of this far out-weighed the doubtful convenience of transporting the solid. The patent claims to produce a gel, which is soluble in water, non-toxic and colorless, in a form from which pure or diluted alcohol can be readily recovered, so that it can be used for making foods, beverages and medicines as well as for technical and industrial purposes, whilst retaining any advantages which might accompany its transport either by land or water, its storage and packing.

Many sugars and polyhydric alcohols form condensation products with acetone, which, since they contain a free hydroxyl group, are capable of forming a sulfuric acid ester, in which one of the replaceable hydrogen atoms of the sulfuric acid is replaced by the diacetone sugar. The sulfuric acid still contains a replaceable hydrogen atom, and hence a metal salt may be prepared. The alkali salts when added to alcohol produce gels of varying stability. The compound giving the most stable gel was the potassium salt of the α-diacetone fructose sulfuric acid. The salt was dissolved in boiling alcohol and the solution allowed to cool. The gel liberated pure alcohol on heating or when compressed mechanically, without changing the chemical structure of the added salt, which could therefore be used again. Since these coagulating agents are soluble in water, the gel can be dissolved in water to give a diluted alcohol, and since the salts are odorless and tasteless, such solutions can be used in exactly the same way as ordinary diluted alcohol. Two methods of preparation were suggested. 20 grams of the potassium salt of α-diacetone fructose sulfuric acid was dissolved in 20 grams of water. The solution was heated to 100° C. and added to 1 liter of 95 per cent alcohol with stirring. After cooling for fifteen minutes, the whole set to a stiff gel. Alternatively, the alcohol was boiled, and then 20 grams of the salt added. A clear solution was obtained, which, on cooling, set to a gel resembling that obtained by the first method.

In addition to methods which involve the preparation of a gel within the alcohol, solid fuels have been prepared by the absorption of the liquid by some porous solid, either combustible or incombustible. There is a very extensive patent literature dealing with such processes, but the majority of them utilize kerosene and solvent naphtha as the fuel rather than alcohol. About 1922, H. Grossmann was granted a patent for the manufacture of a substitute for matches.[40] Little round balls of pumice, siliceous marl or clay powder, etc., were soaked with a liquid fuel such as methylated spirit. These were placed in boxes about the size of match boxes, fitted with little clamps, the jaws of which gripped one of the balls, whenever the clamp was inserted in the box. On removing the clamp from the box, the ball could be ignited by striking it on the box as an ordinary match, and it burnt for about the same time. Combustible solid materials could be used as a base for the fuel, instead of the pumice, etc., and wood, coal or celluloid were suggested by the patentee.

R. Calvert [41] prepared a soap-alcohol gel within the pores of diatomaceous earth. He added 3 parts of soap to hot alcohol (68 parts), and while the solution was still hot, and therefore liquid, poured it over 29 parts of the earth, so that the pores became impregnated with the solution, which, when cold, set to a gel inside the earth.

ALCOHOL SOAPS.

It has been assumed that the washing and cleansing power of a soap depended upon the nature of the lather and also the wetting power of the soap, and its consequent ease or otherwise of dissolving the dirt particles. This power of dissolving the dirt and any fat particles present was said to be dependent upon the rapidity with which free alkali was liberated. Consequently the greater the dilution, and hence, the greater the dissociation, and therefore the amount of free alkali, the more powerful the soap as a detergent. Recent experimental work has shown that this conception must be considerably modified. The more complete dissociation of the soap with much water has resulted in enhanced wetting power, so that the soap has the more easily spread over the fat-covered surface such as the skin, but the dissolving power of the solution is, in consequence of this great dilution, very small. The washing and purifying effect of an alkali solution of the same concentration as the soap solution was found to be extraordinarily small, showing that some other influence than that promoted by the presence of alkali, must be the cause of the marked detergent properties of even quite dilute solutions of soap. There is no doubt that the lather does influence the washing power. The finer the structure of the lather, the greater the mechanical washing effect, as distinct from that due to the alkali formation. The dirt bubbles are tenaciously retained by the foam bubbles, and in the washing process are removed with the lather. Anything which would increase the foam, would increase the washing powers. Since alcohol reduces the surface tension of aqueous solutions and water itself, and therefore increases the foam, it should enhance the washing powers of a soap. Such is found to be its behavior when incorporated in the soap. Moreover, owing to their greater power of dissolving fats, soaps containing alcohol possess distinct advantages over the ordinary aqueous soaps. Owing to its superior wetting powers, alcohol can penetrate further into the pores of the skin. It therefore fetches the dirt particles from the depths of the pores, and introduces them into the foam. If the hands are washed with ordinary soap, and dried, and the apparently clean hands rewashed in alcohol soap, the water from the second washing will contain as much or even more dirt than the water from the first.

A. Kolliger has given a very valuable résumé[42] of the work done upon the germicidal properties of alcohol regarded from the medical standpoint. For medical men, who need some ready means of thoroughly sterilizing the hands, 70 per cent alcohol offered many advantages, but it was rather difficult to transport, and dangerous near a fire, as well as being subject to variations of concentration over which there was very little control. Many attempts to overcome these difficulties by the preparation of solid alcohol or of alcohol-acetone soaps have been made, the most successful of which produced a compound known as "Festalkol," which consisted of 20 per cent palmitic and stearic acids and 80 per cent of 98 per cent alcohol. In the form of a paste it was sold in glass tubes containing enough for a single disinfection of the hands. Denatured alcohol could be substituted for the pure alcohol. The product was markedly superior to corrosive sublimate as a bactericide.

R. Falck[43] has pointed out that when a soda soap prepared from coconut oil in alcohol is rubbed into the skin, and then washed to a lather in water, a very superior means of washing and disinfecting the skin is afforded. Furthermore, apart from the natural disinfecting action of the alcohol, such a soap lent itself readily to the addition of other disinfectants notably coal-tar products, sulfur, resorcinol, salicylic acid, etc., and hence is especially valuable for medical purposes against bacterial infection. Experiments were undertaken showing that an alcohol soap (Sapal) gave, after one and one-half to two minutes washing, almost 100 per cent disinfection using *Bacillus coli* in special cultures.

Resulting from his researches, Falck has invented several processes for the manufacture of soaps, which contain, as a base, alcohol instead of water, and since this solid form of alcohol is likely to assume more importance commercially than the fuel, these processes merit a more detailed description. They are protected by a series of patents[44, 45, 46, 47] put forward during the years 1924 to 1927.

It was very necessary that the soap should be solid, or, at least semi-solid. Many of the alcohol soaps, especially those prepared from olive oil, were paste like in appearance. Moreover, with the solidity, there should not be any brittleness or tendency to disintegrate under the pressure of the hand. The soaps had to possess as high a melting point as was practical, while it was undesirable that the alcohol should be separated by the pressure from the hands or by evaporation. It has been shown how desirable a fine lather is, and the greater the permanency of the lather the better. The majority of these requirements have been met by the increase in the proportion of the soap in the alcohol over that present in the alcohol fuels. As the amount of soap in the alcohol increases, the resulting solid gradually loses its combustible properties and acquires those of a soap.

The invention utilized the common fatty acids, as their sodium salts, in admixture in varying proportions. These proportions were not rigidly fixed, and considerable elasticity in the amounts used was claimed. Coconut oil soap seemed to be the best for the purpose. This soap consists of sodium laurate with admixture in smaller degree of other sodium soaps. A systematic research into the respective merits of the various sodium soaps, revealed some interesting, and, to some extent, astonishing results. As would be expected, the power of forming a compound with the dirt particles, was a factor of the length of the carbon chain, the longer the chain, the greater the power of building compounds. Industrial soap is principally sodium stearate. Only a small amount of this soap is required to solidify alcohol. Unfortunately the product is of very little value as a detergent. On the other hand, soaps prepared exclusively from sodium laurate were too soft to be of any practical value, so that the admixture of the two soaps was suggested. It was found that the addition of small amounts of stearin soap to the coconut oil soap resulted in a much harder product without adversely affecting the washing power. The viscosity, surface tension, and colloidal properties were so modified that the density and stability of the foam bubbles were considerably increased with the result that the washing and purifying properties were actually increased. A pure oleic acid soap in alcohol, containing a high percentage of the acid, itself water free, yielded a soft soap, of which the washing powers were not of a very high order. This behaved in a similar manner to the stearic acid soap, when mixed with coconut oil soap. The smallest addition of oleic acid strengthened the dissolving power towards fat and dirt particles and thereby enhanced the washing powers, without sensibly lowering the melting point, and decreasing the consistency.* The soap which gave the greatest washing and purifying powers was prepared with the following composition: 25 per cent sodium laurate, 10 per cent sodium stearate (or 5 per cent sodium stearate and 5 per cent sodium palmitate[47]), 2.5 per cent sodium oleate in 62.5 per cent alcohol (96 per cent).[44] The sodium salts could very well be replaced by those of potassium.

A drawback possessed by many of these soaps was that syneresis set in on standing, or when they were subjected to pressure. They were intended to be marketed in tubes, from which they were obtained by squeezing, but as a consequence of the syneresis, the pressure often resulted in the alcohol coming out leaving the hard soap behind in the tube. Falck overcame this difficulty by carrying out the preparation in an autoclave under pressure instead of under a reflux condenser, the usual method of preparing these soaps. Owing to the use of high pressure—he used six atmospheres as a rule—it was possible to carry out the preparation at a much higher temperature, and the effect of this seemed to be to give the soap a definite structure in which the alcohol was firmly retained. Whereas by the ordinary methods the soaps were transparent and, apparently, structureless, these soaps, which solidified at a proportionately higher temperature, formed a rigid opaque mass, fungoid in appearance. Under the microscope, the structure was seen as a mass of fine needle-shaped granules matted together and interwoven in the same way as the fibers in a piece of felt. Soap prepared in this manner did not disintegrate under pressure, and when dried in the air gave a gel resembling silica gel in appearance. The foam building and cleansing properties of the soap were twice as powerful as those of ordinary aqueous soaps.

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* As Zsigmondy showed, sodium stearate is an excellent protector (and deflocculator) when its solutions are hot, but the "gold number" rises enormously when the solutions become cold. Sodium oleate appears to act as a colloidal protector to the stearate, thus making it more efficient at lower temperatures. See paper on "Protection" by J. Alexander in Vol. I of this series. J. A.

The quality of the soap was still further improved by using soaps prepared in alcoholic media, rather than soaps prepared in water. For this purpose, the fatty acid and the alkali were separately dissolved in alcohol of a high purity, and the solutions mixed in stoichiometric proportions.[46] The new product resembled very closely the product previously obtained in the autoclave. It had a definite structure in which the particles were woven together as in felt. These needles were readily seen at a fracture. Owing to the production of glycerin as a valuable by-product, the method enabled the soap to be produced much more cheaply.

It has already been stated that alcohol soaps are especially adapted for the admixture of disinfecting agents. This is no doubt due to the superior dissolving powers of the alcohol towards the bactericides, which are usually organic compounds. This property was exploited by P. Villian in 1925.[48] He succeeded in preparing a transparent soap, containing a high percentage of perfume or disinfectant, or other chemical ingredient of medicinal value, such as capsicum, menthol, camphor or iodine, without adversely affecting the detergent properties or the transparency, which was apparently a valuable selling feature.

His method was to add to the hot soap mixture, the composition of which is detailed below, equal parts of methylated spirit, and the perfume or medicant, followed by a soluble derivative of cellulose, such as viscose. This produced a film or coating on the surface of the hardened soap which caused the retention of the volatile component. The harder and purer the fats used, the harder and clearer the soap. To ensure that the soap was colloidal in nature, it was very necessary that no ionizable salt, or, indeed, any substance which easily crystallized should be present in the pan in which the soap was made. The soap mixture was prepared from the following ingredients: Tallow, 55 parts; coconut oil, 25 parts; palm oil, 10 parts; resin, 10 parts. Saponification was carried out in water or spirit. The soap was transferred to a steam-heated pan or still, with a condenser attached to trap any excess perfume. 100 lbs. of the soap was heated to 97° C. with 25 lbs. of methylated spirit. After boiling for a few minutes, the mixture was allowed to cool to about 80° C. (never below 72° C.). At this temperature, the perfume or medicant was added. About 33 per cent by weight was used, essential oils or synthetic products of a crystallizable nature, gums or balsams being avoided, together with 1 to 5 per cent of a solution in an equal weight of alcohol of a cellulose derivative. Viscose, cellulose acetate, butyrate or acetobutyrate were suggested as suitable. The resulting product was allowed to cool slowly, the slower the rate of cooling, the more transparent the soap.

G. Piorkowski[49] has further extended the use of additional disinfecting agents by incorporating with the alcohol soap, sodium persalts and sodium peroxide. These substances increase the natural disinfecting power of the alcohol soap to a very remarkable degree owing to the liberation of activated oxygen within the pores of the skin, the peroxide or persalt being carried there by the alcohol, which, as has been previously noted (*supra*) is capable of penetrating deeper than water into the pores of the skin. Since alcohol is itself an oxidizable substance it is attacked to a small extent by the persalts, but this action seems only to preserve the oxygen compounds from further decomposition. A soap containing 15 per cent sodium persulfate was able to destroy the most resistant bacteria, especially staphylococci, streptococci and *Bacillus pyocyaneus* within 5 minutes. Thus it forms a very superior means of disinfecting the hands. Piorkowski used sodium persulfate, perborate and peroxide, and magnesium peroxide.

MEDICAL PREPARATIONS.

An alcoholic base has been used as an improvement in many face creams.[50] An ordinary cream applied in a thin layer to the skin is impervious to air, and tends to open the pores of the skin promoting an unnatural and unpleasant sweat. The presence of an astringent closes the pores and gives the skin a soft and natural appearance. The use of an astringent alone would cause dryness of the skin, which is equally undesirable. By incorporating with the cream a substance such as eau de cologne, which has an alcoholic base, both these unpleasant features are obviated. Moreover the presence of the saponaceous base with the cream produces a cleansing effect, which could not be obtained by eau de cologne alone. "Frozocolone" is a preparation of this type.

Owing to the superior penetrating power of alcohol, it has been employed as a base for medical preparations which have as their object the relief of various muscular disorders or rheumatism. Thus an alcohol soap embodying about 10 per cent oil of amber and a little succinic acid has been patented as a treatment for rheumatism.[51] The value of iodine for the treatment of such disorders is well known, but as the skin is comparatively impervious to aqueous preparations, ordinary tincture of iodine is of doubtful value for external application. This difficulty has been overcome by mixing the iodine with a soap containing alcohol and so producing a paste. Several such preparations are on the market.

Early attempts to prepare such pastes were hampered by the possibility of the iodine reacting with the solidifying agent. K. Jungmann and O. Kolbert [52] introduced a patent which sought to overcome this disadvantage by the use of a trace of sodium iodide as a stabilizing agent for the iodine. The action depended upon the formation of an addition product of iodine with the iodide, an action which is utilized in the preparation of ordinary tincture of iodine. The preparation of the paste was carried out in the following way: 40 grams of stearic acid was dissolved in 800 cc. of alcohol with warming. At the same time, 3.68 grams of sodium hydroxide was dissolved in another 200 cc. of alcohol. The two solutions were mixed at 65° to 70° C., with the result that the acid was saponified. To the warm solution of the soap, 30 grams of sodium iodide was added, and with continual stirring, 20 grams of iodine in 200 cc. of alcohol. The solution was run into glass tubes, in which it cooled and set, and in which it was marketed. Organic acids other than stearic may equally well be employed, and neutralized by caustic soda or by sodium alcoholate. Thus R. Geller has applied for a patent [53] to use benzoic, stearic, palmitic, phthalic and salicylic acids. He suggested that potassium iodide be used as a stabilizer instead of sodium iodide.

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Editor's Note.

A large American manufacturer of solidified alcohol has kindly given me the following information, much of which has apparently not been published:

The soap method of making solidified alcohol has long been abandoned here, but not because of syneresis which never gave any trouble practically, and was never even observed. The main objection against soap-solidified alcohols is that they liquefy on burning, constituting a very serious fire hazard to the user. Incrustation, excessive inorganic residues and unsatisfactory burning, especially when most of the alcohol has been burned off, are other objections.

From our experience, it appears that the only practical solidified alcohol to be used on a small scale for fuel purposes is one which gels with nitrocotton and the basis of this industry was laid by the Denayrouse French Patent No. 296,132 of 1900, with corresponding British and German Patents, but no corresponding patent was issued in the United States. The "Smaragdin" mentioned by the authors was produced under this patent, the feature of which was the use of an ether-alcohol collodion, from which the ether was permitted to evaporate bringing about solidification of the residue. The large-scale development of this industry is really due to American enterprise, a fact which is true even to-day. While the output of this product in the United States is of a magnitude of highest order, on the Continent it is still a curiosity and what is marketed there is not a solidified alcohol, but in reality compressed metaldehyde, although during the war the belligerents everywhere furnished their soldiers with soap-solidified-alcohol for their outfits.

Real progress, from a technical point of view, in the manufacture of solidified alcohol was made with U. S. Patent No. 1,262,267 and especially No. 1,262,268 of April 9, 1918, issued to Jacob Schaub.

Instead of the use of undesirable ether, Schaub employed other suitable solvents, principally alcohols, and instead of waiting for part of the solvents to evaporate and to bring about the desired solidification, he conceived the very ingenious idea of using water as a precipitant, but in small quantities only so as to bring about the formation of a solid gel. The U. S. patents of Poulton, Brigham and others had a similar object. But it would take me too far to quote all the pertinent facts, which contributed to the building up of this rather substantial industry in the United States.

A highly interesting aspect of this subject, interesting also from a theoretical point of view, is the fact established by Kugelmass in 1922 and McBain in 1926 to the effect that even highly nitrated celluloses form perfect solutions (dispersions?) with absolute alcohol at temperatures of —20°C. These pseudo solutions gel on warming, but liquefy again when brought down to the required degree below zero; this behavior is reversible.

The so-called "Meta" made from metaldehyde by Lonza in Switzerland, is marketed almost exclusively in Europe. It may be mentioned that trioxymethylene (paraformaldehyde) and hexamethylenetetramine, both in compressed form, have also been proposed for the same purpose.

Alkaline and Other Detergents.

THEIR FUNCTION IN LAUNDERING, TEXTILE PROCESSING, AND GENERAL CLEANSING OPERATIONS.

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For the purpose of this chapter the term "detergent" is taken broadly to include all common materials used as aids in general cleansing operations. Its strongest connotation suggests the reagents employed in the laundering of textiles.

Effort Spent for Cleanliness.

Washing contributes largely to *personal* satisfaction, comfort and health; yet quite as large a quantity of "cleansing aids" and the labor incidental to their use, go toward maintaining household and general cleanliness. Enumerating some of these intimate administrations, dish-washing, bathroom and lavatory service may be mentioned.

The maintenance of these personal services constitutes perhaps the largest labor-hour item of all expended human effort in modern civilized society.* The value of the materials employed is correspondingly large. Of the total production of sodium compounds approximately 13 per cent is made into soap and 8 per cent into cleansing materials other than soap. Thus 21 per cent of the alkali produced is devoted to a striving for cleanliness.[1]

Besides their economic and social importance, detergent materials and their application present many interesting colloid-chemical aspects, which will be especially considered here.

Cleansing Processes Are Colloidal.

Cleansing processes are triply colloidal. The dirt or stain to be removed is usually in a colloidal state; the surfaces to be cleansed (textile, skin or other surfaces) are usually of a colloidal nature; and soap, the most important reagent excepting water, is, when functioning, at least partly in a colloidal state. Especially true are the foregoing statements in the common cases where water is the vehicle or dispersing medium; but even in the cases where organic solvents are the dispersing medium, colloidal reagents are added (as dry cleaners' soap), thus maintaining the colloidal aspects of the three important factors, the dirt, the surface to be cleansed, and the reagent.

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* Many animals spend considerable time in keeping clean. Flies, cockroaches, and many other insects continually clean their wings, legs, antennae, etc. Birds frequently preen their feathers and take "dust baths" against lice. Cats and dogs lick themselves clean and pussy often "washes" her face with a moist paw. Elephants bathe. "Wallowing" in mud seems partially at least for protection against insects, but is also cooling and ultimately cleansing. J. A.

Dirt and Stains as Applied to Textiles.

A garment or other textile article ready for the laundry or for dry cleaning is said to be *soiled,* a term really including *dirty* and *stained.*[*] Loosely the three expressions are used synonymously. There is some precedent in the limited writings on cleansing to use the word *stain* to designate the more refractory localized discolorations, and *dirt* the more common soiling bodies. In these senses they are used here. Dirt is simply adsorbed particles, discolorants left on a surface by contact or by evaporation of a dispersing fluid. A stain usually requires treatment other than that accorded in the regular cleansing procedure. Thus in ordinary water washing, chewing gum is a stain, because it is most readily removed by a special solvent, namely carbon tetrachloride. In dry cleaning maple syrup is a stain because water-borne stains are not removed by the usual petroleum solvent.

The greater part of the soil on outer body garments consists of adsorbed particles—dust and smoke—which could be largely removed by prolonged violent agitation of the textile in ordinary water; but such procedure would shorten the useful life of the fabric. Road dust (fine clay particles, pulverized earth in general) is eventually "wet out" in water, peptized, dispersed, hence washed out of the interstices and from the surfaces of the fibers. Soot, on the other hand, consists of fine particles of carbon enclosed in adsorbed film of complex hydrocarbons. It is therefore more difficultly wet out and deflocculated in plain water. Moreover its presence interferes with the dispersion of other solid particles.[2]

Body garments and bed linen, in addition to air-borne dirt, are further soiled by skin excretions, which are more or less of an oily nature.

Table linen, in addition to air-borne dirt, is soiled by foods, some of which make stains. Those of an albuminous nature such as egg, milk, and blood from rare meat, require low temperature for the first cleansing bath, because at elevated temperatures they are coagulated and rendered more refractory to dispersion. Gravy, salad dressing, butter and other foods of the emulsifiable type are easily washed away with soap and water, provided food dyes are absent.

Fruit discolorations are stains. The sugar portion is, of course, water-soluble; but coloring matter, natural or added, contained in fruit foods (including jams, ketchups, etc.) frequently requires special treatment for its removal from fabrics. It is the common occurrence of the residual stains from fruit, coffee, tea, cocoa, chocolate, blood, medicines and (occasionally) mildew, that renders the use of sodium hypochlorite imperative in the commercial laundry.

Another type of dirt is exemplified by candle-wax drippings. Wax-like bodies which the fabric accidentally acquires in the molten form, adhere tenaciously when cooled. They may be dispersed with soap and alkali if the temperature of the cleansing solution is high enough to melt or even soften them. When this procedure is impractical, the most satisfactory method of removing waxes from fabrics is to place the spot between pieces of blotting paper and apply a warm iron. The heat liquefies the wax and the blotter removes the most of it by capillarity.

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[*] *Soil,* derived from the French *souiller,* going back to the Latin *sus,* swine (from which the word *syphilis* is also derived), means to defile or pollute, and is the generic term. *Dirt,* derived from the Middle English *drit* (same in Icelandic) meaning *dirt, excrement of birds,* involves mainly the idea of anything that may make a thing filthy or unclean by adhering to it, such as mud. Colloquially, *dirt* is used as synonymous with *earth,* as in "pay-dirt," "dirt road." *Stain* is a form of *distain,* derived from the French *destaindre,* going back to the Latin *dis,* apart and *tingo* to *tinge.* It means to *tinge with an unnatural color,* and particularly to make a spot which cannot be easily removed. J. A.

Machine grease is a dirt often found on work garments. It is usually removed by ordinary soap and water washing. If refractory to that treatment, it may be removed by applying a 2 per cent solution of oleic acid in kerosene followed by washing in a hot aqueous solution of soda ash. The oleic acid being intimately distributed in the solvent and dirt, forms soap with the alkali and thus facilitates their emulsification. Machine grease often contains dispersed metallic particles, notably iron, which may oxidize on a fabric and impart a stain difficult to remove by ordinary washing. The treatment then indicated is one for iron stain. Oxalic acid is a specific for iron stain. Potassium cyanide is a specific for most other heavy metal stains.

Stains of dye-like nature such as those from ink, leather, grass and walnut, respond either to oxidizing or reducing agents. The oxidizing reagents employed are sodium hypochlorite, sodium peroxide or one of the persalts. In cases of refractory stain demanding a strong oxidizer, potassium permanganate may be used, followed by oxalic acid to remove the resulting manganese stain. A reducing agent commonly effective is sodium metabisulfite (sometimes with addition of zinc dust).

The choice between laundering or dry cleaning is made largely on the nature and dye of the fabric rather than on the character of the dirt. Outer garments made of wool are usually more perfectly restored to a new-like condition by washing in non-aqueous liquids. Wool fabrics tend to felt upon mechanical treatment in aqueous alkaline solutions, which are, nevertheless, desirable for cotton and linen fabrics. Commercialized and household dry cleaning thus fill a niche in methods of renovation of fabrics not readily cleansed in aqueous solutions. Then, too, numerous dyes employed in decorative fabrics are less likely to be damaged by non-aqueous liquids than by water.

Further data concerning stains and their removal are to be found in a chart inserted at the end of this chapter.[3] The expression "removed by the standard washing procedure" means that recommended by the research department of the Laundryowners' National Association for white wash goods. This procedure includes a mild treatment with sodium hypochlorite (one quart of one per cent available chlorine per fifty pounds of goods and a sour bath of acetic acid). In household treatment these reagents are recommended in the cases indicated.

TEXTILE PROCESSING.

Cotton.

The processing of new textiles involves a number of laundering processes, the specific detail varying for each of the commercial textile fibers not only according to the nature of the fiber itself, but also according to the nature of the natural and acquired stain. Thus the stain on gray cotton cloth is a composite of the natural wax-like bodies found in the natural fiber, the oils or size (with their oxidization products) added to facilitate spinning and weaving, together with adventitious dirt acquired from factory handling and the atmosphere. These must all be removed from the cloth before satisfactory bleaching may be done. The wax-like bodies require kier boiling, wherein the cloth is subjected to recirculated currents of hot caustic soda solution in steam-tight iron tanks. The wax-like bodies undergo chemical change,—possibly hydrolysis. Temperature, time and concentration control is required to permit the hydrolysis of the wax-like bodies and to avoid hydrolysis or other chemical action on the cellulose. The other components of the stain are simply dispersed in the cleansing vehicle, the alkali reagent functioning as in ordinary laundering procedure.

Wool.

In preparing fleece for spinning and weaving of wool cloth, the object is to remove various objectionable substances, some simply adsorbed solids, others of grease-like nature. The fatty acids present are converted by the action of the alkali employed into soap which contributes to the dispersion of the remaining dirt. In this process of wool scouring, the detergents also give desirable physical properties to the water in which they are dissolved. Soda ash is the usual detergent in "wool scouring."

Silk.

In boiling off or degumming silk the alkali employed is usually a neutral soap, which aids emulsification and, to a less extent, solution.

This epitome of textile processings is given simply to serve as a background when discussing the function of detergents in the laundering process which involves a wider variety of soiling components. The reagents employed in both operations are of the same nature. Such distinctions as are found lie largely in the dosages and methods of application of the cleansing aids.

LAUNDERING.

Physically, laundering procedure includes: (a) the wetting out of the dirt and textile; (b) the dispersion of the dirt in the dispersing medium; and (c) the removal of the dispersing medium by dilution (rinsing).

Whatever the variables, water and soap are always employed in laundering and with few exceptions an additional alkali, namely a crystalloid, usually a sodium salt of a weak acid. Water is the dispersing medium. Soap is the most important detergent.

Mechanically the essential operations of laundering are: (a) agitation in the cleansing liquid; (b) the removal of the cleansing liquid by repeated dilutions (rinsing); and (c) dewatering the fabric by wringing or centrifuging. (Drying economy has made this almost universal practice.)

Mechanical Features of Laundering.

A primitive method is to pound the fabric, saturated with the soapy water, on stones or boards at the water side. A later improvement is to rub the fabric on the corrugated surface of a washboard. Modern washing machines of the domestic or power laundry types accomplish the same results.

The following is a procedure for home washing approved by domestic science authorities and recommended by the manufacturer of a widely advertised equipment ensemble, a washer of the reversing "dolly" type, with roller wringer.

The machine is filled with soap-water (0.5 per cent soap solution) at a temperature around 80° C. Approximately five pounds (dry weight) of clothes are added, and the agitator started and run for 5 to 10 minutes according to the degree of soiling. The machine is stopped and the clothes removed from the detergent bath, passed through a wringer into a rinse bath of similar volume and temperature, wherein the clothes are thoroughly immersed and agitated. From this rinse bath the clothes are removed and again passed through the wringer into the bluing bath of similar volume, from which the clothes are removed and passed again through the wringer after which they are ready for drying on the line. An average cotton garment, after being passed through a good wringer will retain 110 per cent of water on the basis of the dry weight of the cloth, whereas the same cloth will retain 300 per cent when simply drained for one minute. From this it may be calculated, assuming uniform dispersion and disregarding the possibility of selective adsorption, that the above procedure eliminates all but 0.2 per cent of the total dispersed dirt and detergents present in the first bath. Without the wringer or a similar dewatering device, with the same number of baths of the same volumes, approximately 15 per cent of the dispersed dirt remains and is dried on the fabric.[4] It is thus clearly seen that the wringer is a very important unit of the home washing equipment.

Convenience and detergent economy are obtained by using the same baths for consecutive lots of fabric, complying with esthetic and sanitary requirements by washing table linen first, then bed linen, followed by white body garments, then colored garments. For a weekly wash for an average family of five, one set of baths is sufficient. Furthermore the gradual cooling of the baths fits the scheme by affording the lower temperature desirable for colored clothes.

In the industrialized laundry a typical formula[5] of procedure for white cotton and linen wearing apparel and flat work is as follows:

1st Bath— Run in lukewarm water at a temperature of not over 100° F. to a point that is 2 inches or more above the designated suds water-level. If the washer is not equipped with a thermometer, the use of tap instead of lukewarm water is advised. Add soap and builder * to produce a light suds, run 5 to 10 minutes, depending upon the type of load, and then discharge the bath. It has been found in certain cases that the addition of extra alkali to the break † is advantageous.

2nd Bath—Add hot water until the required suds water-level is reached.‡ Add soap and builder to raise a running suds § and run not over 10 minutes. Discharge the bath. After the wheel has run a moment or two, the temperature should approach 125° F. with a good hot-water condition.

3rd Bath—Add hot water, soap and builder as above. The temperature ordinarily should equal 140° F. after the bath has run a few moments. Discharge the bath at the end of not over 10 minutes.

4th Bath—Run in hot water to the designated suds level, and add dilute Javelle water in an amount not to exceed two quarts of a one per cent solution per 100 pounds of material. Use less if possible. Add soap and builder, as necessary, and run not over 10 minutes. The temperature of this bath ordinarily will range between 155° and 160° F. with a satisfactory hot-water supply.

5th Bath—When the water-supply contains one or more grains of hardness, it is advisable to run the first rinse at a suds water-level for not over five minutes. Otherwise a high rinse level may be used.

6th Bath—Run a hot rinse at a rinse water-level for not more than five minutes.

7th Bath—Repeat last bath.

8th Bath—Repeat last bath.

9th Bath—Follow with a warm (130° F.) high rinse for not more than five minutes.

10th Bath—Sour at a suds water-level at 120° F. for five minutes. Then rinse the water to a rinse level with cold water, blue for five minutes and pull out the load.

The clothes are then placed in extractor basket and centrifuged until sufficiently dry for ironing "flat" pieces (towels, sheets, etc.).

By calculations of consecutive dilutions with the qualifications specified in the case of the home equipment it will be found that the above procedure re-

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* As explained later a "soap builder" is something added to aid the soap, e.g. sodium carbonate, sodium silicate or the like. J. A.

† In the industrialized laundry the initial bath is commonly called "the break."

‡ The initial water-level must allow for a rise due to formation of suds.

§ This means a suds that carries up on the rotating cylinder, but not enough to run out at the outer cylinder door. The amount of soap used is usually about 0.2%, figured on the amount of water in the bath.

moves over 99.9 per cent of the dispersed dirt. Thus in the power laundry process, the advantage attained by the use of the wringer between baths in the home procedure, is gained by a plurality of baths and greater volumes of water.

SOAP.

In a contribution to the chemistry of laundering [6] some years ago the writer stated that no adequate theory picturing the complete functioning of soap and alkaline detergents had been proposed. While the scope of knowledge on the subject has been much enlarged, even now no theory affording satisfactory indices to detergent value has been generally accepted.

An early theory as to the cleansing action of soapy solutions is that of Chevreul [7] (1811). He showed that soap, when it is dissolved in water, decomposes into free alkali and acid salts of the fatty acids, that is, hydrolysis occurs. He then assumed that all dirt particles adhere to surfaces because of a film of fatty substance. The saponification of fatty substance by the free alkali of the soap solution, according to his theory, was thought to release the dirt particles and suspend them in the suds. The fallacy concerning the behavior of the dirt and the quantitative effect of the alkali liberated by hydrolysis seems not to have been detected for a period of nearly one hundred years.

One writer pointed out that alkalis, yielding much higher hydroxyl-ion concentrations than are afforded by soap, were inferior to soap as cleansing reagents.[8] Another showed that the cleansing or emulsifying power of soap was due to the soap *per se,* and not to the alkali of hydrolysis.[9] McBain * and his co-workers have published much fundamental data on soap and soap solutions especially concerning soaps as electrolytes, and have given to the literature the expression "ionic micelle." These and other contributions laid the basis for a colloidal theory of alkaline detergency. The distinctive characteristic is the low surface tension imparted to the solution by the soap and that on this property depends its great power of (a) wetting surfaces, (b) dispersing and suspending small solid particles and droplets of liquids immiscible with water, (c) lubricating surfaces and dirt particles.[10] It would therefore seem strange that the surface tension measurement under some specified conditions should not have been accepted as an index to detergent value.

In this, one factor seems to have been overlooked in the publications of most investigators—the influence of added alkalis other than soap on the surface tension of a soap solution of given concentration. All the common alkali salts of weak acids have this property to a greater or less degree. Even sodium acetate, the salt of so strong an acid as acetic, produces some lowering of the surface tension of soap solutions.[11]

Most commercial soap contains added alkali in varying proportion, and since the soap is more expensive than alkali the surface tension value has not been accepted as a measure of detergency.

Various other methods have been proposed for measuring the detergent value. P. H. Fall [10] devised a procedure to measure the quantity of finely ground manganese dioxide that may be permanently suspended by a given volume of detergent solution of defined concentration. Inasmuch as materials practically found effective in cleansing operations, notably non-soap alkalis in cleansing metals, would fall low in the scale by his test, it is likely that too

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* *See* paper on "Soaps" by J. W. McBain in Vol. I of this series. J. A.

much stress was placed on the permanency of the suspension. Another method with respect to textile cleansing is to test the reagent in a specified washing procedure using definite methods of soiling, concentrations of reagents, volume of bath to quantity of cloth, and exact procedures in washing and rinsing, comparing the soiled washed cloth with a specimen representing the original condition of the cloth.

The soiling material and methods as well as the washing procedure vary, but this method of evaluating detergents and bleaching compounds seems to grow in favor.[12] Such procedure also permits an observation on the effect of the reagent on the tensile strength of the fabric.

In industrialized laundering, the trade has for a number of years been supplied with so-called neutral soap, that is, soap having alkali and fatty acid completely combined it stoichiometric ratio. Fat is more expensive than alkali, so that sophistication was more readily precluded by a "neutral" soap specification.

On the other hand, most good laundry soaps as sold to the household consumer, contain added alkali, notably in the form of a silicate of soda, or sodium carbonate, or both. None of these should be considered as adulterants, provided they are not present in excessive amount.

In the text. e trade, the commercial laundry, and the household, soap generally means sodium soap. Potash soap has a traditional use in laundering and textile processing of wool and silk. Potash has also been the preferred alkali in liquid toilet soaps.

The preference for potash soap is due to its greater solubility in water and in alcohol at low temperatures. In wool and silk washing a low temperature bath is desirable. With a given fatty acid this advantage is not so conspicuous as had been thought. By selecting suitable fatty acids, the desirable physical properties may also be obtained with sodium soap, and it is concluded that sodium soap properly made from suitable fats is even superior to potash soap in wood and silk processing.[13] Ammonium soaps have found some special application, but their use is extremely limited. The soap of commerce consists mainly of the sodium salts of the higher fatty acids, oleic, stearic or palmitic, to mention the principal ones; and the classification of soaps as hard or soft soaps corresponding to the sodium or potassium soaps respectively, is of less significance than formerly.

The purchaser of soap who sets store by numerical constants, demands to know the titer test, the iodine number and sometimes the saponification number as a basis of judgment of soap quality. For cold-water washing of textiles he would select a low-melting fatty acid because of more ready solubility with attendant facility of rinsing; and not too high an iodine value because highly unsaturated fatty acids give soap a pronounced tendency to turn rancid. For hot water washing, a soap whose fatty acid shows a higher titer and a lower iodine number would be selected because such a soap is soluble and may be readily rinsed out at higher temperatures.

Soap for laundry and textile purposes is marketed in the form of flakes, chips or powder. The traditional cake finds use in the household for its many conveniences of application, but for home laundering the flaked form is obviously convenient and is gaining in popularity. Spray-dried "beads" have been recently introduced. Such flakes are sold on a true soap basis usually eighty-eight, or more, per cent of soap.

ALKALINE DETERGENTS OTHER THAN SOAP.

As stated before most soaps sold to the household trade contain as a matter of convenience as well as of tradition some added alkali other than soap. In textile laundering as well as in the industrialized laundry, a non-soap-added-alkali is almost universally employed. Notable exceptions are in the washing of silk and wool in which soap alone is the safest detergent. This practice obtains even where water of "zero hardness" is used—that is water treated to remove all calcium and magnesium ions. In the household soap one use for the added alkali is as a so-called water softener. Most natural waters contain more or less calcium and magnesium ions; and as calcium and magnesium soaps are difficultly soluble and of a sticky nature and are formed by reaction with the sodium soap, the solution is not only deprived of the desired reagent, but is contaminated with an additional dirt which is not only difficult to remove from the textile but which also adsorbs other suspended dirt. These insoluble soaps antagonize sodium soap, breaking down any emulsion already formed. The desirability of soft water has long been recognized; textile industries develop in localities where relatively soft water is to be had. Water-softening materials are employed with the soap as an expedient to compete with the soap in the precipitation of the calcium and magnesium compounds. The sodium salts commonly employed are carbonates, silicates, phosphates, or even sodium hydroxide. For waters high in magnesium the value of silicates and hydroxide are obvious when we consider the insolubility of the resulting compounds. Practically sodium hydroxide was employed because its use accomplished the desired result, and not through a consideration of the fact that it converts bicarbonates to carbonates, thus yielding a precipitant for calcium, and that *per se* it is a good precipitant for magnesium. Likewise with the silicates. They are said to have been introduced as a substitute for the rosin necessary to give desired physical properties to the bar of soap. The manufacturer making soap for wide distribution must meet varied conditions. Hence the established custom of additions to soaps. But with soft water, now found in all scientifically managed textile mills and laundries, and even in many municipalities and homes, the popularity of these alkali additions must be justified by some other useful function.

One of these may be in the suppression of the hydrolysis of the soap. McBain[14] has shown that hydrolysis of soap in water is unimportant except in very dilute solutions; but it is with dilute solutions that the launderer is dealing.

Another function of the added alkali may be to adjust the pH value of the bath to a suitable range to stabilize the suspension or emulsion formed. In the clarification of liquids from suspended matter, it is well known that certain ranges of pH values are suitable for bringing about flocculation and that other ranges are suitable for preventing flocculation. In laundering flocculation of dispersed solids must be prevented.

Another function may be to assist the soap in lowering the surface tension of the bath. As mentioned before, within certain ranges of soap concentration added alkali further lowers the surface tension. These observations constitute a description rather than an explanation.[*] The economy effected

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[*] Zsigmondy found that the protective action of sodium stearate is enormously increased at higher temperatures. Thus its "gold number" at 60° C. is 10.0, while at 100 degrees it is reduced to 0.01, the protective action being thus 1,000 times greater. It is quite possible that beneficial "soap aids" may function by making the soap go into finer dispersion at lower temperatures, or else prevent it from excessive aggregation on cooling after it is dissolved at higher temperatures. Fineness of dispersion means greater kinetic and surface activity, and consequently greater effectiveness. J. A.

by the use of alkalis other than soap in conjunction with soap is beyond question. These alkali materials might logically be called "soap aids," but the expression used in the laundry trade is "soap builders."

As far as the writer knows no work of a disinterested investigator has been published to establish specifications for the "ideal detergent." The total acid neutralizing power as indexed by the percentage of available Na_2O is a specification long employed in the trade. More recently the pH value of a certain concentration of the material in water has been mentioned. Considerations other than maximum detergency must be recognized in certain instances in the selection of the most suitable pH range. For instance borax in proper dosage may be employed with soap in laundering silks and woolens.

The alkalis of commerce with their percentages of total Na_2O and respective pH values in $N/10$ solution at 20° C. are here tabulated (Table 1). By *available alkalinity* is meant the titratable alkalinity with a strong acid, employing methyl orange as an indicator.

TABLE 1.—*Alkalis of Commerce.*

Trade or Common Name	Chemical Name	Formula	Total Na_2O	Available Na_2O	pH Value in N/10 Solution at 20° C.
Baking Soda or Salaratus	Sodium Bicarbonate	$NaHCO_3$	36.9	36.9	8.5
Borax	Sodium Biborate	$Na_2B_4O_7.10H_2O$	16.25	16.25	9.6
Modified Soda	Sodium Sesquicarbonate	$Na_2CO_3NaHCO_3.2H_2O$	41.1	41.1	9.6
Soda Ash	Sodium Carbonate	Na_2CO_3	58.5	58.5	11.6
Sal Soda	Sodium Carbonate Decahydrate	$Na_2CO_3.10H_2O$	21.7	21.7	11.6
T. S. P.	Trisodium Phosphate	$Na_3PO_4.12H_2O$	24.48	16.3	12.2
Water Glass	Silicate of Soda	$Na_2O.3.65SiO_2$, plus water	(on water free basis) 22.0	22.0	11.4
Causticized Ash	Mixture of: NaOH and Na_2CO_3				12.2 for 10%
Caustic Soda	Sodium Hydroxide	NaOH	77.5	77.5	13.0

Modified sodas are made by two methods. One is by crystallizing a pasty mass of the molecular mixture of sodium carbonate and sodium bicarbonate. The resulting material is a grainy powder of irregular crystals. Another method consists in crystallizing $Na_2CO_3.NaHCO_3.2H_2O$ from a mother liquor of definite concentration and temperature.[15] The resulting material is composed of fine needle-like crystals. The advantages claimed by proponents of this material are a reserve of alkalinity with a relative low pH value. Prolonged boiling progressively converts the compound into sodium carbonate.* Baking soda, borax, soda ash, sal soda, trisodium phosphate and caustic soda, being definite well known chemical compounds, need no further discussion.

Water glass is not often used in laundering except as it is incorporated into soap. This is attributable largely to the inconvenience of distributing and handling of a liquid. Anhydrous water glass is difficult to dissolve. However proprietary preparations composed largely of a hydrated silicate of soda are marketed to laundries in a powdered form.

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* The escape of CO_2 gas within the textile mesh should have a mechanical detergent effect, also. J. A.

Causticized ash of various ratios finds extensive market for laundry and general cleansing purposes. It is usually a mechanical mixture of dry soda ash and caustic soda. In the solid state NaOH and Na_2CO_3 do not form mixed crystals.[16] Advantages are high reserve alkalinity and within certain limits, almost constant pH value.

Numerous proprietary compounds are on the market designed for laundry and household cleansing purposes. Many of these are mixtures of soda ash and trisodium phosphate.

It is interesting to note that by variation of the concentration of various alkaline solutions the same pH values may be obtained. Normal sodium carbonate, 0.0545 normal trisodium phosphate and 0.0065 normal sodium hydroxide solutions each show a hydrogen-ion value of 11.35.[17]

The attitude of the writer as to the respective merit of the various alkalis available for detergents is that the dosage and general procedure in the use of the alkali is a matter of more importance than the selection of a particular alkali.

OTHER USES OF ALKALINE DETERGENTS.

The properties of alkaline materials which make of them valuable soap aids in laundering, likewise make them useful wherever soap is used. There are other applications where they are used without soap. One of these is in washing dishes in mechanical washers. However, there are proponents of the use of some soap along with added alkali in this cleaning bath. With hot water and adequate agitation mechanical dish-washers are successfully operated with detergent alkalis containing no soap. The difficulty in emulsifying oils and fats commonly found in foodstuffs without the use of soap does not tend to harmonize the theoretical with the empirical observations.* When the soap is omitted a pH value for the bath of around 11.5 to 12 seems to be most favorable. This condition is met within a 10 per cent causticized ash or by trisodium phosphate or with caustic soda for water containing a bicarbonate alkalinity of four or five grains calcium carbonate equivalent per U. S. gallon.

The washing of milk bottles and beverage bottles involves much the same chemical and physical considerations but differs from dish-washing in the character of dirt and mechanical procedure.

Cleansing Metal Parts.

The cleansing of metal parts of machinery is commonly done by means of a warm aqueous alkaline bath. Soda ash, causticized ash, trisodium phosphate, silicate of soda and various proprietary mixtures of two or more of these alkalis are employed. Inasmuch as the dirts to be removed in this case contain lubricating oils and greases mainly of a petroleum nature which are notably difficult to emulsify in water lacking soap, an explanation of the practical success of the procedure is not obvious. It may be pointed out, however, that lubricating oils and greases may contain traces of fatty acids or calcium soaps which, reacting with the alkali, may yield sodium soaps sufficient to materially aid the emulsification.

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* The presence of some free fatty acids may give some soap, even where there is none added with the alkali. J. A.

De-inking Paper.

Industrially soda ash and caustic soda are extensively used in de-inking salvaged paper, both old news print and magazine paper. The concentration of soda ash in the water used is as low as 0.75 per cent, but the quantity used on basis of weight of paper is from 6 to 10 per cent. Inks are composed of carbon black and inert pigments of very fine particle size dispersed in an oleaginous varnish. Some are adjusted to proper viscosity with non-volatile unsaponifiable oils.

Laboratory experiments indicate that in this process soap would facilitate the dispersion of the ink,* but the cost factors seem to favor the use of the non-soap alkali. When caustic soda is substituted for soda ash the concentration of alkali is reduced so as to give the bath approximately the same pH value. For some purposes the process of de-inking is designed to distribute the ink pigments evenly through the resulting pulp rather than to wash them entirely out.

Abrasive Alkali Mixtures.

Floors covered with ceramic tiles, rubber tile or linoleum are mopped with water containing a little alkali, usually of the modified soda type in concentration around 1 to 2 per cent. The advantage claimed over the use of soapy water is in more ready rinsing and the resulting absence of a film that occurs with the use of soap.

Mixtures of abrasive material with soap powder and soda ash and other alkalis constitute a class of cleaners extensively used in the kitchen and for purposes where scrubbing rather than washing are required. Many brands of this class of cleansers are nationally advertised. They contain soap in quantities varying from one-half to 10 per cent, non-soap alkali from 5 to 15 per cent, and abrasive material from 50 to 75 per cent. A typical percentage analysis is as follows: Soap, 0.6; soda ash, 6.5; trisodium phosphate, 6.4; fine silica, 69.0; moisture and undetermined, 17.5; total 100.0.

A feature of good abrasives of this type is that the particle size is sufficiently large to be an effective scouring material against refractory dirt, and at the same time is free from coarse particles that would scratch the surface being scoured.

The abrasive varies in source as well as in preparation. Kieselguhr, ground pumice, volcanic ash, ground feldspar and ground silica are used. The better grades are sized by water elutriation. The well-known property which these abrasive materials possess of adsorbing colloidal bodies from liquids is an additional factor contributing to the effectiveness of this class of cleansers.†

The disadvantage in the use of any actually *abrasive* material is that the repeated use wears away the surface being cleaned. This is more or less noticeable in time depending of course on the hardness of the surface in question. In some instances a detergent equally effective could be used with the elimination of this disadvantage. For instance this type of cleanser is often employed to clean wash basins and bath tubs of a water line scum or film

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* Bentonite, a highly colloidal clay, has been successfully tried in de-inking paper. *See* reports of the Forest Products Laboratory, Madison, Wisconsin. J. A.

† It must not be overlooked that in scouring powders and "soaps" the added mineral, if it is sufficiently fine, may assist in deflocculating dirt, as Pickering showed. The mineral is thus an active ingredient, and no mere filler. Silica, no matter how finely ground, will scratch most things because of its great hardness. The advantages of a softer mineral and of very fine grinding of the mineral, are both obvious. J. A.

that is due largely to calcium and magnesium soaps. It has been observed that this refractory film is readily removed by wiping with a cloth dampened with kerosene, carbon-tetrachloride or other organic solvent, explainable by the fact that calcium and magnesium soaps are soluble in these solvents. The odor of organic solvents is objectionable to some people, so that many prefer to use the convenient abrasive cleanser even at a sacrifice in the life of the surface cleaned.

The film of calcium and magnesium soap also may be readily removed by wiping with a damp cloth sprinkled with dry soda ash or trisodium phosphate. The limited quantity of water in the cloth slows up the solution of the crystals, which can thus act as an abrasive as well as a source of the desired alkalinity.

Dry Cleaning.

If organic solvents were as cheap, as available, and as free from fire hazard as water, no doubt "dry cleaning" of textiles would be more extensively done, though for the maintenance of the whiteness of undyed fabric through repeated cleansing, water-washing is not to be excelled. But felting of wool with attendant shrinking seldom occurs in dry cleaning, and garments of mixed fabrics demanding different procedures may be dry cleaned unharmed. Besides this many dyes which "run" or "bleed" in water are fast to organic solvents. Dry cleaning is thus a very important adjunct to water-washing in clothes renovation.

When industrialized service is considered, dry cleaning employs procedure and equipment similar to that of laundering. One important engineering feature, however, is added, because the solvent must be reclaimed.

The garments are washed in a revolving cylinder type of washer and a plurality of baths is given after which the garments are spun in a centrifuge to remove as much liquid solvent as possible. The remaining solvent is then evaporated.

The solvent, loaded with dirt, is collected in holders, agitated with a caustic soda solution, settled, and decanted to a storage tank for re-use. After having passed this cycle several times, it is finally necessary to purify the solvent by distillation.

In the cleaning bath a so-called "dry cleaners' soap" is added to the solvent. An adequate description of the function of this "soap" has not been published as far as the writer knows.

The soap is a mixture of oleic acid with an alkaline earth oleate, usually magnesium oleate. If the qualitative function is similar to that of sodium soap in water, the quantitative effect is far less. No phenomenon similar to "suds" is produced.

Two empirical observations are offered for what they are worth: (a) the use of the dry cleaners' soap tends to minimize the fire hazard; (b) without the dry cleaners' soap, water-borne dirt is not so readily removed from the fabric.

Considering the first observation, one source of fire accidents in dry cleaning is thought to be the discharge of static electricity built up by friction of one garment against another in the solvent, which has a high dielectric constant. Data on dielectric constants * and the effect of added material in

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* *See* paper by J. Errera on "Specific Inductive Capacity" (or dielectric constant), pp. 507-14, in Vol. I of this series. J. A.

organic solvents are for the most part a matter for future research. But if we accept prevailing opinion in the trade as fact, the dry cleaning soap dissolved in gasoline must alter the dielectric constant. The obvious way to evade the fire hazard is to use a non-inflammable solvent or to reduce the inflammability by adding carbon tetrachloride as is sometimes done. Here again enters the cost factor.*

The explanation of the second function of the dry cleaning soap, that of aiding in the cleansing process, is also for the present obscure, though its utility is unquestioned. Dry cleaners and household purchasers would not continue to use it if they saw no benefit in its use. How and why it works are hard to explain.

The following observations on the behavior of oleic acid in some organic solvents may be noted. In an attempt to find a quick, convenient method for estimating the relative particle size in certain powdered materials by the rate of settling or by nephelometric methods, it was necessary to use a dispersing fluid other than water. It was found that very fine calcium carbonate, barium sulfate, and Portland cement would settle very rapidly when ten grams of the powder was shaken in 40 cc. of kerosene, benzene or carbon tetrachloride. The rapid settling was obviously due to flocculation. When 0.1 cc. of oleic acid (commercial) was added to the 40 cc. of solvent, the suspension of all but the relatively coarse particles was maintained for a longer period. In some cases a given calcium carbonate that would settle clear in three minutes from kerosene, would remain suspended for one hour when the oleic acid had been added. Since the discrete particles and the flocculated particles settled in accord with Stokes' Law, it seems that the presence of the oleic acid prevented flocculation.

Somewhat analogous to this is the fact that when putty is made of whiting and linseed oil, the presence of a fraction of a per cent of added oleic acid to the oil reduces the proportion of linseed oil required to give a certain consistency to the putty.

Another fact which should be considered in connection with the use of dry cleaning soap is that in the normal condition of textiles to be dry cleaned an appreciable quantity of hygroscopic water is present. The presence of oleic acid and calcium and magnesium oleate in the solvent facilitates the formation of a water-in-oil emulsion.

The function of the caustic soda solution in cleaning the dirty solvent for re-use is to remove the oleic acid and thereby break the emulsion, allowing the suspended dirt to settle into the aqueous layer.

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[1] *Chem. Met. Eng.*, 37, 5 (1930).
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[3] This copyrighted chart is taken from "The Conservation of Textiles," by Elledge and Wakefield, published by the Laundryowners' National Association, who have kindly granted permission to use it.
[4] Ostwald's dilution equation may be applied. Alfred Smith, *Textiles*, 5, 426-5 (1924).
[5] This procedure is reproduced here from "L.N.A. Formulas for Washroom Practice," by permission of the Laundryowners' National Association, owners of the copyright.
[6] Elledge and Isherwood, *J. Ind. Eng. Chem.*, 8, 793 (1916).
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[12] P. Herrmann, *Z. deut. Öl Fett Ind.*, 44, 361 (1924).
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* Carbon tetrachloride tends to decompose in the presence of moisture, yielding hydrochloric acid which attacks the apparatus and goods. Metal probably catalyzes the decomposition. J. A.

[14] *Trans. Chem. Soc.*, **105**, 957 (1914).

[15] Gmelin, under Natrium, p. 763-766. The system Na_2CO_3 $NaHCO_3$, H_2O.

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[17] Max Levine *et al., Ind. Eng. Chem.*, **19**, 1338 (1927). This figure differs materially from other published results, and may be a typographical error. At room temperature these three solutions all show a pH of about 12.1 colorimetrically.

PROCEDURE CHART FOR THE REMOVAL OF STAINS FROM WASH GOODS *

The methods recommended for white goods are equally effective for colored goods, PROVIDED THAT THE REAGENTS USED HAVE NO EFFECT ON THE COLOR OF THE MATERIAL.

Tests should always be made on some hidden portion of the garment before the reagent is applied to the stain.

Begin with the simplest method and work up to the more complex and drastic procedures.

Where the color is changed by perspiration, it may sometimes be restored by sponging with a weak acid or alkali.

KIND OF STAIN	COTTON	LINEN	WOOL	SILK
ALBUMIN	Removed in the standard washing process.			
BLOOD	Removed in the standard washing process. The stain of the hemoglobin will be removed in the bleach bath.		Removed in the standard washing process. The stain of hemoglobin may be removed with hydrogen dioxide solution.	
BLUEING: ULTRAMARINE	Removed in the standard washing process. If this does not remove all of the spots and specks, treatment with "sour" will decompose them.			
PRUSSIAN	Before coming into contact with an alkali, these stains will wash out in clear water. If contact with an alkali has changed the spots to ferric oxide (iron rust), a mixture of acetic and oxalic acids must be used.			
ANILINE	Many of the aniline blue stains will be removed by the standard washing process that includes a bleach bath. Stains that do not respond to this treatment will be removed by a reducing solution of sodium bisulfite and zinc dust.		Wool and silk should not be blued with aniline blues, because aniline colors dye these fibers directly. In case this type of blue has been used, the stain may be treated with a permanganate solution or with sodium bisulfite and zinc.	
COCOA AND CHOCOLATE	Removed in the standard washing process.			
COFFEE	Removed in the standard washing process.			
CREAM AND ICE CREAM	Removed in the standard washing process.			
DYE: "BLEEDING" OF MULTICOLORED FABRICS	Where a multicolored fabric (a stripe or plaid) has bled or run, and the white portion has become colored, it is sometimes possible to remove the stain from the white without affecting the color of the original pattern. Small samples of the material should be tried with javelle water, followed by oxalic acid; permanganate solution followed by oxalic acid or sodium bisulfite; or sodium bisulfite and zinc. The best method can be used on the garment.		In the case of wool and silk, the same methods that are recommended for cotton and linen may be tried, using permanganate solution followed by sodium bisulfite, and sodium bisulfite and zinc. Bleach should never be used on these fibers, but hydrogen dioxide may be substituted for it. Efforts to remedy this condition on wool and silk are not apt to be as successful as on cotton and linen.	
"BLEEDING" OF ONE COLORED GARMENT IN A LOAD OF WHITE GARMENTS	Where a load of white goods has become colored by the bleeding of a ribbon or similar piece of colored fabric, the treatment is the same as given above, with the addition of caustic soda solution for cotton and linen. The success of the treatment is more assured in this case, however. It is advised that a small, inexpensive garment be taken for purposes of determining the best method.			
HAT DYE	Soak in 95 per cent ethyl alcohol, rinse in a clean portion of alcohol and launder as usual. Slight stains remaining after this treatment may be treated as directed above.			
EGG	Removed in the standard washing process.			

PROCEDURE CHART FOR THE REMOVAL OF STAINS FROM WASH GOODS—*(Continued)*

KIND OF STAIN	COTTON	LINEN	WOOL	SILK
FRUIT	Removed in the standard washing process.		Try the following in order: Warm water, oxalic acid, acetic acid, potassium permanganate solution followed by oxalic acid or sodium bisulfite, hydrogen dioxide and sodium perborate.	
GRASS	Removed in the standard washing process.† If any traces remain they may be removed by treatment with javelle water.		Treat with a mixture of equal parts by volume of 95 per cent ethyl alcohol and ethyl ether.	
GREASE	Grease stains are usually removed in the standard washing process. If an exceedingly resistant stain is encountered, it may be softened with a mixture of lard and oleic acid (2 parts of oleic acid to 98 parts of lard, by weight) and washed again. When the oleic acid comes in contact with the soda ash in the usual bath, soap is formed, and being in such intimate association with the grease removes it readily.		Stains surviving the regular laundry process must be treated with an excess of soap by hand or with one of the organic solvents, such as gasoline, carbon tetrachloride, chloroform or ethyl ether.	
GUM OR RESIN	Use the following solvents: Turpentine, benzene, carbon tetrachloride, chloroform, 95 per cent ethyl alcohol, ethyl ether, kerosene, gasoline, carbon disulfide. The specific solvent must be determined by test, since the solubility of different gums and resins varies. The solvent for common chewing gum, or chicle, is carbon tetrachloride.			
INK: **IRON, ORDINARY WRITING**	Treat with warm acetic-oxalic acid mixture.			
ANILINE	See DYES and BLUEING (ANILINE) for the ordinary writing fluids. No remedy that is harmless to the fabric is known for the black aniline marking ink used in the laundry.			
INDIA	Removed in the standard washing process. The stain may be loosened by greasing it with lard previous to laundering.			
BLACK PRINTING	See INDIA INK.			
SILVER NITRATE	Soak in sodium thiosulfate solution until the stain disappears, or treat with javelle water till stain disappears, then soak in a weak solution of ammonia to remove the silver chloride formed. (If this precaution is omitted the stain will reappear.)		Treat the stain with potassium cyanide solution. (POISON!)	
INDELIBLE PENCIL	Removed in the standard washing process. Any traces that remain may be removed with javelle water or with potassium permanganate solution, followed by oxalic acid.		Remove the dye with 95 per cent ethyl alcohol or potassium permanganate followed by oxalic acid. The mineral matter will wash out.	
IRON	See INKS (IRON)			
LEATHER	Light stains are removed in the standard washing process. Deeper stains may be treated with javelle water.		No remedy is known which is harmless to the fabric.	
MACHINE OIL	The oily stain may be removed after the manner described under GREASE. If the stain is caused by a bearing grease, it may contain some iron or other metal, which, however, can usually be removed with the solution used for INKS (IRON).			

PROCEDURE CHART FOR THE REMOVAL OF STAINS FROM WASH GOODS—*(Continued)*

KIND OF STAIN	COTTON	LINEN	WOOL	SILK
MEDICINE: ORGANIC	Removed in the standard washing process. A very heavy stain may have to be treated with javelle water.		Stains not removed in the standard washing process must be treated with permanganate solution, followed by oxalic acid or sodium bisulfite solution.	
CONTAINING SALTS OF THE HEAVY METALS, LIKE IRON, SILVER, ETC.	Iron stains of this type may be treated as INKS (IRON). Argyrol and other silver stains may be removed by treatment with an excess of potassium cyanide solution (POISON!). This reagent converts the metal to a soluble form that can readily be washed out.			
MILDEW	Fresh, light stains are removed in the standard washing process. Old stains, however, must be treated with javelle water alternated with oxalic acid.			
MUD	Removed in the standard washing process. Occasionally there is a residual iron stain that must be treated [see INKS (IRON)].			
PAINT AND VARNISH	These stains are more easily removed if treated before being laundered. Oleic acid is rubbed into the spot, and the stain is washed with a 1 per cent solution of oleic acid in kerosene (prepared by dissolving two ounces of the fatty acid in a gallon of kerosene). Repeat the treatment with the kerosene-oleic acid solution, and wash with warm soda ash solution (6 ounces of soda ash to a gallon of water).		Use the following solvents: Turpentine, benzene, carbon tetrachloride, or chloroform.	
PERSPIRATION	If not removed in the standard washing process, treat with javelle water, or with potassium permanganate solution followed by oxalic acid.		If the stain does not wash out, use potassium permanganate solution followed by oxalic acid.	
SCORCH	Light spots will be removed in the standard washing process, but heavier spots must be specially treated. For this purpose, javelle water, alternated with oxalic acid, may be used; also potassium permanganate solution followed by sodium bisulfite.		Treatment with permanganate solution will partially restore scorched wool and silk, but a heavy scorch can never be removed.	
SYRUP	Sugar is removed in the standard washing process. Fruit syrup stains remaining after this treatment should be dealt with as described under FRUIT.			
TAR OR TARRY	See treatment for PAINT			
TEA	Tea stains are usually removed in the standard washing process.		Such stain as remains after the standard washing process may be treated with hydrogen dioxide, or with permanganate solution, followed by oxalic acid solution.	
TOBACCO: EXTRACT	If not removed in the standard washing process, either javelle water or a solution of potassium permanganate followed by oxalic acid may be used.		The substances comprising a tobacco stain are soluble in 95 per cent ethyl alcohol. Hydrogen dioxide or permanganate solution may be used on any traces that remain after treating with alcohol.	
TARRY RESIDUE FROM PIPES	See treatment for PAINT			

PROCEDURE CHART FOR THE REMOVAL OF STAINS FROM WASH GOODS—(*Continued*)

KIND OF STAIN	COTTON	LINEN	WOOL	SILK
TURMERIC	Usually removed in the standard washing process; if not, treat with javelle water or with potassium permanganate solution. This dye is one of the few permitted to be used in food by the Bureau of Chemistry's interpretation of the Pure Food Law. Some of these permitted dyes resist the action of the above reagents, but they can all be removed with amyl alcohol.		A stain which survives the standard washing process can be treated with potassium permanganate or hydrogen dioxide solution. The discussion of the other dyes used in foods, as given for cotton and linen, holds for wool and silk also.	
VASELINE	See treatment for WAX			
VERDIGRIS	Usually removed in the standard washing process. Older stains may require more drastic treatment, as, for example, with dilute hydrochloric (muriatic) acid.			
WALNUT (BLACK)	Boil in a concentrated soap solution and follow with treatment with javelle water if the gray stain persists. For old stains soak in javelle water, rinse, treat with oxalic acid, and rinse again. This treatment is not always successful.		No treatment can be recommended for wool and silk.	
WAX: PARAFFIN AND OTHER WAXES	These substances must be sponged with a suitable organic solvent (gasoline, chloroform, benzene, carbon, tetrachloride, etc.), or placed between two layers of clean, absorbent material, such as blotting paper, and pressed with a warm iron. The blotting paper removes the paraffin by capillary attraction after the heat has converted it into a fluid state.			

PREPARATION OF SOLUTIONS RECOMMENDED FOR USE ABOVE

1. **HYDROGEN DIOXIDE (hydrogen peroxide)—Use the pharmacopoeial grade, full strength.**
2. OXALIC ACID—Dissolve an ounce of the acid in a gallon of water.
3. JAVELLE WATER—Prepared as directed in the L. N. A. "Standard Formulas for Washroom Practice," Chart No. 1.
4. POTASSIUM PERMANGANATE—Dissolve an ounce of the crystals in a gallon of water. A stronger solution may "burn" the fabric.
5. SODIUM BISULFITE.—Prepare a saturated solution by adding the crystals to water till no more will dissolve. Where zinc is used in connection with it, the zinc should be in powdered form and may be added to the solution in a bag to prevent it from getting on the fabric.
6. WEAK AMMONIA—The ammonia sold by druggists is about 10 per cent solution; dilute ten times before using.
7. POTASSIUM CYANIDE—Dissolve an ounce in a gallon of water. Great care should be taken in using this solution, because of its poisonous character. After using, the solution should never be left standing about, but should be immediately thrown out and the vessel rinsed very thoroughly.

* Reproduced by permission Laundryowners' National Association, 425 First Street, LaSalle, Ill.

† Standard washing process means a recommended dosage of NaOCl, namely 1 qt. of 1% NaOCl to 60 lbs. of goods. This chart was designed for the power laundry.

The Colloid Chemistry of Washing.

By Dr. L. Zakarias.*

Contribution from Dr. L. Zakarias' Physico-chemical Research Laboratory (Prague).

If soaps are typical colloids, so is dirty linen. This plural nature of the laundry process is universally admitted. There is naturally, then, a complex interplay of fabric colloids, soil † colloids and soap colloids in washing. The physico-chemical characteristics of matter in this state of division weave the warp of detergency theory just as truly as the woof is those threads of thought which still are best expressed in the language of classical "molecular" chemistry. Few chemists think of cellulose as merely aggregated glucose, or soot as only carbon, or soap as just the alkali salts of fatty acids. Though the complexities militate against our complete understanding of the washing process, or of soap manufacture, we must develop exact measurement based on purely physico-chemical principles.

But progress toward a rational detergency theory has been meager, compared with the brilliant and economically important advances in other textile fields where many operations have for years been based on firmly established colloid chemical principles. Such rival theories of laundering as have emerged have been limited, till quite recently, by the language of classical "molecular" chemistry. This state of affairs has bred the hitherto accepted axiom, formally recognized by legislation in many countries, that the detergent value of a soap product is strictly proportional to its fatty acid content. In building soaps for particular ends it is true that chemists have recognized the rôles of lathering power, solubility, low salt content and so-called completeness of saponification. But exact methods of measurement have been sadly lacking, confining the analyst largely to fatty acid and alkali determinations. Continual effort has been made to supplement soap by other colloidal bodies aiming to raise its detergent efficiency, e.g., albumin, starch and miscellaneous mucoids. Trial has often shown real aspects of merit to such detergent aids, offset by serious disadvantages in other respects. For example, albumin may be ruled out *a priori* on account of its extreme sensitivity to heat and to dissolved salts.

Pending development of a really satisfactory theory, art has outstripped science. Practical laundrymen in the large dyehouses and commercial laundries have cast off the shackles of classical "molecular" chemistry and have substituted—with lastingly good results—soda for one-third to one-half the soap formerly required,[1] and use a wash water containing 0.25 per cent of soap-soda mixture as best for their practical purposes. This same new laundry technique has been made available to the housewife by soap powder containing soda and perborate.

Very recently, the polysaccharide "Physiol" has been recommended as a similar detergent aid. Several soap technologists have stressed its stability and its virtue in assistance toward better lathering power and increased solution rate. Practical tests have been described by Schaal,[2] Krings,[3] Popp[4] and

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* Translated by Dr. Kenneth P. Monroe, Jersey City, N. J.

† Soil here means the "dirt" that soils the linen.

the author.[5] Experimental data have been presented which should be readily verifiable; certain theoretical aspects have also been discussed.

Still other writers on detergent aids have maintained that mere soap lacks solvent power toward oily and fatty soils. To overcome this there have been recommended such soap adjuncts as cyclohexanol and its homologs, e.g., hexalin.

Soap Evaluation by Physico-chemical Methods.

Attempt was made by Bayrodt and the author [6] to use the purely scientific results of McBain, Spring, Krafft, Zsigmondy, Papaconstantinou and Leimdörfer in practical laundry problems. Clues toward physico-chemical methods for evaluating detergents were sought in particular. Effort was directed to correlate detergent efficiency with such properties as hydration, lathering power, peptization and protective colloid action. This last-named property has been emphasized, especially by the author and his coworkers, as the essential criterion of detergent efficiency. Special technique has been developed for its measurement; the resulting numerical values are termed "Congoruby numbers." Bayrodt [7] details the procedure: "The Congoruby technique is simple yet more accurate than so-called gold number methods. A 0.01 per cent solution of Congoruby * is prepared in rigorously pure distilled water. 10 cc. of this is mixed with 1 cc. protective colloid solution in each of six test-tubes. After five minutes' standing, various amounts of 10 per cent sodium chloride solution are run in from a micro-burette. The amount is varied systematically so that each tube in the series receives an increment of, say, 10 mg. NaCl over its predecessor. After 10 minutes' standing, some of the tubes usually show a definite color change from red to lilac.† For example, Tubes 1, 2 and 3 may show no or insufficient color change while Tubes 4, 5 and 6 are clearly over the endpoint. Assuming 70 mg. NaCl had been added to Tube 4 while Tube 3 had received but 60 mg., the Congoruby number is defined at 60 for the particular protective colloid solution under examination. Blank determination, omitting any protective colloid, usually shows a Congoruby number of 30 to 40, when reagents and technique are satisfactory."

Herites [8] applied this method to dilute soap solutions in distilled water and so found an optimum soap concentration at 0.25 per cent. Data in Table 1 are from this work (*see* table on opposite page).

The author [9] investigated several phases of lathering power by means of his foam-meter.[10] (See Fig. 2.) He attempted to correlate these with detergent efficiency. This work yielded experimental results which could be duplicated accurately and pointed the way to new generalizations. The following are of particular practical interest:

From the colloid chemical viewpoint, saponification may be incomplete in spite of excess alkali as indicated by the usual alcoholic titration. Soaps in aqueous solution develop optimum lathering power at 0.25 per cent concentration. The experimental results bearing on lathering power are shown in Table 2.

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* The German is Congo-rubin.

† Translator's Note: This color change follows coarsening of the colloidal dye aggregates. *Compare* Wo. Ostwald, *Kolloid-Z.*, 24, 67 (1919); *Kolloid chem. Beihefte*, 10, 179 (1918-19), and 12, 92 (1920); Lüers, *Kolloid-Z.*, 27, 123 (1920), and Haller, *ibid.*, 27, 188 (1920).

In a paper entitled "The Nature of the Combination between Fiber and Dye" [*J. Soc. Chem. Ind.*, 30, 517 (1911)], J. Alexander reported on the color changes and ultra-microscopically visible aggregation variations when Benzopurpurin was aggregated by acid in the presence of and in the absence of protective colloids, and showed that the changes of color on silk and wool resembled those in the presence of good protectors like gelatin and gum arabic, while on cotton the changes resembled those in the presence of starch, a poor protector. J. A.

TABLE 1.*—*Variation of Congoruby Number with Time and Concentration in Aqueous Solutions of Two Commercial Soaps at Room Temperature.*†

Trade Name of Soap	Soap Concentration Per Cent	Congoruby Number after Endpoint Designated in Minutes				
		5	10	Average 10	15	30
Pilnaček Ovalseife	0.25	70 70 75 70	60 60 65 60	61	55 55 60 60	55 55 60 55
	0.125	75 75 75 75	70 60 60 65	63.7	60 60 60 60	60 60 60 60
	0.0625	55 55 55 55	50 50 50 50	50	50 45 45 45	50 45 45 45
Meiszner Kernseife with Colloid Addition	0.25	80 75 80 80	80 75 80 80	78.7	80 75 75 75	60 55 55 60
	0.125	75 75 75 75	70 70 70 70	70	70 65 70 70	70 65 65 65
	0.0625	50 50 50 50	50 50 50 50	50	45 45 50 45	45 45 45 40

* Translator's Note: Herites quotes Bayrodt, *loc. cit.*, to the effect that substantially the same Congoruby number is obtained at 0.5 per cent as at 0.25 per cent soap concentration.

† Results of 4 duplicate titrations are given for each solution; in addition to the 10-minute endpoint described in the text, data are also given for 5-, 15- and 30-minute endpoints.

TABLE 2.—*Variation of Height and Bubble Number* * *of Lather with Concentration in Aqueous Solution of a Commercial Soap at Room Temperature.*†

Soap Concentration Per Cent	Cc. of Soap Solution, Converted into Lather	Lather Height mm.	Bubble Number in 9 sq. mm.	Lather Quantity Index ‡
0.5	3.1	121	81	1986
0.4	2.5	120	100	3054
0.3	2.2	112	100	4319
0.25	1.8	93	144	5259
0.2	1.4	84	144	7634
0.1	0.9	39		11030
0.05	0.5	15		15270

* Translator's Note: A 3 mm. square was cut out of a larger piece of paper; the paper was held against the tube so that the center of the square was at the midpoint of the lather column. Bubbles visible within the 9 sq. mm. were counted by aid of a lens.

† 4 cc. soap solution was shaken for 10 seconds in a cylinder 18 mm. in diameter.

‡ Lather quantity index is added by the translator who calculated it as cubic centimeters of lather obtained per gram of soap consumed. The trend of values so disclosed is not against the author's thesis that 0.25 per cent is the optimum soap concentration for washing. Practical limit to the volume of wash water necessitates considerable reserve soap to replace that consumed by soil; *quality* as well as *quantity* of lather is important.

Alkalinity was measured by Wulff's[11] foil colorimeter (see Fig. 1), a simple and reliable instrument for this purpose.

Some details of technique warrant further description: 0.25 per cent soap solution was shaken repeatedly in the foameter, froth being separated from residual solution each time until this latter had practically lost its lathering power. At this point it is reasonable to assume removal of active soap colloids.* Inspection of Table 3 shows clearly that alkalinity diminishes steadily, and that the non-lathering fatty residue finally left behind actually reacts acid. Parallel results have been obtained in commercial laundry practice, where atmospheric carbon dioxide accentuates the condition still more. The conclusion is strengthened that soaps may be, in practical effect, deficient in alkali despite 0.05 to 0.1 per cent excess caustic indicated by the usual (phenolphthalein) titration in alcoholic solution. Technologists have, therefore, operated according to sound principles in using soda as a soap adjunct.

TABLE 3.—*Lather Exhaustion Test of 0.25 Per Cent Commercial Soap Solution at 15° C.**

Cc. Soap Solution Converted into Lather	Lather Height mm.	pH	Color
1.6	95	Over 9	Deep red violet
1.5	90	7	Red violet
0.5	35	6.7	Rose
0.3	13	6.5	Faint rose cast

* The boiled soap used contained 80 per cent fatty acids. Solutions were prepared, then stood for 7 hours before testing. One drop of phenolphthalein solution was added.

Very recently the author has shown that rational methods for measuring protective colloid action must comprehend more than the usually accepted passive function of such colloids in preventing coagulation. A truly positive action toward further peptization must also be considered. From this point of view Zsigmondy's technique for evaluating soaps and other such colloids is lacking.† A truly comprehensive method must, for example, take into account the effect of pH. Thus, a 0.25 per cent soap solution had a Congoruby number 60 at pH 9, but the corresponding number at pH 6.7 was only 30. A number of neutral polysaccharide solutions of same (0.25%) concentration, on the other hand, had Congoruby numbers over the range 60 to 80. In the near neighborhood of neutrality, therefore, such polysaccharides clearly excelled the soaps.

Walter[12] applied surface tension measurements to finding optimum conditions for peptization by protective colloids. Another recent investigation in this field was made by Brauer.[13] To be sure, Krafft and Zsigmondy had already emphasized the proportionality between surface tension lowering and detergent efficiency. But these earlier workers were apparently out of touch with commercial laundry practice. Walter, on the other hand, investigated practical usage as regards soap concentration and confirmed this to the extent of finding an optimum surface tension effect in 0.25 per cent soap solutions (containing 0.12 to 0.15 per cent fatty acids).

We see, therefore, that the various methods—Congoruby number, protective colloid action, lathering power and surface tension—all agree to define 0.25 per cent as the optimum soap concentration for laundry practice, a figure

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* Soap solutions so dilute as 0.25 per cent are practically free from micelle. But there may be colloids of still finer dispersion.

† Zsigmondy showed ("Colloids and the Ultramicroscope," Eng. ed. 1909) the enormous difference between the protective action of hot and of cold sodium stearate solutions. *J. A.*

in good accordance with current empirical usage. It is quite customary for commercial laundries to employ 0.25 per cent soap solution, and to require 100 liters of such solution, with added soda, per 25 kilograms of soiled goods.

In addition to such indirect physico-chemical methods described above there are direct procedures for [14] assaying soaps such as proposed by Rhodes and Brainard. Their technique is indeed direct but it does not seem well adapted to practical ends. Test fabric is soiled as uniformly as feasible by lampblack emulsified in fat, then washed, under conditions exactly reproducible, on a laboratory wash wheel modeled after the larger wheels of commercial laundry. Measurement of remaining soil after washing showed that the optimum soap concentration lay between 0.1 and 0.25 per cent. The principal uncertainty in this method lies in the nature of the soil and its

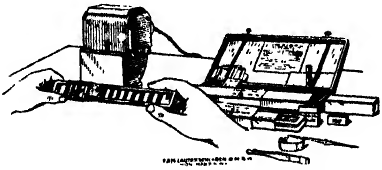

FIG. 1.—Layer colorimeter (Wulff).

FIG. 2.—Foam-meter (Zakarias).

manner of attachment to the fabric, for neither of these duplicates the normal condition of dirty laundry. True, we have here such soils as soot and dust but these are very finely dispersed in binding media which may include miscellaneous fatty substances, coagulated albumin and other misplaced food residues, not to mention a wide and varied range of epithelial discards and excreta—all more or less inter-emulsified one with the other. The laundry process is, therefore, not a mere desorption or emulsification of soot. The binding media such as fat, for example, have a firm hold on the textile which must be loosened, in some cases by actual saponification. In this process the dispersing power and protective colloid action of the soap are of prime importance. No synthetic soil yet devised duplicates the complex conditions met in actual laundry practice, so results obtained with such methods lack practical bearing. No laundryman, for example, would use the 3 to 6 per cent wash waters indicated by the technique just described.

DETERGENT AIDS.

Investigating proposed detergent aids, the author and his coworkers have used experimental methods indirectly but firmly based on physico-chemical principles. The most recent publication in this series includes data on certain organic solvents. Such solvents have been described by Krings [15] and termed, from a purely empirical standpoint, the most important class of detergent aids. But the author has shown [16] that such liquids actually lower the detergent efficiency of soap, measured by the Congoruby and foameter methods. This depressor action is due to the active soap colloids' going preferentially to the oil-water interface—thus they are used up in emulsifying the oily solvent. Such oils are, of course, not truly soluble in water to any appreciable extent. In Table 4 are presented data on the protective colloid properties of such compounded detergents.

TABLE 4.—*Congoruby Numbers of 0.25 Per Cent Aqueous Solutions of Soap-solvent Mixtures * at Room Temperature.*

Admixed Solvent	Per Cent Solvent	Congoruby Number after Endpoint Given in Minutes		Difference between Solution and Blank	
		5	10	In Congoruby Units	In Per Cent
Blank		30	30	0	0
Pure Soap			70	40	133
Methyl Hexalin	5		65	35	117
	10		65	35	117
	50		50	20	67
	100	45	40	10	33
Calmett Oil	5		60	30	100
	10		65	35	117
	50		50	20	67
	100	35	35	5	17

* Each mixture was prepared from the required amounts of 0.25 per cent commercial soap solution and 0.25 per cent uniform aqueous suspension of the particular solvent.

Percentages of solvent given are based upon the sum of soap and solvent present.

These results are confirmed amply by laundry practice, where it is known generally that such detergent mixtures have no particular virtue toward normal soiled fabric. On the other hand, they are very useful for abnormally greasy soils, e.g., goods smeared with mineral oil. Here the soap and solvent mixtures are rightly valued by practical people because otherwise such goods are washable—and then with great difficulty—only by prodigal amounts of soap.

Using the technique recently developed by the author and his coworkers, Spiske[17] found that neither sulfonated oils nor the so-called wetting-out agents raised the detergent efficiency of soap. His results are summarized in Table 5.

TABLE 5.—*Congoruby Numbers of 0.25 Per Cent Aqueous Solutions of Mixed Detergents,* Prepared from a Commercial Soap with Various Sulfonated Oils and Wetting-out Agents as Adjuncts.*

Trade Name of Adjunct	Per Cent Adjunct	Congoruby Number 10 Minute Endpoint
Blank		30–40
Pure Soap		100
Finishing Oil	10 50 100	100 80 50
Avirol A H..............	10 50 100	100 80 30–40
Neopyridit	10 50 100	90 70 40–50
Nekal B X..............	10 50 100	90 70 40–50
Laventin	10 50 100	100 80 40–50
Servirol	10 50 100	90 70 40

* Mixtures were prepared and percentages given as noted in Table 4. Measurement was at room temperature.

Experiments by Sauer[18] have demonstrated increased stability of soaps toward calcium salts when certain polysaccharides are also present. The author[19] also investigated protective colloid actions of detergents, compounded of soap with a great variety of other substances usually considered very effective protective colloids. Surprisingly enough he found many of these practically ineffective in the presence of soap. Barring "Physiol," almost none of the higher polysaccharides tested had any virtue as a soap adjunct. As a rule the polysaccharides coagulated in the soap solution, forming slimy precipitates smearing the fabric. Even "Physiol," free from this drawback, has only a very moderate positive effect in raising the protective colloid action. But "Physiol" and certain other suitable polysaccharides are rightly esteemed for their property of so modifying the precipitated calcium soaps, that these have little or no tendency to foul the goods. Such polysaccharides are used in the laundry chiefly because they tend toward a whiter wash, a superior lather and a cosmetic effect. Results are summarized in Table 6.

TABLE 6.—*Congoruby Numbers of 0.25 Per Cent Aqueous Solutions of Mixed Detergents,*[*] *Prepared from a Commercial Soap with Various Polysaccharides as Adjuncts.*

Adjunct	Per Cent Adjunct	Congoruby Number
Blank		70
Pure Soap		90
Tragacanth	20	90
Gum Arabic	20	90
Physiol A 11..............	5	95
	20	100

[*] Mixtures were prepared and percentages given as noted in Table 4. Measurement was at room temperature.

Colloid silicic acid in the water-glass of commerce (38° Baumé, empirical formula $Na_2Si_3O_7$) may be used effectively as a detergent aid. Up to 0.15 per cent in the wash water it is harmless to fabric. Silicate[19] has other important textile application, for its buffer action reduces hazards in the liquid bleach process.

WATER SOFTENING AND DETERGENCY.

The author expects to complete and publish, shortly, researches on two novel methods for testing the efficiency of detergents as water softeners. This new technique enables the analyst to test relative as well as absolute stability against calcium salts. For example, preparations of soap with organic solvents, sulfonated oils, wetting-out agents, or even soda and certain polysaccharides, cannot be classed as absolutely stable against calcium salts; all these mixed detergents yield finer or coarser precipitates with hard water. In case of certain soluble wetting-out agents and sulfonated oils, the precipitated calcium soaps are very fine grained, whence harmless as regards smearing the fabric. By the author's classification such detergents are relatively stable toward calcium salts. Certain refined polysaccharides, on the other hand, are absolutely stable because these yield no precipitates in ordinary hard water of, say, 20° to 40° on the French scale. A good preliminary estimate of any water softener may be carried out as follows: Equal amounts of hard water are mixed with regular increments of softener in a series of vessels, standard soap is then added to each up to 0.05 per cent soap concentration. The lather is then tested. The amount of water softener consumed before a good lather is obtained is taken as an inverse measure of its efficiency. In testing polysaccharides the soap concentration should be raised to 0.08 per cent because these bodies have a considerable tendency to combine with soap themselves.

Not only is it a poor protective colloid, but soap also falls short of being an economical detergent in its sensitivity to hard water. In this latter respect it compares unfavorably with "Physiol." Using the stabilized polysaccharide solution "Wasch-Physiol," of pH 10.5,* the author[20] demonstrated its virtue as a water softener as well as a detergent. 100 liters of hard water (23° French scale) was sufficiently softened by 1 kilogram of "Wasch-Physiol" that a good lather was obtained at 0.08 per cent soap concentration. Since the polysaccharide solution contained but 10 to 11 per cent solids, it follows that 0.1 per cent dry substance sufficed to soften the water. For best results the procedure used above must be adhered to, namely, the polysaccharide must *first* be added to the hard water, followed by soap after heating the softened water to 50° to 60° C.

While this work was in progress, Sieber conducted other exact tests on "Physiol" at the Forschungsinstitute für Textilindustrie in Reichenberg. He demonstrated this polysaccharide excelled soap for laundering wool, viscose and acetate silk, and that it had no harmful effect on silk, cotton and linen.

One may, of course, soften the water by such reagents as caustic soda, water-glass, soda ash and bleaching soda. But very few laundrymen do this because the calcium and iron salts are precipitated on the goods, necessitating expenditure of considerable soap to remove the stain.

Complete water-softening by special installations is out of the question because such water damages the fabrics. If, on the other hand, 6° to 7° (French scale) of hardness are left in, the precipitated calcium soaps frequently smear the fabrics worse than usual. Common laundry practice is not to soften the water completely, whether intentionally or by faulty operation of water-softening equipment.

Aside from the nuisance of precipitated calcium carbonate, the soda process of water softening takes time, which is an economic drawback of prime importance in the laundry industry. By the use of polysaccharides, softening and washing proceed simultaneously, thus saving time.

Even so, "Physiol" cannot be advanced as the ideal laundry agent. If the iron content of the raw water exceeds a certain level, yellow smudging of the fabric by precipitated iron soap occurs in spite of "Physiol" and just as when soap alone is present. In extreme cases the goods actually become progressively yellower the longer they are washed! †

But the "Physiol" laundry technique may be proofed against such occurrence by the following simple and economical precaution: Before adding "Physiol," a little lime water is poured into the warm wash water and the wash wheel is run about 2 minutes. This suffices practically to remove the iron; excess lime is taken care of by the "Physiol."

It is true that some polysaccharide solutions which are good detergent aids alter on long standing, to all appearances by the formation of insoluble precipitates. But this is illusory, for the phenomenon is really a kind of syneresis. If the apparently altered solution be shaken thoroughly the precipitate dissolves completely and the liquid regains its high viscosity.

We have now seen some of the improvements in laundry practice yielded by applying colloid chemical knowledge. These advances in technique are only typical of what has been accomplished by this same science in the more general field of modern chemical industry. As examples of what turn future progress may take the author might cite certain new detergents—recently submitted for test—proof against iron and calcium salts and which suffice for washing without any added soap.

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* The translator has not examined this product but found considerable silicate in another "Physiol" preparation of nearly the same pH in water solution.

† Such firm setting of insoluble iron soap on the fiber is a species of mordant dyeing. It may be avoided by dissolving sufficient soap for good lather *before* immersing the goods.

WASHING WITHOUT SOAP.

By continued laboratory and plant scale investigations the author has been able to adapt "Wash-Physiol" to the various requirements of laundries, dye houses and other textile processing plants. It has been possible to carry out such operations as laundering, dyeing and fulling without soap.

Good results were obtained in laundering at higher temperatures by using "Physiol" and soda. For washing woolens, silks and artificial silks at lower temperatures it was found sufficient to supplement "Physiol" with a small amount of cheap fat solvent in addition to the soda.*

The most recent results of this work simplify the hitherto very confusing and complicated situation which has existed in the field of detergents for laundry and textile operations. Costly water softeners and, indeed, the whole drudgery of water softening are unnecessary when soap is replaced by more efficient detergents. How great this advantage is may be emphasized by detailing some of the complications attending the use of soap in textile operations. If soap is used, then it is also necessary to: (1) Remove any film of wax or grease from the fiber; (2) soften the water; (3) remove iron and manganese from the water; (4) remove humic acids and suspended mud from the water; (5) exercise care not to add too much soda; (6) use good control in removing all traces of soap from the fabric by hot and cold rinsing.

In certain textile operations it is known that satisfactory results cannot follow unless efficient fat solvents are used at some stage of the process. But if one tries to simplify the operation by washing with soap and solvent together, these reagents lower each other's efficiency, sometimes completely.

Such is not the case with "Physiol," the polysaccharide detergent which the author has used to replace soap completely in practical operations with conspicuous success. Some advantages of this reagent are:

(1) "Physiol" may be used to remove films of wax or grease from the fiber.

(2) It is absolutely insensitive to hard water;

(3) Barring abnormally high iron content of the water, it removes iron and manganese. When very much iron is present, it is advantageous to supplement Physiol by the prior addition of a little milk of lime.

(4) It does not hinder the action of fat solvents, and may be used with such without lowering the efficiency of either reagent.

(5) It renders humic acids and suspended mud harmless to the fabric.

(6) It may be used together with high concentrations of soda in the wash water.

All these effects may be obtained in one operation, during washing, and the efficiency of "Physiol" is practically unaffected by hard water.

"Physiol" is a sterile polysaccharide which is unaffected by ironing, so that it is immaterial whether it is rinsed completely out of the goods or not after washing. The entire nuisance of rinsing, whether hot or tepid, is eliminated.

Accurate colorimetric measurements by the Textil-forschungsinstitute in Reichenberg have shown that test pieces of goods washed with "Physiol" are significantly whiter than pieces of the same goods washed with a well-known brand of soap flakes. Tensile strength determinations at the same Institute have also demonstrated that the strength of alkali-sensitive fabrics such as wool is surprisingly greater after washing with "Physiol" than with soap. These results are in harmony with other smaller scale laboratory experiments, some of which may be described:

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* It would not be within the scope of this article to give detailed recipes but such may be obtained from the manufacturers of Physiol, the Polydyn-Werke, G.m.b.H, in Prague, X.

Equal amounts of snow-white grained soap (Grade 1a) and of "Physiol" were dissolved in distilled water. Strips of bleached cotton fabric were immersed in both solutions, which were then boiled. The strip immersed in soap solution, and also the soap solution itself, acquired a yellowish tint. The strip immersed in "Physiol" solution emerged whiter than ever, and no discoloration of the solution was observed. Since the distilled water was absolutely free from iron or similar contaminant, it is obvious that the white soap yellowed the fabric on boiling while the polysaccharide did not.

If 2 to 10 per cent "Physiol" is added to a 5 per cent starch solution, the starch is soon hydrolyzed but causes no discoloration on ironing.

In plant scale experiments the interesting observation was made that "Physiol" wash water did not lather much at the concentration most effective for washing, but did show increased lather when approaching exhaustion. This recalls the fact that saponine produces an excellent lather but is a poor detergent. Since "Physiol" is an excellent detergent but lathers poorly, the author has revised his previous assumption that lathering is a perfectly general index of detergent efficiency. Only among soaps is this true. It cannot apply generally among all classes of detergents. The paradox is completed by the fact that soap solutions lather freely at concentrations efficient for washing but the lather becomes poor as soap becomes exhausted from the wash water. "Physiol," on the other hand, lathers poorly at concentrations efficient for washing, and only begins to lather well as the "Physiol" concentration approaches exhaustion! *

The author then turned to surface tension measurement as a possible common denominator for evaluating soaps and polysaccharide detergents. But this failed also. There finally remained only one property common to soaps and polysaccharide detergents, namely, protective colloid action. In this the soaps are inferior to the polysaccharides.

Protective Colloids in the Textile Industry.

The author has found a simple explanation for the wide-spread use of ordinary soap in the textile industry, not only for mere cleansing, but also as a wetting agent in such operations as bucking, fulling and dyeing. Obviously the soap functions partly as a protective colloid, partly as a peptizing reagent.

In bucking, the soap is solely a protective colloid since peptization of the fiber is accomplished by the caustic soda solution. The impurities removed from the fiber by bucking combine with the soap, partly to form systems of mixed colloids, partly by mere emulsification.

In fulling and felting it is necessary to swell the wool fiber in order to erect the microscopic scales which have previously lain flat on the fiber. The erected scales of one fiber then interlock with those of other fibers and the whole structure is gummed together by the peptized surface layer of protein. The reagents used in fulling, therefore, serve merely to swell the fiber. H. Arnold [21] has shown by extensive investigation that felting depends upon swelling of the fibers and that this result may be obtained by simple alkalis in the absence of soap. The so-called wetting agents have practically no utility in felting. In this operation, therefore, it is evident that soap functions merely as an alkali. But its protective colloid action may also be helpful because protective colloids have a so-called filming effect which renders the alkali less harmful to the fiber. The more efficient the protective colloid, the more

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* This may be that, as Sheppard showed with gelatin, dilution increases the degree of dispersion. J. A.

pronounced is this filming effect, which is utilized in medicine for alleviating the action of irritants.[*]

In dyeing, it is quite evident that soaps, sulfonated oils and so-called wetting agents function principally as protective colloids. These reagents peptize and form protective films around the dye particles, thus stabilizing the dye suspension which is otherwise so sensitive toward coagulants such as common salt and Glauber's salt. This uniformity of dye dispersion in the bath also causes more uniform absorption of dye by fiber, hence yields a brighter and more level dyeing.[†] In the dye bath, therefore, it is important to have protective colloids because these act as peptizing agents. Capillary activity and surface tension are of minor significance. When hard waters must be used for dyeing, much of the soap, sulfonated oil or so-called wetting agent must be consumed to soften the water.

The above examples are enough to show how soaps are used in the textile industry for their protective colloid action and their peptizing effect. The foregoing discussion also shows that, in the light of modern developments, soaps are not economical reagents for these purposes. We now know far more efficient protective colloids and peptizers, proven by practical test.

There are obvious similarities between washing, on the one hand, and dyeing, on the other. The function of protective colloids is identical in both operations: toward finer dispersion of the soil in one case and of the dye in the other. But this difference in the two processes exists: in washing there are used such crystalloids as soda, caustic soda, etc., which function as swelling agents to distend the fiber; in dyeing the crystalloids, such as common salt, Glauber's salt, etc., act as precipitating agents.

There is an old theory that soap somehow conditions textile fiber in such a way that, for example, soil is more readily removed by washing. This is incorrect. Such conditioning is principally a result of alkalinity. It should be remembered also that traces of soap left in goods after washing may give rise to fatty acids which eventually go rancid.

A THEORY OF DETERGENCY.

Progress in general detergency theory received its first impulse in the classical experiments of Spring. He first demonstrated that *merely* alkaline solutions could not peptize soot sufficiently to pass through the pores of filter paper. To attain filtrable dispersion it is necessary to have some such protective colloid as soap, to loosen the adsorptive forces between soot and cellulose. The author [22] has suggested that filtrability may only be obtained by capillary active bodies, such as tend actually to peptize the cellulose. It is futile to consider capillary activity as a mere wetting of the pores, a point of view confirmed by Norris' [23] experiments. Let us now consider this principle in its bearing on the experimental data, obtained by physico-chemical methods and presented in foregoing sections of this article. We have seen that detergent efficiency reaches a simultaneous maximum with lowering of surface tension, or, in other words, with peptizing action.

Another property which parallels these two above is protective colloid action. This is dual in nature, for it includes an active tendency toward increased dispersion as well as toward preventing coagulation. With pure soaps, testing the lathering power is a simple and effective experimental attack because lathering power parallels protective colloid action. But this method

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[*] Gums tragacanth and arabic, and marshmallow are among the *demulcents* used in pharmacy. J. A.

[†] *See* J. Alexander, "Colloid Chemistry," New York, D. van Nostrand Co., 1929, 3rd ed.

alone is inadequate toward mixed detergents containing polysaccharide as well as soap.

To harmonize these facts and theories the author submits the following:

Step (1) of washing is mere aqueous saturation of the dry soiled fabric. During this stage the textile pores, more or less clogged with soil, become distended. The soil itself includes dust and soot emulsified in colloid binding media—misplaced food residues, perspiration, etc. All this must first be wetted by the detergent solution. After wetting, the pores are enlarged and the fabric is more permeable to colloids, as the author has demonstrated by filtration experiments. Higher temperature accelerates this opening of the pores, as well as speeds up the emulsification of fatty soils; this latter effect is noticeable as low as 60° C.

Step (2) is probably formation of a new soluble complex by intermingling of detergent colloids with soil colloids. Such combination is hastened by agitation by the laundry wheel. This new colloid soon becomes uniformly and stably suspended in the wash water, serving to keep emulsified such solid or semi-solid soot and dust aggregates—of microscopic size and larger—derived from the original soil.

It is obvious that complete removal of soil—or, rather, of the colloid complex between soil and detergent—can only attend repeated rinsing with pure water. Thereby the mixed colloidal solution is diluted progressively.* This rinsing process may, indeed, be considered as a species of dialysis of the textile. The whitening of fabric which attends it may be regarded as a stripping process, just as that used in the textile industry to remove dyes adsorbed on or even chemically combined with the fiber. Soaking of the goods before actual washing may, in turn, be looked upon as a preliminary peptization period, during which the surface soil begins to react with detergent to form mixed colloid.

In conclusion, "kierboiling" of raw cotton rests upon the same principles just discussed. The raw fiber pores are clogged with dry crusts of difficultly saponifiable fat, removable only by prolonged cooking with alkali, or by solvent treatment which softens and facilitates subsequent removal, whether by emulsification or saponification. In dye-house parlance such solvents are "wetting agents" although they do not truly wet the cotton fiber. Similar function must be ascribed to the solvents and some of the so-called wetting agents used in the laundry. For these are only useful with abnormally greasy soils, especially where much unsaponifiable oil or wax is present. It is only after such removal of oily film that the usual aqueous detergents can enter the textile pores.

SUMMARY.

(1) General application of physico-chemical principles to evaluating detergents has been discussed. Bearing on this there have been detailed the rôles of: (a) protective colloid action, including protective action in the former limited sense of the word, and also positive tendency towards finer dispersion, (b) surface tension, (c) peptizing action, and, (d) in case of pure soaps, the lathering power. "Indirect" experimental methods have been developed on these bases.

(2) For pure soaps it has been demonstrated that highest detergent efficiency is obtained at 0.25 per cent concentration.

(3) The customary (phenolphthalein) alcoholic titration has been shown

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* **Translator's Note:** Better, by repeated rinsing with progressively diluted soap solutions, thereby eliminating all danger of re-coagulating the soil by dilution with water alone.

illusory as regards optimum ratio of alkali to fatty acid in soaps. Even when 0.05 to 0.1 per cent excess alkali is so indicated, the soap may be alkali deficient in practical effect, and to such an extent as to be uneconomical in laundry. More economical are the mildly alkaline mixtures of soap and soda.

(4) Merits of the following as detergent aids have been discussed and pertinent experimental data have been presented: organic solvents for fats, wetting out agents, sulfonated oils and certain polysaccharides. In general, it developed that these are of little or no value as soap adjuncts.

(5) Concerning absolute stability toward calcium salts, the conclusion was reached that this is only attained by certain detergents containing no soap but consisting of polysaccharides. Relative stability toward calcium salts was also discussed but as of secondary importance. Data were presented that, near the neutral point (pH 7), certain polysaccharide detergents clearly excel soap in protective colloid effect.

(6) The advantage was shown of certain polysaccharide detergents which soften the water simultaneously with the laundry process. It was pointed out that the usual time-consuming processes of softening water prior to washing may be so avoided.

(7) A theory of detergency was outlined briefly. According to this, important rôles are played by wetting and peptization of the soil colloids as well as of the textile colloids. It is proposed that a new colloidal complex follows the union of detergent colloid with soil colloid. This complex is assumed to be readily soluble in water and easily removed by rinsing.

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The Foam Method of Extinguishing Fire.

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Even in the early days of the oil industry it became necessary to devote some attention to the subject of extinguishing oil fires. Hand in hand with the development of the industry went an ever-increasing destruction of life and property by fire.

Water is, and perhaps always will be, the universal fire extinguisher, but it is obvious that water, when used at oil fires, except for cooling nearby tanks, is not only useless but often becomes a positive menace. The heavier water will sink below the surface of the burning oil without putting out the fire and eventually will float the oil over the sides of its container, thereby spreading the fire to adjacent property, or, if the oil has a boiling point higher than the boiling point of water, the formation of steam will cause the burning oil to "boil" over the sides of the tank in a most disastrous manner.

It soon became apparent that the proper method of coping with these fires was to provide some means for smothering them. Carbon dioxide would answer all the requirements, if it could be applied. However, free carbon dioxide alone cannot be used successfully on large open oil fires because the heat will expand the gas and dissipate it and the draft from such fires naturally carries it away. But free carbon dioxide, *trapped in minute bubbles* with strong, tenacious cell walls, may be used to form a thick smothering blanket over burning oil surfaces and over a great variety of other burning surfaces as well.

The early history of the foam method of extinguishing fires is rather obscure, but the subject is known to have been studied as early as 1900, although no successful results were obtained until several years later. The action of an acid on a carbonate, to form carbon dioxide, is usually attended with a certain amount of froth, but this is in no sense a foam stable enough to withstand being applied to a fire. Aluminum sulfate, reacting with sodium bicarbonate, will produce a much more durable bubble wall, and perhaps this is due to the colloidal nature of the aluminum hydrate formed in the reaction. But this froth, although an improvement on the acid froth, is in no wise adaptable to the extinguishment of fires. After years of patient experimental work, it was found that when aluminum sulfate and sodium bicarbonate solutions react in the presence of a suitable colloid, a foam is produced which is more or less lasting and tenacious, depending on the quantity and character of the colloid used.

It will be conceded that for this foam method to become applicable to commercial use, all of the substances used to produce the foam must be relatively inexpensive and easily obtained in almost unlimited quantities and they must be soluble in water with a minimum of sediment. The colloid must be free from a tendency to change or decompose, either in its free state or when combined with one of the solutions, and it must produce the maximum in strength and durability of bubble wall.

The aluminum sulfate and the sodium bicarbonate answer their requirements very well. The crux of the whole matter, then, lies with the colloid employed. Such materials as egg albumen, glue, glucose, gelatin, extract of soap bark, various resins and other substances of like nature have been investigated, but each one falls short of the requirements.

In 1909, a report by a United States Consul to Germany described a foam system in which the foam stabilizer used was extract of licorice root. Although the ordinary licorice products of commerce are known to possess, to a remarkable degree, the ability to produce foam, they are relatively expensive and, due to the fact that they contain starch and certain sugars, they have a tendency to ferment and decompose in the presence of much moisture. When, therefore, in 1914 experiments were conducted with a further extraction product of licorice root and this was found to have even more desirable qualities than the primary extract with none of the disadvantages, a great forward stride in the art was made.

Using approximately 3 per cent of this special extract with 8 per cent sodium bicarbonate and 89 per cent water as one solution, and a 13 per cent solution of aluminum sulfate as the other, means may be provided for the protection of large oil tank farms and refineries. The two solutions are kept in separate tanks until needed, when they are pumped simultaneously through twin lines of piping to appropriate mixing chambers on the oil tanks. Here they meet and mix and the freshly formed foam flows out over the burning oil surface. Hose stations are provided at suitable points to make the system as flexible as possible and to provide protection outside the oil tanks as well as inside. All hose lines are twin—a line for each solution—and the solutions meet and mix at a common nozzle, insuring, as in the case of the mixing chamber, that the foam produced will be subjected to a minimum of loss from friction.

An average foam system installation in the oil fields would be represented by 100,000 gallons of each solution, stored in appropriate tanks and a twin duplex horizontal steam pump capable of delivering 500 gallons of each solution per minute to suitable mixing chambers and hose stations. There are smaller systems than this in use in the oil industry and there are also much larger ones. The engineering problems involved in setting up such systems are much greater than would appear on the surface and they will not be touched upon here.

It is now known that the foam method of extinguishing fires may be applied to a great variety of risks other than those encountered in the oil industry. The 2½-gallon foam fire extinguisher and the 40-gallon portable engine have come into general use in homes, offices, institutions, public buildings and factories. Modern steamships, such as the "Majestic" and "Leviathan" and a host of others, are equipped with foam systems for protecting the oil hazard in their boiler rooms.

City fire departments are turning to the use of foam, not only for oil hazards, but for general hazards as well. This is brought about, not only because of the superior fire fighting ability of foam, but also because its use cuts down "water damage" to a surprising extent.

Colloidal Aspects of Waste Treatment.

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The following discussion will be limited to a consideration of those colloidal problems which arise in connection with "water carried wastes," namely, industrial or trade wastes and domestic sewage.

CONSTITUENTS OF SEWAGE.

Containing as it does body wastes (excreta), household wastes, community wastes (street washings, etc.) and, in manufacturing cities, the byproducts of industry, the combined waste liquor carries a very complex mixture of chemical substances. These substances may be of animal, vegetable or mineral origin. The animal or vegetable substances, "organic matter" will be found to include considerable material from all three of the principal biochemical groups, that is, the fats, carbohydrates and proteins as well as many decomposition products of the members of these groups. The mineral or inorganic constituents include sand and clay as well as the common mineral salts found in the water supplies. They may also include acids, alkalis, and salts in high concentrations as a result of the discharge of such substances from manufacturing plants.

Not only is there a wide difference between the composition of sewages from different communities but there is great variation in the composition of sewage from a given city. The laboratory assay of sewage is a difficult matter. A large number of samples must be taken at different times for examination and the results interpreted with care.

The living organisms in sewage are naturally limited to unicellular forms, i.e., bacteria and protozoa, although spores and cysts of various higher forms are present. In this group the variety of organisms is almost as great as the variety of chemical substances present. The presence of acids, alkalis or certain salts from manufacturing wastes may produce a practically sterile sewage. Domestic sewage will contain large numbers of intestinal organisms. And wastes from the so-called "fermentation industries," a very wide group, including some dairying processes, some tanning processes, commercial solvents, etc., will each carry characteristic fauna and flora.

The object of sewage treatment is primarily to prevent nuisance rather than to control disease. The prevention of disease can only be accomplished by disinfection and, as was stated in the discussion of water purification, the most economical point for the application of the disinfectant is in the water treatment plant rather than in the sewage treatment plant. If the organic matter of the liquor is reduced to a sufficiently low concentration so that it will not cause a nuisance the matter of disinfection can easily be accomplished by chlorination.

Nuisance results from the putrefactive decomposition of organic matter.

This decomposition produces substances which quickly consume the dissolved oxygen in the water, after which hydrogen sulfide, mercaptans and many other foul-smelling compounds are observed.

The depletion of oxygen causes the death by suffocation of practically all of the higher animals such as fish. The consumption of oxygen by sewage is called the "biochemical oxygen demand" and may be determined in the laboratory by diluting the sewage with a known amount of aerated pure water of known oxygen content and determining the oxygen consumed during the incubation of the diluted sewage for a definite time at a definite temperature.

Besides the depletion of oxygen by putrefaction or biochemical action purely chemical reactions may occur which consume oxygen, for example, oxidation of ferrous sulfate from pickle liquors or sulfite from pulp mills. When such substances are discharged into streams they are frequently more harmful to aquatic life than organic wastes, partly because the consumption of oxygen is very rapid and partly because they frequently cause an increase in acidity.

While the most important characteristic of a sewage or waste liquor is its oxygen-consuming power, more data are available in the literature on the amount and character of nitrogenous compounds in wastes than on their oxygen demand.

The total amount of organic matter in sewage is surprisingly small. It seldom amounts to more than 500 mg. per liter and is usually about half that amount. A few industrial wastes will exceed these values.

Approximately one-third of the impurities in water-carried wastes are of such a size and specific gravity that they will settle readily in a quiescent tank within one and one-half to two hours. The remaining two-thirds are in a colloidal state of dispersion and must be removed by some one of several more or less complicated processes involving a variety of colloidal reactions.

In the following pages we shall first present an outline of these processes and then discuss some of the more important colloid problems in detail.

METHODS OF DISPOSAL.

Dilution. It is obvious that if any material is uniformly dispersed in a sufficiently large amount of some neutral substance it will apparently disappear as far as ordinary methods of observation are able to discern. The amount of dilution necessary depends therefore on the accuracy of the observational methods employed. If the organic matter does not reduce the dissolved oxygen below the requirement of normal aquatic life, disposal by dilution may be considered successful from that standpoint.

It is just as essential that the matter carried by the sewage be uniformly dispersed, as that the amount of diluting water be sufficient. Otherwise there will be local accumulations of sludge which will putrefy and cause nuisance, and masses of unsightly floating solids will also be observable. There are few cases where coarse screens can be dispensed with and in most instances fine screens or sedimentation should be used prior to dilution. The consensus of opinion appears to be that where a flow of less than 2,000 to 3,000 gallons per capita per day is available for dilution, foul conditions are sure to result, and that where the flow is more than 6,000 to 8,000 gallons per capita per day no nuisance results except from large floating objects and the formation of sludge banks.

BROAD IRRIGATION OR SEWAGE FARMING.

Broad irrigation or sewage farming has been rather extensively used in Europe and to some extent in this country in districts with low rainfall. The waste liquid from which the settleable solids have been removed is distributed over a given area of land by means of ditches and allowed to seep away. The colloids are adsorbed on the soil particles. Where the soil is not of an open texture, the land is tilled. It is not possible to dose any one area continuously, several areas are dosed in rotation. The land is cultivated during the proper season of the year, thus taking advantage of the small manurial value of the sewage. In arid regions the sewage is of advantage for the water it furnishes. The area required is frequently larger than the area of the city served, and irrigation is practically limited to communities where large areas of sandy soil are available.

FISH PONDS.

Under proper biological control it is possible to dispose of sewage by running it into fish ponds. The process is by no means as simple as it might appear. The fish do not take up the organic matter directly but feed upon the smaller aquatic life whose growth is stimulated by the sewage. It is a case of "big bugs have little bugs upon their back to bite 'em," etc.* The proper relation between the various plants and animals must be maintained or the whole cycle will break down. The care required to maintain these fish ponds is so great that they would perhaps better be classified with artificial means of treatment. The area required is even greater than is necessary for broad irrigation.

ARTIFICIAL TREATMENT.

The completeness of the treatment necessary for any given installation depends so much on local conditions and requirements, especially on such factors as the strength of the sewage and the volume of the body of water into which the effluent is to be discharged, that generalized statements regarding it cannot be made. A great variety of treatment devices are in use ranging in effectiveness from coarse bar screens which remove only large floating debris, to elaborate works turning out an effluent which would meet the drinking water standard so far as appearance and dangerous bacteria are concerned. A rather generalized and somewhat idealized flow sheet for complete treatment is given in Figure 1.

The raw sewage passes first through screens made of bars spaced three-fourths of an inch or more apart. The bar screens are used primarily to catch pieces of boards and other large objects which would clog the channels or damage the pumps. They ordinarily catch a considerable amount of finer material in addition, such as paper, vegetable peeling and some feces. The amount of organic matter in these screenings is sufficiently large so that it cannot be spread out on the ground without breeding flies and causing a nuisance. It may be buried or composted or digested with the settleable solids if tank treatment is used.

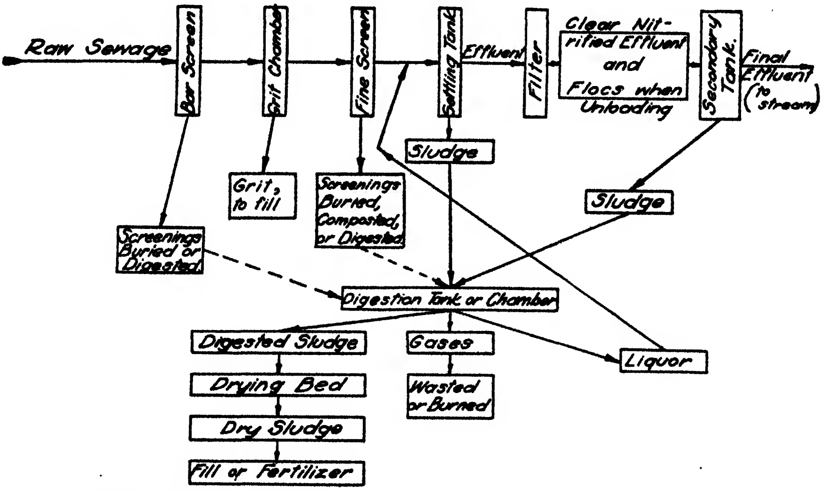
*** This comparison was put into verse by Jonathan Swift as follows:**

"So, Nat'ralists observe, a Flea
Hath smaller Fleas that on him prey.
And these have smaller Fleas to bite 'em,
And so proceed *ad infinitum.*"

(From "On Poetry: a Rhapsody," printed 1773.) J. A.

The sewage next passes to the grit chamber where the velocity is decreased by increasing the cross section of the channel so that coarse, heavy particles settle out. With a velocity of about 1 foot per second, gravel, cinders and similar matter will be deposited, below this velocity coarser particles of organic matter will also be deposited. The proper adjustment of the velocity yields a sediment containing so little organic matter that it can be used for grading or fill without the danger of odors or nuisance.

From the grit chamber the sewage may be passed through "fine screens" or it may pass directly to the sedimentation tanks. Fine screens usually have openings of one-quarter inch or less and are mechanically operated so that the screenings are continuously removed and the openings kept clear. If the sewage contains a large amount of coarse floating matter such as vegetable hulls, matches, etc., screens will be found especially useful. They remove particles which would not settle out in the sedimentation tanks but which would produce scum and also clog the filter nozzles. In some cases where the available dilution is sufficiently large, screening may be sufficient treatment.



Courtesy Chemical Catalog Co., Inc.

FIG. 1.

The screenings are largely organic in nature and unless disposed of promptly will become very offensive. They may be drained and hauled away and buried or plowed into the soil, or the screenings may be mixed with the digesting sludge in the sedimentation tank and reduced with them.

The next step in the purification is sedimentation. This may be accomplished either with or without the aid of chemical coagulants and in tanks of various designs. The use of chemical coagulants, usually lime, lime with ferrous sulfate, or alum, is advantageous in certain trade wastes. For domestic sewage it does not appear to be regarded with favor at the present time because of the large amount of sludge which must be disposed of.

Horizontal flow sedimentation tanks are usually built from 6 to 10 feet deep, of such width that the velocity of flow will be less than the critical settling velocity of the settleable solids and of a total capacity to give the necessary detention period for sedimentation. They may be built deeper at the inlet end where the heaviest accumulation of sludge occurs and where the sludge is drawn off, or the bottoms may be built hopper-shaped to facilitate sludge removal. When the plant is designed for separate digestion the sludge must be removed when fresh, every day or every few days, to avoid a nuisance.

Recently the use of mechanical devices to thicken and remove the fresh sludge has become very popular. They may be installed in either circular or rectangular tanks. Since they are automatic and continuous in their action they overcome the principal objection to plain sedimentation tanks, namely, the disagreeable laboriousness of removing the sludge from the sedimentation tank to the digestion tank. These mechanical thickeners also produce a sludge of lower moisture content than is obtained simply by sedimentation. Expensive steep sloping bottoms are not necessary in settling tanks equipped with such devices.

Septic tanks are designed with sufficient capacity to allow the accumulation and digestion of the sludge to take place in the sedimentation chamber. Septic tank sludge is not removed until "ripe" or digested. The effluent from a septic tank is fouled by the products of the anaerobic digestion of the sludge.

It will be noted that the sludge produced in all of the above tanks, except in the septic tank, is removed while still fresh and allowed to digest in a separate compartment.

The labor of handling the sludge and the disturbing effect of sludge digestion on sedimentation are both avoided by the use of *two-story tanks.* These tanks are built with the sedimentation chamber over the sludge digestion chamber and communicating with the latter by means of a slot. The bottom of the sedimentation chamber is sloped toward the slot so that the sludge slides down into the digestion chamber below. The Travis tank was originally designed so that a portion (one-fourth to one-tenth) of the fresh sewage passed into the digestion chamber displacing the septic liquor which was discharged with the effluent from the sedimentation tank. This design has not been adopted in this country. Dr. Karl Imhoff of the Ruhrverband has designed a two-story tank commonly called the Imhoff or Emscher tank. The general construction is similar to the Travis tank but there is no outlet to the digestion chamber except for the drawing off of sludge and hence no flow of fresh sewage through the digestion chamber. The slots at the bottom of the sedimentation chamber are baffled to prevent gaseous products of digestion from rising through the sedimentation chamber, thereby fouling the liquor and disturbing sedimentation. These tanks are usually built rather deep (25 feet or more) for the purpose of improving the quality of the sludge.

Sedimentation, if at all successfully carried out, removes from 25 to 40 per cent of the organic matter from the sewage, the effluent being milky and colloidal but free from settleable suspended matter.

If the body of water into which the sewage is to be discharged is not large enough to receive the settled effluent without damage, it may be further purified by so-called *"filtration."* The results are obtained by contact of the colloidal liquid with microbial growths on the surface of the material of which the "filters" are made rather than by true filtration. The contact material may be gravel, crushed rock, clinker, coke, brush, etc. Where gravel, rock, clinker or coke is used it is usually screened to a fairly uniform size. The various sizes used range from quarter to half inch up to 2 or 3-inch or even larger. The finer material furnishes more surface per cubic foot but becomes clogged more readily and therefore requires more care.

The material is arranged in beds from 5 to 10 feet deep and is dosed from the top by means of troughs or sprinklers. The sprinkler is more commonly used, whence the name "sprinkling filter" which is generally applied to filters of this type. The dosage is intermittent, the cycle being determined by local conditions. The organic matter in the tank effluent, which is largely colloidal, is almost completely removed in its passage through the filters, part of it being precipitated in the microbial jelly which soon collects on the surfaces and part oxidized to carbon dioxide and nitrate. The effluent from the filters should be perfectly clear except for flocs of the microbial growth which break off and pass out of the filter. At times, especially in the spring and fall, this breaking off of flocs, called "unloading," is very extensive. These flocs settle readily and if desired may be removed in a "secondary" sedimentation tank. The effluent from the final tank should be clear and stable, that is, it should contain sufficient oxygen dissolved or as nitrate to oxidize any remaining organic matter.

If the treated liquor is to be discharged near a bathing beach or a water supply it may be disinfected with chlorine.

"Intermittent sand filters" operate much as do trickling or sprinkling filters. Because of the very fine grained material the top layer of sand must be cleaned frequently to prevent clogging. For the same reason they must be dosed at a relatively low rate so that they are practically limited to relatively small installations. When properly operated sand filters turn out a very high quality effluent.

The settled solids as already indicated are allowed to undergo a *digestive* or *rotting* process by which the less stable compounds are liquefied and decomposed. This action is brought about by various microorganisms commonly present in the sludge. The principal final products of this reaction are gases, notably carbon dioxide and methane, dissolved substances, and a black humus residue which has an earthy or tarry odor. This residue, the digested sludge, as drawn from the tanks carries 5 to 10 times its weight of water and is run out onto sand beds where the water readily drains away leaving an inoffensive residue of an earthy consistency. This material may be used for fill or for enriching poor soil.

The activated sludge process may be substituted for sprinkling filters or for both sedimentation and filters. Activated sludge consists of flocs of microbial growth similar to that which is found on filter stone. This floc may be built up by blowing air through the sewage for a time, allowing it to settle decanting and feeding with fresh sewage. In large plants operated on a continuous flow plan the sewage from the screens or from sedimentation tanks passes into an aeration chamber, where it meets a predetermined amount of activated sludge from the sedimentation of previously treated sewage and is stirred by compressed air introduced through porous plates, or by mechanical aeration devices. The floc as it comes in contact with the liquor under aerobic conditions acts much as it does in filters, taking up colloidal organic matter, part of which is used in the growth of the floc and part oxidized to carbon dioxide and nitrate. After the necessary aeration period (roughly two to six hours) the liquor passes to sedimentation tanks where the sludge settles and the clear liquor is discharged. The required amount of sludge is returned to the aeration chambers and the remainder is digested or pressed for fertilizer.

The area required for an activated sludge plant depends upon local factors, but is much less than that required for tanks and filters (1/10 to 1/15). The first cost is also less but the operation cost is much higher.

A well-operated activated sludge plant should give a somewhat better effluent than is obtained from trickling filters.

Summary of Sewage Disposal Methods.

The various means of sewage disposal are summarized in the following outline, which is given in a more abbreviated form in Figure 1.

Sewage Disposal Methods [1]

- A. Without Treatment
  - 1. Irrigation
  - 2. Dilution
- B. With Treatment
  - 1. Separation of solids and liquids
    - a. Coarse solids by racks
    - b. Floating and coarse suspended solids by screens, scum boards or skimming chambers.
    - c. Grit, by grit chamber
    - d. Settleable solids, by tanks
    - e. Suspended solids, by
      - (1) Sedimentation
      - (2) Chemical precipitation
      - (3) Flotation
      - (4) Centrifuging
      - (5) Sand filtration
    - f. Colloids by precipitation or filtration
  - 2. Treatment of liquid
    - a. Oxidation (Note: Some possible exceptions to this classification have been noted by the authors)
      - (1) Dilution
      - (2) Irrigation
      - (3) Sand filtration
      - (4) Contact bed
      - (5) Sprinkling filter
      - (6) Activation
      - (7) Miles acid process
    - b. Disinfection
      - (1) Liquid chlorine
      - (2) Bleach
    - c. Sterilization
      - (1) Heat
      - (2) Chemicals
  - 3. Disposal of effluent
    - a. Irrigation
    - b. Dilution
  - 4. Treatment of solids
    - a. Screenings and scum
      - (1) Burying
      - (2) Burning
      - (3) Composting
    - b. Grit—used as filling
    - c. Sludge
      - (1) Removed undigested as liquid
        - (a) Covered in furrows
        - (b) Lagooned
        - (c) Dumped at sea
      - (2) Digested
        - (a) In full stream of sewage, septic tank, biolytic tank.
        - (b) In small amount of sewage, Travis tank.
        - (c) Without sewage, Imhoff tank, separate digestion.
      - (3) Removed, digested as liquid
        - (a) Covered in furrows
        - (b) Sprayed in fertilizer
        - (c) Lagooned
        - (d) Dumped at sea
      - (4) Concentrated (either digested or undigested).
        - (a) Sedimentation and decantation.
        - (b) Mechanical thickeners.
      - (5) Removed, concentrated as a liquid, then
        - (a) If undigested, treated as (1) or digested separately as in (2)c above
        - (b) If digested, treated in (3) above or dewatered as in (6) below
      - (6) De-watered to spadable condition
        - (a) Sand beds, draining and evaporation
        - (b) Pressing
        - (c) Centrifuging
        - (d) Exhausting Oliver filter
        - (e) Wringing, between rollers
      - (7) Removed as cake or in spadable condition
        - (a) Dumped at sea
        - (b) Used as filling
        - (c) Used as fertilizer
        - (d) Mixed with fuel and burned
      - (8) Dried in a kiln by heat
        - (a) Used as fertilizer
        - (b) Used as fertilizer base

Removal of Colloids from Sewage.

The effluent from a well-designed settling tank still carries sixty-five per cent or more of the putrescible matter with it. This organic matter is largely in a colloidal state of dispersion although some is in true solution and a small amount in suspension. A further coagulation and clarification occurs when this liquor is held for a week or more, but the improvement is not sufficient to warrant such treatment. Alum or copperas as coagulants are effective, but produce a large amount of objectionable sludge. It was early recognized that the colloids could be quickly and effectively removed by means of contact surfaces if aerobic conditions were maintained to a sufficient degree.

TYPES OF CONTACT SURFACES.

An outline or suggested classification of the various types of contact surfaces is given in the accompanying outline.

Contact Surfaces.
- Fixed
  - In the air (elevated)
    - "Filters" (sprinkling, contact, etc.)
    - Aerated filters
      - Basiakine's
      - Slate aerators,
      - etc.
  - In water (not elevated)
    - Colloiders
    - Slate beds
    - Tauchkorper (aerated)
- Movable (not elevated)
  - Intermittent motions
    - Nidus racks
  - Continuous motion
    - Activated sludge
    - Drehkorper

The slow sand filters, earth filters and sewage farms were the earlier developments. Their action is more nearly true filtration. The coarser grained types of surfaces are of more recent development. Several of the types listed in the classification have not passed the experimental stage. The sprinkling filters and contact beds are widely used and there are a large number of activated sludge plants in use. The Travis colloiders have been installed in a number of tanks and there are now fifteen installations of Imhoff's Tauchkorper (contact aerators) in use in Germany. Imhoff[2] points out that there is a loss of head through all those types in which the active surfaces are exposed to the atmosphere, while this is not the case with immersed surfaces like activated sludge, Tauchkorper, etc.

The effect of these contact surfaces is to remove the colloidal organic matter, leaving a practically clear liquid. At the same time a certain amount of oxidation occurs, as the result of which carbon dioxide and nitrates are formed.

Two opposing theories have been suggested for the explanation of the reactions taking place during the removal of colloids by contact surfaces. One might be called the Physicochemical theory of Travis—the Hampton Doctrine—and the other the Biochemical theory of Dunbar. Ardern[3] summarized these two theories as follows:

The earliest theory advanced with respect to the mechanism of the purification changes effected by the "filtration" of "sewage" was based on the work carried out at the Lawrence Experimental Station, Mass., in respect to the development of the intermittent sand filters as advocated by Frankland, as a practical means of sewage purification.

According to this theory, the suspended solids applied with the sewage or tank effluent are arrested mechanically in the filter by virtue of its fine pores, and subsequently oxidized, and the organic matter in solution is directly oxidized and mineralized by bacterial agency during the course of its passage through the filter, with the accumulation within the filter of small quantities of "humus" which is very resistant to further fermentation. Presumably colloids are included in the organic matters in solution, although they were not referred to specifically.

This simple representation of the purification process received almost universal support, notably by Stoddart as late as 1909.

Dunbar assumed that it was not possible to bring about the complete oxidation of the complex organic matter present in solution in sewage during the short period of time taken by the liquid in passing through the filter, and as the result of a series of experiments extending over a considerable period (1897-1900) carried out by him and his colleagues at the Hamburg Hygienic Institute (*vide* "Principles of Sewage Treatment"), he advanced what is known as the "absorption theory" of sewage purification.

For a full discussion of the difference between the theory of preliminary absorption of colloidal matter and of its direct coagulation and deposition in the filter, the reader is referred to a paper presented by Travis to the meeting of the Association of Managers of Sewage Disposal Works at Leicester, (July 4th, 1908), which appeared in the July 10th, 1908, issue of the *Surveyor*, and the discussion thereon which ensued between the author and Lubbett, of the Hamburg Hygienic Institute.

The evidence available with respect to the mechanism of the removal from sewage of organic matter in pseudo-solution may be summarized thus:

(I) The experiments of Stoddart designed to show its direct oxidation by bacterial agency cannot be considered conclusive. On the other hand it has not been demonstrated that under the favorable conditions present in an efficient filter, in which the sewage passes in thin films over a net work of media covered with an active bacterial slime, the mean time of passage is insufficient to allow of direct biolytical oxidation of some portions of the organic matter in pseudo-solution.

(II) While it is accepted that sewage colloids may be precipitated or coagulated by intimate surface contact, this desolution theory can scarcely represent the whole phenomena of colloid removal otherwise such action would continue in the absence of microorganisms.

Mention may be made of Dunbar's experiment in which a solution of albumin containing nitrogen equivalent to the organic nitrogen content of an average sewage was applied to a mature filter, with the result that almost quantitative oxidation of the sulfur was obtained, while 58 per cent of the total nitrogen appeared in the filter, 10 per cent as ammonia, 20 per cent as nitrate and 25 per cent as organic nitrogen. Thus 42 per cent of the nitrogen disappeared either in the gaseous form or accumulated in the "humus." A considerable part of the carbon of the albumin also disappeared as gaseous carbonic acid, but a part also went to form the "humus" which accumulated in the filters.

Chemical analyses of the affluent and effluent reveal still greater differences in the character of each. The affluent shows relatively large amounts of free ammonia and albuminoid nitrogen, organic nitrogen, and "oxygen consumed." Nitrates, nitrites and dissolved oxygen are present in very small amounts, if at all. On the other hand, the settled filter effluent is low in free ammonia and albuminoid nitrogen, organic nitrogen and "oxygen consumed." Nitrates, nitrites and dissolved oxygen are present in fairly large amounts. These conditions give to the effluent its "stability," or freedom from putrefactive decomposition.

Mumford[4] explains the mechanism of nitrification by the oxidation of ammonium salts in several stages. Hydrogen atoms are successively hydroxylated, with the subsequent elimination of water from the molecule. In support of this theory, she has found hydroxylamine salts and salts of hyponitrous and nitrous acid in the reaction mixture during such an oxidation.

Clark and Adams [5] have shown that nitrification ceases when the carbon to nitrogen ratio in the sewage becomes too great. Good purification and production of a satisfactory effluent can be secured, nevertheless, if the filter is gradually accustomed to such sewage by the application of increasingly larger doses.

In the light of recent developments in the field of colloid chemistry, it is felt that certain of the phenomena in the purification process can be explained on a more rational basis. The correct interpretation of the phenomenon of adsorption will undoubtedly throw much light on the mechanism of purification, and as W. C. McC. Lewis says, "There can be no doubt that more complete information of this purely physical phenomenon is the first step toward a rational understanding of the more complicated phenomena of the dye-house and the filter-bed." It is believed that such indefinite terms as "enormous pressures" and "adsorption" used by Dunbar, and such vague terms as "desolution" and "physical forces" used by Travis can be replaced by a more exact analysis of the fundamental principles underlying the whole process of purification.

As postulated in the older theories, coarse suspended solids are arrested and held by the slimy bacterial film. Such action is attributed to the gelatinous nature of this growth and to the formation of fine pores by adjacent films, through which large particles cannot pass. However, the growth which accumulates in a mature filter is characterized by an extremely large surface area, and hence exhibits, to a maximum degree, the surface phenomenon of adsorption.

Gibbs[6] has determined from thermodynamic considerations, that, when a change in surface tension takes place due to the formation of a solution, a change in concentration also occurs, the surface film having a different concentration from the main portion of the solution. Film concentrations tend to change so as to decrease surface tension. In other words, if a solute increases the surface tension of the solution, the film will be more dilute than the main portion of the solution; if it decreases the surface tension, then the solute will concentrate in the surface film. The rule is expressed mathematically by the equation: *

$$C = -\frac{c}{RT} \cdot \frac{ds}{dc}$$

Thus, when the surface tension decreases with increasing concentration of solute, $\frac{(ds)}{(dc)}$, the concentration of solute, (C), in the surface layer is positive and hence greater than in the main body of the solution.

Most salts and all strong bases increase the surface tension of water; but ammonia and nitric and hydrochloric acids decrease it.[7] Gibbs' rule applies only to substances in true solution, but a similar phenomenon has been found to occur in colloidal solutions. Many substances like soaps and proteins form colloidal solutions which have lower surface tensions than pure water.[8] Ramsden [9] found such substances to concentrate in the surface film. Our interest in these substances arises from the fact that such organic material must be removed from sewage in order to destroy its putrescibility. It has been shown by Willows and Hatschek [10] that surface concentrations of such colloids

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* This simplified form of the Gibbs equation is true in a qualitative sense only.

as Congo red, methyl orange, etc., are 20 to 100 times as great as those calculated from the formula. No expression has been derived to cover the behavior of colloids in this respect.

In sewage, we have colloidal soaps and proteins which tend to concentrate in a surface film as pointed out above. This need not be only the air-liquid interface, but can be the interface between the bacterial jelly and the sewage. For example, Donnan and Lewis,[11] in using oil drops to measure surface concentrations of colloids, obtained some results which showed large discrepancies from the calculated figures. They ascribed this to colloidal gelatinization or flocculation on the oil surface and stated that it may be regarded as excessive adsorption due to the marked lowering of the surface tension, resulting in the overstepping of the solubility of the solute and the consequent flocculation on the surface layer.

The substances which concentrate at the jelly-sewage interface are attacked by the bacterial and biological life of the jelly. As rapidly as these substances are removed by digestion, others come to the interface until the surface tension is reduced to its previous value. Thus a dynamic equilibrium is maintained between the removal of organic matter from the interface by digestion, and the addition of more organic matter to the interface by virtue of surface tension lowering.

Soluble products, such as ammonia, which lower the surface tension of water, obey Gibbs' rule closely and therefore concentrate at the interface. Because of their solubility, they may also be removed by direct preferential absorption into the living cells present in the jelly.

The bacterial film or jelly always contains dissolved and probably adsorbed oxygen, obtained chiefly from the air drawn into the bed, but to some extent from that dissolved in the incoming sewage. In the presence of oxygen, bacterial and biological agencies decompose the organic matter with the final production of nitrate, carbon dioxide and a humus-like residue. It is certain that enzymes play an important part, at least in the initial states of the decomposition ot proteins.[12] Nitrates raise the surface tension of water and are therefore driven away from the interface into the main body of the liquid and thus pass out of the filter. The humus remains on the stones and materially increases the effective surface. Salts like sodium chloride pass directly through without being adsorbed, since they raise the surface tension of water and do not concentrate at the interface. The fallacy of using sodium chloride to determine the detention period of organic matter in a filter is obvious.

The ammonia originally adsorbed from the sewage, together with that formed in the decomposition of protein by bacterial activity, may undergo at least one of several fates. It may be used in the formation of living protoplasm by bacterial cells; it may be oxidized to nitrates by bacteria in order to meet energy requirements; it may be oxidized by organized or unorganized catalysts. When the adsorbed ammonia and oxygen meet on the film, we have conditions similar to those existing in the oxidation of organic substances in the presence of a catalyst possessing enormous surface area. It is not unreasonable, then, to postulate the catalytic oxidation of ammonia on the bacterial film. Since the amount of nitrate in the filter effluent represents only about 50 per cent of the ammonia in the sewage, it is evident that the difference between the sum of the nitrate and ammonia in the effluent and the ammonia in the sewage must be accounted for by some other reactions.

That there is a need for intermittency in dosing a filter is shown by the following considerations. Particles of organic matter concentrated at the interface of the jelly and sewage are liquefied by enzymes. They are then taken into the living cells at a rate dependent upon the utilization of these substances inside the cell. Since the predominant reactions in a filter are oxidations, this utilization depends largely upon the amount of oxygen available for this purpose. Thus the absolute amount of oxygen available, as well as the oxidation potential, regulates the oxidation of substances in the cell. This, in turn, regulates the rate of entry of organic molecules into the cells. Finally, dependent on this rate, is the rate of concentration at the interface. Hence the more oxygen available, the more colloids can be concentrated at the interface, dissolved, diffused into the cell and finally oxidized.

Since one liter of saturated water at 20° C. contains about eight milligrams of dissolved oxygen, and one liter of air contains 250 milligrams of oxygen, it can be seen that a given quantity of air in contact with the bacterial jelly contains thirty-one times as much available oxygen as the same quantity of saturated water or sewage. Furthermore, as it is being dissolved or adsorbed by the jelly, the diffusion of more oxygen molecules to the jelly is far more rapid through air than through sewage, since diffusion rates depend largely upon the viscosity of the media. If a continuous flow of sewage is allowed to trickle over the jelly, the necessary oxygen must come from that dissolved in the sewage. The intermittent sand filter is a very good illustration of the fact that there is not enough oxygen in solution in sewage to permit purification. We have secured some data which point to the same conclusion.

On the other hand, when intermittent dosing is employed, air is drawn into the bed to replace the receding sewage. With the far greater amount of oxygen thus introduced, and the higher rate of diffusion to the jelly, the necessary oxygen is rapidly absorbed. The activated sludge process illustrates the fact that as more oxygen is furnished the amount of nitrification increases.

The current conception of the mechanism of the purification process may be summed up briefly:

1. Colloidal and soluble substances which lower the surface tension of water concentrate at the jelly-sewage interface.
2. These adsorbed substances are attacked by enzymes, bacteria and higher forms of animal life and the ammonia thus liberated is subsequently oxidized by bacterial or chemical means.
3. A flocculent, humus-like residue of large surface area accumulates in the filter until the periodic unloadings.
4. Since sufficient oxygen for the reactions cannot be obtained from that dissolved in the liquor, it is necessary to operate the beds intermittently and allow atmospheric oxygen to come in contact with the bacterial film.
5. The application to the purification process of the law of mass action and its analogy to adsorption and several biological phenomena leads to the conclusion that the bulk* of the purification is effected in the upper part of the filter where the sewage is most concentrated.

REMOVAL OF COLLOIDS FROM SEWAGE BY ACTIVATED SLUDGE.**

In the "activated sludge" process the removal and partial oxidation of colloids are accomplished by a biological jelly as is the case in sprinkling filters. Although the chemical and colloidal reactions are about the same in both cases, the mechanical steps differ widely. The "activated sludge" consists of gel-like flocs of material similar to that which collects on the "filter" stones. The sewage and sludge are aerated together in tanks provided with air diffusers or

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* Although obviously incorrect, current practice in filter design is to assume that the purification accomplished, plotted against depth, gives a straight line.

** See also "The Activated Sludge Process" by Arthur J. Martin (London: Macdonald and Evans).

mechanical agitators. When purification is complete the sludge is allowed to settle from the clarified liquor. The liquor is sufficiently pure or stable to be discharged and the sludge is used in part to maintain the process. The remainder may be dried for fertilizer or subjected to an aerobic stabilization. The voluminous literature on this subject has been ably summarized by Martin (*loc. cit.*) and more briefly by Buswell (*loc. cit.*).

In reviewing the opinions of experimenters with regard to the theory underlying the activated sludge process of sewage disposal, one soon comes to the conclusion that two main lines of action are held responsible for the results obtained. The mechanism of the reaction is sometimes described as that of adsorption of the colloidally dispersed matter by sludge already present in the sewage, for example:

> "The sludge embodied in sewage and consisting of suspended organic solids, including those of a colloidal nature, when agitated with air for a sufficient period, assumes a flocculent appearance very similar to small pieces of sponge. Aerobic and facultative aerobic bacteria gather in these flocculi in immense numbers, some having been strained from the sewage and others developed by natural growth." In other words, the usual suspended particles in sewage grow by the accretion of material colloidally dispersed, thus producing activated sludge.*

Other writers refer to the "scrubbing action" of suspended particles, and compare the action of activated sludge to that of alum coagulation.[13] The process is often referred to as one of oxidation, assuming that oxidation is a principal step in the purification of sewage. Another definition states that activated sludge must be of "a character to absorb colloidal matter," and another author [14] refers to the "clotting" of the colloids in the sewage. Such expressions seem to indicate what might be called a colloidal or mechanical theory for the mechanism of the action of activated sludge, similar in many respects to the Hampton doctrine of the action of sewage filters.

Another theory, which in reality seems to have been the first to be proposed, is what might be called the biological theory and resembles Dunbar's theory of sewage filters. Those emphasizing this viewpoint of the action of activated sludge call attention [15] to the analogy between the action of slate beds, contact beds, and sprinkling filters and the action of activated sludge. The sludge is referred to by these writers, not as a clotted, agglomerated or coagulated sludge produced by the mechanical growth of suspended particles in the sludge, but as biological growths arising from the germination and propagation of microorganisms whose "spores" are always present in sewage. The term "cultivated sludge" used by one author,[16] and "animate energy" used by another,[17] contrast as strongly as any with the term "coagulated" or "agglomerated" sludge, used by those favoring the colloidal theory.

If one examines particles of activated sludge under the microscope he is immediately impressed with the fact that they are composed largely of active, growing, microscopic organisms of varieties ranging from true bacteria up through the giant bacteria, with occasional molds and yeasts, and also a variety of free-swimming and attached protozoa.[18] These communities of microorganisms obtain food from the colloidal and dissolved matter and salts in the sewage. From what we know of the metabolism of micro-organisms it is probable that the unicellular forms absorb through their membranes such soluble forms of organic matter as are able to pass through this membrane, and that they also secrete enzymes which are capable of peptizing or liquefying colloidal particles too large to be directly absorbed. Protozoa, on the other

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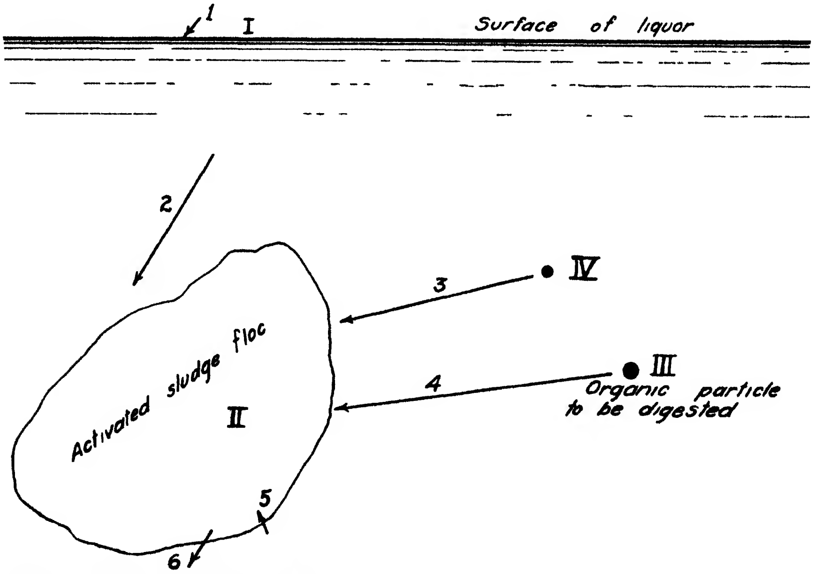
* Similarly, the cream layer in milk has a much larger bacterial content than the lower "skim milk" layer. J. A.

hand, can easily be seen to approach and ingest visible particles of organic matter.

Various terms more descriptive of the process have been suggested to supersede the earlier one, "activated sludge." Of these "bio-aeration" seems to have much to commend it. Shive and Buswell[19] call attention to the fact that both dissolved and colloidal matter are removed by the activated sludge process and suggest that the reactions take place in two steps. For the first they suggest the term "bio-precipitation," while the second step is one of oxidation and nitrification.

Clark,[20] in 1912, called attention to this viewpoint in the following manner: "In experiments upon aeration of sewage tried during the past twenty-five years by various investigators, as described by Drown, Dupré and Dibdin, Mason and Hine, Black and Phelps, etc., the chief object of each study has been to learn the oxidation changes induced by such treatment. The collection of suspended and colloidal matters, as here described, is an entirely new feature of aeration work."



Courtesy Chemical Catalog Co, Inc

Fig. 2.

A more detailed analysis of the steps in the process is given by Buswell.[21] When air is blown into the aeration chamber of an activated sludge plant it does three things: (1) It maintains the sludge in suspension; (2) It maintains aerobic conditions; (3) It stirs up the mixture, allowing fresh liquor to come into contact with the sludge. We are not able to tell, therefore, which one of these three factors determines the critical minimum air requirement. In mechanical aeration processes we also have the same three factors determining the critical velocity, namely, one and one-half feet per second, which is found necessary to maintain in the circulating chamber. The importance of maintaining the sludge in suspension is due to the fact that otherwise the sludge could not come into contact with the liquid and also to the fact that if the sludge is allowed to stand it very soon begins to putrefy and redisperse and the work done in building it up is lost.

If we consider the various steps which must take place in the activated-sludge process it will be apparent that stirring is of great importance. There are apparently four important points involved in this process, each of which are represented in Figure 2 as follows: (I) The water surface, by a straight line; (II) an activated-sludge floc, by a rough oval; (III) a colloidal particle of organic matter, by a large dot; (IV) a dissolved molecule of organic matter, by a small dot.

THE SIX STEPS OF THE PROCESS.

(1) The air must saturate the liquor or water immediately below the surface of contact. Langmuir has shown that enough molecules strike such a surface to saturate it in an infinitesimally short time, giving a thin layer of water saturated with oxygen immediately in contact with the air surface.

(2) This oxygen must then diffuse to the activated-sludge particles. This is an exceedingly slow process, as was pointed out more than twenty years ago by Noyes and Whitney and later emphasized by Phelps.

(3) The dissolved molecular organic matter must diffuse to the activated-sludge particles. This, also, being a diffusion process, is slow.

(4) The colloidal particles must get to the activated-sludged floc somehow or other. Although these particles are in rapid motion (Brownian movement), the actual change of position of colloidal particles is practically zero.

(5) The organic material and the oxygen must be taken up and worked over by the organisms of the sludge floc. As far as we are able to tell this is a comparatively rapid process.

(6) The by-products of the biological growth must diffuse away from the sludge floc; otherwise they will accumulate and poison it.

Of the six steps which must take place, all except (1) and (5) are comparatively slow. The only way that we can speed up the other four steps in this process is by stirring. Stirring will sweep away the saturated film from the air surface and bring it down in contact with the activated-sludge particles. It will move the dissolved and colloidal organic matter about so that they come in contact with the floc and will sweep away the metabolic products of the sludge organisms. In view of this analysis it does not seem so strange that stirring should prove to be more important than air in the carrying out of this process. Stirring by means of blowing air through sewage is, however, a rather inefficient process. We do not get as much stirring for the power input as we would if the power were applied in some other way. When air is blown into sewage, the activated-sludge floc, air bubbles and liquid are all driven in the same direction. The most efficient process would be one in which the air surface and flocs would be held stationary while the liquor is caused to flow past them.

In the earlier literature [22-27] some mystery was attached to the fact that activated sludge contained from 3 to 7 per cent of nitrogen, while settled and digested sludges contained less than 2 per cent. The realization that the activated sludge is composed largely of microbial protein removed the mystery.

To demonstrate further the occurrence of bio-precipitation, Shive with Buswell [28] cultivated *B. subtilis* in pure culture in large flasks of peptone broth, maintaining a vigorous agitation throughout the incubation. At the end of the incubation, the growth of subtilis was allowed to settle and the supernatant liquor analyzed.

The data showed that as much as seventeen per cent of the nitrogen was removed from solution in 48 hours.

One of the attractive features of the activated sludge process has been the high nitrogen content of the sludge and hence its value as a fertilizer. Bartow and Hatfield[29] made an extensive investigation of this subject and demonstrated by pot cultures that activated sludge had high manurial value. Many subsequent confirmations of this conclusion are available. "Milorganite," a dried activated sludge fertilizer, is a well known commercial product.

Drying of Activated Sludge.

One of the most serious problems in the development of the activated sludge process has been the handling and drying of the sludge. The sludge produced by the process is a biological jelly containing 96 to 99.5 per cent of moisture. The water is combined with the gel to so large an extent that the ordinary physical means such as draining, settling, centrifuging, or filter pressing are relatively ineffective. Treatment with various chemical reagents which are known to cause gels to shrink and extrude water makes it possible to filter this material by means of pressure or vacuum filters to a cake of 70 to 85 per cent moisture. From this point it must be dried with heat.

The chemical treatment of the sludge to prepare it for filtration has been the subject of numerous investigations, particularly in the United States and in England. Bartow and Hatfield[29] tried a variety of reagents. They found that sulfuric acid when added to produce a pH of about 4.5 greatly increased the rate of filtration but that even better results were obtained with aluminum sulfate. About the same time (1917) Pearse[30] tried the use of acid on a commercial scale. The advantages of this treatment he found to be:

1. The yield and capacity of press are increased.
2. The nitrogen and fat content of the sludge are increased.
3. The filter cloths do not clog as rapidly.
4. The sludge cake does not become septic on storage.

The only objections to the use of acid were:

1. The cost of the acid.
2. The addition of another step in the process, as well as the requirement of more equipment.

Later investigations, a mere bibliography of which would require considerable space, have only served to confirm and make more specific these conclusions. Mohlman[31] finds the necessary dose of aluminum sulfate to be from 4 to 10 pounds per thousand gallons of sludge containing 98.5 per cent moisture. The treatment with alum was far more effective than treatment with sulfuric acid (3.5 to 5 cc. per gal.).

The relative efficiencies of various astringents are given in Table I by Mohlman and Palmer (*Eng. News-Record,* Jan. 26, **1928**).

Theoretically, it is assumed that the aluminum ion combines with the "solution link" groups of the organic gel lessening their tendency to bind water. The acid treatment is based on the assumption that the gel is sufficiently uniform in composition to have a definite iso-electric point or point of minimum swelling.[32]

In spite of all that has been done, the drying of activated sludge remains a problem and the cost is greater than the market value of the fertilizer obtained. In some cases it will be necessary to carry this loss as a charge against the cost of sewage treatment.

In the study of the microbiology of activated sludge in its development

Table I.—Comparison of Equal Weights of Iron and Aluminum Salts.
April 11, 1925

Weight of Conditioner per 1000 Gal. Sludge	Time to Filter 200 cc. Filtrate Min.	Sec.	Total Time of Filtration Min.	Sec.
10 lb. of aluminum sulfate $Al_2(SO_4)_3.18H_2O$	4	35	9	18
10 lb. aluminum nitrate $Al(NO_3)_3.9H_2O$	4	00	9	37
10 lb. aluminum chloride $AlCl_3.6H_2O$	2	10	3	40
10 lb. ferric sulfate $Fe_2(SO_4)_3$	2	15	3	53
10 lb. ferric nitrate $Fe(NO_3)_3.9H_2O$	1	52	3	00
10 lb. ferric chloride $FeCl_3.H_2O$	1	42	2	18
Specific gravity of sludge				1,014
Maximum vacuum				18 in.

from raw sewage there seems to be a definite succession or addition of forms, as the sludge develops. Beginning with the characteristic microorganisms of raw sewage as it is taken into the aeration chamber, there is predominance of the minute flagellates and ciliates, with occasional Peritrichs and Holotrichs. In a few days the minute forms diminish in number until they become a negligible quantity while Peritrichs, Holotrichs, and Heterotrichs increase in number, the Peritrichs predominating throughout. As the minute forms become insignificant, the gelatinous masses of the Chlamydobacteriacae and Nematodes appear, to be followed in a few days by the sudden appearance of Peritrichs.

The animal inclusions of the sludge made up a very small part of the entire mass. The base of the sludge was composed of zooglœal masses intermixed largely with filamentous bacteria and occasional *Zoogloea ramigera.*

It appears that the filamentous forms overwhelmingly predominate the sludge. The literature on filamentous forms is scattered and rather uncertain taxonomically. Certain polyspora, *Sphaerotilus dichotomus* and *Zoogloea ramigera* were undoubtedly present, however, in large numbers.

BACTERIAL SURFACE.

Hering[3] long ago pointed out the importance of bacterial surface in sewage purification, though few definite data have been developed since his paper on the subject. From the microscopic studies of Buswell and Long[24] we may obtain a notion of the order of magnitude at least of the sludge surface in the activated sludge process. Take a case where two million standard units of zooglœal masses were found per cubic centimeter in the aeration chamber. Each floc must have a lower surface equal at least to the upper surface, so that leaving out the side surfaces we would have four million standard units of 0.0004 mm. sq. each or 16 cm. sq. of surface per cubic centimeter of volumes. This figure does not include the surface of the protozoa or the free-swimming bacteria. If increased by fifty or one hundred per cent it would probably approach more closely the correct value. This would mean a surface of approximately 500 sq. ft. of sludge surface in 1 cu. ft. of the aeration chamber.

Both activated sludge and sprinkling filters produce effluents of very high quality, often carrying less organic matter than the streams into which they are discharged. Tanks, on the other hand, remove only a third of the organic matter. There are many cases where an intermediate degree of purification would be satisfactory. Partial treatment with filters is impracticable, but partial treatment with activated sludge has been employed to relieve the load on trickling filters.

An intermediate device between activated sludge and trickling filters is also needed. In the filter the amount of active surface per cubic foot is low while in activated sludge it is high. An activated sludge plant of given capacity is from one-tenth to one-fifteenth as large as a tank and filter installation of like capacity. The operating costs of the former are high as is also the construction cost of the latter. A device more compact and less costly to build than filters and not expensive to operate would find wide use. The colloiders of Travis, lath placed in the sedimentation chamber on six- to nine-inch centers, represented a step in the right direction. But the amount of surface was small and the accumulated growths became septic and redispersed. The lath filters of Black and Phelps were subject to the same limitation. Many filters made of rather fine-grained material have been used in experimental and large scale installations from time to time but have not come into general use because of the danger of clogging. Brushwood has frequently been employed. Favorable results were reported on a large brush filter in Toronto.[34] Richards and Weeks [35] have experimented with straw filters and Buswell [36] is operating a small corn cob filter. Woody vegetable material will decompose in time and at present data are not available to determine whether the cost of replacement will offset the saving in cost of installation. A recent experiment with an aerated sand filter was reported by Basiakine.[37]

Shive and Buswell [28] have described an experimental device so arranged that 24 square feet of active surface was available per cubic foot of tank volume. Provision was made to shake or agitate the active surface at intervals of about eight hours in order to remove the accumulated growths. Circulation and aeration were obtained by means of compressed air, the amount used being less than 0.1 cubic foot per gallon. A removal of 30 to 50 per cent of the colloids was reported. The devices were referred to as "nidus racks."

Imhoff [38] has recently described a similar device which he calls "Tauchkorper" or "contact aerators." The middle third of the sedimentation chamber of an Imhoff tank is filled with brushwood, underneath which an oscillating aerator introduces compressed air. The intermittent aeration removes the growth accumulations which settle in the last third of the chamber. Using 0.1 cubic foot per gallon Imhoff obtains about the same degree of purification as was obtained by Shive and Buswell. Several installations of this sort are being built in the Ruhr District.

STABILIZATION OF SOLIDS.

In nature organic matter is worked over and over by succeeding generations and classes of microorganisms until it has been broken down into simple substances, principally ammonia, nitrates and gases, and a black residue vaguely referred to as humus.

The chemical reactions which occur during the progressive change of fresh organic matter to oxidized or stabilized products may be of two kinds: (1) oxidation, resulting if complete in the formation of water and carbon dioxide and (2) formation of insoluble products. These insoluble compounds may be either solid or gaseous and may be the result of the following reactions:

(a) *Reduction,* resulting in the formation of methane and under some conditions hydrogen and the hydrocarbons of higher molecular weight.

(b) *Hydrolysis* or lytic actions in general, resulting in the formation of carbon dioxide and a variety of other products.

(c) *Humus formation.* Whether oxidation, reduction, or lysis appear to be the dominant reactions in the decomposition of organic matter, there is almost invariably a resistant, rather stable residue formed which is called "humus." This humus is of rather indefinite character and varies in composition, depending upon the method and the material from which it is formed.

(d) *Bio-precipitation.* This process is best exemplified in the activated sludge process. It does not stabilize organic matter but removes it from dispersion in the sewage.

STABILIZATION OF THE SOLIDS IN SEWAGE.

The solid organic matter which is deposited from sewage by sedimentation is usually associated with 90 to 95 per cent of water from which it is not easily separated. It is soluble to a considerable extent although it goes into solution slowly and by means of rather complicated reactions. The animal and vegetable matter of which it is composed consists largely of organic compounds containing either hydroxyl, carboxyl or amine groups or all three. These groups are soluble in water and act as solution links tending to favor the dispersion of the compounds in water. Many of these compounds are characteristically sticky or gluey, tending to take up water, first swelling to gels and then dispersing to sols. If solution, or perhaps more properly dispersion, of these solids is allowed to take place in such a manner that the liquefied products are returned to the main body of the sewage liquor, the reduction in oxygen demand accomplished by sedimentation will be proportionately offset. The solids are of such a nature that they cannot be removed and exposed in the open air without creating a nuisance. They are allowed to undergo a rotting process while submerged in a compartment or tank separated from the sewage liquors. The object of this rotting, as intimated in the discussion above, is to produce a relatively insoluble, inert, and stable organic residue of a compact granular texture, which may be separated readily from the associated liquid by draining. This process is most often referred to as digestion but is sometimes called septicization.

From the standpoint of the resulting products this rotting appears to take place in two phases. Imhoff early designated them as the "putrid phase" and the "odorless phase." [39] In a discussion by Thumm and Reichle published in 1914 [40] the first phase was said to be of an acid character and the second phase of an alkaline character. Somewhat later Imhoff [41] uses the terms "acid digestion" and "methane digestion" to distinguish these two phases in the sludge rotting process. Groenewege [42] has also emphasized the occurrence of acid production during the early stages of putrefaction and a number of other workers have made similar observations. More recently Rudolfs [43] has studied the progress of putrefaction following the change in hydrogen-ion concentration as the process proceeds.

Acid Phase. When freshly settled sludge from domestic sewage is first drawn it has a pH in the neighborhood of 7. (By the "pH of a sludge" is meant the pH of the liquor associated with the sludge.) If this sludge is allowed to stand at room temperature active biological action sets in within a few hours. There is an active evolution of gas, a considerable portion of the sludge is floated by the gas bubbles and the liquid portion becomes increasingly milky. At the same time the pH drops sometimes as low as 5 and an exceedingly foul odor develops, in which that of hydrogen sulfide seems to predominate. If this acid condition is allowed to persist all action practically ceases.

During the "acid phase" there is relatively little decrease in the volume of sludge and little improvement in its drainability. In fact the early stages of acid digestion result in an increased stickiness. That the pH range, 5 to 6, is unfavorable for rapid peptization of nitrogenous compounds follows from the fact that the isoelectric points of those for which the data are known, mostly lie a little below pH 5. This condition naturally retards the digestion of nitrogenous organic matter. Neave and Buswell[44] have shown a marked increase in the solubility of the organic matter in fresh sewage solids as the pH increases up to about 7.8.

The evolution of gas at this stage is relatively rapid. This rapid evolution of gas coupled with the sticky viscous character of the sludge presents ideal conditions for the formation of the foamy[45] scum which is the frequent worry of operators of new plants. The gas which is formed during this acid phase contains a relatively large amount of carbon dioxide, frequently as high as 50 per cent. The quantity of methane is proportionately less, ranging from 50 to 65 or 70 per cent. It is difficult to say, from the data at present available, to what extent the low methane content is due to the diluting effect of the carbon dioxide and to what extent it is due to less active methane fermentation than occurs in later stages. Some evidence favors the former explanation, namely, that methane is actively produced from the first, but is diluted by the carbon dioxide until the evolution of carbon dioxide drops off.

In some cases, both in laboratory experiments and in actual plant operation, this acid condition predominates persistently and the digestion produces a foul sticky sludge which drains poorly. Numerous examples might be mentioned. We cite the experience of Stevenson,[46] in which a tank operated poorly and was persistently acid. The difficulty in this case was attributed to the high amount of fats in the sewage.

Alkaline Phase. Under proper conditions the acid phase of digestion is followed by an "alkaline phase,"[40] sometimes referred to as the "non-putrid" or "methane" digestion. During this stage the pH rises to between 7 and 8, the foaming usually ceases, there is a slight earthy or tarry odor, the amount of carbon dioxide in the gas drops and the amount of methane rises, the liquor loses most of its milkiness and the sludge becomes more granular.

This general improvement is due to the decomposition of the material which is more easily attacked by bacteria leaving a more stable, less soluble residue. Rudolfs,[47] for example, has shown that the biochemical oxygen demand of the sludge decreases rapidly as digestion proceeds. He found that in "ripe" sludge, i.e., sludge sufficiently digested to drain well and to undergo no further active fermentation during draining, the biochemical oxygen demand determined after 24 hours' incubation at 20° C. amounted to from 1,000 to 1,500 ppm. for each per cent of organic matter. For fresh sludge the biochemical oxygen demand is several times as great.

Neave and Buswell[48] have shown that during digestion a decrease in the "fixed carbon" of the organic matter occurs, similar to the change which takes place in coal in passing from lignite to anthracite. This change is not sufficiently great to permit the use of the fixed-carbon determination as a control test, but it does indicate the trend of the reaction toward stabilization.

In a well-operating digestion chamber to which fresh solids are added continuously as in the Imhoff tank, or at short intervals as in separate sludge digestion, the alkaline or non-putrid digestion should predominate. The acid condition should not recur after the first "working in" or "ripening" which occurs when the tank is first put in operation. Occasionally acidity has been observed in tanks from which nearly all of the digested sludge was drawn and on the other hand new tanks which were started off with an initial quantity of ripe sludge have been found to pass through the undesirable acid stage much more rapidly than those which were not thus treated. Thumm and Reichle[41] emphasized the importance of maintaining a proper ratio of "acid-binding" material to fresh sludge in any digestion chambers and securing a good mixture of the "acid-binder" with the incoming sludge. All of the present methods of maintaining an alkaline reaction ("acid-binding") during sludge digestion were given by these authors. These are:

(1) By maintaining the alkalinity of the fresh sewage liquor which may be caused to enter the digestion chamber.

(2) By introducing tap water which will both neutralize and dilute the acid.

(3) By introducing nitrogenous matter which during digestion forms ammonia (i.e., sludge which has passed the acid stage).

(4) By the addition of alkali (lime, limestone, etc.) to the chambers.

The necessity of having a considerable excess of ripe sludge over fresh solids to maintain alkaline or non-putrid digestion in the chamber was thus early recognized. Imhoff[49] suggested a special device to mix a predetermined amount of ripe sludge with the fresh solids, basing his patent on the above observations. The amount of ripe sludge necessary to maintain proper digestion he states[50] will vary with local conditions, but suggests the retention of ripe sludge equal to one month's accumulation on 1 part of fresh solids to 30 parts of ripe sludge. For a separate digestion system at Birmingham, Watson[51] uses 1 part ripe sludge to 5 parts of fresh sludge with most excellent results.

Optimum pH for Digestion. Rudolfs has further observed that the best digestion occurs at Plainfield when the pH lies between 7.3 and 7.6. About the same range for good digestion was noted by Baity.[47] An increase of the ratio of fresh solids to sludge lowers the pH and results in poorer digestion. This is in accord with earlier observations of Imhoff and others.

There are cases where the addition of lime is not found as beneficial as it was by Stevenson (cited above) and Rudolfs. Imhoff[52] reports that in Germany, liming of digestion chambers has been tried repeatedly but never with success.

The optimum pH range of 7.3 to 7.6 determined by Rudolfs is apparently not of universal application. Dr. W. D. Hatfield[53] states that at Decatur, Illinois, where an exceptionally well-digested sludge is obtained, the pH is in the neighborhood of 6.8. At this plant the temperature of the incoming sewage is near 35° C., due to industrial wastes.

Three explanations may be given for the maintenance of a relatively high pH in the digestion chamber in the presence of an excess of ripe sludge. The microbial population of the ripe sludge may overgrow and choke out the acid producers which apparently thrive on the fresh material alone, or, what seems more probable, the alkaline products produced by the decomposition which occurs in the second phase are more than sufficient to neutralize the acids produced in the first. In other words, the ripe sludge acts as an alkaline buffer maintaining a relative constant pH. An important factor is the fact that under normal conditions the acids are decomposed by bacterial action instead of neutralized.

It is apparent that the acid produced in the first stages of digestion may arise (1) from the decomposition of carbohydrates, (2) from the hydrolysis and oxidation of fats and (3) from the hydrolysis and deamination of proteins. Experimenters seem quite well agreed that very little protein decomposition occurs during the first stage. That leaves carbohydrates and fats as the source of the acid. The simpler carbohydrates (e.g., the sugars and starches) are easily and rapidly decomposed, but the usual chemical tests fail to reveal more than very small quantities of these substances in fresh sewage sludge. The more complex carbohydrates, such as natural "ligno-cellulose," are only very slowly attacked, their decomposition requiring months. That the amount of acid observed in the first stage of sludge digestion comes largely from the carbohydrates seems improbable. Numerous references in the literature indicate that grease is broken down during sludge digestion.

O'Shaughnessy,[54] for example, stated that the fats and soaps are about 30 per cent decomposed and recently Neave and Buswell[55] have made a similar observation. The latter authors found the same per cent of "grease" in fresh solids and digested sludge, indicating that the digestion of this material kept pace with that of other organic matter. (*See also* Bach and Sierp.[56]) Later work by the same authors[58] indicates that the "grease" or "fats" are largely decomposed during the first phase of digestion to give acetic, butyric and others of the lower fatty acids.

The alkaline reaction of the second phase of digestion is generally considered to be due principally to the ammonia produced by the decomposition of nitrogenous matter. The decomposition of fatty acids also tends to reduce the acidity thus:

$$C_nH_{2n}O_2 + \frac{(n-2)}{2} H_2O = \frac{(n+2)}{4} CO_2 + \frac{(3n-2)}{4} CH_4$$

In a number of separate sludge digestion installations abroad the practice is to carry on the digestion in two stages. The fresh sludge is allowed to remain in the first digestion tank for about half the total time required for digestion and then removed to a second tank for the completion of the process. This procedure precludes any possibility of the presence of undigested particles in the sludge when drawn off to the drying beds. An exceptionally good sludge is obtained at Birmingham, England, in this way. The Kremer design of tank used in Germany operates on this plan.

The net effect of all of these biochemical reactions is to break down some of the less complex compounds to the gaseous end-products carbon dioxide and methane, and at the same time to remove the solution link groups from the more complex compounds, thus leaving a relatively inert solid residue which has a greatly decreased affinity for water. Spillner,[57] describing an early and extensive series of experiments on the drying qualities of both fresh and digested sludge, gives considerable data illustrative of this change. Fresh sludge when drained to a gel of spadable consistency retained 71 per cent moisture while spadable digested sludge retained only 55 per cent moisture. The fresh sludge required 33 days to drain, the digested sludge 16. Digested sludge usually contains 80 to 85 per cent moisture when drawn from the tanks and occasionally runs as low as 70 per cent, while fresh sludge seldom carries as little as 90 per cent moisture. These figures indicate clearly the presence of water-binding colloids in fresh sludge.

The stable residue is commonly referred to as "humus." The term "humus" is one of rather indefinite significance and may be used to designate the resistant material which remains after the decomposition of organic matter by various chemical reagents or by microorganisms. The chemical composition of humus depends upon the character of the material from which it is formed as well as upon the method of its formation.

The amount of this humus residue varies considerably with the character of the raw sludge. O'Shaughnessy[54] reported that the amount of sludge decreased to the extent of 30 per cent in about seven weeks but the product was sticky. A further period of several weeks was required for a physical change in the sludge as a result of which it became granular. A digestion period of several years still left 40 per cent of the organic matter undissolved. Early investigators claimed a much higher degree of liquefaction. In modern practice about 25 to 35 per cent of the organic matter is liquefied and gasified during digestion. The *volume* of the sludge is reduced in a much greater ratio than is the weight, due to the destruction of the water-binding colloidal character of the organic matter. The volume reduction may frequently amount to 75 per cent.

The effect of increase in temperature during digestion is to greatly increase the rate of organic decomposition. The optimum temperature for rapid stabilization of solids appears to be about 26° C.[56] Whether or not the temperature changes the course of the reaction has not yet been established. The increase in rate of gas production goes along with increased decomposition of solids, but appears to reach a maximum at a temperature 5° to 10° C. lower.

Since with an increased temperature the rate of digestion is increased, a smaller tank capacity may be used to handle a given amount of sludge if artificial heating is provided. The advantages of such an arrangement have not so far been generally considered worth the extra operation expense. There are some cases in which the cost of heat is distinctly less than the interest on the extra cost of larger tanks. The quantitative relation between temperature and rate of digestion is difficult to define because of rather wide differences in the methods of measuring digestive progress. Sierp[58] has shown that the evolution of gas is best at 25° C. but that liquefaction is most rapid at 37° C. He does not recommend heating above 25° C. in practice. He found that gas production was arrested at 6° C. but that there was still some decomposition at that temperature.

The earliest investigators appear to have realized that the gases given off during putrefactive fermentation contained considerable amounts of methane, and various arrangements were made from time to time to use the methane as a source of heat or power. Cameron used the gases from his plant at Exeter, England, for lighting more than twenty-five years ago. Gas from sewage tanks was used at Matunga, Bombay, for driving a gas engine in 1897,[59] by Hommon[60] for lighting in 1915 and by Watson[61] in Birmingham in 1920 for power production. Moss-Fowler[62] in 1923 reported the work of Flicker begun in 1911 in Australia on the production and collection of gases from sewage tanks. Several of the devices for stimulating gas production and collection have been patented.

Recently Imhoff[63] has described certain installations in Germany completed in 1922 for the collection and use of the gas. Incidentally the substitution of gas collectors for gas vents increases the area of the sedimentation chamber about 25 per cent.

The amount of gas obtained from sludge digestion is naturally variable. A summary is given by Pearson and Buswell in the table on following page.

As the result of a recent study[64] of two-stage digestion the process has been summarized as follows:

There is at first a relatively rapid fermentation which results in the decomposition of the simpler compounds and the production of a large quantity of gas, including most of the hydrogen sulfide. This fermentation is apparently complete in a very few days. This observation is in accord with that of Hatfield[65] and others, who have observed that 50 per cent of the gas is evolved in the first 24 hours. After this fermentation has reached completion, it is still necessary to allow the sludge to undergo some sort of ripening process.

Plant	Corrected Population	Solids per Capita	Volatile Matter per Capita	Gas Yield		Reference
				Per capita	Per gram volatile matter added	
		Grams	*Grams*	*Liters*	*Liters*	
Antigo, Wis.	5,600	34.7	25.0	18.2	0.73	*Public Works*, **59**, 134 (1928)
Plainfield, N. J.	45,500	33.6	....	28.3[a]	1.13	*Ibid.*, **58**, 342 (1927)
Marion, Ohio	40,000	37.5	....	....	....	*Ibid.*, **57**, 350 (1926)
Expt. Plant	200	28	21	11.05	0.53	Water Survey, *Bull.* **29**
Expt. Plant	200	42	32	17.0	0.41	*Sewage Works J.*, **3** (April, 1931)
Expt. Plant	200	40.2	31.3	19.8	0.495	
Fitchburg, Mass.	40,000	45	....	....	....	*Public Works*, **57**, 343 (1926)
Salem, Ohio	7,000	54	35	....	....	*Sewage Works J.*, **2**, 30 (1930)
Salem, Ohio (plus activated sludge)	7,000	84.6	55	28.0	0.333	
Flint, Mich.	130,000	....	37	....	....	*Public Works*, **61**, 24 (1930)
Chicago (Calumet), Ill.	4,400	....	44.5	22.5	0.505	*Sewage Works J.*, **1**, 173 (1929)
Bloomington, Ill.	40,000	74	....	....	....	*Ibid.*, **2**, 404 (1930)

[a] Estimated, 1931.

The exact nature of this is not understood, but the net result is that the sludge loses its water-binding properties and can then be drained on sand beds.

The ripe granular sludge resulting from thorough digestion is ordinarily pumped or siphoned from the bottom of the digestion chamber on to sand beds. The sand beds are usually provided with underdrains and are bounded by low walls extending a foot or two above the sand. In some cases [66] glass-covered beds have been used to hasten drying and avoid odors. The sludge though carrying as low as 70 per cent moisture in some cases is sufficiently fluid so that it may be pumped and distributed to the various sand beds by means of troughs. In ordinary weather the sludge will drain and evaporate sufficient moisture in two to three weeks so that it may be easily handled with a shovel (spadable). It is then shoveled into carts or narrow-gage cars and hauled away to be used for fill or fertilizer. The value of the sludge for fertilizer depends upon its humus character rather than on its content of plant foods such as nitrogen and phosphorus. The nitrogen content ranges from 1 to 2 per cent on the dry basis and the phosphorus about the same. At Rochester, New York, for example, a small price is received for the air-dried sludge.[67]

Van der Meulen and Smith [68] have found that the rate of filtration of ripe sludge is greatly increased by the use of alum. Sulfuric and sulfurous acids were less effective. The amount of alum used was 6.7 pounds per cubic yard and a cake of 80 per cent moisture content was obtained in four minutes. Following these experiments, Rudolfs, Downes and Campbell [69] found that the addition of 3 pounds of alum per cubic yard decreased the draining time of ripe sludge on sand beds by one-half.

Undigested sludge or sludge obtained by chemical precipitation is sometimes filter-pressed and heat-dried for fertilizer, but this process has found only limited application, especially in America. Centrifuges have been used for fresh sludge and screenings with some success in Germany. Dumping at sea and plowing under the soil are methods which are sometimes adapted to local conditions.

The production of gas and coke by destructive distillation of sludge was suggested by some of the earlier investigators.[70] About 7,000 cubic feet of gas was produced per ton of dry solids as compared with 8,000 to 12,000 cubic feet from a like amount of peat or soft coal. The amount of moisture to be dealt with limits the advantage of such a method of treatment. A recent patent [71] describes a process whereby the ammonia produced by the destructive distillation of sludge is absorbed in sulfuric acid and recovered as ammonium sulfate.

From a sanitary standpoint, there is little danger in using digested sludge for fertilizer,[72] although fresh sludge may frequently be the source of infection if so used.

INDUSTRIAL WASTES.

A comprehensive treatment of this sub-topic would require a volume of several hundred pages. Only a few examples can be given of the applications of colloid chemistry in this field. The use of alum or alum and lime is frequently useful in clarifying relatively small volumes of highly concentrated industrial wastes. The manifold effects of the reagent, alum, should be noted in this connection. (1) It reacts with the alkaline substances found in most natural waters to form a flocculent precipitate which may in a mechanical way sweep impurities out of the water. (2) This floc, because of its large surface, may adsorb large amounts of dissolved or colloidal matter from the water, or it may coat the sand grains of the filter and thus act as an adsorbent. (3) Aluminum sulfate hydrolyzes when dissolved in water, yielding hydrogen ions, i.e., it is in effect a weak acid. Hence it may be used, though not necessarily economically, where acidity is desired. (4) It yields the trivalent positive aluminum ion (Al^{+++}) which has been shown to be very effective in precipitating negative colloids. (5) It yields the divalent negative sulfate ion which has a precipitating effect on positive colloids, such as "colloidal iron" or "colloidal alumina."

An interesting commercial scale application of the principle of film concentration to waste treatment was made by Imhoff. Wool washing wastes are passed through tanks provided with specially constructed aerating devices. A voluminous foam is produced in which a major portion of the fats and soap are concentrated. The foam is skimmed by revolving paddles which just clear the surface of the liquid. Treatment with sulfuric acid breaks the foam and causes a separation of lanolin in a salable condition. The remaining liquid is sufficiently reduced in concentration so that it may be discharged to any ordinary sewage treatment plant without upsetting its operation.

Mertens (Brit. Pat. 328,606) uses paddles instead of compressed air and A. T. King[73] uses an injector to produce the foam. Halvorson[74] has recently described a chlorination process for the precipitate of colloids, mostly proteins and fats from packing wastes. To the effluent from primary sedimentation chlorine is added, and the precipitated material removed in the second clarifier amounts to roughly 2 tons per day. The chlorine is applied in quantity to insure a residual chlorine value of 50 parts per million in the precipitation tanks and represents a ratio of 1.5 lb. of chlorine per pound of total nitrogen present in the effluent from the plain settling tank. A pH of 4 or thereabouts appears to be the optimum condition for the precipitation and maximum nitrogen recovery. It is possible to precipitate 90 per cent of the organic nitrogen content of the wastes if they are fresh. Stale wastes yield as low as 60 per cent nitrogen recovery. In plant practice the average has been 73 per cent recovery of organic nitrogen and 98 per cent removal of suspended solids.

The ultimate success of this process depends on the filter pressing and sale of the sludge.

Boruff and Buswell[75] have recently developed a technique for controlling anaerobic fermentation whereby colloidal and dissolved organic matter, such as occurs in distillery wastes, can be handled rapidly and continuously without preliminary coagulation. This process as mentioned above converts the organic matter into CO_2 and CH_4. The latter gas is present in quantities sufficient to produce a combustible mixture of more than 500 B.t.u. per cu. ft.

It may be stated as a generalization that most industries use larger volumes of water than is necessary, thus producing large volumes of dilute wastes. If the volume is reduced to a minimum, the chances of economic recovery of by-products are greatly increased. An example is the production of cattle food by the evaporation of starch distillery or beet sugar wastes.

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INDEX TO AUTHORS *

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