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CONTENTS.

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CHEMICAL ENGINEERING, PLANT, AND MACHINERY.

By F. Rumford, Ph.D., B.Sc., F.R.I.C., M.I.Chem.E.,
Royal Technical College, Glasgow.

The Report of Progress for 1945 hailed the development of atomic energy as being the most remarkable feat of chemical and mechanical plant design of all time. It is the more regrettable, therefore, from a disinterested scientific viewpoint, that all full-scale plant aspects of this discovery, and any developments that may have occurred since the original publication of the two official pamphlets, are still a closely guarded secret.

The present year has been notable for a very large number of reports on the German chemical industries, published under Government auspices. These reports have been on specific factories, and have in general dealt with processes from a chemical rather than an engineering viewpoint. Careful scrutiny and correlation will be required before any general picture of chemical plant development can be obtained. It would appear that no novel principle was exploited during the war on the German side, although some very difficult and sensitive substances were handled in the preparation of acetylene derivatives and of concentrated hydrogen peroxide.

In the realms of chemical engineering literature, the appearance of a Unit Operations Review, published in the industrial edition of *Industrial and Engineering Chemistry* for January, should be noted. The review, citing some 450 references, many not available in this country at the moment, forms a very valuable bibliography of the last two or three years, and will be repeated every January in future. It may also be noted that the well known *Chemical and Metallurgical Engineering* has changed its name to *Chemical Engineering* since July, 1946.

Fluid Flow.

H. E. Rose[1] has attempted to derive a general expression for the pressure drop given by fluid flow through beds of granular material. The expression is based on a Reynolds value in which particle size is taken as the linear dimension, while velocity is calculated on the total cross-section of the conduit (empty tube velocity). The critical value for the criterion appears to be about 90, and above this value the pressure

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[1] *Proc. Inst. Mech. Eng.*, 1945, **153**, 141; B., 1946, I, 217.

drop is almost independent of viscosity. A. R. Morcom,[2] however, suggests that previously published work has given a critical range for the criterion of 10—40, and traces a relationship between pressure drop and Reynolds value for all fluid velocities. A composite function of pressure drop, fluid properties, and particle shape factors is shown to give a linear relation with the modified Reynolds criterion. P. J. Rigden[3] has pointed out that experiments on the flow of gases through plugs of powder in a narrow tube often give misleading results, due to the slip of gas along the tube walls.

H. V. Allen[4] has conducted experiments on the rate of flow and pressure drop through deep beds of bauxite and fuller's earth, as used in petroleum refining. His tests were made with beds of solid 6 in. in diameter and 10 ft. high, which should be large enough to nullify the edge effect indicated by Rigden. His final conclusions were expressed in the form of a plot of "friction factor" against Reynolds number, based on particle diameter as before. L. A. Galin[5] has published a mathematical study of the flow of a fluid through an unrestricted porous medium, with flow at right angles to the force of gravity. In another connexion, J. Hiles and R. A. Mott[6] have presented a formula for the resistance to gas flow through a bed of coke; the expression contains factors for coke size and voidage, and may be extended to a general form.

K. F. Tromp[7] has given an account of the phenomena met with when a spherical body falls through viscous fluid in a narrow tube, so that there is a considerable upward flow of fluid through the annular space. An expression is derived for the terminal velocity of fall, and results are compared with experimental values for the fluid velocity necessary to support spherical particles in slightly tapered tubes. V. B. Korbin-Kroukovsky[8] correlates the sharp increase in resistance to motion, shown when a moving body accelerates up to the speed of sound, with the separation of fluid from behind the moving body. The degree of this separation is partly determined by the ratio of particle size to mean free path of the fluid molecule; this ratio appears to have some critical value at which the degree of separation, with gaseous fluids, changes sharply. The author indicates that more experimental data are required.

R. L. Stoker[9] has discussed the means available for the production of a fixed velocity distribution in a fluid traversing a conduit. He suggests that a wire grid or a smoothed Venturi throat will give a regular velocity distribution, and gives a relation between maximum and average velocity in terms of (*a*) pressure drop across the resistance, (*b*) relative area of

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[2] *Trans. Inst. Chem. Eng.*, 1946; B., 1946, I, 191.
[3] *Nature*, 1946, **157**, 268; B., 1946, I, 217.
[4] *Petrol. Refiner*, 1944, **23**, 245; B., 1946, I, 152.
[5] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **47**, 246; B., 1946, I, 191.
[6] *Fuel*, 1945, **24**, 135, 158; B., 1946, I, 53.
[7] *Ibid.*, 126; B., 1946, I, 117.
[8] *J. Franklin Inst.*, 1945, **240**, 477; B., 1946, I, 118.
[9] *Ind. Eng. Chem.*, 1946, **38**, 622; B., 1946, I, 278.

conduit and throat. F. A. Schwertz[10] has calculated the rate at which carbon monoxide and hydrogen can be separated by diffusion into another gas stream, through a boundary consisting of a thin perforated metal plate. Such problems were successfully overcome in the separation of the uranium isotopes, and a slight indication of the plant involved is given by J. F. Hogerton,[11] whilst M. C. Fox[12] has given an even briefer description of the pilot plant for separation of these isotopes by thermal diffusion.

HEAT TRANSFER.

The increasing demands made on technologists for greater economy in heat usage are reflected in a number of papers on improved heat transfer in recuperators, waste gas–air heat interchangers, and efficient thermal insulation. At a conference[13] on the last topic, G. N. Critchley dealt with the economics of pipe-line insulation, citing very short repayment times for large pipes on heavy duty. The influence of texture on insulating properties was also discussed; for compounded granular materials, the porosity of the insulating mass should decrease as the temperature increases if the insulating efficiency is to remain constant. At the same conference, A. H. Leckie and J. H. Chesters stressed the advantages of cold gastight outer walls as the final stage in furnace insulation, although it was necessary to warn against overstressing of refractories by too efficient local insulation. L. R. Barrett, S. Pexton, and J. E. Davies described the problems of heat economy in ceramic kilns and in gasworks practice, while G. C. Allfrey gave an estimate of the relative costs of certain types of lagging for boilers.

C. Tasker[14] described the methods used in the United States for the thermal insulation of hot underground piping, used in conveying steam or hot water for district heating; the main difficulty arises from the tendency of soil moisture to infiltrate into the porous lagging material. G. N. Critchley[15] has suggested means for analysing the efficiency of tubular metal recuperators, and sets out curves to show the effect of gas velocity, external fins, spiral baffles, and similar factors. F. H. Green and L. S. King[16] show that a suitable tube form in such recuperators is that of a partly flattened cylinder, with dimpled markings; the increased rates of heat transfer with these tubes were not accompanied by a proportionate increase in pressure drop. G. E. Tate and J. Cartinhour[17] have given details of four typical disc-on-tube heat exchangers, whilst tubes of a similar type have been incorporated into boiler furnaces.[18]

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[10] *Physical Rev.*, 1945, [ii], **68**, 145; C., 1946, 138.
[11] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 98; B., 1946, I, 117.
[12] *Ibid.*, 102; B., 1946, I, 118.
[13] *J. Inst. Fuel*, 1945, **19**, 20; B., 1946, I, 45.
[14] *Inst. Fuel Bull.*, 1946, *April*, 146; B., 1946, I, 277.
[15] *Ibid.*, *Feb.*, 100; B., 1946, I, 150.
[16] *Trans. Amer. Soc. Mech. Eng.*, 1946, **68**, 115; B., 1946, I, 350.
[17] *Ibid.*, 1945, **67**, 687; B., 1947, I, 1.
[18] *Eng. Boiler House Rev.*, 1946, **60**, *Mar.*, 60; *April*, 106.

Finned tubes have also been studied by R. M. Armstrong[19] and E. A. Schryber[20]; the results obtained in heat transfer are compared with those for plain tubes in tube and shell heat interchangers, and the ease with which variations in surface may be obtained during fabrication is indicated. D. L. Katz, K. O. Beatty, and A. S. Foust[21] have compared the performance of tubes with integral spiral fins with the results given by plain tubes.

Fundamental data for the performance of multi-tube heat exchangers are given by M. Fishenden and O. A. Saunders.[22] They have established values for forced convection transfer from streaming fluids to banks of tubes lying at various angles across the fluid stream. The work is also extended to fluid inside the tubes, and to certain cases of radiation from hot gases, with suggestions for the determination of the effective radiating mass of the gas stream. Z. F. Tschuchanov[23] has suggested a direct correlation between the Reynolds and Nusselt numbers for a stream of gas flowing over a plane surface, with the value of the Prandtl number remaining approximately constant.

E. W. Thiele[24] has reviewed the present state of knowledge on heat transfer from a fluid to a bed of granular solids. He suggests that theoretical mathematical analysis has gone further than actual experiment, and indicates fields in which further experiment would be desirable. C. L. Norton[25] has described a novel heat interchanger, which comprises a moving mass of refractory pebbles, flowing countercurrent against (1) a heating gas and (2) gas to be heated. Heat transfer rates up to 650 B.Th.U./ft.^{3}/hr./° F. are claimed with superheated steam as the gas, and still higher rates are indicated for hydrogen. The cooled pebbles are elevated continuously from the bottom to the top, heating half of the tower. A very important application of the principle of heat interchange between suspended solids in a gas stream and cooling surfaces has been reported by P. C. Keith.[26] The gas stream formed the reacting mixture in a Fischer–Tropsch synthesis, with the solid particles acting as a fluidised catalyst. With the whole mass, gases and catalyst alike, moving around suitable cooling surfaces, it was possible to secure much more efficient cooling and temperature control than in the normal systems of narrow tubes, with fixed catalyst beds, adjacent to cooling surfaces.

T. C. Finlayson and A. Taylor[27] have made measurements of heat transfer and efficiency with various types of packing in a large model regenerator. They note, rather surprisingly, that the rate of heat

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[19] *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 675; B., 1947, I, 1.
[20] *Ibid.*, 683; B., 1947, I, 1.
[21] *Ibid.*, 665; B., 1947, I, 1.
[22] *J. Inst. Fuel*, 1945, **19**, 62; B., 1946, I, 77.
[23] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **48**, 100; B., 1946, I, 213.
[24] *Ind. Eng. Chem.*, 1946, **38**, 646; B., 1946, I, 277.
[25] *Chem. Met. Eng.*, 1946, **53**, *No.* 7, 111; B., 1946, I, 349.
[26] *Oil and Gas J.*, 1946, **45**, *No.* 6, 102; B., 1946, I, 319.
[27] *J. Inst. Fuel*, 1946, **19**, 82; B., 1946, I, 189.

transfer is proportional to the square root of the gas velocity, and derive expressions for convective heat transfer coefficient and pressure drop. An expression is also given for the height of the various packings required to give a definite value for the efficiency.

In a report to the Gas Research Board, A. L. Roberts and R. Long[28] have detailed tests on the emission spectra of various refractories. In the drying of a number of stoving enamels by radiant heat, which they also investigated, the absorption spectra of the enamels are unimportant if the metal underneath can absorb the radiation, but with highly reflective metal surfaces it may be necessary to increase the absorptive power of the enamel. Synthetic resins of the Perspex type absorb the radiation from a gas-fired surface-combustion unit more efficiently than they absorb shorter-wave radiation from a tungsten-filament lamp. J. B. Carne[29] has studied the influence of shape on rates of infra-red drying. He points out that a curved surface loses heat by convection more rapidly than does a flat surface, while radiant energy is absorbed at a rate independent of curvature ; unless some attempt is made to check convection loss, heating and drying of flat surfaces will be more rapid than with curved surfaces of similar absorption characteristics.

K. J. C. Connell, O. W. Humphreys, and J. L. Rycroft[30] have contrasted the methods available for heating solid objects of varying shape and physical properties. Natural convection will supply heat at a rate of about 1 B.Th.U./sq. ft./hr./° F., and heat input increases with radiant, dielectric, and eddy-current heating up to a maximum of 5×10^6 B.Th.U./sq. ft./hr. with surface eddy currents. Choice must be determined by the circumstances in each case, and a comprehensive bibliography of the various means for electrical heating is appended. A. J. Maddock[31] trances the connexion between the various types of molecular polarisation and the effectiveness of dielectric heating. It is suggested that dipole polarisation is the predominant factor in homogeneous dielectrics, but interfacial polarisation is the most important when laminated material is heated. The power factor of a typical system varies more widely with frequency than does the dielectric constant, and a frequency should be specifically chosen for each material. In a review of the present uses of dielectric heating the author cites a wide diversity of processes, from the setting of plywood to the reheating of meat pies. P. W. Schutz and E. K. McMahon[32] have shown that the electrical properties of beds of granular solids vary with particle size, and dielectric heating rates vary accordingly ; thus alumina particles of 2 mm. size heat up ten times as rapidly as granules of 0·1 mm. size and of idential composition.

On the vexed question of heat transfer to boiling liquids, M. T. Cichelli

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[28] *Rept. of Joint Gas Res. Commee.*; B., 1946, I, 117.

[29] *Gas J.*, 1945, **246**, 435 ; B., 1945, I, 369.

[30] *J. Inst. Elect. Eng.*, 1945, **92**, *Part* II, 385 ; B., 1946, I, 1.

[31] *J. Sci. Instr.*, 1946, **23**, 165 ; B., 1946, I, 349.

[32] *Ind. Eng. Chem.*, 1946, **38**, 179 ; B., 1946, I, 190.

and C. F. Bonilla[33] suggest a maximum rate of heat flux, at pressures approximating to one third of the critical pressure. Alternatively, if rates of heat flow are kept constant and well below the maximum value, values for the film coefficient of heat transfer increase steadily with pressure up to ranges close to the critical pressure. The experimenters worked with an electrically heated metal disc, and found great difficulty in obtaining reproducible results unless the boiling surface was kept scrupulously clean. Soiled (perhaps slightly roughened) surfaces increased both film coefficient and maximum boiling rates. They noted certain abnormalities with binary mixtures of hydrocarbons, which could hardly be explained by a later discovery[34] that the liquids used were not the pure hydrocarbons, but mixtures of several components.

R. S. Silver,[35] in a discussion on the rates of heat transfer obtainable in evaporation or condensation at a surface, suggests that the highest resistance to heat transfer in such a system will ultimately lie in the film of condensing vapour. Details for heat interchange between hydrocarbon vapours and oils are set out in an American patent,[36] whilst a modified form for a tube-and-shell heat interchanger, in which the tube bundle is given a twist to produce a waisted shape, is claimed[37] to increase heat transfer without increased pressure drop.

K. G. Denbigh[38] notes that, for water and a large number of typical organic liquids, the Prandtl number (Pr) is related to the molal latent heat (H) at normal boiling point by the formula $-\log Pr = (0{\cdot}2H/RT) - 1{\cdot}8$. J. A. Storrow[39] has measured the film coefficient of heat transfer by natural convection for coils immersed in a tank of water; he notes that the results are higher than previously accepted figures for both horizontal cylinders and vertical surfaces. A paper[40] on the rate of heat transfer in a small annulus, by F. G. Carpenter, A. P. Colburn, and E. M. Schoenborn, suggests that the characteristic linear dimension for these conduits should be the difference between inner and outer diameter, as this gives a change from stream-line to turbulence with a Reynolds criterion of about 2000. Heat transfer rates across the inner wall of the annulus could then be effectively correlated by a plot of Colborn's J factor against this Reynolds criterion.

The use of organic silicates as heat-transfer fluids appears to be on the increase, and the use of tetracresyl (tetratolyl) silicate in transferring heat from an anthracite stove to a cooking oven has been described.[41] This silicate boils at 436°, while a mixture of tetraphenyl and tetracresyl

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[33] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 755; B., 1946, I, 213.
[34] *Ibid.*, 1946, **42**, 411; B., 1946, I, 350.
[35] *Engineering*, 1946, **161**, 505.
[36] U.S.P. 2,379,519.
[37] B.P. 570,115; B., 1945, I, 348.
[38] *J.S.C.I.*, 1946, **65**, 61; B., 1946, I, 217.
[39] *Ibid.*, 1945, **64**, 322; B., 1946, I, 45.
[40] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 165; B., 1946, I, 350.
[41] *Coke*, 1946, **8**, 68.

silicates is claimed[42] to remain liquid down to −20°. A special design of heating stirrer, for use in a vacuum boiling pan, and consisting of a series of hollow coils mounted on a common axle, has been patented.[43] The problem of cooling viscous liquids, which deposit crusts on the cooling surface, has been partly overcome[44] by a synthetic thick wall in which a third fluid circulates as a mixture of liquid and saturated vapour.

H. C. Hottel and A. Kalitinsky,[45] in tests on the measurement of gas stream temperatures by means of thermocouple probes, show that conversion of kinetic energy into heat occurs with consequent rise in the indicated temperature; they have devised a form of probe which gives a recovery of this kinetic energy with an efficiency approaching 98%.

DISTILLATION.

Mass transfer between liquid and vapour in distillation has been so rapid, in comparison with the parallel case of gas absorption, that little attention has been paid to film resistances. With the growing demand for very narrow distillation cuts has come the necessity for a closer study of these film resistances. Until recently, measurements have been confined to wetted-wall columns (*Ann. Repts.*, 1945, **30**, 10), but R. L. Geddes[46] has shown how to apply diffusion rates in liquid and vapour phases to a measurement of film resistances and hence of Murphree efficiencies in a normal bubble-cap plate; he compares his calculated results with published figures for plate efficiencies and finds reasonable agreement in most cases, though certain large and unexplained discrepancies are noted. R. E. Peck and E. F. Wagner[47] combine the normal McCabe–Thiele diagram with a mass transfer construction in which the line indicating concentration head is sloped to the axes in accordance with the relative magnitudes of the film coefficients; suitable values for this slope are obtained by trial and error in a stated case, and the relative magnitudes of the coefficients are assessed thereby. With a wetted-wall column, resistance was entirely in the gas film, while in a packed column or bubble-cap plate the resistances of both films were approximately equal.

A. M. Clark[48] has presented a mathematical analysis of the separation of binary mixtures by distillation, based on previously derived equations for the equilibrium between liquid and vapour. An expression is obtained for the number of theoretical plates required under total and partial reflux, and the number compared with other figures calculated on the basis of (*a*) diffusion and (*b*) heat transfer; a simple relation is shown to exist between all three figures. K. Wohl[49] has reviewed the work of Van

[42] U.S.P. 2,335,012; B., 1946, I, 254.
[43] U.S.P. 2,335,131; B., 1946, I, 120.
[44] B.P. 575,749; B., 1946, I, 255.
[45] *J. Appl. Mech.*, 1945, **12**, A, 25; B., 1946, I, 153.
[46] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 79; B., 1946, I, 216.
[47] *Ibid.*, 1945, **41**, 735; B., 1946, I, 216.
[48] *Trans. Faraday Soc.*, 1945, **41**, 738; B., 1946, I, 118.
[49] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 215; A., 1947, I, 14.

Laar, Margules, and others on the relation between liquid and vapour, and extended their mathematical treatment to ternary complexes. W. D. Harbert,[50] assuming constant relative volatility and constant internal reflux, has derived a series of equations connecting number of plates with composition change, for both binary and multicomponent mixtures.

This problem of multicomponent mixtures continues to attract attention, and several other attempts at simplification have appeared. E. G. Scheibel and C. F. Montrose[51] present a method for the determination of the minimum reflux ratio required in a multicomponent separation. This ratio is based on (*a*) a minimum reflux for a pseudo-binary mixture of two key components and (*b*) the increase in this ratio required in order to strip the key components at each end of the column ; this latter increase is expressed in the form of an empirical equation based on relative volatilities. E. G. Scheibel[52] then suggests a similar method for the determination of a positive reflux ratio, to be applied to a key component binary system ; the method is claimed to give, by normal graphical means, the number of plates and the position of the feed plate required for a given separation. W. C. Edminster[53] has evolved a somewhat complicated "stripping factor" determined by plate number and by reflux ratio, for which he gives a graphical solution. This factor, applied to a multicomponent mixture with fixed volatility ratios, gives from a defined product a feed plate composition, and from the bottom plate discharge an alternative value for the feed plate. Trial values of the stripping factor are applied until a satisfactory single solution for the feed plate composition is found.

The processes of azeotropic and extractive distillation (the latter being defined as the process of addition of a selective non-volatile component) are being more widely employed. A. P. Colburn and E. M. Schoenborn[54] have discussed the selection of the agent to be employed in either case. The general efficiency of an agent may be expressed in the form of a change in the activity coefficient; in general, differences in these coefficients diminish as the temperature of the system rises, and much published material cannot be successfully correlated because of this fact. When, however, satisfactory figures exist for two binary systems having a common component, the corresponding figures for a combined ternary system can be calculated. M. Benedict and L. C. Rubin[55] have laid down suitable conditions for the choice of active agents in either system of distillation, and they point out that agents for extractive distillation are much easier to find than suitable azeotrope formers. The same two workers, with C. A. Johnson and E. Solomon,[56] suggest a triangular

[50] *Ind. Eng. Chem.*, 1945, **37**, 1162 ; B., 1946, I, 118.
[51] *Ibid.*, 1946, **38**, 268 ; B., 1946, I, 216.
[52] *Ibid.*, 397 ; B., 1946, I, 216.
[53] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 15 ; B., 1946, I, 215.
[54] *Ibid.*, 1945, **41**, 421 ; B., 1945, I, 370.
[55] *Canad. Chem.*, 1945, **29**, 746 ; B., 1946, I, 78.
[56] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 371 ; B., 1945, I, 346.

diagram, based on determinations of activity coefficient, for the study of ternary distillation systems. O. L. Updike, W. M. Langdon, and D. B. Keyes[57] tested a wide range of organic liquids for their effect in separating aromatic from paraffinic hydrocarbons. Most notable changes in relative volatility were obtained with nitromethane, acetonitrile, and furfuraldehyde. No particular property of these successful separating agents could be singled out as a guide to activity.

This separation of aromatic from paraffinic constituents was of great importance during the war in the preparation of toluene, and a number of patents have recently appeared dealing with this process. Thus[58] a mixture of acetone, methanol, and water, added to toluene–paraffin, gives a residue of toluene and aqueous alcohol, with an overhead of acetone–paraffin. Alternatively, a mixture of acetone and methanol is used alone,[59] while a mixture of methyl ethyl ketone and water,[60] or nitromethane,[61] has also been suggested. It is a matter for note that none of these separating agents increased the volatility of the toluene *vis-a-vis* the paraffin, a point also made by Updike and his co-workers.

A notable achievement in extractive distillation has been reported by J. Happel[62] and his collaborators. By the use of aqueous furfuraldehyde it was possible to modify the relative volatilities of the C_4 hydrocarbons very considerably, and eventually to obtain a nearly pure butadiene concentrate as a residue from a complex mixture. Two sixty-plate columns were used, of standard cap and bubble type, and it was notable that the plate efficiency, based on published data for activity coefficients, was relatively low—about 25%.

R. H. Ewell and L. M. Welch[63] have reported the existence of an unusual ternary azeotrope in the system methanol–acetone–chloroform; this ternary complex has neither the lowest nor the highest boiling point, so that for certain mixtures the boiling point first falls, then remains steady, and then rises again. R. S. Dicks and C. S. Carlson[64] have compared the capacity of a column when separating by straightforward fractional distillation and when operating with an added component for extractive distillation. In a typical case, extractive distillation gave the same results that would have been obtained by normal distillation in a column four times as high and of the same cross-section.

The method of assessing fractionating column efficiency by comparison with theoretical plates, or height equivalent thereto, has come under criticism by J. A. Gerster, J. H. Koffolt, and J. R. Withrow.[65] They

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[57] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 717; B., 1946, I, 215.

[58] B.P. 572,897; B., 1946, II, 33.

[59] B.P. 572,297; B., 1946, I, 56.

[60] U.S.P. 2,388,040.

[61] U.S.P. 2,385,610.

[62] J. Happel, P. W. Cornell, D. Eastman, M. J. Fowle, C. A. Porter, and A. H. Shuttle, *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 189; B., 1946, II, 405.

[63] *Ind. Eng. Chem.*, 1945, **37**, 1224; A., 1946, I, 114.

[64] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 789; C., 1946, 159.

[65] *Ibid.*, 393; B., 1945, I, 370.

argue that this efficiency will vary with the slope of the equilibrium curve and with the reflux ratio chosen, and results can rarely be comparable; that such consistent figures for plate efficiency have been reported in the past is due to the constancy of reflux ratio and flatness of the equilibrium curve in the plant chosen for measurement. J. E. Mitchell, jun.,[66] has described the purification of styrene by vacuum fractionation, when the need for checking polymerisation made it necessary to work with a maximum pressure drop from bottom to top of column of less than 35 mm. of mercury. This problem of fractional distillation under reduced pressure has been the subject of a patent[67] which describes a column with a series of rotors, compressing the vapour sufficiently for pressure drop to be negligible from top to bottom of the column. L. Dostrovsky and E. D. Hughes[68] have given an account of a very efficient small column equivalent to 450 theoretical plates, for the separation of heavy water; this column was 12 ft. long, packed with wire gauze rings, and automatically controlled.

Difficulties in the proper distribution of liquid in a packed column are claimed[69] to be overcome by a method of flooding the packings, in this case wire gauze cylinders, before operation; the apertures in the wire remain covered during subsequent working. A perforated-plate column has been built[70] in which the size of the vapour passage diminishes from the bottom to the top, while another, which should be simple to construct, has[71] the perforated plates of wire gauze with dished edges, and pyramidal projections to provide spacers and phase paths. A helical wire coil for packing[72] and a bubble-cap tray[73] made up from corrugated plates have been patented. Methods for the control of a fractionating column by pressure drop,[74] by the viscosity of a selected fraction,[75] and by the boiling temperature of a sample of the product[76] have been described. D. F. Othmer and F. R. Morley[77] have devised an equilibrium still which is suitable for use at pressures up to 200 lb. per sq. in.

Main developments in molecular distillation have been in connexion with the pumping system. A detailed paper[78] by P. Alexander, on the design of vapour diffusion pumps, criticises the prevailing conception of operation as gaseous diffusion through a slot, of width approximating to the mean free path of the vapour molecules. Many pumps may be shown to have a pumping speed in excess of a maximum calculated on

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[66] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 293; B., 1946, I, 407.
[67] U.S.P. 2,333,712; B., 1946, I, 49.
[68] *Nature*, 1946, **158**, 164.
[69] B.P. 578,309; B., 1946, I, 360.
[70] U.S.P. 2,206,502; B., 1946, I, 7.
[71] U.S.P. 2,336,060; B., 1946, I, 193.
[72] U.S.P. 2,332,110; B., 1946, I, 49.
[73] U.S.P. 2,339,561; B., 1946, I, 281.
[74] U.S.P. 2,386,778.
[75] U.S.P. 2,198,325; B., 1946, I, 6.
[76] U.S.P. 2,340,026; B., 1946, I, 281.
[77] *Ind. Eng. Chem.*, 1946, **38**, 751; C., 1946, 299.
[78] *J. Sci. Instr.*, 1946, **23**, 11; B., 1946, I, 118.

this basis, and the vapour stream must therefore act as an entraining jet. In support of this theory, pressure measurements in the throat of a typical pump are cited, and it is shown that one of the most critical points in pump design is the avoidance of a break-back of gas molecules along the walls of the pumping chamber. A pump designed to suit these conceptions is described, and claims are made for a very high pumping speed. A recent patent[79] is reminiscent of the same idea of a high fluid velocity over the cooling and condensing surfaces ; a jet of liquid is used, which is partly vaporised between the entraining nozzle and the condensing surface. The relative merits of petroleum oils (several proprietary types) and two typical silicones as pumping agents in vapour diffusion pumps have been determined[80] by G. P. Brown ; the highest obtainable vacuum and the best resistance to oxidation at boiling temperature were both registered with a silicone oil.

ABSORPTION AND EXTRACTION.

Some attention has been paid to the simple spray tower, with no packing, as a unit for mass transfer. H. F. Johnston and H. Bliss[81] have compared the rates obtained in a small solvent-extraction tower of this kind with those obtained in packed towers ; they suggest that the spray tower is well suited to liquid systems of low interfacial tension, especially in the case of high concentration head between phases. S. K. Nandi and T. R. Viswanathan[82] have detected a possible source of error, in small-scale experiments with towers of this type, caused by undue turbulence at the jets of the spraying system ; they worked with a small column, and, subject to the criticism above, they suggest that the effective H.T.U. is independent of concentration head. R. C. L. Bosworth,[83] in a study of the rate of absorption of a gas by a falling liquid drop, argues that the amount of gas absorbed, so long as equilibrium is not reached, will be proportional to the square root of the time of exposure. As, for a freely falling drop, the height fallen will vary as the square of the time, it follows that the amount absorbed will be proportional to the fourth root of the tower height ; the rate of absorption of carbon dioxide in a typical case was shown to follow this rule. It is presumed that a steady falling rate was never attained, or the second premise would hardly apply.

W. E. Lobo, L. Friend, F. Hashmall, and F. Zenz[84] have reviewed published data on the limiting flow rates (flooding points) of packed towers. They suggest a packing factor, determined by packing surface and percentage of voids, to modify a normal equation of the dimensional type correlating these flooding velocities ; the factor would need to be carefully determined, as they show that the percentage of voids in

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[79] U.S.P. 2,338,583 ; B., 1946, I, 282.
[80] *Rev. Sci. Instr.*, 1945, **16**, 316 ; B., 1946, I, 118.
[81] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 331 ; B., 1946, I, 352.
[82] *Current Sci.*, 1946, **15**, 162 ; B., 1946, I, 352.
[83] *J. Proc. Austral. Chem. Inst.*, 1946, **13**, 53 ; B., 1946, I, 253.
[84] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 693 ; B., 1946, I, 215.

ordinary ring packing varies widely according to the method of filling used.

In an extraction unit[85] for gases, the gas is introduced at the base of a tall liquid column under a fine-mesh wire screen, which is vibrated to break up the gas bubbles into a fine dispersion. A rotary extractor for solids has been patented[86] in which solution flows down the rotating cylinder against lifting helical fins which convey the solid to the top; the liquid does not overflow the fins, and a long countercurrent path is created.

EVAPORATION.

C. F. Bonilla[87] has shown mathematically that in multiple-effect evaporation, the distribution of areas of heating surface in each effect to give the minimum total surface shall be such as to make the ratio of effect surface to temperature drop constant for each effect; despite the marked alteration in area this arrangement demands, the total surface does not change markedly from that required for the normal arrangement with equal heating surfaces in each effect. A practical commentary on this calculation is provided by S. C. Spencer,[88] who urges the importance of such practical factors as tube fouling; in the design of a multiple-effect system it is always essential to bear in mind the necessity for high liquid rates over heating surfaces where fouling is likely to occur.

L. A. Tromp[89] has shown diagrams of the more important types of jet condenser now in use; he suggests that parallel-flow jet-ejection units, dispensing with both vacuum pumps and barometric leg discharge, are likely to prove most popular in the future, while wet vacuum pump systems are becoming obsolete. H. E. Byer[90] recommends the use of barometric jet condensers, countercurrent where the vapour load is steady, and parallel flow where the load is intermittent, as in final vacuum pan finishing for sugar; he agrees with Tromp that wet vacuum pump systems are obsolete. P. Freneau[91] points out that a steam-jet ejection system can be a valuable check on the working of a plant; as the suction pressure, for a given jet, is an indication of the amount of non-condensible gas being handled, this pressure becomes a measure of the amount of air leak plus the amount of gas being evolved during the operations in the plant.

P. Sporn, T. Baumeister, and E. R. Ambrose[92] have drawn attention to the use of vapour recompression in evaporation as a means for utilising surplus electrical power, and have urged the application of the heat pump generally in a factory system for the conservation of fuel. The deposition

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[85] B.P. 572,242; B., 1946, I, 50.
[86] U.S.P. 2,199,928; B., 1946, I, 6.
[87] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 529; B., 1946, I, 79.
[88] *Ibid.*, 1946, **42**, 407; B., 1946, I, 352.
[89] *Inst. Sugar J.*, 1946, **48**, 94; B., 1946, I, 253.
[90] *Ibid.*, 44; B., 1946, I, 153.
[91] *Chem. Met. Eng.*, 1946, **53**, *No.* 6, 104; B., 1946, I, 391.
[92] *Ibid.*, 98; B., 1946, I, 349.

of a calcium sulphate scale is a frequent phenomenon in evaporation processes, and J. W. Waser and F. N. Alquist[93] describe the removal of such scale by boiling with a concentrated (30—40%) solution of caustic soda; a large brine evaporation system was treated very successfully in this way. A patent[94] on the use of inert solvent vapour in the concentration of concentrated aqueous solutions describes the dehydration of caustic soda solution in a packed tower; the solution flows down countercurrent to kerosene vapour, and substantially anhydrous soda collects at the base; the supply of kerosene vapour is from a diphenyl boiler.

L. M. K. Boelter, H. S. Gordon, and J. R. Griffin[95] have given experimental values for the evaporation of water from a horizontal plane surface; the data can be correlated to some extent by a dimensional equation, or by a simple empirical equation reminiscent of the earlier work of Hinchley and Himus. E. Simons[96] has reduced the formulæ for the design of cooling towers previously published (*Ann. Repts.*, 1942, **27**, 14) to a series of nomograms, which facilitates the design of this particular multi-deck type; at the same time, the importance of avoiding marine growth by sterilisation (chlorine treatment) is emphasised. The older type of pyramidal wooden cooling tower is being gradually replaced by the double-cone, hyperboloid section tower, in concrete. F. K. T. van Iterson[97] has indicated the manifold advantages of this latter type as regards mechanical stability; very considerable deformation of the reinforced concrete construction, due, *e.g.*, to foundation subsidence, can occur without the structure collapsing.

MIXING.

J. H. Rushton[98] has again stressed the point that no general criterion of effective mixing exists. In a review of published data, he points out that power consumption can generally be related to cube of speed, fifth power consumption can generally be related to cube of speed, fifth power of diameter (or other linear dimension), and density of fluid being stirred. The effects of viscosity are confined to a relatively small region which can be defined by a modified Reynolds number. D. F. Riley[99] has classified liquid mixers into the three main classes of paddle, turbine, and propellor; he suggests appropriate fields and power consumption formulæ for each type. I. S. Brumagin[100] has made a study of the flow forms produced by propellor and turbine mixers, and suggests that the former is unsuitable for liquids of high viscosity, unless the containing vessel is streamlined to eliminate dead-space; turbine mixers can give effective mixing of viscous

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[93] *Ind. Eng. Chem.*, 1946, **38**, 394; B., 1946, I, 253.

[94] U.S.P. 2,326,099; B., 1946, I, 278.

[95] *Ind. Eng. Chem.*, 1946, **38**, 596; B., 1946, I, 277.

[96] *Chem. Met. Eng.*, 1945, **52**, *No.* 6, 106; B., 1945, I, 345.

[97] *Proc. Ned. Akad. Wetensch. Amsterdam*, 1946, **49**, 113; B., 1946, I, 189.

[98] *Canad. Chem.*, 1946, **30**, *No.* 5, 55; B., 1946, I, 352.

[99] *Manufg. Chem.*, 1946, **17**, 274; B., 1946, I, 352.

[100] *Chem. Met. Eng.*, 1946, **53**, *No.* 4, 110; B., 1946, I, 215.

liquids in regularly shaped vessels, but they lack the shearing action of a propellor mixer.

E. S. Bissel, H. J. Everett, and J. H. Rushton[101] have shown that the problem of maintaining effective agitation in shallow layers of liquid, such as may be present in an emptying tank, is a very real one. Propellor mixers require a seal of at least 1·5 times the propellor diameter in order to avoid vortex formation, while for really effective mixing the liquid depth should never be less than half the tank diameter. If a tank is to be emptied slowly, with maintenance of mixing, the stirring devices should carry two impellors, and the tank bottom should be cone-shaped or provided with a small well for the lower impellor and outlet.

DRYING.

In a paper by W. B. Senseman,[102] the advantages of combining size reduction with drying are pointed out, and a special system is described in which a very wet feed may be dried and disintegrated. High-speed hammer or squirrel-cage breakers are used, with a fan and cyclone separator in closed circuit; moist air from this circuit is continuously displaced by hot waste gas from a furnace, and wet feed is mixed with partially dried and recirculated material. For large units drying and grinding can be arranged with the solid flowing partially countercurrent to the hot gas supply, thus increasing thermal economy. Short working times and the rapid cooling of the hot gases make the process suitable for thermally unstable substances. The dual function of air circulation in direct drying—heat transfer and moisture entrainment—has been analysed by V. P. Victor,[103] who suggests equations for the determination of the optimum amount of recirculation in a reheating system.

D. B. Broughton[104] argues that the movement of moisture in a porous slab drying in a current of air is governed by diffusion under concentration head forces; resistance to flow is determined by the liquid viscosity, which in turn varies with the liquid temperature. The argument is developed to show that a plot of the ratio drying rate/air temperature against water content will give a straight line with an intercept on the axis indicating critical water content. The mechanism of moisture movement in porous material has also engaged the attention of L. E. Stout, K. J. Caplan, and W. G. Baird.[105] They note that flow appears to follow the same laws with both convective and infra-red drying, even though the drying rate may be much faster in the latter case; the difference is often so marked that air currents may diminish the total heat input in a radiant-heat dryer.

J. W. Payne and C. H. Nachthaler[106] have described a dryer for free-flowing solids, the operation of which is reminiscent of "through washing"

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[101] *Chem. Met. Eng.*, 1946, **53**, *No.* 1, 118; B., 1946, I, 152.
[102] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1897; B., 1945, I, 370.
[103] *Chem. Met. Eng.*, 1945, **52**, *No.* 7, 105; B., 1945, I, 345.
[104] *Ind. Eng. Chem.*, 1945, **37**, 1184; B., 1946, I, 117.
[105] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 283; B., 1945, I, 345.
[106] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 105; B., 1946, I, 117.

in a filter press. The drying chambers are arranged, as thin slices between inlet and outlet air chambers, assembled in batteries as in a filter press. The sides of the drying chamber are of wire mesh, and the drying air flows across the chamber as the stream of granular material flows downward to an outlet port at the base. H. F. Reichard[107] suggests the use of an additional spray to increase the capacity of a dipping-drum dryer. A device[108] for producing strings of paste from a slurry, followed by drying of these strings, has been patented, while a combination[109] of drying and elutriation in a single chamber may be of interest.

FILTRATION AND GAS CLEANING.

B. F. Ruth[110] shows that electro-osmotic effects may play an active part in filtration, especially where electrolyte concentration is changing, as in normal washing. The liquid streaming potential which is set up increases the apparent resistance of the filter cake. It had been noted by previous workers that the permeability of a porous material appeared to vary with the testing fluid, and these potential effects may well have been the cause. It follows that measurements of filtration rates can be applied in calculations only when it is specified that identical electrochemical conditions obtain. A. J. Luettgen, K. S. Whisler, and H. D. Bauman,[111] working on the caustic soda solution obtained after incineration and lixiviation of lignate residues in paper mills, have found that a filter bed of graded anthracite coal is most effective in the removal of finely divided carbon.

A combined pressure-leaf and centrifugal unit for separating liquids and solids has been described[112] in which the solid is first deposited by fluid flow through the filter leaves, and then flung off by centrifugal force. It is claimed[113] for another centrifugal separator that the continuous discharge of friable solids, such as sugar crystals, can be obtained by suitably sloped walls, thus avoiding the breakage caused by normal mechanical discharge devices.

C. E. Beaver[114] has reviewed the present position of electrostatic precipitation in gas cleaning. He notes that the principal cause of failure is a high electrical resistance offered by the precipitated material; this can be overcome by the addition of water spray or ammonia vapour to the gas before treatment. Typical treatment times are from 2 to 5 seconds, and precipitation efficiencies range from 90 to 98%; recent successful applications have been the coagulation of carbon black and the recovery of "fluidised" catalyst. New forms of precipitator are still

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[107] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 118; B., 1946, I, 117.

[108] U.S.P. 2,339,979; B., 1946, I, 279.

[109] B.P. 576,056; B., 1946, I, 311.

[110] *Ind. Eng. Chem.*, 1946, **38**, 564; B., 1946, I, 278.

[111] *Ibid.*, 832; B., 1946, I, 406.

[112] B.P. 574,896; B., 1946, I, 219.

[113] U.S.P. 2,335,794; B., 1946, I, 120.

[114] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 251; B., 1946, I, 392.

appearing and a typical patent[115] describes three stages—ionising, precipitation on a collecting electrode as agglomerates, which may then be re-entrained, and final collection in a chamber with corona discharge. In another type,[116] the collecting electrode forms a moving wall, which carries the dust out of the circuit to collecting nozzles.

Other methods of gas cleaning have not been neglected. In a series of papers[117] on the removal of tar fog from coal gas, E. H. M. Badger indicates that tar precipitation is an important auxiliary function of a turbo-exhauster, when this is used to remove gas from the retorts and force it through a purifying train; the type of exhauster chosen should depend on this auxiliary purpose, for which a single-stage machine working at high speeds is more effective than multi-stage units of slower speed. A cyclone separator[118] which has been very successful in the cleaning of boiler-plant waste gas has been built up from a number of small cyclones in parallel; the unit cyclones were only 6 in. in diameter, with an inner tube of 4 in., to give a very narrow annulus. Efficiencies of more than 90% were claimed for grate-fired boilers, while over 80% of the dust was recovered with powdered-coal firing. An account has just been published[119] of a novel German design for cyclones, with an axial inlet.

F. S. Gilg[120] has recorded some experiences with blast-furnace gases cleaned in various ways and then used as a boiler fuel. Unless the gas was very thoroughly cleaned, deposits always formed in the flues; these deposits were particularly difficult to remove when the gases were water-washed, and formed hard scales on the heating surfaces. Dry cleaning of the gases by cyclones etc. gave deposits which were easily removed by blowing and brushing. C. C. Hermann,[121] after reviewing the methods available for dust collection, has indicated the best means for disposing of waste dust from dry cleaning; after discharge from collecting hoppers by means of a double valve, or a rotating pocket, the dust is wetted to a fluid sludge and fed to settling tanks from which a heavy sludge is withdrawn to dumping trucks or barges.

W. Francis[122] has given a detailed description of the processes being used to reduce the sulphur content of waste gases to a statutory limit. Where effluent is allowable, the matter is straightforward, and the sulphur is rejected as a dilute calcium sulphite–sulphate mixture. Non-effluent processes reduce to washing with a concentrated solution of sulphates and sulphites, buffered with alkali, and withdrawing some fraction continuously for working up to solid salts or liquid sulphur dioxide.

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[115] U.S.P. 2,199,390; B., 1946, I, 7.

[116] U.S.P. 2,333,431; B.P. 570,630; B., 1946, I, 51; 1945, I, 350.

[117] *J.S.C.I.*, 1946, **65**, 166; B., 1946, I, 284.

[118] *Elect. Times*, 1945, **108**, 768; B., 1946, I, 77.

[119] *Brit. Coal Util. Res. Assoc. Bull.*, 1946, **10**, 50; B., 1946, I, 310.

[120] *Iron Steel Eng.*, 1945, **22**, *No.* 3, 47; B., 1945, I, 347.

[121] *Chem. Met. Eng.*, 1946, **53**, *No.* 5, 136; B., 1946, I, 278.

[122] *Power and Works Eng.*, 1946, 17; B., 1946, I, 309.

SIZE REDUCTION.

A notable paper[123] by T. K. Prentice claims that a reasonably constant figure of 3·5 ft.-lb. per sq. ft. of surface produced is required in the crushing of South African quartzite; the figure was based on the breakage of standard fragments by bending, compression, and tension, followed by surface measurement by liquid adsorption and/or Carman's permeability method. Application of these results to actual grinding figures for bulk industrial grinding of the same rock suggested grinding efficiencies of the order of 25—35%. Subsequent discussion[124] on the paper, however, suggested that further work on the subject would be necessary before the generalisation could be considered as firmly established. It should be noted that F. C. Bond has claimed[125] that crushing strength tests on rocks are of little use as a guide to resistance in gyratory crushers or ball mills; he argues that a better criterion is given by impact shattering, and has devised a twin-hammer impact machine for this test.

H. Heywood and E. J. Pryor[126] suggest that ground mineral particles tend to assume a common form—that of a truncated tetrahedron. They draw up a table on this basis to show the distribution of surface in samples of definite size range; the table shows very clearly the large amount of surface associated with particles of below normal sieving size. In another paper,[127] H. Heywood indicates the possible errors in normal sifting analyses, showing that sieving on standard B.S.I. sieves in different laboratories can give deviations of ±8% from a mean value. A. R. Steinberg[128] suggests that the true form of finely ground particles approximates to a flattened plate of height from 0·2 to 0·5 times the linear dimension of the irregular base; this base diameter is most correctly measured by Martin's method—the length of a bisecting line—as surface measurements calculated from this are in agreement with those of hydraulically equivalent spheres.

F. Warnecke[129] contends that distribution of weight in subsieve samples can be effectively determined by Gaudin's hypothesis (that a linear relation exists between log of weight and log of size). The slope of the line expressing this hypothesis can be determined by plotting points around the 200-mesh range; material of below 1 mμ. is neglected as being colloidal in character and not produced by grinding. The individual fragments may be assumed, according to Warnecke, to approximate to spheres, and determinations of surface based on this assumption are tabulated.

C. Benedicks and P. Sederhohm have calculated[130] the effect of a liquid on the strength of a solid particle with existing cracks. It is shown that

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[123] *Bull. Inst. Min. Met.*, 1946, *No.* 477; B., 1946, I, 190.

[124] *Ibid.*, *No.* 478.

[125] *Amer. Inst. Min. Met. Eng.*, 1946, *Tech. Publ.* 1895; B., 1946, I, [illegible]

[126] *Bull. Inst. Min. Met.*, 1946, *No.* 477; B., 1946, I, 190.

[127] *Ibid.*; B., 1946, I, 190.

[128] *J.S.C.I.*, 1946, **65**, 314; B., 1947, I, 3.

[129] *Chem. Eng. Min Rev.*, 1946, **38**, 323; B., 1946, I, 351.

[130] *Jernkont. Ann.*, 1945, **129**, 107; B., 1946, I, 79.

the form of the crack determines the effect of the liquid ; with a short wide crack, the liquid reduces the strength of the solid, while with a narrow deep crack, the strength is increased. Benedicks and G. Rubin[131] then go on to show experimentally the effect of liquids on solid strength tests. Tensile, bending, and fatigue tests on metals all give lower values when the metal is immersed in water, while glass in similar circumstances has its strength reduced by over 30%. The effect of different liquids was measured in this latter case, and it was found that the transverse strength of a glass specimen was reduced 23% by ethyl alcohol and 21% by glycerin. Tensile strength tests on steel bolts showed that failure occurred at scratches which had been previously wetted by water. It is not clear how this effect would influence wet grinding as opposed to dry working, but certainly another factor has been recognised in a very confused system. G. S. Smith[132] has mentioned the effect of surface cracks on strength tests, and a paper[133] by L. C. Verman on the mechanical strength of bonded materials may also be of interest.

D. P. Brown and R. Hess[134] have made a detailed analysis of the working of a pan grinding plant and screening unit ; they compared such factors as the possible throughput of fines with the actual throughput, and the effect of changes in the circulating load. Although no specific generalisations were established, a number of useful working figures for clays of varying hardness were determined. H. R. Banks[135] proposes that the feed to a ball mill should be screened to remove large fragments, so that smaller balls may be used in the mill proper ; this increases the capacity of the mill, which is roughly proportional to the grinding surface present. The use of rubber linings is to be deprecated, as throughput is reduced to a much greater extent than is compensated for by any saving in wear or power consumption. The author also suggests that cascade mills, which dispense with ball charge, are of use only for certain types of ore easily fractured by impact. N. A. Macleod[136] has measured the relative rates of ball wear in a small rubber-lined mill, with batch grinding. When sulphur-containing ores were being ground, the rate of wear was increased by aëration ; with siliceous materials no aëration effect could be traced. This chemical corrosion will clearly make it impossible to correlate ball wear as between siliceous and pyritic ores on the basis of a grindability test.

C. E. Berry[137] suggests that for dry grinding to sub-sieve sizes the machine should be either a high-speed hammer mill or a jet pulveriser (fluid energy unit) according to the type of material being handled For tough, resilient fragments the hammer mill, with internal classifier,

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[131] *Jernkont. Ann.*, 1945, **129**, 37 ; B., 1946, I, 79.
[132] *Metallurgia*, 1945, **33**, 55 ; B., 1946, I, 78.
[133] *J. Sci. Ind. Res., India*, 1946, **4**, 459 ; B., 1946, I, 214.
[134] *J. Amer. Ceram. Soc.*, 1946, **29**, 147 ; B., 1946, I, 278.
[135] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1890 ; B., 1945, I, 370.
[136] *Ibid.*, 1918 ; B., 1946, I, 78.
[137] *Ind. Eng. Chem.*, 1946, **38**, 612 ; B., 1946, I, 351.

is recommended; power consumption here may be as high as 50 h.p. hours per ton of 5—20-mμ. material. For hard, brittle solids a fluid energy system should be used, in which the fragments are entrained and disintegrated by internal friction. The fluid stream may work with a centrifugal swirl, or with a circular ring tube, or with a long straight conduit. Details of all these units are given and claims made for reduction to below 5 mμ. in size. The amount of fluid required may be up to ten times the weight of solid, and pressure drops of 100 lb. per sq. in. across the unit are suggested.

The use of a ball race as a means for fine grinding continues to attract attention, and a relatively simple arrangement of two upright cones, with the ball race forming the annular floor between them, has been patented[138]; the space between the cones acts as a preliminary classifier. Another patent[139] describes a series of ball races mounted on a common rotor; the material to be ground passes through each race in turn. As a contrast to the positive grinding action of the ball race, another pulverising unit has been described[140] in which a rotor turns in a vertical cylindrical chamber, with ample clearance between rotor blades and the walls; disintegration is caused by vortex action in the clearance space, and an upward current of air removes fines.

W. H. Coghill, G. D. Coe, and I. L. Feld[141] have described a new type of upward-current classifier of relatively simple design, with a long narrow lower tube discharging into a wider head, which acts as a preliminary sorting chamber; several of the lower tubes can be built to deliver into the head section. In a second paper, the same workers, with M. F. Williams,[142] set out a number of results obtained with this classifier, working on both size and density separation.

MATERIALS.

The use of "Karbate," or compressed carbon block, appears to be extending. According to M. R. Hatfield and C. E. Ford,[143] the best base for construction is graphite, and this may be cemented with a wide range of synthetic resins, the choice being based on the usage required. It has been possible to make up a calandria heater for steam pressures of 40 lb. per sq. in., with a surface of 90 sq. ft., and a commercial size cooler-absorber for hydrochloric acid gave absorption rates of 10 lb. of HCl per hr. A further use[144] for silicone derivatives has been found in the manufacture of thermally resistant insulating material, allowing the use, according to H. F. Horrell, of much higher temperatures in electrical plant. Polymerised tetrafluoroethylene is now available on an

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[138] U.S.P. 2,196,642; B., 1945, I, 372.

[139] U.S.P. 2,204,140; B., 1946, I, 81.

[140] U.S.P. 2,324,208; B., 1945, I, 373.

[141] *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3844; B., 1946, I, 189.

[142] *Ibid.*, 1946, *Rept. Invest.* 3851; B., 1946, I, 189.

[143] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 121; B., 1946, I, 215.

[144] *Paper Trade J.*, 1945, **121**, *No.* 22, 18; B., 1946, I, 77.

experimental plant scale, and M. M. Renfrew and E. E. Lewis[145] have made some striking claims for its resistance to all types of chemical attack. The polymer is unattacked by all common reagents, from caustic soda to fuming nitric acid, and is insoluble in any type of organic solvent. Up to a temperature of 300°, the only reagent to show any appreciable attack was molten sodium, and the mechanical properties of the material were quite satisfactory from this temperature down to $-100°$. The only drawback appears to be that no satisfactory bond to metals has yet been devised.

M. G. Fontana[146] has listed and compared the various synthetic rubbers and plastics now available for plant fabrication, and B. W. Whitehurst[147] has described the erection of large plant units in Pyrex glass. R. W. Porter[148] gives an account of the manufacture of fluorine in commercial quantities, and it would appear that the corrosive properties of fluorine and hydrofluoric acid have been successfully overcome; the fluorine is made by normal electrolytic methods, using steel cathodes and carbon anodes, and the fluorine is led off through mild steel pipes, purified by cooling, and compressed into steel cylinders, with monel metal valves.

Plant Design and Control.

C. F. Roe[149] suggests that the various formulæ which have been put forward for the design of thick-walled pressure vessels can be reduced to a general form in which the ratio of pressure to wall stress is equated to the ratio of wall thickness to external diameter; the results given by this simplification are compared with those calculated from the formulæ of Lamé, Claverino, and others. S. M. Jorgenson[150] has presented formulæ and diagrams for the calculation of stresses in vessels under both internal and external pressure. A special design[151] for the latter type of vessel (*e.g.*, vacuum still) has been patented, with corrugated walls and external stiffening rings.

H. G. Elrod[152] shows that slight economies in multiple-stage gas compression may be obtained by varying the compression ratio to suit the temperature to which the gas is cooled between stages. A proportioning pump has been devised[153] with telescopic plungers, the length of which may be adjusted by means of a micrometer handwheel. C. H. Butcher,[154] in the course of a general review of chemical plant details, has indicated the advantage of a bursting disc over a spring-loaded safety valve, which is apt to stick when exposed to chemical plant atmospheres.

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[145] *Ind. Eng. Chem.*, 1946, **38**, 870; B., 1947, II, 21.
[146] *Chem. Met. Eng.*, 1946, **53**, *No.* 4, 102; B., 1946, I, 253.
[147] *Ibid.*, *No.* 7, 112; B., 1946, I, 370.
[148] *Ibid.*, 106; B., 1946, I, 368.
[149] *Ibid.*, *No.* 3, 114; B., 1946, I, 253.
[150] *Petrol. Refiner*, 1945, **24**, 381; B., 1946, I, 213,
[151] U.S.P. 2,329,970; B., 1945, I, 371.
[152] *Ind. Eng. Chem.*, 1945, **37**, 789; B., 1945, I, 347.
[153] *Chem. Age*, 1946, **55**, 76.
[154] *Ind. Chem.*, 1946, **22**, 324; B., 1946, I, 277.

J. D. Pull[155] has given some instances of the growing use of electronic devices in modern plant control, and J. D. Zeigler[156] has suggested that control systems can be classified as proportional, proportional with reset, and proportional with reset and maximum rate control. S. D. Ross[157] shows that normal valves and taps are not well suited to the operations of an automatic control system, and proposes special types, with specific relation between movement and size of opening obtained. J. L. More, F. J. Quail, and J. W. Bain[158] claim that the most desirable setting of a temperature-regulating device is one which gives a recovery curve of 25% amplitude ratio (each swing one quarter of the one preceding); they give experimental data for the performance of such a system.

Boiler Water Treatment.

L. Streicher[159] claims that certain feed waters can be softened economically by a simple electrolytic treatment. A diaphragm cell separates the water into an acid anolyte, which is rejected, and a basic catholyte, which is passed to a settling tank; here the basic water deposits calcium carbonate and magnesium hydroxide in a convenient form; the softened water is also quite free from dissolved oxygen. In a typical case the current consumption was 7 kw.-hr. per 1000 gallons of softened water, with a diminution of total hardness by 75%. Direct addition of chemicals to the boiler at fixed intervals can maintain alkalinity and phosphate concentration at desirable levels, but H. Gaunt[160] points out that such treatment gives no protection to the feed water heater, or any other pre-boiler plant. He proposes the adoption of a method whereby a proportion of the boiler water is added to the raw feed water, while direct dosage of the boiler continues as before. It is claimed that the total blowdown is greatly reduced as compared with the normal continuous conditioning process for feed water.

The return of condensate to a boiler is generally accompanied by troubles with entrained oil. This may be absorbed by base-exchange material, presumably acting as active surface. G. von Breitenstein and H. Berger[161] have detailed the use of "Invertitmasse" in reducing oil content; reactivation is by flushing with cold water and salt solution. J. H. Richards[162] recommends coagulation with a chemical precipitate, such as aluminium hydroxide, followed by filtration, as the only effective means of oil removal. One of the troubles frequently traced to oil is foam formation, but causes of this condition are many, and it may be desirable to add a foam-reducing agent. If an electrode[163] is fixed in the

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[155] *Chem. and Ind.*, 1946, 205.
[156] *Ind. Eng. Chem.*, 1946, **38**, 360; B., 1946, I, 215.
[157] *Ibid.*, 878; B., 1947, II, 46.
[158] *Ibid.*, 1945, **37**, 279; B., 1946, I, 149.
[159] *Civil Engineering*, 1946, **16**, 312; B., 1946, I, 309.
[160] *Elect. Times*, 1945, **108**, 356; B., 1946, I, 118.
[161] *Glückauf*, 1944, **80**, 261; B., 1946, I, 151.
[162] *Int. Sugar J.*, 1945, **47**, 321; B., 1946, I, 151.
[163] B.P. 572,759; B., 1946, I, 83.

vapour space just above the desirable liquid–foam level, rises in the foam can complete an electrical circuit and start a pump supplying antifoaming agent. Such an agent[164] should contain hydrophilic radicals connected by long unsaturated carbon chains, a composite molecule which is claimed to give stable surface films; a typical substance mentioned in the patent claim is cetyl β-stearylethanesulphonate.

B. G. Houseman[165] has set out the advantages of vegetable extracts, such as tannins, in the treatment of boiler water; it is claimed that calcium carbonate is precipitated as an easily suspended sludge, that corrosion of various kinds is checked, and that traces of oil are coagulated on the carbonate precipitate. A patent[166] for the preparation of nitrogen-containing phosphates for conditioning described the heating of phosphoric acid with urea or urethane at 140° until a white porous solid has formed. S. J. Hopkins[167] has described the use of organic ion-exchange agents for the preparation of low-conductivity water.

Failure of boiler tubes is often due to factors quite outside the control of boiler water conditioning processes, and V. Walker[168] cites a number of instances of such failures. The causes range from thermal stress cracking, usually starting at surface scratches, and a number of purely mechanical factors to external corrosion by fuel ash. A further paper of interest on this point, by W. T. Reid, R. C. Corey, and B. J. Cross,[169] describes some sixteen cases of external corrosion on furnace wall tubes, and indicates that a frequent cause is the condensation of alkaline compounds on the tubes, followed by reaction with the iron and oxygen to form enamels.

MISCELLANEOUS.

S. E. Anderson[170] points out that the batch production of a chemical which is stored for gradual use will involve (*a*) production cost and (*b*) capital investment. In these circumstances, as batch size increases, a diminishing cost per unit of production is offset by increasing storage cost, and for any process some optimum batch size exists. Most works chemists will have had at some time to determine the interface position between two liquid phases, and will appreciate a series[171] of paints, for use on dipsticks, made up with preferentially soluble pigments.

C. Buck, T. Hayes, and R. R. Williams[172] have discussed the development of chemical processes through the pilot-plant stage, and suggested proper functions for the chemist, chemical engineer, and mechanical engineer in this development.

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[164] U.S.P. 2,328,551; B., 1945, I, 372.

[165] *Fuel Econ. Rev.*, 1945, **24**, 25; B., 1946, I, 1.

[166] U.S.P. 2,338,987; B., 1946, I, 279.

[167] *Manufg. Chem.*, 1946, **17**, 285; B., 1946, I, 309.

[168] *Elect. Times*, 1945, **108**, 696; B., 1946, I, 118.

[169] *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 279; B., 1946, I, 149.

[170] *Chem. Met. Eng.*, 1946, **53**, *No.* 7, 137; B., 1946, I, 351.

[171] B.P. 575,517; B., 1946, I, 219.

[172] *Ind. Chem.*, 1946, **22**, 324; B., 1946, I, 227.

FUEL.

By H. L. Riley, D.Sc., A.R.C.S., D.I.C., F.R.I.C.,
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During the past year the Coal Industry Nationalisation Act, 1946 (9 and 10 Geo. VI, c. 59), has come into force. The Coal Commission, which is dissolved under the terms of the Act, made its Final Report[1] to the Minister of Fuel and Power for the year ended March 31st, 1946; payment of compensation (£69,000,000) to royalty owners has been made and the transference of all unworked coal in Great Britain from private to public ownership is thus complete. The main provisions of the Nationalisation Act[2] are as follows. A National Coal Board of nine persons has been formed to acquire colliery undertakings, manage the industry, and secure its efficient development; the Board is subject to general directions by the Minister of Fuel and Power. Compensation for assets transferred to the Board is to be paid in Government stock; the global sum has been fixed at £164,660,000. Two consumers' councils, industrial and domestic, are to advise the Minister. The Act provides not only for the nationalisation of the working, getting, and supplying of coal, but also for allied activities such as coke ovens, manufactured fuel plants, transportation works, merchanting property, and welfare activities connected with the collieries. Eight Divisional Boards,[3] each of six members, have been set up to carry out the reorganisation of the coal mining industry. These far-reaching changes, which take effect from January 1st, 1947, are being made under conditions of extreme difficulty; although the fall in the production of coal apparently has been arrested and estimates for 1946 indicate an increased production of more than 6 million tons, this has been more than offset by increased demand. The closing months of 1946 have seen the compulsory curtailment of industrial activity because of the shortage of fuel. This condition of economic disequilibrium is likely to persist during the early months of 1947: the re-establishment of equilibrium will require a large expenditure of free energy. Various factors are responsible for the serious shortage of solid fuel[4]: the percentage of miners aged over 40 rose from 34·5 in 1931 to 43 in 1945; in the same period the percentage between 14 and 17 fell from 9·6 to 4·8; the number of underground workers decreased by 69,000; between 1913 and 1944, the percentage of seams over 6 ft. being worked decreased from 11·6 to 8·1, and the percentage between 5 ft. and 6 ft.

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[1] H.M. Stat. Off., 1945; *Coll. Guard.*, 1946, **173**, 95.

[2] H.M. Stat. Off., 1945.

[3] *Times, Sept.* 13, 1946.

[4] *Statistical Digest*, 1945, H.M. Stat. Off., *Cmd.* 6920, 1946; see also *Times, Oct.* 2, 1946.

decreased from 17·5 to 12·7, while the percentage under 3 ft. increased from 18·8 to 25·7; during the same period the percentage of coal cut mechanically increased from 7·7 to 80·2.

Fuel Efficiency.—The serious consequences of this shortage of solid fuel have been mitigated somewhat by more efficient utilisation. O. Lyle[5] has estimated, however, that savings of 80 million tons of coal a year could readily be achieved if the urge to economise was sufficiently great; he has suggested that the imposition of a heavy excise duty on coal, subject to appropriate rebates for exported products, would greatly assist the attainment of this end as it would impel all coal users to economise, would stimulate a desire for education, and would improve the teaching of thermal technology. The Institute of Fuel has continued to give valuable assistance in the fuel economy campaign: a symposium on waste-heat recovery was arranged at which J. R. Rylands and A. B. Tillotson[6] discussed technical and economic aspects of waste-heat recovery in economisers, E. C. Evans and A. H. Leckie[7] its use in the iron and steel industry, J. L. Harvey[7] in copper refining, and A. E. Balfour[7] in the zinc industry; J. G. King and F. J. Dent[8] dealt with its utilisation in the carbonisation industries and W. A. Moorshead[9] in the glass container industry. Its utilisation in high-temperature carbonisation processes has also been reviewed by H. D. Edwards.[10] In a discussion on fuel efficiency in the iron and steel industry C. Hulse and R. J. Sarjant[11] have compared solid (including pulverised), liquid, and gaseous fuels and furnace practice and design; examples of plant survey work are given, together with a list of problems requiring solution. N. H. Turner and F. A. Gray[12] concerned themselves with problems connected with heat conservation and the economical use of gaseous fuels. The factors to be considered when determining the most efficient and economical system of supplying given proportions of power and process steam have been studied by W. A. Pain.[13] The second progress report on fuel efficiency in the coal industry, which has been issued by the Coal Industry Joint Fuel Efficiency Committee,[14] deals with the utilisation of low-grade fuels, particularly those produced during coal preparation at the collieries.

Atmospheric Pollution.—The inefficient utilisation of solid fuel and atmospheric pollution almost invariably go together and far too little attention has been given to the evil consequences, both social and economic, of the latter. The Manchester City Council on the recommendation of its Public Health Committee has decided to include in its next General

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[5] *Inst. Fuel Bull.*, *Oct.*, 1946, 1.

[6] *Ibid.*, 1945, *Dec.*, 72; B., 1946, I, 150.

[7] *J. Inst. Fuel*, 1946, **19**, 166—175; B., 1946, I, 297.

[8] *Ibid.*, 134; B., 1946, I, 222.

[9] *Ibid.*, 180.

[10] *Brit. Coal Util. Res. Assoc. Bull.*, 1945, **9**, 333; B., 1946, I, 159.

[11] *J. Iron and Steel Inst.*, 1946, **153**, 165P; B., 1946, I, 269.

[12] *Ibid.*, 183P; B., 1946, I, 269.

[13] *Inst. Fuel War Time Bull.*, *Oct.*, 1945, 1; B., 1946, I, 2.

[14] *Coll. Guard.*, 1946, **172**, 62.

Powers Parliament Bill a clause which will permit the setting up of smokeless zones; the Common Council of the City of London has agreed to make application to Parliament for powers "to require that in new buildings, plans and specifications for heating arrangements, whether for the generation of power, the warming of rooms, the heating of water, or the cooking of food, should be submitted to the Corporation for approval," and also to give the Corporation power to declare any area of the City a smokeless zone.[15] The D.S.I.R.[16] has given an account of a survey of (1) the distribution of atmospheric pollution in the neighbourhood of Leicester; (2) the principal agents concerned; (3) the variation in pollution in relation to habits of population and meteorological conditions, and (4) the method of escape of pollution from the town atmosphere; suggestions have also been made with regard to smoke abatement, sulphur control, and town planning.

The Committee of Inquiry, under the chairmanship of Sir G. Heyworth,[17] set up in 1944, to review the structure and organisation of the gas industry and to advise what changes have become necessary in order to develop and cheapen gas supplies, has recommended the compulsory purchase of all existing gas undertakings and the appointment of ten regional boards to run the industry.

FUEL RESOURCES.

Coal production in different countries has been analysed by W. R. Gordon,[18] who has pointed out that until the process of reconstruction is further advanced, Europe will continue to be short of coal; France is the only producing country to reach an average monthly output equal to that of 1935–38. The Fuel Research Board (D.S.I.R.)[19] has issued a first appraisal of the results of a rapid survey of our national coal reserves and production: an estimate is given of a total 20,000 million tons output between 1942 and 2042 with an average annual production during the first 10 years of approximately 238 million tons and a decline in output towards the end of the period; information is also given regarding reserves and the rate of production of particular classes of coal. An account of the history and geological structure of the Lancashire coalfield has been given by N. Simpkin.[20] M. Macgregor and W. J. Skilling[21] have described the geological structure of the Scottish coalfield and discussed the character and quantity of the reserves of coal. The vertical distribution of spore types in the coal seams of North Staffordshire has been studied by J. O'N. Millot,[22] who, together with F. W. Cope and H. Berry,[23] has given some

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[15] *Smokeless Air*, 1945, *No.* 59, 26.

[16] "Atmospheric Pollution Research," H.M. Stat. Off., 1945.

[17] H.M. Stat. Off., 1945, *Cmd.* 6699; *Times*, *Dec.* 5, 1945.

[18] *Coll. Guard.*, 1946, **173**, 114.

[19] *Fuel Research Survey Paper No.* 58; H.M. Stat. Off.

[20] *Inst. Fuel Bull.*, *Dec.*, 1945, 54; B., 1946, I, 157.

[21] *Ibid.*, *June*, 1946, 204; B., 1946, I, 282.

[22] *Coll. Guard.*, 1945, **171**, 592.

[23] *Ibid.*, 1946, **172**, 533; *Trans. Inst. Min. Eng.*, 1946, **105**, 528; B., 1946, I, 396.

interesting data on the coal seams encountered in a deep boring in the same area. An account has been given of the microspores in the productive coal measures of the central coalfield of Scotland by E. M. Knox.[24] Regional Survey reports on the Bristol and Somerset,[25] the South Wales,[26] and the Forest of Dean[27] coalfields have been issued. Borings for oil[28] at Gringley-on-the-Hill on the borders of Yorkshire, Nottinghamshire, and Lincolnshire have led to the discovery of seams of good-quality coal; two are 7 ft. thick and several 4 ft. thick. C. E. Marshall[29] has given a description of the petrology and field relations of the Barrow Hill intrusion associated with the coal measures in South Staffordshire.

The total output of coal in Eire,[30] largely anthracite from Castlecomer and Ardagh, was raised from 118,000 tons in 1939 to about 200,000 tons in 1944; the total import of coal in 1944 was 740,000 tons. S. K. Roy[31] has described the distribution of the coalfields in India and the properties of the coals produced : Sir C. Fox[32] has estimated that India's reserves of coking coal amount to 1500 million tons. A detailed account of the composition, properties, and occurrence of the Victorian brown coals has been given by A. B. Edwards.[33] The annual consumption of coking coal in South Africa[34] is approximately 4 million tons : the life of the known reserves has been estimated to be 37·5 years with a possible extension of a further 15 years by blending non-coking coals with the coking slacks; the life of the coking coal reserves at the present rate of consumption might be increased to approximately 163 years by their exclusive use for coke manufacture. From the borehole results of several Orange Free State gold mining companies, it appears that important coal seams exist vertically above the gold reefs.[35] P. E. Hall[36] has given details of the seams examined and proximate analyses of borehole samples in a survey of possible sources of coking coal in the Transvaal. The production of both coking and steam coals from the Witbank coalfield and the possibility of conserving reserves of coking coal have been discussed by L. A. Bushell, S. B. Gass, F. W. Quass, and R. F. J. Teichmann.[37] The output of coal from the Enugu colliery, Nigeria,[38] rose from 323,266 tons in 1939 to 668,158 tons in the year ended March 31st, 1945. In the same year Canada consumed slightly more than 41 million tons of bituminous coal

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[24] *Trans. Inst. Min. Eng.*, 1945, **105**, 137, 268; B., 1946, I, 221.
[25] H.M. Stat. Off., 1946; *Coll. Guard.*, 1946, **172**, 339.
[26] H.M. Stat. Off., 1946; *Times, April* 3, 1946.
[27] H.M. Stat. Off., 1946.
[28] *Times, Sept.* 13, 1946.
[29] *Quart. J. Geol. Soc.*, 1946, **101**, 177.
[30] H.M. Stat. Off., 1946; *Engineer*, 1946, **181**, 211.
[31] *J. Sci. Ind. Res., India*, 1945, **4**, 197, 335.
[32] *Gas World*, 1946, **124**, *Coking Sect.*, 20.
[33] *Proc. Austral. Inst. Min. Met.*, 1945, *No.* 140, 205; B., 1946, I, 362.
[34] *Iron Coal Tr. Rev.*, 1946, **152**, 982.
[35] *Coll. Guard.*, 1945, **171**, 671.
[36] *J. Chem. Met. Soc. S. Africa*, 1945, **46**, 124; B., 1946, I, 157.
[37] *Ibid.*, 45; B., 1946, I, 52.
[38] *Iron Coal Tr. Rev.*, 1945, **151**, 769.

and more than 4 million tons of anthracite; of the bituminous coal burned approximately 17 million tons were produced in Canada and the rest imported from the United States.[39]

Belgian coal reserves to a depth of 1200 m. have been estimated to amount to 6000 million tons and, on the basis of the 1939 production, to be ample for Belgium's needs for over 200 years[40]: production in 1945 was 15,750,000 tons, or little more than half that of 1939.[41] Production of coal in Poland[42] has steadily increased; with the addition of 24 collieries acquired from former German territories, she now owns 80 mines and planned to reach an output of 48 million metric tons in 1946, with an export to Russia of 8 million tons: the nationalised industry is managed by a Central Coal Board. W. G. Cass[43] has reviewed the development of Russian coal resources since 1913; then they were estimated at 230,000 million tons; coal output is on the increase; in 1937 the reserves were estimated to be 1,654,000 million tons.[44] The lignite output of Turkey is progressively increasing, the eventual objective being an annual production of a million tons[45]: G. Ladame[46] has described the properties and published analyses of some Turkish sub-bituminous coals. The economic aspects of the Greenbrier coalfield, West Virginia, has been discussed by W. Crichton[47]; since 1921, annual production has increased from 52,000 to nearly 3½ million tons; reserves are estimated at over 2000 million tons. The carbonising properties of the Powellton Bed from Coal Mountain Mine, Guyan, Wyoming, W.Va., have been described.[48] A. C. Fieldner and coworkers[49] have given an account of the Tennessee and Georgia coalfields and analytical data of the coals. In 1943 Japan produced 52 million metric tons of coal (estimated): the reserves of all kinds of coal have been put at nearly 17,000 million tons.[50] Coal output in Brazil[51] in 1939 was 1,046,975 metric tons; it increased progressively to 2,034,310 tons in 1943 but declined in 1944 to 1,855,591 tons; the coal, which is of poor quality and contained 30—35% of ash and 4—7% of sulphur, is sub-bituminous.

COAL MINING AND PREPARATION.

The twenty-third Annual Report (1944) has been issued by the Safety in Mines Research Board[52]; amongst other topics, it deals with coal-dust and fire-damp explosions, mining explosives, shot-firing, and fires

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[39] *Inst. Fuel Bull., Oct.*, 1946, 37.
[40] *Coll. Guard.*, 1946, **172**, 474.
[41] *Iron Coal Tr. Rev.*, 1946, **152**, 134.
[42] *Ibid.*, **153**, 156.
[43] *Chem. Eng. News*, 1946, **24**, 1725.
[44] *Soviet News, Feb.* 20, 1946, 3.
[45] *Iron Coal Tr. Rev.*, 1945, **157**, 727.
[46] *Maden Tetkik. Arama, Ankara*, 1944, **32**, 257.
[47] *Min. Congr. J.*, 1945, **31**, 24.
[48] *U.S. Bur. Mines*, 1946, *Tech. Paper* 683; B., 1947, I, 97.
[49] *Ibid.*, 1945, *Tech. Paper* 671; B., 1946, I, 52.
[50] *Ibid.*, *Foreign Minerals Survey*, 1946, **2**, *No.* 5.
[51] *Iron Coal Tr. Rev.*, 1945, **151**, 1030.
[52] H.M. Stat. Off., 1945.

in coal mines. The work of the Geological Survey in locating unworked coal between the surface and deeper colliery workings and the influence of geological factors in determining the methods of open-cast mining have been described by S. Buchan.[53]

Dust.—Continued attention has been given to the suppression of dust in mining operations because of the silicosis and pneumokoniosis hazards. The use of water jets and sprays for the reduction of dust has been described by H. W. Smith and H. F. Banks[54] and by C. G. Warner.[55] E. Thomas and I. Hartmann[56] have investigated the use of calcium chloride for the suppression of dust in mine roadways and F. H. Price[57] has described experiments at a Kent colliery in which foam was employed during drilling and coal cutting. Several papers have appeared on the use of aluminium powder and hydrated alumina for the prophylaxis of human silicosis and for relieving the symptoms of the disease. P. J. Bamberger[58] has reviewed experimental studies and concludes that hydrated alumina and metallic aluminium both seem to be effective in relieving the symptoms of silicosis in a significant number of cases : the hydrate seems to be superior to the metal powder and deserves further clinical study.

Cleaning.—E. T. Wilkins[59] has pointed out that improved standards of coal cleaning are becoming necessary for hydrogenation, electrodes, pulverised and colloidal fuels, etc., and has described the wartime use in Germany of acid extraction and electrostatic dry cleaning for the production of low-ash coal. A. Crawford[60] has given an account of ash extraction by means of caustic soda, used by the Germans. A pilot cyclone coal washer in which centrifugal force is used for cleaning fine coal in heavy liquids was the subject of a paper by M. G. Driessen.[61] K. F. Tromp[62] has discussed the economic limits of separation of middlings in dense-medium washers and the manner of breakdown of washery middlings. The coal-cleaning performance of pneumatic jig, pneumatic table, and Baum-type jig have been compared by H. F. Yancey and M. R. Geer,[63] who have also studied the cleaning of coals from the Matanuska field of Alaska. The influence of particle size on the efficiency of flotation agents for bituminous coal slurries has been investigated by H. Menzel.[64] J. S. V. J.

[53] *Coll. Guard.*, 1946, **172**, 46.

[54] *Trans. Inst. Min. Eng.*, 1945, **104**, 602 ; B., 1946, I, 85.

[55] *J. Ind. Hyg.*, 1943, **25**, 303 ; B., 1946, I, 313.

[56] *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3828 ; B., 1946, I, 85.

[57] *Iron Coal Tr. Rev.*, 1946, **152**, 629.

[58] *Ind. Med.*, 1945, **14**, 477.

[59] *Chem. Eng. Group and Inst. Chem. Eng., Feb.*, 1946 ; B., 1946, I, 122 ; *Combined Intelligence Objectives Sub-Commee., Item* 30, *File* XXXIII–6, H.M. Stat. Off., 1946 ; *Coll. Eng.*, 1946, **23**, 176.

[60] *Brit. Intelligence Objectives Sub-Commee., Item* 30, *Final Rept.* 522 ; *Iron Coal Tr. Rev.*, 1946, **153**, 322.

[61] *J. Inst. Fuel*, 1946, **19**, 33 ; B., 1946, I, 85.

[62] *Ibid.*, 112, 115 ; B., 1946, I, 193, 194.

[63] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1888 ; B., 1945, I, 376. *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3840 ; B., 1946, I, 193.

[64] *Glückauf*, 1944, **80**, 367 ; B., 1946, I, 157.

Spee[65] has pointed out that the simplified formula previously given[66] for the velocity of fall of particles in a washery medium is to be applied only to conditions of teeter existing in a washing bed and not to conditions of free fall. The effect of the shape of the particles, the ash content, the free water content, and the particle size distribution on the dewatering characteristics of small coal has been considered by F. Hopkinson.[67]

Briquetting.—The wider use of coal cleaning has brought an increase in the production of washery slurries and coal fines; provided that these can be cleaned and dried, briquetting offers a method of making them suitable for the domestic market. Several ovoid briquetting plants, which were ordered by the Ministry of Fuel and Power in 1942, are now in operation and their ultimate output on a double-shift basis should be approximately 900,000 tons of ovoid briquettes per annum.[68] The annual production of the American fuel-briquetting industry[69] reached a new high level of 2,464,960 tons in 1944; in 1944, 322,416 tons (83%) more anthracite and 152,127 tons (11%) less bituminous coal were used than in 1943; asphalt binders remain the preferred type. H. Lafuma[70] has reported that in 1943, the French production of coal briquettes reached 800,000 tons, for which 35,000 tons of sodium silicate were employed as binder: the sodium silicate is introduced: (*a*) as the vitreous disilicate which is pulverised and added dry, (*b*) as a solid emulsion of pitch and sodium silicate (maximum 65%) which is applied like ordinary pitch, and (*c*) as a dispersion of pitch (20—25%) in sodium silicate solution. L. D. Schmidt, W. T. Reid, W. Seymour, and J. W. Myers[71] have described the physical and combustion characteristics of packaged fuel composed of anthracite fines, coking coal, and petroleum asphaltic binder. B. W. Johnson[72] has given an account of the manufacture of coke-breeze ovoid briquettes which have proved satisfactory for forced-draught furnaces but not for domestic use. Details of the manufacture of fuel bricks from sawdust, wood shavings, flax straw, sunflower-seed husks, charcoal, etc., bound with such materials as starch and dextrin, have been given by J. Cruellas.[73]

PHYSICAL AND CHEMICAL PROPERTIES OF COAL.

A marked increase (20%) in the apparent specific gravity of damp powdered coal brought about by 0·1% of kerosine has been reported by A. A. Agroskii and V. S. Zagrebilnaja.[74] In agreement with other

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[65] *Fuel*, 1946, **25**, 92; B., 1946, I, 313.
[66] B., 1936, 770.
[67] *Gas World*, 1945, **122**, *Coking Sect.*, 51, 60; B., 1945, I, 351.
[68] *Iron Coal Tr. Rev.*, 1946, **153**, 156.
[69] *U.S. Dept. Interior, Washington, M.M.S., No.* 1312.
[70] *Chem. Tr. J.*, 1945, **117**, 609.
[71] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3882; B., 1946, I, 314.
[72] *Gas J.*, 1945, **246**, 397, 403; B., 1945, I, 351.
[73] *Ind. y Quim.*, 1945, **7**, 315; B., 1946, I, 85.
[74] *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech.*, 1945, 190; *J. Inst. Petroleum*, 1945, **31**, 376A; *see also Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **49**, 273.

workers, A. Kumpan[75] has found, by means of X-ray diffraction, an increase in the crystallinity of coal with rank. C. E. Marshall[76] has studied cokes formed by the intrusion of an igneous dyke into coal measures, using optical and X-ray methods. S. J. Gusev[77] has detected the presence of dithio-ethers in Kizelow coals : their thio- and dithio-ether content increases with increasing depth and bears no apparent relation to the total organic sulphur content of the coal.

The action of fuming nitric acid followed by alkaline permanganate on bituminous coal fractions, rich in particular petrographic constituents, has been studied by G. Schultz and H. C. Howard[78] ; the yields of total benzenoid acids and mellitic acid obtained decreased in the order : fusain, opaque attritus, anthraxylon, and transluscent attritus, resins, *i.e.*, as the C/H ratio fell : the yields of mellitic acid were respectively 25·4, 13·5, 6·2, and 1·5% on the dry ash-free basis. I. Berkovitch and A. McCulloch[79] have investigated the effect of admixed sulphur on the behaviour of coking coals in the Gray–King assay apparatus ; like oxygen, sulphur adversely affected coking power and increased the yield of fixed carbon. A. Gillet and M. L. Fastré[80] have identified the changes taking place in a high-volatile coal exposed to moist air as (i) fixation of oxygen and loss of hydrogen over the first 48 hours, (ii) fixation of oxygen without loss of hydrogen by the end of the 10th day, (iii) slow oxidation during the next 10 days ; the oxidation is partly reversible and is inhibited by treating the coal with quinol. N. W. Franke and M. W. Kiebler[81] have described a process for the production of large yields of benzenepolycarboxylic acids by the action of oxygen on coal at 200—300° and 500—1200 lb. per sq. in., in the presence of caustic alkali. Information on the nature, occurrence, and possible commercial utilisation for varnishes etc. of the resins found in coal has been summarised by W. A. Selvig.[82]

Humic Acids.—E. Ganz[83] has extracted humic acids from a young lignite by means of ammonia and subjected them to heat in nitrogen, air, and hydrogen ; a marked decomposition was observed at 350° ; hydrogenation of the ammonium nitrohumate in dioxan with molybdenum sulphide as catalyst gave a 30% yield of propyl*cyclo*hexane. G. Bouilloux[84] has concluded that in the majority of cases, humates in solution are ill-defined, hydrolysed, and in equilibrium with the anion of the alkaline salt used to peptise the humic acid. The simultaneous adsorption and ion exchange shown by humic acid in the free state or associated with a mineral support has been studied by Á. Boutserin-Galland.[85]

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[75] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **49**, 590.
[76] *Fuel*, 1945, **24**, 120 ; B., 1946, I, 9.
[77] *J. Appl. Chem. Russ.*, 1944, **17**, 362 ; A., 1945, I, 284.
[78] *J. Amer. Chem. Soc.*, 1946, **68**, 994 ; A., 1946, I, 295 ; B., 1946, I, 362.
[79] *Fuel*, 1946, **25**, 36, 69 ; B., 1946, I, 257.
[80] *Bull. Soc. chim. Belg.*, 1944, **53**, 83 ; B., 1946, I, 85.
[81] *Ind. Chem.*, 1946, **22**, 433 ; *also Chem. Industries*, 1946, **58**, 580 ; B., 1946, II, 231.
[82] *U.S. Bur. Mines*, 1945, *Tech. Paper* 680 ; B., 1946, I, 397.
[83] *Fac. des Science de l'Université de Paris, Thesis.*
[84] *Bull. Soc. chim.*, 1944, [v], **11**, 38 ; *Chim. et Ind.*, 1944, **51** 930 ; A., 1946, II, 60.
[85] *Ibid.*, 1945, [v], **12**, 116 ; A., 1946, I, 81.

Solvent Extraction.—G. Bouilloux[86] has extracted a coal (38% volatile matter) in turn with boiling benzene, morpholine (b.p. 128°, yield 18%), and boiling hexachlorodiphenyl (b.p. 360—370°, yield 16%); he concluded from his experiments that during its formation, the temperature of the coal did not rise above about 100° and that the process did not involve the formation of humic acids as intermediates. A. Gillet[87] used anthracene oil at 350° to extract a coal (31% volatile matter) and obtained 77·8% dissolved in 15 minutes; two fractions extracted from the coal with aniline were also examined. D. J. W. Kreulen[88] has summarised his conception of the nature of coal solvent extracts; he considers them to be organosols consisting of oily and micellar phases. Work carried out during the war on the extraction of ester waxes from British lignite and peat by the Fuel Research Station (D.S.I.R.)[89] has been described and G. Palmer, G. S. Shillitor, and A. Macmaster[90] have given an account of the German montan wax industry.

Inorganic Constituents.—A. Dooley[91] has reviewed the work published since 1939 on the occurrence of sulphur in coal, the part played by sulphur compounds in atmospheric pollution, the behaviour of various forms of sulphur in coal during carbonisation, various reactions of sulphur dioxide and hydrogen sulphide, and the action of sulphur compounds on the materials used in furnace and boiler construction. The recovery of iron pyrites from colliery refuse at Horden Collieries has been described by F. B. Champness.[92]

In a study of the distribution of coal ash components in the Petschora basin, G. N. Egorov[93] has found that the silica content of the ash is uniform, increasing slightly in the eastward direction of the polar Urals: Al_2O_3, Fe_2O_3, MgO, and SO_3 contents vary in the same sense and CaO in the opposite sense. W. A. Selvig and F. H. Gibson[94] have given chemical analyses of 200 coal-ash samples representing all the major coal-producing areas of the U.S.A. A spectrographic study of the coals of the Charleroi basin has been made by M. Legraye and P. Coheur,[95] who found that no single element or group of elements characterised any one bed. J. Endell and K. Endell[96] have described the technique of *X*-ray analysis as applied to the characterisation of mineral matter in coal and given some typical microphotometer curves for Ruhr coals. In an investigation connected with the preparation of pure coal M. T.

[86] *Bull. Soc. chim.*, 1942, [v], **9**, 779; B., 1946, I, 194.
[87] *Bull. Soc. chim. Belg.*, 1942, **51**, 23; B., 1945, I, 376.
[88] *Fuel*, 1946, **25**, 99, 104; B., 1946, I, 314.
[89] *Fuel Research Tech. Paper* 52.
[90] *British Intelligence Objectives Sub-Commee.*, 1945, *Final Rept.* 13, *Item* 22; B., 1946, I, 260.
[91] *Inst. Fuel War Time Bull.*, *Oct.*, 1945, 30; B., 1946, I, 9.
[92] *G.E.C. J.*, 1945, **13**, 178.
[93] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **47**, 489; B., 1946, I, 194.
[94] *U.S. Bur. Mines*, 1945, *Tech. Paper* 679; B., 1946, I, 397.
[95] *Ann. Soc. géol. Belg. Bull.*, 1944–5, **68**, 63.
[96] *Feuerungstech.*, 1943, **31**, 137.

Mackowsky[97] has characterised the common and rare minerals occurring in coal. F. V. Schachov and M. E. Efendi[98] have studied the nickel content (0·001—1%) of a number of coal samples from the Kuznetsk basin; the nickel content and the ash content are not related. V. M. Ratinski[99] has discussed the occurrence of germanium in coal.

CARBONISATION.

The pyrolysis of a Campine coal (31·2% volatile matter) between 340° and 900° has been studied by A. Gillet, J. Willemme, and M. L. Fastré[100]; they found that the products evolved in a stream of nitrogen differ from those given off in a stagnant atmosphere. A. Gillet and G. Dauvister[101] have reported that the progressive loss of volatile matter with rising temperature in a current of hydrogen follows closely that obtained in a current of nitrogen.

The moisture sorption of coals in relation to their coking quality has been investigated in the coal-testing laboratory of the South Metropolitan Gas Co.[102]; it has been concluded that the agglutinating, coking, and swelling properties of a coal depend largely on the sorptive power of the infusible humic components for the "resinic" components during the fusion stage of the latter. In a study of the behaviour of bituminous coals on heating, H. Macura[103] has reported the results of experiments on (*a*) the softening of coal mixtures, (*b*) the relations between shrinkage, ash, and volatile matter content, and (*c*) caking power as a function of rate of carbonisation and particle size of coal. H. E. Blayden, H. L. Riley, and F. Shaw[104] have investigated the relative effects of the addition of finely-divided crystalline and colloidally dispersed inorganic compounds on the caking properties of a large number of coals; if the quantity of inert material added is just sufficient to suppress swelling during carbonisation the strength of the coke is increased, whereas further additions have adverse effects, a modified Campredon test is described. The use of sucrose, glucose, coal-tar pitch, and synthetic resins as binders for active carbon has been described by J. J. Morgan and C. E. Fink.[105]

Coking Practice.—The experimental determination of the factors which govern the design of regenerators, with special reference to coke ovens, has been described in detail by T. C. Finlayson and A. Taylor.[106] H. S. Auvil, L. D. Schmidt, and H. G. Graham[107] have investigated the determination of bulk density by the following methods: (*a*) shovelling the

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[97] *Feuerungstech.*, 1943, **31**, 143.
[98] *Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **51**, 139; A., 1946, I, 360.
[99] *Ibid.*, 1945, **49**, 119; A., 1946, I, 328.
[100] *Bull. Soc. chim. Belg.*, 1944, **53**, 27; B., 1946, I, 9.
[101] *Ibid.*, 1945, **54**, 5; B., 1946, I, 283.
[102] *Fuel*, 1946, **25**, 42; B., 1946, I, 194.
[103] *Oel u. Kohle*, 1940, **36**, 117, 161; 1944, **40**, 227, 269; B., 1946, I, 221, 314.
[104] *Fuel*, 1946, **25**, 13; B., 1946, I, 123; C., 1946, 82.
[105] *Ind. Eng. Chem.*, 1946, **38**, 219; B., 1946, I, 194.
[106] *J. Inst. Fuel*, 1946, **19**, 82; B., 1946, I, 189.
[107] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3935; B., 1946, I, 314.

coking slack into a 1 cu. ft. box (A.S.T.M. method), (*b*) dropping it into the box from a conical hopper, and (*c*) filling a box (8 × 18 × 24 in.) from a rectangular hopper with a hinged bottom ; the results obtained by method (*c*) agreed most closely with measurements made on a full oven charge. F. D. Lohr and G. V. McGurl[108] have patented a method of regulating the bulk density of coke-oven charges by mixing oil (less than 0·5%) with the coking slack. A full-scale machine for charging coke-ovens by allowing the coal to fall 15 ft. from a hopper through guiding slots into the oven has been described by H. H. Lowry and H. J. Rose[109] ; it is claimed that this procedure gives a uniform density of the coal, 15% greater than normal. H. Zollikofer[110] has given an account of 25 years' experience of the dry-quenching of coke, a subject of considerable importance in view of the need for fuel economy. W. W. Stevenson[111] has found that by replacing the mild-steel bottom plates of coke cars by an alloy steel containing C 0·07, Cr 1·00, Cu 0·42, Si 0·87, Mn 0·23, P 0·156, and S 0·033% their life was increased from 14 to 25 months. By sweeping out the top free space of the oven by means of stripped gas G. Cellan-Jones[112] has obtained increased yields of benzole.

Blending.—S. R. Illingworth[113] has claimed that by blending coals it is possible to control the formation during carbonisation of the plastic layer which favours the pyrolysis of volatile matter and the deposition on the coke of carbon of low combustibility. D. A. Reynolds and J. D. Davis[114] have reported that coke from high-volatile (31—38%) coals is improved by blending them with suitable low-volatile (15—20%) coals in the ratio 7 : 3 ; coke from strongly coking, medium-volatile coals is slightly weakened by the admixture of 70—80% of high-volatile coal to the slack. F. H. Read, H. W. Jackman, and P. W. Henline[115] have found that Illinois coal could replace some of the Appalachian coals carbonised in the Chicago and St. Louis districts, with a saving in transport. It has been reported by J. D. Clendenin, K. M. Barclay, and C. C. Wright[116] that the size grading and strength of coke made from a blend containing 5% of anthracite fines cannot be correlated with the density, volatile matter content, or size of the anthracite ; grinding and heating the anthracite to 950° before blending tend to increase the strength of the resultant coke. Substitution of 5—6% of anthracite for part of the low-volatile coal in a blend has been found by D. L. Newkirk[117] to increase the size and shatter index of the coke, unless the carbonising time was reduced from 16·75 to 16·25 hours ; the coke from the anthracite blend was stronger, harder,

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[108] U.S.P. 2,378,420.

[109] *Combined Intelligence Objectives Sub-Commee.*, *Item* 30, *File* XXXI–24.

[110] *Monatsbull. Schweiz. Ver. Gas u. Wasserfachm.*, 1945, **25**, 121.

[111] *Gas World*, 1946, **125**, *Coking Sect.*, 65 ; B., 1946, I, 314.

[112] *Coke*, 1946, **8**, 8 ; B., 1946, I, 222.

[113] *Gas J.*, 1946, **247**, 848, 853 ; B., 1946, I, 257.

[114] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3936 ; B., 1946, I, 314.

[115] *Ind. Eng. Chem.*, 1945, **37**, 560 ; B., 1945, I, 377.

[116] *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 405 ; B., 1946, I, 158.

[117] *Blast Furn. Steel Plant*, 1945, **33**, 461 ; B., 1946, I, 158.

and more brittle than that from the normal blend, and its blast-furnace performance was satisfactory. A. G. V. Berry and R. Edgeworth-Johnstone[118] have made a compact, non-porous petroleum coke by carbonising at 800° mixtures of primary petroleum coke with either petroleum residuum (volatile matter 70%) or cracked asphalt (volatile matter 45%), provided that the primary coke had a volatile matter content of less than 11% and that the calculated volatile matter content of the blend was less than 22%; if it was greater than 22%, strong but porous cokes were obtained.

Coke.—A coke which burned very well in an open domestic grate has been made by G. M. Gill and J. Roberts,[119] who carbonised a graded ($2\frac{1}{2}$—$1\frac{1}{2}$-in.) non-coking (Barnsley Top-Hard) coal, at high throughput, in continuous vertical retorts; the coke was about the same size grading as the original coal. C. G. Thibaut[120] has attempted to give an index of the quality of blast-furnace cokes based on metrical characteristics such as size grading, porosity, impact strength, and chemical analysis: he has related the index to the behaviour of a coke in the blast furnace. The relationship between the flow of gases through beds of coke and other granular materials and the average size of the individual pieces, and the nature of their surface and the voidage in the bed, has been discussed by J. Hiles and R. A. Mott.[121]

Carbon.—U. Hofmann[122] has reviewed recent work which indicates the similarity of the electron structure of graphite with that of polynuclear aromatic compounds. W. Rüdorff[123] has given a comprehensive account of the lamellar compounds of graphite in which he suggests a new structure for the lamellar complex, graphite monofluoride. J. B. Nelson and D. P. Riley[124] have determined the thermal expansion of graphite by means of X-rays and discussed its theoretical significance. By carbonising hexaiodobenzene, J. Gibson, M. Holohan, and H. L. Riley[125] have obtained carbons which give little coherent scattering of X-rays; they give X-ray evidence in support of a disordered cross-linked structure for such carbons. F. Trombe, M. Foëx, and J. Berdet[126] have studied the purification of graphite by heating it electrically to high temperatures; heating for 5 minutes at 2650° removes all impurities except about 0·001% of magnesium and boron, and this can be reduced to about 0·0002% by prolonging the heating to an hour.

COMBUSTION.

Solids.—A spectroscopic study of the combustion of carbon filaments at 1000—1300° has been made by R. Audubert and C. Racz[127]; they found

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[118] *Ind. Eng. Chem.*, 1945, **37**, 551; B., 1945, I, 377.

[119] *Coke*, 1946, **8**, 35, 41; B., 1946, I, 221.

[120] *Rev. Mét.*, 1943, **40**, 129; B., 1946, I, 9.

[121] *Fuel*, 1945, **24**, 135, 158; B., 1946, I, 53.

[122] *Naturwiss.*, 1944, **32**, 260; A., 1946, I, 12.

[123] *Wien. Chem.-Ztg.*, 1944, **47**, 172.

[124] *Proc. Physical Soc.*, 1945, **57**, 477, 486; A., 1946, I, 39.

[125] *J.C.S.*, 1946, 456; A., 1946, I, 304.

[126] *Ann. Chim.*, 1945, [xi], **20**, 701; B., 1946, I, 257.

[127] *Bull. Soc. chim.*, 1945, [v], **12**, 318; A., 1946, I, 72.

that the apparent activation energy for the production of the radiation at 1050—1250° was approximately 68 kg.-cal. at a pressure of 250 mm., 84 kg.-cal. at 100 mm., and 90 kg.-cal. at 50 mm.; emission of radiation of wave-length 2000 A. indicated the accumulation of 150 kg.-cal. in a single molecule; the bearing of the results on the mechanism of carbon combustion was discussed. J. R. Arthur[128] has carried out experiments in order to determine to what extent carbon dioxide is a secondary product in carbon combustion; very fine water-cooled gas-sampling tubes were used. The gas within a fraction of a mm. of the burning carbon surface was found to contain 0·5—2·0% of carbon monoxide; away from the surface the carbon monoxide content of the gas was negligible; when inhibitors (chlorine, carbon tetrachloride, phosphorus oxychloride) were added to the gas stream, up to 22% of carbon monoxide was found in the gas stream about 1 mm. from the carbon surface. G. W. Bridger[129] has found that the $CO/(CO_2 + CO)$ ratio in the gases produced by the combustion of coke in air is increased by the presence of chlorine or chlorine compounds; the very low amount of carbon dioxide produced in the inhibited combustion of coke suggests that carbon monoxide is the primary product in the oxidation of carbon at 1000°. M. Letort and J. Martin[130] have reported that the rate of combustion of powdered graphite at 510° is greatly increased if before the experiment it is burnt for a few minutes in air and then stored in nitrogen; the abnormally high combustibility gradually disappears.

R. E. Jones and D. T. A. Townend[131] have drawn attention to the importance of the formation of peroxidic substances during the oxidation of coal; at the ignition temperature the peroxygen content rises to a high value and then falls as the coal ignites. The seven conditions which favour the spontaneous combustion of coal have been found by J. L. Elder, L. D. Schmidt, W. A. Steiner, and J. D. Davis[132] to be as follows: (1) lowness of rank, (2) high temperature during storage, (3) newly mined coal, (4) availability of oxygen, (5) accessible surface area, (6) low moisture content, and (7) low ash content. When air is directed obliquely downward into a deep enclosed fuel bed through a slit, the width of which can be varied from 0 to 2 mm., M. W. Thring and R. Mayorcas[133] have found that the carbon dioxide content of the exit gases rises to a maximum for a value of the air delivery pressure which is nearly independent of the rate of air supply, but depends on the nature of the fuel.

J. F. Barkley, L. R. Burdick, and R. Wiggers[134] have reported that it is possible successfully to burn mixtures of anthracite fines and bituminous

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[128] *Nature*, 1946, **157**, 732; A., 1946, I, 395.
[129] *Ibid.*, **158**, 236.
[130] *Ibid.*, **157**, 874; *Compt. rend.*, 1946, **222**, 1049; B., 1946, I, 362.
[131] *Inst. Gas Eng.*, 1945, *Comm.* 287; B., 1946, I, 123.
[132] *U.S. Bur. Mines*, 1946, *Tech. Paper* 681; *Amer. Gas Assoc. Month.*, 1945, **27**, 411; B., 1946, I, 221.
[133] *Coke*, 1947, **8**, 104; B., 1946, I, 221.
[134] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3916; B., 1946, I, 314.

coal slacks on industrial stokers and recommend mixing by loading into trucks in alternate layers. In the course of investigations of the mode of combustion of coal on a chain-grate stoker, W. G. Marskell, J. M. Miller, M. R. Webb, and J. E. Rayner[135] have studied (*a*) the effect of rate of combustion on composition of the fuel bed, (*b*) the effect of primary air temperature and air rate on combustion, (*c*) stoker-link temperature, and (*d*) the behaviour of sulphur in fuel beds.

Vapours and Gases.—The various factors which affect the stability of burner flames have been studied by J. E. Garside, J. S. Forsyth, and D. T. A. Townend.[136] H. Behrens has discussed the effect of the diffusion of hydrogen on the structure of flames[137] and described the form of small-jet flames with excess of combustible gas.[138] An account has been given, by F. Brinsley and S. Stephens,[139] of a sensitive and rapid method of determining experimentally the minimum proportion of air required to burn the gases completely, it is based on the appearance of the flame; they have suggested that the colour of the flame observed is due to S_2.

A summary of work carried out on the combustion of carbon monoxide and a discussion of the reaction mechanism have been given by J. R. Arthur.[140] V. N. Kondrateev[141] has shown that small quantities of hydrogen extend the pressure limits of ignition of carbon monoxide-oxygen mixtures and discussed the bearing of this result on the chain mechanism of the reaction, he has also described[142] a jet method of measuring ignition limits which depends on a rapid fall in pressure. G. Whittingham[143] has investigated the oxidation of sulphur dioxide during the slow combustion of carbon monoxide: with a $CO + 3O_2$ mixture containing 1% of sulphur dioxide no formation of sulphuric acid mist was noted until 600° was reached, but thereafter it increased in intensity up to the ignition temperature at 665°. N. Tschirkov[144] has continued his experiments on the oxidation of methane and found that at 630° water vapour has little effect on the induction before explosion, in contrast with the shortening of the induction period observed below 600°; he has discussed the kinetics of the reaction. A. D. Walsh[145] has found that the point of oxygen attack in the combustion of paraffins is almost exclusively a tertiary CH bond if present; the first step in low-temperature hydrocarbon combustion is the formation of peroxides. A. C. Egerton and G. J. Minkoff[146] have obtained up to 30 g. of hydrogen peroxide per

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[135] *Fuel*, 1946, **25**, 4, 50, 78, 109; B., 1946, I, 397.
[136] *J. Inst. Fuel*, 1945, **18**, 175; B., 1945, I, 351.
[137] *Naturwiss.*, 1944, **32**, 297; A., 1946, I, 4.
[138] *Ibid.*, 299; A., 1946, I, 22.
[139] *Nature*, 1946, **157**, 622.
[140] *Brit. Coal Util. Res. Bull.*, 1946, **11**, 129; B., 1946, I, 400.
[141] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **49**, 37; A., 1946, I, 281.
[142] *Ibid.*, 116; A., 1946, I, 316.
[143] *Nature*, 1946, **157**, 550.
[144] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **46**, 368; A., 1945, I, 312.
[145] *Trans. Faraday Soc.*, 1946, **42**, 269.
[146] *Nature*, 1946, **157**, 266; A., 1946, I, 226.

100 c.c. of condensate during the explosive combustion of hydrogen and oxygen at low pressure with rapid cooling. A. G. Gaydon[147] has reported that atomic oxygen is present in the carbon monoxide and hydrogen flames and also in the cool carbon monoxide flame. E. K. Rideal and A. Robertson[148] have published three papers dealing with the reaction kinetics of the oxidation of liquid hydrocarbons : the first is concerned with the formation of hydroperoxides and their decomposition, the second with the energy chain mechanism in the thermal oxidation of tetralin, and the third with the chain mechanism of the benzoyl peroxide-sensitised oxidation of tetralin.

N. B. Nisbet[149] has stated that, as expected from theory, 2 : 5-dimethylfuran has a high blending octane number. F. C. Burk, G. H. Bloud, and W. F. Aug[150] have studied the effect of ignition quality and volatility of fuels on the performance of automotive Diesel engines. The results of experiments on the effect of adding ignition accelerators, especially organic peroxides, to Diesel fuels on engine performance have been described by A. W. Schmidt and F. Mohry.[151] From the results of tests carried out in a multicylinder Diesel-injection, two-cycle engine, F. G. Shoemaker and H. M. Gadebusch[152] have drawn up criteria for correct Diesel fuel specifications. E. Starkman[153] has investigated ignition delay in Diesel engines and found that it has two components, a fuel vaporisation time and a chemical reaction time. G. W. Jones and W. R. Gilliland[154] have determined the compositions of limit mixtures of gasoline and dry air which are inflammable : the effects on these limits of progressive additions of nitrogen, engine-exhaust gases, carbon dioxide, and commercial chlorofluoromethanes have been studied.

Manufactured and Substitute Fuels.

Methane.—Further details of road-car trials using methane and of the storage and production of liquid methane have been given by Sir A. C. Egerton, T. A. Hall, and M. Pearce.[155] C. E. Boast[156] has revealed that over a million miles were covered during the war by cars using methane from the Croydon sewage works. A. Weddige and J. Bosten[157] have reported that more than 3 million cubic metres were recovered in the first year of systematic tapping of coal seams in the Ruhr. Possible methods of drawing off methane when working gassy seams have been outlined by R. Forstmann and P. Schulz.[158]

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[147] *Trans. Faraday Soc.*, 1946, **42**, 292.
[148] *Proc. Roy. Soc.*, 1946, **185**, **A**, 288, 309, 337.
[149] *J. Inst. Petroleum*, 1946, **32**, 162 ; B., 1946, I, 224.
[150] *J. Soc. Auto. Eng.*, 1945, **53**, 166T ; B., 1945, I, 352.
[151] *Oel u. Kohle*, 1940, **36**, 122 ; B., 1946, I, 224.
[152] *Oil and Gas J.*, 1946, **44**, *No.* 36, 74 ; B., 1946, I, 224.
[153] *Trans. Amer. Inst. Chem. Eng.*, 1946, **42**, 107 ; B., 1946, I, 224.
[154] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3871 ; B., 1946, I, 285.
[155] *Inst. Fuel Bull., June*, 1946, 193 ; B., 1946, I, 284.
[156] *Ibid.*, 238.
[157] *Glückauf*, 1944, **80**, 241 ; B., 1946, I, 158.
[158] *Ibid.*, 175 ; B., 1946, I, 160.

Power Alcohol.—L. C. Verman and K. A. Nair[159] have described road tests in which the behaviours of leaded petrol and alcohol were compared; they state the adjustments required when using alcohol. The economics and advantages of the use of hydrous beet-sugar alcohol as a motor fuel have been discussed by M. Martraire,[160] and J. Retel[161] has described the advantages of fuel injection in the utilisation of alcohol as a motor fuel; he has claimed that when engines designed solely for alcohol injection are available it will be possible to produce in France sufficient alcohol to replace imported petrol.

A. D. Puckett[162] has determined the knock ratings of paraffins and olefines C_1—C_4 and of carbon monoxide and the antiknock qualities of ethyl and butyl alcohols, acetone, and ether; under proper conditions of use all these compounds are satisfactory. J. T. Duck and C. S. Bruce[163] have tested a number of substitute fuels and blends in order to compare their efficiences with that of petrol in automobile engines: they have reported that the use of low-proof alcohol is uneconomic.

Coal-in-Oil.—According to E. Boye[164] the term "Fliesskohle," used originally as a trade name, now describes generally intimate mixtures of finely-divided (not colloidally dispersed) coal with a suitable fuel oil: it is possible to utilise coarser coal by transforming the oil into a liquid gel.

FURNACES AND BOILERS.

In a paper, citing 120 references, C. G. Thibaut[165] has comprehensively reviewed the factors influencing coke consumption in the blast furnace. H. L. Saunders and R. Wild[166] have described experiments with small-scale models, which has been carried out in a detailed study of the effect of various factors such as size, density, shape, etc. on the flow of the burden through a blast furnace. The influence of coke size, drying the blast, and charging bushy turnings on gas flow and coke consumption in the blast furnace has been discussed by K. Neustaetter.[167] An investigation of blast-furnace blowing rates has led R. S. Wilcox[168] to the conclusion that the most economical rate is that just above the point at which flue-dust production begins to increase rapidly. A. D. Williams[169] has found that although the output of iron from a blast furnace is increased by removing excess of water vapour from the blast, it is decreased if the concentration of water vapour is reduced beyond a certain point; the optimum humidity corresponds with a dew point of 9—10°. T. L.

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[159] *J. Sci. Ind. Res. India*, 1946, **4**, 601; B., 1946, I, 285.

[160] *Bull. Assoc. Chim. Suer.*, 1945, **62**, 204; B., 1946, I, 196.

[161] *Mém. Soc. Ing. Civ. France*, 1945, **98**, 16; B., 1946, I, 125.

[162] *J. Res. Nat. Bur. Stand.*, 1945, **35**, 273; B., 1946, I, 196.

[163] *Ibid.*, 439; B., 1946, I, 222.

[164] *Chem.-Ztg.*, 1944, **38**, 187.

[165] *Rev. Mét.*, 1944, **41**, 369, 409; B., 1946, I, 176.

[166] *J. Iron and Steel Inst.*, 1945, **152**, 259P; B., 1945, I, 369.

[167] *Blast Furn. Steel Plant*, 1945, **33**, 825; B., 1946, I, 175.

[168] *Ibid.*, 986; B., 1946, I, 175.

[169] *Rev. Mét.*, 1941, **38**, 113; B., 1946, I, 175.

Joseph[170] has discussed the theory of operating blast furnaces at high top pressures and F. Janecek[171] has described the alterations made to a furnace in order to make it suitable for operating at an increased top pressure of 10 lb. per sq. in., together with the experience gained with operating at this pressure.

Assuming the excess of air to be constant, K. Cleve[172] has calculated the zones of maximum temperature for several idealised cases of pulverised-coal firing. G. Schaper[173] has given an account of theoretical considerations and practical tests in a study of temperature range, gas mixture, and heat transfer in pulverised-fuel furnaces for high-radiation boilers. H. Schwiedessen[174] has discussed factors affecting the heat consumption of industrial furnaces in relation to load and throughput, and M. W. Thring and J. W. Reber[175] have given consideration to the effect of output on the thermal efficiency of industrial boilers and furnaces.

The burning of bituminous and sub-bituminous coals on an anthracite, ash-removal type, domestic stoker has been investigated by H. F. Yancey and K. A. Johnson.[176] H. G. Meissner[177] has suggested that fuel burning rates in boiler furnaces would be more conveniently expressed as heat released per sq. ft. of grate area per hour than as the weight of coal burnt. M. Ledinegg[178] has derived formulæ for calculating flue-gas temperature at the exists of the primary and secondary combustion chambers, allowing for the fusion point and thermal properties of the ash.

An account of the history and occurrence of external corrosion of furnace wall tubes and of the significance of sulphate deposits and sulphur trioxide in corrosion mechanism has been given by W. T. Reid, R. C. Corey, and B. J. Cross[179]: X-ray diffraction studies of "enamel" deposits show them to consist primarily of a solid solution of K_2SO_4, Na_2SO_4, and alkali metal ferric trisulphates, *e.g.*, $K_3Fe(SO_4)_3$. P. O. Rosin[180] has made calculations on the total, recoverable, and returnable heat in combustion gases and discussed the limitations on the recovery of "waste" heat in boilers and in recuperators. G. N. Critchley[181] has given data and equations for calculating the heat content of waste furnace gases and the amount returnable to the furnace, he has also discussed counter- and parallel-flow metallic recuperators. J. A. Kilby and W. G. Cameron[182] have given consideration to the factors pertinent to the installation of waste-heat boilers and their ancillary plant, with particular reference to the iron and steel industry.

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[170] *Blast Furn. Steel Plant*, 1945, **33**, 699; B., 1946, I, 176.
[171] *Iron Steel Eng.*, 1946, **23**, *No.* 2, 88; B., 1946, I, 297.
[172] *Warme*, 1944, **67**, 157; B., 1946, I, 213.
[173] *Ibid.*, 31, 55.
[174] *Arch. Eisenhuttenw.*, 1944, **18**, 43; B., 1946, I, 189.
[175] *J. Inst. Fuel*, 1945, **19**, 12; B., 1946, I, 45.
[176] *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3849; B., 1946, I, 194.
[177] *Combustion*, 1945, **17**, *No.* 4, 41; B., 1946, I, 149.
[178] *Wärme*, 1943, **66**, 256; B., 1946, I, 149.
[179] *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 279, 289; B., 1946, I, 149.
[180] *J. Inst. Fuel*, 1945, **19**, 53; B., 1946, I, 77.
[181] *Inst. Fuel War Time Bull.*, *Feb.*, 1946, 100; B., 1946, I, 150.
[182] *J. Inst. Fuel*, 1946, **19**, 193; B., 1946, I, 309.

ANALYSIS AND TESTING.

J. T. McCartney[183] has described the preparation of slides of very fine coal powder suitable for electron micrography and the determination of particle size distribution by means of the electron microscope. The British Standards Institution[184] has issued a specification for screen analysis of coal down to $\frac{1}{32}$ in. which includes a note on the theory of sampling. A chart has been devised by B. G. Šimek[185] for calculating the gross and net calorific values of coals from the water and ash contents, the ash factor, and the calorific value of the dry, ash-free coal. By the correlation of a large number of bomb-calorimetric determinations with analytical data, H. Lefebvre and C Georgiadis[186] have deduced formulæ for calculating calorific values of coals and cokes The prediction of the clinkering behaviour of fuels from small-scale tests has been discussed by J. J. Reilly,[187] and E. Rousseau and J. Delorme[188] have described apparatus for the determination of the softening curves of fuel ash and the evaluation of the temperature at which agglomeration occurs. J H. Jones[189] has quoted results of carbon and hydrogen determinations which indicate that the modified rapid Fenton method, although suitable for normal work, cannot yet replace the Liebig method when results of the highest accuracy are required. R. F. J. Teichmann[190] has described a laboratory method for determining the suitability of South African coal and coal blends for the manufacture of metallurgical coke. K. Hoehne[191] has described modifications in the Koppers method of determining the carboxy-reactivity of coke ; changes in reactivity from minute to minute are followed by measuring the rate of flow of the exit gas, instead ot its composition.

G. Blecher[192] has given a graphical representation of Le Chatelier's formula for determining the inflammability of a number of gas mixtures, by means of which, with tables of data, it is possible to determine the inflammability limits of mine gases. R. Heinze[193] has described a laboratory carbonising apparatus made of iron for studying the low-temperature carbonisation properties of coal ; it gives a higher tar yield than the Fischer aluminium retort.

R. Reed[194] has found that a simple method of detecting aldehydes in flue gases from furnaces fired with natural gas or oil (and therefore incomplete fuel combustion) is to pass the gas through basic fuchsin in an aqueous solution of sulphur dioxide.

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[183] *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3827 ; C., 1946, 82.
[184] *Brit. Standard* 1293 ; 1946.
[185] *Glückauf*, 1944, **80**, 33 ; C., 1945, 233.
[186] *Compt. rend.*, 1941, **212**, 1152 ; C., 1946, 82.
[187] *Brit. Coal Util. Res. Assoc. Bull.*, 1945, **9**, 172 ; B., 1946, I, 158.
[188] *Chim. et Ind.*, 1945, **54**, 134 ; C., 1946, 14.
[189] *Inst. Fuel War Time Bull., Oct.*, 1945, 37 ; C., 1946, 6.
[190] *J. Chem. Met. Soc. S. Africa*, 1945, **45**, 202 ; C., 1945, 232.
[191] *Gluckauf*, 1943, **79**, 166 ; C., 1945, 233.
[192] *Ibid.*, 489 ; C., 1945, 286.
[193] *Oel u. Kohle*, 1943, **39**, 973 ; C., 1945, 233.
[194] *Trans. Amer. Soc. Mech. Eng.*, 1944, **66**, 407 ; C., 1945, 286.

GAS, DESTRUCTIVE DISTILLATION, TAR, AND TAR PRODUCTS.

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The gas industry has not found the first post-war year to be easy going. It has had no particular advantages apart from the return of some of its staff and the end of the risk of damage by enemy action On the contrary, coal supplies have been difficult in regard to both quantity and quality , in consequence it has not always been possible to maintain full pressure. There have been stoppages due to labour disputes.

The Gas Engineering Advisory Boards have continued to serve after the cessation of hostilities and their reports indicate the maintenance of a high degree of efficiency of carbonisation and of fuel utilisation.[1] Collaboration with the Ministry of Fuel and Power has been accomplished by the action of the Co-ordinating Committee of these Advisory Boards in inviting the Director and members of the staff of the Gas and Electricity Division to its meetings

The announcement by the Government of its intention to nationalise the gas industry has naturally resulted in there being no papers read on the subject of the reorganisation and integration of the industry such as are summarised in the 1945 and 1944 Reports [2]

In the Ministry of Fuel and Power Statistical Digest 1945[3] the sections on coal, coke, gas, and electricity have been expanded, as compared with the 1944 Digest. There are entirely new sections on coke ovens and petroleum products, including oil from coal. The provisional figures for total gas available in 1945 show an increase of about 4% over those for 1944. It is a little surprising to find that, of the total gas made at coke ovens, about 2% is still being bled or burned to waste. Reference will be made to the statistics relating to benzole and tar products later in this report.

W. Hodkinson and H. B. Taylor have discussed the technical and economic factors in the organisation of the grid of the West Yorkshire Gas Distribution Co., which buys gas from coke ovens and gas undertakings and supplies it by the United Kingdom Gas Corporation Ltd. over an area of 450 square miles.[4] This is one of the few papers which discuss extensions of activities of the industry.

The use of gas for steel heating in Sheffield has resulted in smoke abatement combined with considerable heat economy. According to

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[1] *Inst. Gas Eng.*, 1946, *Comm.* 301.

[2] *Ann. Repts.*, 1944, **29**, 41; 1945, **30**, 46.

[3] *Cmd.* 6920.

[4] *Inst. Gas Eng.*, 1946, *Comm.* 297; B., 1946, I, 399

H. A. Fells,[5] in the operation of gas-fired furnaces in which non-scaling atmospheres are readily controlled, coke-oven gas has replaced nearly three times its thermal equivalent of coal.

The Institution of Gas Engineers has given some attention to the structure of gasholders and a paper on roller carriages for spirally-guided gasholders was presented at the meeting in November, 1946, by F. M. Birks.[6] Wind-tunnel experiments on models of a spirally-guided gasholder were carried out at the National Physical Laboratory by G. A. Hawkins and G. H. Lean. A digest of this report was made by S. M. Milbourne.[7] N. G. Mathers[8] has detailed recommended procedure and precautions in purging gasholders. Inert combustion gas should be used for the initial stage until the vent gas contains not less than 9% of carbon dioxide. Air or coal gas then follows according to whether the holder is coming off or going on duty.

A renewed interest is being shown in regard to the utilisation of constituents of coal gas as raw materials for the chemical industry. The Northern Industrial Group, Newcastle, which has for its object the increase of industrial activity in Durham and Northumberland, has set up a Coal Processing Industries Panel. The latter has investigated ways and means for integrating all industries based on coal consumption. In the first and second reports[9] reference is made to the large supplies of coke-oven gas in the area from which could be separated constituents of value as raw materials for chemical manufacture. As an example, the separation of ethylene has been studied, and organic chemicals which could be produced from it are enumerated. The subject has been studied at greater length by N. Booth.[10] Ethylene and propylene can be obtained by chemical means. Propylene may be particularly useful but the amount is small. Methane, hydrogen, and carbon monoxide can be separated by diffusion. Hydrogen is used in ammonia synthesis and hydrogenation, *e.g.*, fat hardening. Carbon monoxide can be converted into acrylonitrile. In view of the large proportion of methane, possible uses are considered in some detail. These include the production of carbon black and of chlorinated derivatives. Processes of this nature have been carried out at a Belgian coke-oven works, and are the subject of a report by an investigating team.[11] Separation was carried out mainly by liquefaction, and included hydrogen for ammonia production. Carbon monoxide was catalytically reduced to methyl alcohol, which was subsequently converted into formaldehyde. Ethyl alcohol, produced from ethylene by means of sulphuric acid, was converted into acetone by interaction with steam.

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[5] *Inst. Fuel Bul.*, 1946, *June*, 210; B., 1946, I, 278.

[6] *Inst. Gas Eng.*, 1946, *Comm.* 303.

[7] *Gas Res. Board, Comm. GRB.* 28.

[8] *Gas J.*, 1946, **247**, 195; B., 1946, I, 124.

[9] *First and Second Repts. of the Coal Processing Industries Panel, Northern Industrial Group, Newcastle.*

[10] *Inst. Gas Eng.*, 1946, *Comm.* 294; B., 1946, I, 399.

[11] *Combined Intelligence Objectives Sub-Commee.* (*C.I.O.S.*), *File* II-11.

Ethylene production from coke-oven gas has also been reviewed by D. D. Howatt.[12] The annual output in Britain is of the order of 150,000 tons, contained in coke-oven gas. To be economic, recovery must not cost more than £20 per ton. Processes for this recovery are outlined, and it is pointed out that for many purposes the complete removal of methane is unnecessary. The fundamental problems of the separation of gases have been investigated by the Gas Research Board.[13] These include the vapour–liquid equilibrium at low temperatures. In respect of the latter, new results have been obtained for oxygen at 11 atmospheres and for carbon dioxide over the temperature range —43° to —45°.

The possibility of using liquid methane as a fuel has been the subject of investigations by Sir A. C. Egerton in collaboration with the Gas Research Board.[13] Results of road trials with an omnibus are given in two papers[14] Liquid methane was carried in a vacuum-jacketed tank. In a 10,000-mile trial the performance was 5 miles per gallon, which includes the small loss of 2½% by evaporation during the night. The corresponding petrol mileage was 7·2. The engine was cleaner, with less valve pitting and less cylinder wear than with petrol. In estimating fuel costs, the price of liquid methane has been assumed to be 6d., which gives an overall cost equivalent to 8·6d. per gallon of petrol. In a second trial of 12,500 miles, and a compression ratio of 8, as against 5·5 in the earlier trial, the performance was 5·15 miles per gallon. Some data were obtained on the partial liquefaction of coal gas, involving a preliminary separation of ethylene, and a scheme was drawn up for avoiding interference with the seasonal calls on the gas industry. In this connexion it may be noted that in Germany plans had been made for the use in auto engines of coal gas enriched with methane made by the Fischer–Tropsch process.[15]

The tar and by-products industry has not encountered any major problems in the transition from war to post-war conditions. It may be said that there has been no transition, as demand exceeds production in respect of all products with the possible exception of benzole and naphthas. In some instances this position is due to the expansion of certain industries, notably plastics. Questions have been asked in the House of Commons regarding the supply of phenol and *m–p*-cresol for plastics production. The recovery of these from coal tar was maintained at a maximum, but expansion of phenol production from benzene was planned, and erection of plant was in hand. Price control of tar products has been continued almost unchanged but there has been considerable relaxation in the regulations regarding distribution and disposal licence procedure has been simplified.

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[12] *Coke,* 1946, **8**, 177, 200, 222, 229; B., 1946, I, 400.

[13] *Gas Res. Board, 7th Ann. Rept.,* 1946, *Comm. GRB.* 24.

[14] *J. Inst. Fuel,* 1945, **18**, 161; B., 1945, I, 351. *Inst. Fuel Bull.,* 1946, *June,* 193; B., 1946, I, 284.

[15] *Brit. Intelligence Objectives Sub-Commee. (B.I.O S.), Final Rept.* 511.

The various branches of the carbonisation industries and the tar industry in Germany have been investigated by teams of industrialists from Britain and the U.S.A. The general conclusion reached is that in Germany there have been few developments of note during the war. It is, of course, possible that the Germans interrogated have been sufficiently astute to conceal these, and the damage to plants would render discovery difficult. There is, unfortunately, evidence of much overlapping in these investigations, the same target being repeatedly visited by different teams; for instance, two almost identical reports are given of visits to the tar works of Rutgerswerke A.-G. at Rauxel by two separate teams.[16]

CARBONISATION.

One of the duties assigned to the National Coal Board was to conduct research on the utilisation of fuel, and the Board has shown wisdom in the appointment of Professor H. L. Riley to be Director of Carbonisation Research.[17]

The output of publications on the fundamentals of coal carbonisation was small during 1946. Apparently A. Gillet and his co-workers were able to carry out some research during the occupation of Belgium, and their results became available.[18] The pyrolysis of a coal was carried out in controlled conditions of heating between 340 and 900° in a stream of nitrogen. The products so evolved differed from those evolved in a stagnant atmosphere. The distillation was consistent with a series of partial reactions, beginning with the loss of CH_2 at 350°, passing through various stages of carbon, hydrogen, oxygen, and other losses, ending with methane evolution at 640—890°. Similar results were obtained by heating in a current of hydrogen.

I. Berkovitch and A. McCulloch[19] carbonised intimate mixtures of coking coals and sulphur in the Gray-King assay apparatus. The coking power of the coal was adversely affected by the sulphur but the yield of fixed carbon at a carbonising temperature of 630° was increased. With sulphur contents up to 5% of the coal, the evolution of gas, tar, and liquor was affected in a somewhat complex manner. The effect of sulphur on the yields and composition of the products is recorded in a series of tables and graphs. These results are discussed in relation to the theories of the structure of coal. When large amounts of sulphur are present it appears that the outermost molecular structures in the coal can be bridged by long sulphur chains; consequently, the increase in yield of coke is accompanied by a progressive and related increase in the sulphur content of the coke.

The results of work carried out by H. Macura on the behaviour of

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[16] (*a*) *B.I.O.S., Final Rept* 660 and 940; (*b*) *C.I O.S., File* XXXII-3; (*c*) *B.I.O.S., Final Rept.* 816; (*d*) *ibid.*, 507.

[17] *Nature*, 1946, **158**, 867.

[18] *Bull. Soc. chim. Belg.*, 1944, **53**, 27; 1945, **54**, 5; B., 1946, I, 9, 283.

[19] *Fuel*, 1946, **25**, 36, 69; B., 1946, I, 257.

bituminous coals on heating have become available.[20] Plasticity–time curves were used to assess the coking power of coals and to determine the influence of size, compression of the coal sample, and admixture of other coals and of pitch. The shrinkage of a series of anthracites, and of coking and non-coking coals, was influenced mainly by the behaviour of the petrological constituents and only to a smaller extent by the content of ash and volatile matter. Experiments on caking power showed that the maximum strength of the coke was obtained with a specific particle size. The results have been evaluated to show the optimum rates of carbonising in coke ovens for given periods.

H. E. Blayden, H. L. Riley, and F. Shaw[21] have shown that the strength of coke is increased by the addition to the coal of just sufficient inert material to suppress swelling during carbonisation; the strength is diminished by additions in excess of this amount. S. R. Illingworth[22] has shown how the formation of a plastic layer can be controlled by blending: this is a means of avoiding the pyrolysis of volatile matter and the lowering of the combustibility of the coke. D. A. Reynolds and J. D. Davis[23] have also investigated blending by tests carried out in the BM–AGA (Bureau of Mines–American Gas Association) apparatus. The coke from coals containing 31—38% of volatile matter was improved by blending them with suitable coals of low (15—20%) volatile matter content. On the other hand the coke from a strongly coking coal of medium volatile matter content could be blended with 70—80% of coal having a high content of volatile matter. This question of blending was also investigated by F. H. Read, H. W. Jackman, and P. W. Henline,[24] using an electrically-heated test oven taking a 500-lb. charge. Reproducible results close to those of full-scale practice, in respect of yields of gas and coke and properties of coke, could be obtained. Illinois coal could replace some of the Appalachian coals carbonised in the districts of Chicago and St. Louis, which would allow a saving in transport.

Some American workers prefer to use anthracite as part of the low-volatile addition. D. L. Newkirk[25] found that the coke had a higher shatter value when 5—6% of anthracite was used as part of the addition. A similar result was obtained by J. D. Clendenin, K. M. Barclay, and C. C. Wright,[26] but they were unable to correlate the effect with the physical characteristics of the anthracite; they were able to increase the strength of the coke still further by pulverising and heating the anthracite to 950° before blending with the coal. In order to produce active carbon, S. Boyk and H. B. Hass[27] chlorinated coal at 200—225° and carbonised the product at 500°, subsequently activating by steam at 800°.

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[20] *Oel u. Kohle*, 1940, **36**, 117, 161; 1944, **40**, 227, 269; B., 1946, I, 221, 314.

[21] *Fuel*, 1946, **25**, 13; B., 1946, I, 123.

[22] *Gas J.*, 1946, **247**, 848; B., 1946, I, 257.

[23] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3936; B., 1946, I, 314.

[24] *Ind. Eng. Chem.*, 1945, **37**, 560; B., 1945, I, 377.

[25] *Blast. Furn. Steel Plant*, 1945, **33**, 461; B., 1946, I, 158.

[26] *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 405; B., 1946, I, 158.

[27] *Ind. Eng. Chem.*, 1946, **38**, 745; B., 1946, I, 314.

The 37th Report of the Refractory Materials Joint Committee of the Gas Research Board and the British Refractories Research Association includes a section on the measurement of temperatures in gas retorts.[28] Thermocouples were inserted in the charge close to the refractory in horizontal and continuous vertical retorts, and in the brickwork of a continuous vertical retort. In the horizontal retort the temperature varied, of course, with the time but there were fairly considerable variations according to position. Temperature fluctuations of the charge and of the walls in the case of the continuous verticals were considerable, amounting to between 400° and 500° over periods of about one hour; such fluctuations were irregular. The effect of these variations on the life of the refractories is discussed. Other subjects reviewed in the Report of the Refractory Materials Committee included further work on the behaviour of firebricks on reheating in relation to the furnace atmosphere, *i.e.*, whether oxidising or reducing; the use of aluminous grog–clay coatings and the addition of aluminium powder to fireclay grog–clay coatings; the behaviour of porcelain under stress at a high temperature; the study of the clay–quartz system, comprising experiments with tridymite and cristobalite. Mention must also be made of a paper by J. S. Smith and P. F. F. Clephane[29] read at the meeting of the Institution in November, 1946, on the behaviour of quartz in fireclay refractories. The reaction between quartz and clay was the cause of several failures of refractories. The formation of a glass of low refractoriness was found to take place, and the change was accompanied by considerable shrinkage.

The amount of heat available for recovery in carbonising processes is not negligible and the questions involved have been reviewed by J. G. King and F. J. Dent[30] and by H. D. Edwards.[31] Proven methods for heat recovery are known and to some extent such recovery is practised, *e.g.*, from sensible heat in flue gases, and in coke where dry cooling is carried out. Edwards formed the opinion that the reason for failing to carry out such fuel economies is the preference of those in control for the simplest, most compact, and most easily supervised types of plant.

The use of different gases for purging tar vapours during carbonisation has been considered by S. Chopin,[32] who found hydrogen to be inefficient; butane was satisfactory but the author recommended the use of steam for practical reasons.

An experimental setting of horizontal carbonising chambers, erected at Wandsworth, is described by R. M. Furror.[33] The purpose was to economise ground space. The chambers were of rectangular cross-section, measuring 21 ft. × 2 ft. 3 in. high × 13 in. wide; they replaced ten horizontal retorts. The throughput was 317 tons per 24 hours, compared

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[28] *Gas Res. Board*, 1946, *Comm. GRB.* 25.

[29] *Inst. Gas Eng.*, 1946, *Comm.* 305.

[30] *J. Inst. Fuel*, 1946, **19**, 134; B., 1946, I, 222.

[31] *Brit. Coal Util. Res. Assoc. Month. Bull.*, 1945, **9**, 333.

[32] *Chim. et Ind.*, 1945, **54**, 327; B., 1946, I, 53.

[33] *Inst. Gas Eng.*, 1945, *Comm.* 289; B., 1946, I, 123.

with 239 tons with the earlier retorts ; the rate per square foot of ground space was also higher. Considerable cracking of the tar took place ; the gas yield was normal but the coke yield was greater.

War-time experiences in carbonisation at Dumbarton are described by A. McFadyen[34] ; by careful attention to the structure and operative control of the producers, throughput of the plant was increased. G. M. Gill and J. Roberts[35] carbonised in vertical retorts coal from the Barnsley Top-Hard seam ; the coke obtained burned very well in an open domestic grate. A. Cole[36] has considered the gas industry as producers and suppliers of two fuels, gas and coke, and in particular the methods to be followed in order to produce, from lean coal, a coke which burns readily in domestic grates.

A setting of vertical retorts is claimed in a patent to be particularly suitable for a gasworks of moderate size.[37] Water-gas generator chambers are provided, alternating with the retorts and communicating with them at a low level. Producer gas is used for heating both retorts and chambers. According to a patent of the Gas Light and Coke Co.,[38] agglomerates of carbonaceous material are prepared in a rotating drum from tar and comminuted material such as coal, coke, or charcoal ; the nodules so obtained are baked at 200° and then carbonised in a continuous vertical retort.

In 1938 the Fuel Research Board undertook, in collaboration with the industry, an investigation of the effect of type of oven on the properties of the coke, but this work was suspended at the outbreak of war.[39] It consisted of full-scale tests in six different types of coke-oven installations and one intermittent vertical chamber oven. The intention was to carbonise six coals obtained from five different coalfields, but it was possible to complete the experimental work only on three of the coals chosen. The work cannot now be completed as the original ovens are no longer available, but such results as were obtained have been published, as the method of planning may be of value in future work of similar type. It was not possible to arrive at definite conclusions, but certain indications were observed, as follows. An increased rate of coking appeared to cause a decrease in the size of coke, and in the strength of coke as measured by the shatter test. There appeared to be no general relation between the resistance of coke to abrasion and either rate of coking or width of oven. The same conclusion applied to the reactivity of the coke. The size of the pores was greater with narrower ovens and a slower rate of carbonisation.

[34] *Gas J.*, 1946, **248**, 564 ; B., 1946, I, 397.

[35] *Coke*, 1946, **8**, 35 ; B., 1946, I, 221.

[36] *Gas J.*, 1946, **247**, 25 ; B., 1946, I, 86.

[37] Standard Furnace and Setting Co. Ltd., A. W. H. Priestley, A. W. Dixon, and J. E. Dixon, B.P. 576,289 ; B., 1946, I, 321.

[38] With H. W. Cartwright, N. E. Siderfin, and R. S. Chaplin, B.P. 577,792 ; B., 1946, I, 286.

[39] "Experiments on coking practice," *Fuel Research, D.S.I.R.*

War-time experiences with a silica coke-oven battery have been related by W. A. P. Hoskins.[40] The effect of increased throughput and of the poorer quality of coke was to cause distortion, slagging, and erosion. It was necessary to devise methods of repairing the ovens without letting them down, although eventually complete renewal of the sole blocks had to be carried out. American experiences have also been reported by W. Seymour.[41] Reserves of high-grade coking coals have been depleted and it has been necessary to examine the suitability of other coals for blending. Since 1942 the average ash content of blast-furnace coke has increased at the rate of 0·5% per annum. L. N. Wilputte and F. Wethley have given their impressions of improvements in coke-oven design and operation[42]; these are mainly in connexion with the charging, but reference is also made to the effect of an increase in the thickness of top brickwork in improving working conditions on the tops of batteries, and in reducing heat losses. In assessing testing methods for controlling bulk densities in coke ovens, H. S. Auvil, L. D. Schmidt, and H. G. Graham[43] compared the results of different ways of filling a box of 1 cu. ft. or 2 cu. ft. capacity and were able to obtain a close agreement with measurements of a full oven charge.

Some German coke-oven installations have been inspected, including the Reichswerke A.-G. Hermann Goering Works at Watenstedt, near Brunswick,[44] and the Nordstern Plant, Gelsenkircher Bergwerks A.-G.[45] The main features of interest at both of these large installations seem to have been the ancillary plant, *e.g.*, Velox boiler and 4000-h.p. gas turbine at the former and plant for separating methane and ethylene at the latter.

Low-temperature carbonising plants have attracted quite a considerable attention, but it is doubtful whether any useful purpose was served by repeated visits to the same plants. The officials at the Wanne–Eickel Plant of Krupp–Lurgi explained the absence of records and drawings by a statement that eleven "commissions" had already inspected the works; although the number eleven may be an exaggeration, the published reports[46] indicate four visits, and the findings of the four teams do not vary greatly. An interesting feature of this plant is its interconnexion with a Fischer–Tropsch plant. Waste gases from the latter were used for heating the retorts of the low-temperature carbonisation plant. Part of the coke so made was utilised for the production of the water-gas required for the Fischer–Tropsch plant. The carbonisation plant comprised iron retorts built in 1943, incorporating improvements in design of the older plant built in 1937. Production of low-temperature coke was about 200,000 tons per annum. The by-product side had been

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[40] *Gas World*, 1946, **125**, *Coking Sect.*, 85; B., 1946, I, 397.
[41] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3907; B., 1946, I, 397.
[42] *Blast Furn. Steel Plant*, 1946, **34**, 355; B., 1946, I, 397.
[43] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3935; B., 1946, I, 314.
[44] *C.I.O.S. File* XXXIII-37.
[45] *Ibid.*, XXXIII-40.
[46] *Ibid.*, XXXI-30 and XXV-25; *B.I.O.S.*, *Final Rept.* 616 and 817.

little developed, and the tar was used without further treatment as fuel oil by the Navy. Some experiments had, however, been carried out on the separation of hydrocarbons from the gas by cooling and the use of active carbon. These hydrocarbons were bottled and supplied to steelworks.

Reports[47] give the results of interrogations regarding the activities of the Lurgi group of companies, itself a subsidiary of the Metallgesellschaft. Various systems of low-temperature carbonisation are mentioned, including carbonisation by direct (Spulgas) and indirect heating; one of these was operated by the Deutsche Erdol A.-G.

Reference may be made here to the carbonisation of other materials. The exploitation of peat has been developed to some extent,[48] and gas making from peat has been tried, but apparently with no great success. A survey of the wood carbonisation industry in Germany is the subject of a report.[49] There were three principal companies carbonising wood. The retorts are internally heated by the gas, after removal of the tar and other useful by-products. The greater part of the charcoal was used in the production of carbon disulphide, but this was an uncertain market, as brown-coal coke could be used for this purpose much more cheaply Three interesting products were made from the tar, viz., a plasticiser for reclaimed rubber, a froth flotation reagent, and a gum inhibitor for motor benzole. No research had been carried out and the prospects for the industry were very poor.

PURIFICATION.

A report of the Gas Research Board on the corrosion of water heaters may lead to a change of views regarding the extent to which purification should be carried This report gives an account of experiments with instantaneous water heaters carried out by N. Booth, P. C. Davidge, G. H. Fuidge, and B. Pleasance.[50] The tests consisted in the running of water continuously through each appliance and lighting and extinguishing the heater at intervals of 3¾ minutes. Assuming that the corrosion mainly occurs during the warming up period, the rate of corrosion was very considerably accelerated. After 1200 heating operations, the corrosion deposit was collected and examined. It was found that when the sulphur content of the gas was reduced from 17 to 3 grains per 100 cu. ft., there was an almost corresponding reduction in the amount of corrosion. In an experiment using gas with a sulphur content of 0·1 grain per 100 cu. ft., it was unexpectedly found that the amount of corrosion was greater than with gas containing 3 grains per 100 cu. ft.; the deposit was also different in composition, more nitrate than sulphate being present.

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[47] *C I O S., File* XXXI–23, XXXII–14, XXXII–91.
[48] *B.I.O.S., Final Rept.* 479.
[49] *Field Information Agency, Technical (F.I.A.T.), Final Rept.* 444.
[50] *Gas Res. Board, Comm. GRB.* 27.

The conventional method of removing hydrogen sulphide by means of iron oxide is the subject of several papers. C. Whitehead[51] has described the tests he employs for purifier charges; these comprise activity, bulk density, and quantity of material passing a $\frac{1}{40}$-in. mesh, the two latter giving an indication of the back pressure which will be thrown. The activity of iron oxides prepared in various ways is discussed by H. Thibon and A. Maillard[52]; they prepared ferric oxide by calcining ferric nitrate at 300°, obtaining an active material, and showed that activity was related to the micro-crystalline structure as shown by *X*-ray examination. H. K. Whalley[53] reduced "red mud," *i.e.*, bauxite residue, in coal gas at 400—550° and then oxidised in a mixture of air and steam at 250—300°, obtaining a material approaching a mixture of bog ore and peat in its quality as an industrial absorbent of hydrogen sulphide; the mechanism of fouling before and after revivification was also investigated. F. A. Sullivan has patented a process[54] for manufacturing a purifying material by the atmospheric oxidation of a mixture containing finely-divided iron, paper pulp, and shavings. The recovery of ferrocyanides and sulphur from spent oxide by the Chemische Fabrik Wesseling A.-G. has been investigated but no unusual feature is described.[55]

According to the Standard Oil Co.,[56] hydrogen sulphide and carbon monoxide can be removed from gas by washing with an alkaline solution of a mixture of *o*- and *p*-chlorophenol, and the spent solution can be regenerated by heat. Particulars have been given of Alkazid M and DIK, alkaline solutions used in Germany for the removal of carbon dioxide and hydrogen sulphide from coke-oven gas or water-gas: Alkazid M is a condensation product of acetaldehyde, methylamine, and hydrocyanic acid; DIK is made from formaldehyde, dimethylamine, and hydrocyanic acid. A high absorptive capacity is claimed and the solution can be regenerated by heat. At the I.G. Farbenindustrie A.-G. Works, Leuna, sodium glycine solution was used for the selective removal of hydrogen sulphide, while only a small proportion of carbon dioxide was dissolved.[57]

The survey of typical town gases undertaken by the Gas Research Board in 1945 has been continued[58] and earlier results have been confirmed. In the Jubilee Memorial Lecture, J. G. King has given some account of the removal of organic sulphur from town gas, and of the problem of gum formation.[59]

The hydrogenation of organic sulphur compounds has been investigated by a number of independent workers, using a variety of catalysts.

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[51] *Gas J.*, 1946, **247**, 274; B., 1946, I, 159.
[52] *Chim. et Ind.*, 1945, **54**, 315; B., 1946, I, 60.
[53] *J.S.C.I.*, 1946, **65**, 217; B., 1946, I, 399.
[54] U.S.P. 2,202,174; B., 1946, I, 12.
[55] *F.I.A.T.*, *Final Rept.* 809.
[56] U.S.P. 2,196,281; B., 1946, I, 379.
[57] *C.I.O.S.*, *File* XXX-6 and XXXII-107.
[58] *Ann Repts.*, 1945, **30**, 53.
[59] *Chem. and Ind.*, 1946, 462.

E. B. Maxted and A. Marsden[60] have studied the conditions under which cobalt thiomolybdate was effective, and E. B. Maxted and J. J. Priestley have given an account of the full-scale tests carried out at the works of Mirfield Gas Co.[61]; thiophen, however, was not affected by this treatment and the same disadvantage applied to the molybdenum sulphide and copper–chromium catalysts examined by the Gas Research Board.[13] In the production of gas mixtures of very low sulphur content, it was found that iron oxide was ineffective for the low concentrations of hydrogen sulphide present after the hydrogenation of organic sulphur and it was necessary to use solid nickel hydroxide. N. Booth and L. J. Jolley have taken out two patents for catalysts for the hydrogenation of organic sulphur. In one[62] iron is deposited on supporting material by the thermal decomposition of iron carbonyl; spent catalyst is reactivated by oxidation and subsequent reduction. In the other[63] the catalyst is prepared by heating a mixture of ferric oxide and an alkali carbonate.

An entirely different type of method for removing organic sulphur, which also removes unsaturated hydrocarbons, is described by Sir A. C. G. Egerton[64]; it consists in bubbling the gas mixture through liquid methane, whereby the impurities are condensed and retained.

E. H. M. Badger has examined the value and limitations of high-speed turbo-exhausters for the removal of tar fog from carburetted water-gas and coal gas.[65] A three-stage exhauster running at 2400—3900 revolutions was used. At the first stage practically all particles above a size depending on the peripheral speed of the rotor were removed. In this way the concentration of tar fog was reduced from 700 to 27 grains per 100 cu. ft. The efficiency of removal could be increased by cooling the inlet gas. Some operating particulars have become available of the Lurgi electrostatic system of tar precipitation at a coke-oven plant in Germany.[66]

The prevention of gum formation in purified town gas is the subject of a patent by Koppers Co.[67]; the gas is subjected to a brush electrical discharge which probably acts by decomposing the oxides of nitrogen which promote the formation of gum.

BENZOLE, TAR, AND TAR PRODUCTS.

The statistics of the Ministry of Fuel and Power in relation to benzole production are shown for each year from 1938 to 1945.[3] The influence of war requirements can be clearly traced in that the production reached a maximum in the years 1943–44, viz., over 100 million gallons, and

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[60] *J.S.C.I.*, 1946, **65**, 51; B., 1946, I, 257.
[61] *Gas J.*, 1946, **247**, 471, 515, 556, 593; B., 1946, I, 195. See B.P. 490,775.
[62] B.P. 572,471; B., 1946, I, 54.
[63] B.P. 574,776; B., 1946, I, 162.
[64] B.P. 578,872; B., 1946, I, 321.
[65] *J.S.C.I.*, 1946, **65**, 166; B., 1946, I, 283.
[66] *Brit. Coal Util. Res. Assoc. Month. Bull.*, 1945, **9**, 344; B., 1946, I, 160.
[67] U.S.P. 2,195,431; B., 1945, I, 379.

declined somewhat in 1945 to 96 million gallons. Production of pure toluole also was at a maximum in those years (12 million gallons), with a sharp fall in 1945 (8½ million gallons). It may also be noted that the information given, and presumably available, for the years 1943, 1944, and 1945 becomes more detailed. Pre-war exports of benzole were less than 50,000 gallons, but in 1943 rose suddenly to 31½ million gallons, and to 45 million gallons in 1944. These exports consist presumably of shipments to U.S.A. under lease-lend arrangements. Board of Trade returns[68] show that exports of benzole fell to just over one million gallons in 1946.

Statistics relating to production of coal-tar products are equally illuminating, although figures prior to 1942, *i.e.*, prior to the functioning of the machinery of the Coal Tar Control, are not available. The amount of crude tar distilled has remained very constant at just over 2 million tons; the corresponding figure for 1938 is approximately 1·9 million tons. A substantial contribution to the demand for liquid fuel was made by the production of approximately 600,000 tons per annum of creosote–pitch mixture. The effect of pressure from the Coal Tar Control is shown in the gradual increase of phenol production from 8200 tons in 1942 to 9200 tons in 1944. The relaxation of regulations in regard to the phenol content of tar products is shown by the drop to 8200 tons in 1945. The breakdown of some of the bulk items would be very interesting, *e.g.*, the various qualities of creosote oil and of cresylic acid; it is to be hoped that these figures will be released in due course.

The coal-tar industry in India has been assessed by C. J. Fielder.[69] The annual production was 95,000 tons per annum, of which 88,000 tons were from coke ovens. During the war some refined products were produced, including naphthalene, phenol, and cresylic acids, but further development was possible.

From an American source there came the news that the coal-tar industry in Germany was re-commencing operations.[70] The two largest distilleries in the Ruhr district began supplying pitch, heavy oils, and road tar. Refined products, *i.e.*, anthracene, naphthalene, phenols, and cresols, were also to be produced.

G. H. Thomson[71] has reviewed the literature on coal tar, covering the period January, 1944, to May, 1946. This review deals with the utilisation of coal tar, coal-tar fuels, methods of separation and identification of coal-tar constituents, and the new compounds identified.

The chemical engineering problems involved in the tar industry have been studied by R. Scott,[72] using a semi-scale distillation unit of 500 gallons capacity. Heat transfer data were obtained relating to tar, pitch, and

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[68] Board of Trade Returns.
[69] *J. Sci. Ind. Res., India,* 1946, **4**, 467, 528; B., 1946, I, 222.
[70] *Chem. Eng. News,* 1946, **24**, 698.
[71] *Brit Coal. Util. Res. Assoc. Month. Bull.,* 1946, **10**, 225.
[72] *Soc. Chem. Ind., Chem. Eng. Group, Oct.,* 1946; B., 1946, I, 400.

various distillates. The conditions for a maximum oil yield were established. Studies were made of the method of calculating the size of fractionating columns, and of the continuous recovery of tar acids by decomposing sodium phenolate solutions with carbon dioxide. In a further paper[73] the author considers some aspects of tar distillation in a single-flash tube still (Foster Wheeler). In this plant the pitch production was reduced by 10%. Coke formation might cause trouble, and corrosion was particularly severe in the continuous plant. This corrosion was in two forms, one due to the presence of ammonium chloride, and the other to organic substances, probably tar acids of high boiling point. Methods for the extraction of tar acids and bases are briefly described.

A patent in the name of Yorkshire Tar Distillers and D. W. Milner[74] describes a method of separating aromatics from paraffinic hydrocarbons. The tar is fractionated into cuts of 5°, which are then washed free from tar acids and bases. The neutral oils so obtained are found to have a much wider boiling range, up to 20°. These are then re-fractionated, when the aromatics are concentrated in the lowest-boiling part, whilst the higher-boiling part of the fraction contains up to 87% of paraffinic hydrocarbons. It will be apparent that such a process should be of particular interest in connexion with naphthas or light oils.

The results of work by E. Larsson on the composition of peat tar have become available.[75] The proportion of phenols, bases and neutral oils was determined.

The Gesellschaft fur Teerverwertung G.m.b.H. distilled three quarters of the tar produced in Ruhr coke ovens, *i e.*, over 800.000 tons per annum. It is reasonable to expect that any new developments in the tar industry would be found there, which may account for the number of inspections of the plant at Duisberg–Meiderich.[76] The only feature of special interest was a continuous vacuum-distillation plant handling 12 tons of tar per hour. The advantages of this system were economy in heat and labour, and an increased yield of oil. In addition to normal tar products, the works produced a fuel oil for marine purposes, and a flame-thrower fuel. Pitch–creosote fuel was not made regularly.

The Rütgerswerke A.-G., Castrop-Rauxel, handled 450,000 tons per annum in peace time.[16a] The dehydrated tar was distilled in batch stills through columns having 40 bubble plates, at an absolute pressure of 200 mm. A plastic compound was made by oiling back with anthracene oil an air-blown pitch. Hard pitch was made by treating soft pitch with superheated steam.

Other tar works inspected were Deutsche Erdöl A.-G. Mineralölwerke, Rositz,[16b] Gewerkschaft Rheinpreussen Utfort/Moers,[16c] and Dr. F. Raschig

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[73] *Inst. Fuel Bull., April,* 1946, 155; B., 1946, I, 284.
[74] B.P. 582,681; B., 1947, I, 98.
[75] *Chalmers Tekn. Högsk. Handl.,* 1942, *No.* 13; B., 1945, I, 377.
[76] *C.I.O.S., File* XXXII–93; *B.I.O.S., Final Rept.* 596, 615, 941.

G.m.b.H. Chemische Fabrik, Ludwigshafen.[16d] Distillation of tar under reduced pressure appears to have been standard practice. There is a surprising statement that at the Raschig plant tar was worked in a continuous plant erected in 1912 and not subsequently improved.

Benzole production is presumably a standard operation and, therefore, there is little published on this subject. However, G. Cellan-Jones[77] recommends sweeping out the top free space of ovens with stripped gas in order to increase the yield of benzole. G. W. Robson[78] has given an account of benzole recovery at Morpeth by active carbon. Woodall-Duckham (1920) Ltd., D. Rider, and W. J. Chadder[79] have described a modification of the rectifying section of a debenzolising still. The benzole vapour is split, part going to the rectifier and the remainder to a heat exchanger cooled by feed wash oil; the latter acts as a selective condenser. The corrosive action of benzole absorbing oils has been shown by C. M. Cawley and H. E. Newall[80] to be due to ammonium thiocyanate and chloride; these salts are less soluble in gas oil than in creosote and hence little corrosion occurs when the fomer is used.

Considerable attention has been given to the purification of benzole. H. Kiemstedt has given evidence[81] that mercaptans are formed during the refining of benzole with sulphuric acid, as a result of reactions between hydrogen sulphide and unsaturated hydrocarbons. According to J. Bougault, E. Cattelain, and P. Chabrier,[82] large amounts of benzene and toluene can be freed from thiophen and its homologues by means of Raney nickel.

W. J. Chadder and H. M. Spiers[83] have reviewed the subject of benzole distillation. Carbon disulphide and *cyclo*pentadiene can be separated from the fore-runnings. Improved fractionation is obtained by working with alternating periods of total and zero reflux. Azeotropic distillation, using methyl alcohol, may be required to produce nitration-quality toluene. The authors give tables of boiling points and other data for use in finding the composition of mixtures of benzene, toluene, and xylene. W. C. Holmes and Co. Ltd. and T. Taylor[84] have patented a method of separating forerunnings by thermostatic control of the reflux condenser.

A patent in the names of Midland Tar Distillers Ltd., F. G. Broughall, and R. Scott[85] has for its object the prevention of loss of hydrocarbons in benzole fore-runnings. The gas is scrubbed with a refined naphtha fraction. The carbon disulphide which is also dissolved is removed by

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[77] *Coke*, 1946, **8**, 8; B., 1946, I, 222.
[78] *Gas J.*, 1945, **246**, 687; B., 1946, I, 10.
[79] B.P. 573,659; B., 1946, I, 89.
[80] *J.S.C.I.*, 1945, **64**, 285; B., 1946, I, 10.
[81] *Oel u. Kohle*, 1943, **39**, 833; B., 1946, I, 160.
[82] *Nature*, 1946, **158**, 631
[83] *Coke Oven Managers' Assoc. Midland Sect.* 1946, *Preprint*; B., 1946, I, 398.
[84] B.P. 580,124; B., 1946, I, 403.
[85] B.P. 575,553; B., 1946, I, 197.

means of ammonium polysulphide. The product is then mixed with the main distillate to form a motor spirit.

Toluene was the most important constituent of benzole but the supply position was never so serious as in 1914–18. A number of schemes were propounded for producing toluene but not all were translated into practice. In the first place, it was possible to operate the washing plants at the gasworks in such a way as to favour toluene extraction. Nitration-quality toluene could be separated from paraffinic crudes by means of azeotropic distillation. This was carried out in Scotland but not in England. D. A. Howes[86] has summarised the various methods by which toluene could be produced from petroleum distillates; these include: liquid–liquid extraction with sulphur dioxide; azeotropic distillation; extractive distillation; and non-destructive dehydrogenation with a molybdenum catalyst. Details of the method of extractive distillation are given by C. L. Dunn, R. W. Millar, G. J. Pierotti, R. N. Shiras, and M. Souders, jun.[87]

J. Griswold and R. H. Bowden[88] have identified the impurities which can be separated from "industrial pure" benzene by azeotropic distillation with acetone; these consist of *cyclo*hexane, various paraffins, and naphthas. R. F. Marschner and W. P. Cropper[89] have determined the boiling ranges of azeotropes of benzene with ten non-aromatic hydrocarbons. Aluminium Plant and Vessel Co. Ltd., G. A. Dummett, and S. J. Ralph[90] have developed a method involving the use of an entrainer of different polarity from that of the components of the mixture and having a lower boiling point; as an example they recommend a mixture of acetone and methyl alcohol for a mixture of aromatics and non-aromatics.

Chemical methods of producing toluene form the subject of a number of patents. The Gas Light and Coke Co., with co-patentors, is responsible for three of these. In the first[91] toluene is obtained by the hydrogenation of phthalic acid or anhydride using a catalyst of vanadium, tungsten, or molybdenum oxide or sulphide. In the second[92] naphthalene is hydrogenated in the presence of tin or a tin compound; it is claimed that under the conditions specified (500° and 200 atmospheres) hydronaphthalenes are not formed. According to the third patent[93] benzene and dimethyl ether react at 250—600° and at a pressure of 50—200 atmospheres to form toluene and xylenes; phosphate catalysts are used. A process patented by C. Weizmann[94] relates to paraffinic benzole or naphtha; dienes are first

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[86] *Ind. Chem.*, 1946, **22**, 403.
[87] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 631; B., 1946, I, 88.
[88] *Ind. Eng. Chem.*, 1946, **38**, 509.
[89] *Ibid.*, 262; A., 1946, I, 206.
[90] B.P. 572,297; B., 1946, I, 56.
[91] With R. H Griffith, B.P. 577,816; B., 1946, II, 320.
[92] With R. H. Griffith and J. H. G. Plant, B.P. 577,818; B., 1946, II, 320.
[93] With A. R. Morcom, W. B. S. Newling, and J. H G. Plant, B.P. 577,314 B. 1946, II, 277.
[94] B.P. 575,768; B., 1946, I, 197.

removed by heating with activated clay and the product is passed over a hydrogenation–dehydrogenation catalyst at 600—700°.

A toluene plant operated by Midland Tar Distillers Ltd. on behalf of the Ministry of Supply has been described[95]; it is a continuous unit comprising four columns for handling crudes and a separate still for re-distilling the toluene fraction.

The benzole refinery at Amalia, Bochum, has been inspected.[96] The crude benzole was handled at the rate of 200 tons per day in a pipe still fitted with a column having 55 bubble plates. Batch stills were used for obtaining the finished products.

The demand for naphthalene is expected to continue, and the petroleum industry is doubtless interested. An American patent[97] of the Socony-Vacuum Oil Co., Inc., gives a method for the production of naphthalene by the cracking of gas oil.

A method has been patented[98] by Reilly Tar and Chemical Corporation, F. E. Cislak, and T. P. Carney for extracting phenols direct from tar; the extraction is carried out at a temperature above 100°, and at a pressure above atmospheric, using a dilute solution of caustic soda.

A system was in operation at the works of Lurgi Gesellschaft, Frankfurt-am-Main, for the extraction of phenols from tar oils by dilute methyl alcohol, the purpose being to produce a high-grade Diesel oil.[99]

G. Murdoch and M. Cuckney[100] have described the recovery of phenols from gasworks ammoniacal liquor, as carried out by the Gas Light and Coke Co. The liquor is washed with a creosote fraction in Holley-Mott washers. The partition factor is maintained at 4—5 by the addition of small quantities of oils containing tar bases. Reference is also made in the Eighth Report[101] of the Liquor Effluents and Ammonia Committee of the Institution of Gas Engineers to the work being carried on at Hinckley on the recovery of phenols from liquor. At the coke-oven installation of Reichswerke A.-G. at Watenstadt, near Brunswick,[43] extraction with benzole was employed for the recovery of phenols from liquor. Recovery of phenol from liquor was also carried out by Lurgi Gesellschaft für Wärmetechnik[99]; small concentrations of phenol, however, were destroyed by a bacterial process.

An inspection of the phenol plant of I.G. Farben Fabrik, Wolfen, showed that no developments had been made, in regard to either plant or products[102]; batch distillation units were used with manual control. The report on the Lurgi organisation[46] directs attention to the high *m*-cresol content of the low-temperature tar.

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[95] *Ind. Chem.*, 1946, **22**, 203.
[96] *B.I.O.S.*, *Final Rept.* 835.
[97] U.S.P. 2,336,244; B., 1946, I, 325.
[98] B.P. 580,926; B., 1947, I, 15
[99] *B.I.O.S.*, *Final Rept.* 623.
[100] *Inst. Chem. Eng.*, 1946, *Advance proof*; B., 1946, I, 399.
[101] *Inst. Gas Eng.*, 1946, *Comm.* 304.
[102] *B.I.O.S.*, *Final Rept.* 560.

N. M. Cullinane and S. J. Chard[103] have studied the action of methanol on phenol in the presence of alumina; they were able, by using activated alumina, to control the reaction so as to obtain improved yields of anisole, cresols, and hexamethylbenzene.

It has been mentioned earlier that cresylic acid of high *m*-cresol content, as used in the manufacture of plastics and plasticisers, was in short supply. Special interest, therefore, attaches to the work of J. N. Shreve and C. J. Marsel[104] on the hydrolysis of chlorotoluene. When *o*- and *p*-chlorotoluenes were hydrolysed, *m*-cresol was found in the cresols formed. Cresol mixtures containing up to 60% of *m*-cresol could be obtained. The best results were obtained by carrying out the reaction in an autoclave at 350° for 2 hours. An excess of sodium hydroxide was required, the most suitable ratio (molar) being 2·5 of sodium hydroxide to 1 of chlorotoluene.

The xylenols are becoming increasingly important as raw materials for chemical industry but their isolation from the mixtures obtained from coal tar is difficult. H. A. Basterfield and Imperial Chemical Industries Ltd.[105] have patented a method for the separation of *m*-4-xylenol from *p*-xylenol; the mixture is treated with butene and sulphuric acid, when the *m*-4-xylenol is preferentially butylated. A further separation is effected by means of caustic soda solution, the sodium salt of 2 : 4-dimethyl-6-*tert*.-butylphenol being soluble; the butyl group is then removed to re-form the desired dimethylphenol.

Pyridine and its homologues continue to receive attention. W. Shive, E. G. Ballweber, and W. W. Ackerman[106] have employed ozonolysis as a method for elucidating their structure; oxygen containing 5% of ozone was passed through a solution of the base, and the product was examined for formic acid, acetic acid, pyruvic acid, pyruvaldehyde, glyoxal, and glyoxylic acid. M. A. Phillips[107] has set out methods for the preparation of various derivatives of pyridine and of esters and substituted compounds. The formation of addition compounds of sulphur dioxide with pyridine and the picolines has been studied by K. R. Hoffman and C. A. Vander Werf[108]; they found that pyridine and *β*-picoline form only one addition compound with sulphur dioxide, whereas both *α*- and *γ*-picolines each form two addition compounds.

Special attention has been given to *β*-picoline, presumably because of its value as a raw material for chemical syntheses, such as the production of nicotinic acid. L. U. Lemmerman, A. W. Davidson, and C. A. Vander Werf[109] have investigated the formation of compounds between the picolines and *o*-chlorophenol. *o*-Chlorophenol forms a stable 1 : 1

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[103] *J.C.S.*, 1945, 821; A., 1946, II, 79.
[104] *Ind. Eng. Chem.*, 1946, **38**, 254; B., 1946, II, 313.
[105] B.P. 582,057; B., 1947, II, 44.
[106] *J. Amer. Chem. Soc.*, 1946, **68**, 2144.
[107] *Ind. Chem.*, 1946, **22**, 283.
[108] *J. Amer. Chem. Soc.*, 1946, **68**, 997; A., 1946, I, 350.
[109] *Ibid.*, 1361; A., 1947, I, 24.

compound with each of the three picolines, as shown by freezing point curves; β-picoline, however, forms a second compound with 2 mols. of *o*-chlorophenol.

Methods for the separation of β- and γ-picolines and 2 : 6-lutidine have been developed by E. A. Coulson and J. I. Jones.[110] These three cannot be separated by a straight distillation, but azeotropic distillation can be used. Acetic acid can be used as an entrainer, but the difference in boiling point is only 2 or 3 ; consequently a column with not less than 70 theoretical plates was required. The base and acid could then be separated by the distillation of each fraction with trimethylpentane.

International Bitumen Emulsions, Ltd., J. A. Montgomerie, P. K. Archibald, and L. C. Bradshaw[111] have described a process for the emulsification of pitch with water. Coal-tar pitch having a melting point above 50° is mixed with a natural asphalt, fatty acid pitch, or fatty acid, emulsification may be assisted by a protein compound and bentonite. A method for the treatment of pitch has been patented by Turner and Newall, Ltd., H. L. Riley, J. J. Hudspith, and E. G. Hancock,[112] wherein the pitch is heated with magnesia to 700°, the friable residue can be extracted with water plus carbon dioxide under pressure, when a fine carbon is obtained. Magnesia and carbon dioxide can be recovered from the solution and re-cycled.

E. A. Coulson and J. I. Jones[113] have pointed out that the coal-tar constituents which have the widest and most varied uses are only those which are most easily isolated. In their opinion fresh, varied, and valuable outlets could be found for the constituents less readily accessible. The petroleum industry was undertaking the supply of organic chemicals present in coal tar. J. I. Jones[114] has directed attention to a new raw material for plastics available in coal tar, viz., acenaphthene. It could be dehydrogenated, with the aid of suitable catalysts, to acenaphthylene; the latter would polymerise to form a resin, and also copolymerise with a number of other materials, including styrene and methyl methacrylate. According to B.X. Plastics and R. S. Colborne,[115] unsaturated hydrocarbons, such as styrene and indene, which are of interest to the plastics industry, can be separated from aromatic hydrocarbons by solubility differences in suitable solvents, such as formic acid, glycols, and glycol esters.

It may be pointed out that at the large German tar works, to which reference has already been made,[16,76] a wide range of special pure constituents was prepared. This was made easier by the procedure of submitting the crude tar to fractional distillation. Constituents available included indene, 1- and 2-methylnaphthalenes, acenaphthene, quinoline,

[110] *J.S.C.I.*, 1946, **65**, 169; B., 1946, II, 313.
[111] B.P. 573,169; B., 1946, I, 90.
[112] B.P. 572,860; B., 1946, I, 90.
[113] *Coke*, 1946, **8**, 108, 120. *Ind. Chem.*, 1946, **22**, 445, 579.
[114] *Brit. Plastics*, 1946, **18**, 286; B., 1946, II, 388.
[115] B.P. 573,111; B., 1946, I, 90.

acridine, indole, carbazole, and benzonitrile. It was stated, however, that the demand was small except in the case of acenaphthene. About 8 tons per month of the latter were supplied by the Duisburg–Meiderich works.

GASIFICATION.

J. Hiles and R. A. Mott[116] have published the results of experimental work on the flow of gases through beds of coke and other granular materials. A generalised formula for all granular materials was thereby derived and the effect of gases other than air was determined. Published data were collected and the results were applied to the formula derived by the authors.

A further account has been given[117] of the work carried out in the laboratories of the Gas Research Board and the Fuel Research Board on the synthesis of methane. The work had reached the stage where an intermediate-scale apparatus was needed, and such an apparatus was constructed at Poole. Some preliminary results are recorded. The laboratory work was mainly concerned with the catalysts, as regards variations in composition and methods of preparation. Progress was made in the evolution of simpler and more effective catalysts.

The enrichment of coal gas with methane was practised in Germany during the war,[118] by bringing about the interaction between hydrogen and carbon monoxide already present in the gas. The purpose of the methanisation was to provide a substitute fuel for road transport. In addition to raising the calorific value of the gas, the process removed constituents causing deterioration of storage cylinders. Plants were installed at roadside filling stations, and the gas produced was compressed to 300 atmospheres. The Germans had another scheme for improving the quality of coal gas, viz., integration of carbonisation with the Fischer-Tropsch process.[119] The smallest Fischer-Tropsch unit that could be economically operated was being erected at the Leipzig gas-works. It was intended to raise the calorific value of the town gas, and at the same time to supply some much-needed liquid and solid products. According to a visit by Dr. Lowry to Koppers G.m.b.H. at Essen, however, the only research on gas production carried out in Germany was on the gasification of pulverised coal with steam and air.[120]

The Westinghouse Electric International Co. has patented a method for the production of a fuel gas suitable for use in the heat-treatment of metals.[121] A protective gas of uniform composition is produced from a fuel gas, such as town gas, of variable composition, by effecting incomplete combustion in two stages, using a catalyst; in the first stage free

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[116] *Fuel*, 1945, **24**, 135, 158; B., 1946, I, 53.
[117] *Seventh Ann. Rept., Gas Research Bd.*, 1946, *Comm. GRB* 24.
[118] *C.I.O.S., File* XXXIII–5.
[119] *Ibid.*, XXVII–68.
[120] *Ibid.*, XXXI–31.
[121] B.P. 573,445; B., 1946, I, 89.

carbon is deposited, to be taken up by the gas in the second stage. According to a patent of M. Steinschlaeger[122] the sensible heat developed by the combustion of gases, oil, or tar in compressed air or oxygen in the presence of steam or carbon dioxide is used to crack further quantities of the fuel; the resultant gases are used, after removal of condensible substances, for power raising or for purposes of synthesis or hydrogenation.

The U.S. Bureau of Mines has issued a progress report for the year 1944 on the gasification of lignite and sub-bituminous coal.[123] Carbonisation and gasification were carried out in laboratory retorts, Glover–West retorts, a water-gas plant, and a pilot plant. In connexion with the last-named it was shown that lignite and sub-bituminous coals which contract on heating could be gasified with steam to yield gas having a ratio of hydrogen to carbon monoxide which could be controlled within the limits of 1·6 to 12·0.

A patent of F. L. Duffield[124] aims at producing a water-gas with a high content of hydrogen, by carrying out the gasification at a temperature of 600°; this favours the reaction $C + 2H_2O = CO_2 + 2H_2$. Superheated steam is employed at a pressure of 20 atmospheres. The carbon dioxide is removed by scrubbing. Several patents have as their object the production of a water-gas suitable for use as a synthesis gas, *e.g.*, for the Fischer-Tropsch process.[125]

A summary of a number of reports from Germany has been made by D. D. Howatt.[126] These show the advantages of using oxygen, a cheap supply of which was available. In water-gas production, "make" could be carried on continuously, instead of the intermittent "make and blow." All available information regarding Winkler water-gas generators in Germany was collected by a team of investigators.[127] There were five large Winkler plants in Central Germany and Czecho-Slovakia. It is concluded that the process is technically sound, but is economic only where a supply of cheap fuel, such as brown coal, is available; moreover, the gas is too low in calorific value to be used as town gas but it serves as a raw material for chemical production such as the production of ammonia or methanol.

A translation is available of a report by Oberingenieur Sabel on "Ten years of oxygen-gasification at Leuna."[128] A difficulty in this sytem of producing a nitrogen-free water-gas was the risk of slagging but this had been overcome, one precaution being the thorough mixing of the steam and oxygen before admission to the generator. The methane content of the gas was low, even when using uncarbonised dry brown coal. The latter result was not obtained in a plant treating materials such as

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[122] B.P. 577,906; B., 1946, I, 321.

[123] *U.S. Bur. Mines*, 1946, *Rep. Invest.* 3901; B., 1946, I, 398.

[124] B.P. 570,007; B., 1945, I, 353.

[125] B.P. 573,923, 574,048, 578,332; U.S.P. 2,198,553; B., 1946, I, 89, 126, 321, 162.

[126] *Chem. Age*, 1946, **55**, 661.

[127] *B.I.O.S., Final Rept.* 333.

[128] *Ibid.*, 199.

brown coal with oxygen under pressure, according to W. Offenbach[129]; analysis of the purified gas shows nearly 23% of methane. From Canada results are reported of the gasification of coke in an oxygen–steam blast.[130]

In order to study the kinetic theory of reactions in the gas producer, M. Prettre[131] used a simplified model consisting of a cylindrical column of regular layers of graphite spheres. It was assumed that three combustion zones existed. In the initial zone equal volumes of carbon monoxide and dioxide were formed ; in the final zone dioxide was reduced to monoxide ; both reactions occurred in an intermediate zone. Calculations were made of the temperature of thin layers, from energy balances, and were compared with the actual temperature distribution. The relation between size of particle, blast velocity, and efficiency was determined. Above a certain limit blast velocity has little influence on efficiency. The effects of enriching the blast with oxygen or of increasing the pressure up to 4 atmospheres were also investigated. E. M. Brown[132] has also discussed the effects of the size and type of fuel, control of the fuel bed, and various other aspects of practical importance on the efficient operation of producers. W. P. Smith[133] has given the results of tests carried out at Rochdale on the control of producers. Better results were obtained with a closed-door producer and steam-injected air than with the open-front type having watered bars. The use of a fan and addition of steam gave even better control ; by introducing coal gas below the hot zone up to 50% of the thermal output was provided.

Some particulars have been given by M. M. Gray and G. C. Allfrey[134] of provision made for emergency gas supplies by producers in case of failure of industrial gas supply due to enemy action. 825 producers with an output of 5 therms per hour and 315 producers with 20 therms per hour were available. These would provide gas having a calorific value of 117—140 B.Th.U. per cu. ft., operating on coke or anthracite nuts. Mobile producer units using inferior grades of fuel are described by B. Sengupta and V. V. Apte[135] ; the special feature of these down-draught producers was the shape designed to ensure uniform distribution of air. T. P. Hignett and E. L. Stout[136] have reported on the construction and operating results of a slagging type of producer for pilot-plant gas supply ; the producer, which was 2 ft. in diameter and 5 ft. high, gave 7000 cu. ft. of gas per hour when fed with a mixture of coke and blast-furnace slag.

A Swedish design for an electrically heated gas producer is given in

[129] *Stahl u. Eisen*, 1943, **63**, 936 ; B., 1946, I, 123.
[130] *Canad. Chem.*, 1946, **30**, *No.* 8, 34 ; B., 1946, I, 399.
[131] *Mém. Soc. Ing. Civ. France*, 1945, **98**, 1 ; B., 1946, I, 123.
[132] *Ind. Chem.*, 1945, **21**, 591 ; B., 1946, I, 53.
[133] *Gas J.*, 1945, **246**, 294 ; B., 1945, I, 352.
[134] *Inst. Fuel Wartime Bull.*, 1946, *Feb.*, 94 ; B., 1946, I, 159.
[135] *J. Sci. Ind. Res., India*, 1945, **4**, 301 ; B., 1946, I, 86.
[136] *Chem. Met. Eng.*, 1946, **53**, *No.* 1, 136 ; B., 1946 I, 159.

the patent of Stora Kopparbergs Bergslags Aktiebolag[137]; the solid carbonaceous fuel is heated by electric arcs and the gases are directed to travel near the walls in preference to along the centre.

A German report[138] has given working results of a slagging-type gas producer using oxygen, of the Thyssen'sche Gas und Wasserwerke G.m.b.H., Duisberg-Hamborn. These relate to a pilot plant with a throughput of 2 tons of coal per day. A 40-ton unit developed from this was destroyed soon after being put into operation.

J. W. Gibson[139] has described the operation of the Burns-Gibson plant for complete gasification. It is developed from the Pintsch type, the retort being heated by the blow gases, whilst the blast gases are utilised in a waste-heat boiler. The blow and run periods are automatically controlled by thermocouples located in the gas off-take and the blast outlet. Particulars are given of a Scottish plant producing 82 gaseous therms per ton of coal, at a cost of approximately 6·8d per therm. The gas, enriched by cracking tar, had a calorific value of 425 B.Th.U. per cu. ft.

The Pintsch-Hillebrand system of complete gasification is the subject of a report from Germany.[140] The plant at Wesseling was fed with brown coal briquettes. It was not possible to use fuel having an ash which softened below 1300°.

A patent of M. H. M. Arnold, D. R. Pryde, R. J. Morley, and Imperial Chemical Industries Ltd.[141] gives the design of a plant for the carbonisation and gasification of powdered coal. Two separate vessels are used and in each the solid is maintained in a fluid state. In the carbonising chamber the lifting medium is part of the coal gas made, re-injected by a fan. The coke particles from the bottom of this chamber are lifted by air through the producer, to be dropped in a higher, wider section. The incandescent coke then returns to the carbonising chamber, and its sensible heat is transferred to the coal feed.

Experimental work on the gasification of coal in hydrogen under pressure has been continued by the Gas Research Board and progress is reported in the seventh annual report.[142] In experiments using a mixture of hydrogen and water-gas it was found that at a higher gas flow the influence of carbon monoxide in forming methane by synthesis was less marked. The addition of steam to hydrogen was also found to reduce the yield of methane. Tests on the effect of size grading of coal were also carried out, using doubles, singles, and coal crushed to pass $\frac{1}{4}$ in.; the yields of methane were 128, 115, and 109 therms per ton respectively. It was also found that the coke residue from the crushed coal was of the largest size grading. Investigations of temperature conditions inside the charge indicated that complications were being

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[137] B.P. 571,878; B., 1946, I, 11.
[138] *C.I.O.S., File* XXIX–51.
[139] *Gas J.*, 1945, **246**, 884; B., 1946, I, 86.
[140] *F.I.A.T. Final Rept.* 425; *Coke*, 1946, **8**, 218; B., 1946, I, 399.
[141] B.P. 578,711; B., 1946, I, 364.
[142] *Seventh Ann. Rept. Council of Gas Res. Board, Comm. GRB.* 24.

introduced by heat losses, owing to the difficulty of ensuring adequate heat insulation of the retort used.

Publication of the results of work carried out by the Joint Research Committee of the Gas Research Board and Leeds University in 1938–39 on the use of oxygen and high pressure in gasification was withheld for security reasons. These were made available in 1946 as "Part IV. Synthesis of gaseous hydrocarbons at high pressure."[143] The report opens with a comprehensive discussion of the possibility of the application of high-pressure methods to gas manufacture, under the headings: (1) the Lurgi process; (2) a two-stage gasification process; (3) a two-stage process involving gasification and contact-conversion; (4) a modified two-stage gasification, allowing coke production. A new series of experiments was completed on the hydrogenation of coal in a retort without the application of external heating other than preheating of the hydrogen feed. Difficulty was encountered owing to the coking of the coal charge: this was overcome by separating the fines below $\frac{1}{8}$ in., and passing these down the walls of the retort, which were water-cooled. All types of fuel hydrogenated rapidly but the results indicated that the yield of hydrocarbons was limited, and that the presence of carbon monoxide had a considerable influence as regards the nature of the type of coal which could be handled.

Information regarding the Lurgi system of high-pressure gasification is given in a report from Germany.[144] The most striking feature of the system in the complete gasification of coal with oxygen and steam at high pressure was the increase in the formation of methane and the consequent raising of the calorific value of the gas. A necessary condition was that the coal should be non-caking and it should be noted that some coals which did not cake when carbonised at atmospheric pressure developed marked caking properties when carbonised at high pressures. There was an optimum ratio of oxygen to steam, this being the factor which controlled the temperature in the combustion zone. Cost comparisons with conventional methods of gas production depended on the value to be given to the saleable coke produced in those methods.

GASEOUS COMBUSTION.

A summary of the papers which are essential to a clear understanding of the more important factors in the oxidation at high temperatures of carbon monoxide has been prepared by J. R. Arthur.[145] The subject is covered from the classical experiments of Dixon in 1877 to the present time. The author concludes that the experimental data can be best interpreted in terms of material chain mechanisms. Reference is made to those features as yet inadequately explained, viz., the rôles played by

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[143] *Gas Res. Board*, 1946, *Comm. GRB*. 26.
[144] *B.I.O.S., Final Rept.* 521, *Gas J.*, 1946, **248**, 889.
[145] *Brit. Coal Util. Res. Assoc. Month. Bull.*, 1946, **10**, 129.

hot surfaces and the influence of those substances which promote combustion ; in technical combustion practice, however, the predominating factors are aerodynamic in character.

Further results are reported by G. W. Culshaw and J. E. Garside[146] in connexion with the study of aërated burner flames. The earlier work related to ethylene–air and carbon monoxide–air mixtures, and showed that the ignition velocity was independent of burner diameter, shape of burner tip, and rate of mixture feed, varying only with working temperature and pressure. This conclusion was found to be valid for a mixture of propane and air, which was chosen on account of its low ignition velocity. During the course of this work it was observed that for mixtures containing a considerable excess of combustible gas, the inner cone, when separated from the outer mantle, assumed an unusual form, described as "polyhedral" ; investigations of this phenomenon were put in hand.

F. E. Vandaveer and C. G. Segeler[147] have investigated the partial combustion of gas with a deficiency of air, using natural gas, coke-oven gas, and butane. The air supply was varied from 10% to 100% of that necessary for complete combustion. The lower limits for air content for self-supporting combustion were found to be below 65%, 53%, and 60%, respectively, of those necessary for complete combustion. The composition of the products of combustion was also examined.

J. E. Kilham[148] commenced an investigation into the transfer of energy from flame gases to solids. Attention was directed in the first place to transfer by forced convection, and the laws relating thereto have been recapitulated. Experimental work was carried out using rods having various refractory coverings. Uranium oxide and rouge reached a temperature of 850°, whilst alumina and magnesium oxide reached 1200° under the same conditions. Nevertheless, the radiation from the latter was less than that from the former. These preliminary results were in agreement with the theory that heat transfer was by forced convection. A description is given of the apparatus set up to measure flame temperatures, based on the method of the reversal of sodium lines. The effect of the composition of the gas mixture on flame temperature was studied.

A gas burner for "concentrated combustion" has been described by J. Palser.[149] Combustion takes place within a cylindrical tunnel in a refractory block and the hot gases which escape at a high velocity can be directed in a desired direction. The industrial applications of this device are described. Technical and economic data on the application of gaseous fuel for commercial uses have been collected and discussed by W. Johnson and W. F. Moore.[150]

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[146] *Inst. Gas Eng., Comm.* 306.
[147] *Ind. Eng. Chem.*, 1945, **37**, 816; B., 1945, I, 377.
[148] *Inst. Gas Eng.*, 1946, *Comm.* 307.
[149] *Gas J.*, 1946, **247**, 104; B., 1946, I, 86.
[150] *Inst. Gas Eng.*, 1946, *Comm.* 297; B., 1946, I, 399.

A report has been issued on the findings of a team which investigated German developments in industrial heat-treating furnaces.[151] It was concluded that practically no progress had been made during the war in connexion with gas-fired furnaces. Automatic control was almost unknown. Even where elaborate instrument panels had been installed, manual control was retained. Some difficulty was caused by the removal of methane from town gas. Use of such gas resulted in oxidising conditions, with consequent scaling.

Analysis and Testing.

A laboratory method for determining the suitability of coal and coal blends for the manufacture of metallurgical coke is given by R. F. J. Teichmann.[152] The ground sample is heated in a Woodall–Duckham "D" oven from cold to 900° in about 3 hours; the assessment is based on the visual examination of the coke. A German method for carrying out a low-temperature assay[153] consists of heating the coal in thin layers on a series of trays; tar yields are higher than those obtained by the Fischer assay.

W. F. Gardner[154] has described an instrument used for determining the oxygen content of the mixture of hydrogen and coal gas in barrage balloons; the instrument was designed for the use of R.A.F. personnel. The principle of the instrument was the combination of the oxygen with hydrogen on the surface of a heated platinum filament; the fall in pressure was indicated on an instrument of the aneroid type.

The use of mercuric sulphate in sulphuric acid as an absorbent for ethylene was recommended by A. W. Francis and S. J. Lukasiewicz.[155] According to F. R. Brooks, P. Benjamin, and V. Zahn[156] this reagent also oxidises carbon monoxide to dioxide; the error so introduced can be corrected by absorbing carbon dioxide in caustic soda solution. The authors of the original paper agreed to this amendment.

V. E. Clifton has described[157] a modified constant-volume method for the analysis of coal gas. A Russian investigation[158] of reagents for the analysis of water-gas contains some innovations, viz., a solution of cuprous sulphate and β-naphthol in sulphuric acid for carbon monoxide, and a solution of silver sulphate and nickel sulphate in sulphuric acid for heavy hydrocarbons. For the determination of tar fog in gas E. H. M. Badger and D. S. Wilson[159] have modified the Blackie impingement apparatus, and have added a preliminary settling vessel; deposited water should be estimated by means of the Fischer reagent.

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[151] *F.I.A.T.* 434.

[152] *J. Chem. Met. Soc. S. Africa*, 1945, **45**, 202; C., 1945, 232.

[153] R. Heinze, *Oel u. Kohle*, 1943, **39**, 973; C., 1945, 233.

[154] *Gas J.*, 1945, **246**, 847; C., 1946, 1.

[155] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 703; C., 1946, 16.

[156] *Ibid.*, 1946, **18**, 339; C., 1946, 160.

[157] *Ind. Chem.*, 1946 **22**, 200; C., 1946, 158.

[158] R. Zelvianskaja, *Trans. All-Union Conf. Anal. Chem.*, 1944, **3**, 175; C., 1945, 15.

[159] *J.S.C.I.*, 1946, **65**, 119; C., 1946, 158.

About half of the sulphur content of crude benzoles is present as carbon disulphide but the nature of the remainder was not known, owing to the lack of precise methods of analysis. G. Claxton and W. H. Hoffert[160] have put on record the experimental work carried out since 1932 with the object of identifying and estimating these sulphur compounds. The authors have now given details of satisfactory methods of analysis for the complete examination of the following sulphur forms in benzole: hydrogen sulphide, mercaptans, carbon disulphide, other sulphides and disulphides. For the estimation of small quantities of total sulphur in benzoles, *i.e.*, of the order of 0·01%, K. H. V. French and G. Claxton described a modified form of the S.T.P.T.C. apparatus for burning the sample without a diluent.[161] Two reagents for the colorimetric determination of less than 0·001% of sulphur as thiophen in pure benzole are given by K. H. V. French[162]; the first (which is the more sensitive) consists of sulphuric acid containing isatin and anhydrous ferric sulphate, whilst the second (which is more stable) is alloxan.

According to L. Bettelheim,[163] for the analysis of mixtures of phenol and cresols, the sample is shaken in a special form of vessel with sodium benzenesulphonate solution, water is then added, and the volume of separated "cresol" is read after 8 hours' settling; corrections must be applied to this observed volume. A colorimetric method for the determination of phenols in petroleum and allied products is described by L. Lykken, R. S. Treseder, and V. Zahn.[164] The sample or a caustic extract is dissolved in acetic acid, nitrous acid is added to form the nitrosophenol, and finally an excess of alcoholic ammonia is added; the intensity of the colour of the resulting quinonoid salt is measured with a photo-electric colorimeter. The method has the advantage of being unaffected by many organic and inorganic materials. The colorimetric method of B. N. Afanasiev[165] depends on the formation of a yellow or brown colour with chloramine-*T*.

Two rather similar methods for the analysis of mixtures of phenol and its homologues are based on spectra. D. H. Whiffen and H. W. Thompson[166] used the infra-red spectra, whilst W. W. Robertson, N. Ginsburg, and F. A. Matsen used the ultra-violet absorption of vapours.[167]

In connexion with the separation of cresols by the process of butylation–fractionation–debutylation, D. R. Stevens and J. E. Nickels[168] have presented data for the analysis, by determinations of freezing point and cloud point, of binary cresol and butylated cresol mixtures.

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[160] *J.S.C.I.*, 1946, **65**, 333, 341.

[161] *Ibid.*, 344.

[162] *Ibid.*, 15; C., 1946, 85.

[163] *Svensk Kem. Tidskr.*, 1942, **54**, 194; C., 1946, 85.

[164] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 103; C., 1946, 86.

[165] *J. Appl. Chem. Russ.*, 1944, **17**, 335; C., 1945, 239.

[166] *J.C.S.*, 1945, 268; C., 1945, 239.

[167] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 746; C., 1947, 68.

[168] *Ibid.*, 260; C., 1946, 164.

A British Standard for disinfectant and sanitary powders specifies the separation of phenols by a dry distillation in admixture with powdered magnesite.[169] The Sub-committee on Methods of Soap Analysis, of the Society of Public Analysts, has published methods for the determination of phenols in soap.[170] Phenols and cresols are separated from the soap by distillation. In the case of high-boiling tar acids, soap is salted out from a solution by calcium nitrate and the tar acids are dissolved in benzene.

I. Gad and J. Hald[171] describe a method for the colorimetric determination of small quantities of pyridine in aqueous ammonia; the sample is treated with cyanogen bromide followed by sulphanilic acid. A. Hamer, R. Pomfret, and W. V. Stubbings[172] have given a method for the determination of the pyridine content of technical pyridine. Separation by distillation through a seventy-plate column was found to be unsatisfactory and the method adopted was based on the sparing solubility of pyridine perchlorate, the perchlorates of picolines and other homologues being readily soluble. A convenient test for β-picoline has been described by G. Riethof, S. G. Richards, S. A. Savitt, and D. F. Othmer.[173] γ-Picoline and 2 : 6-lutidine react with phthalic anhydride in the presence of acetic acid to form pyrophthalones, whilst β-picoline does not react in this way. The test for purity depends on the yellow colour of the pyrophthalones: these compounds are precipitated in alkaline solution, and the reaction may be used for purifying β-picoline.

A method for the estimation of naphthalene in absorbing oil, described by P. E. Reichardt and D. L. White,[174] consists in volatilising the naphthalene in a stream of warm air, and subsequently absorbing it in picric acid solution. J. A. Hinckley, M. C. Wilson, H. McKnight, and B. B. Corson[175] have given details of a method for the determination of small amounts of sulphur in naphthalene. The naphthalene vapour is burned in a current of air and the sulphur dioxide is absorbed in soda. The sulphite formed is oxidised with bromine, and determined as barium sulphate turbidimetrically. The most interesting feature of the paper is the description of the apparatus, which includes a variable high-current, low-voltage transformer, a gas-lift absorber, and an infra-red device for volatilising the sample.

Two British Standards have been published during the year, which may be appropriately mentioned here: "Classification of wood preservatives,[176] and "Coal tar pitches."[177] The former has a section on tar oil

[169] B.S. 1013:1946.
[170] *Analyst,* 1946, **71**, 301; C., 1946, 259.
[171] *Dansk Tidsskr. Farm.*, 1941, **15**, 105; C., 1946, 20.
[172] *Analyst,* 1946, **71**, 419; C., 1947, 12.
[173] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 458; B., 1946, II, 408; C., 1946, 253.
[174] *Ibid.*, 286; C., 1946, 163.
[175] *Ibid.*, 1945, **17**, 462; C., 1946, 9.
[176] B.S. 1282 : 1945.
[177] B.S. 1310 : 1946.

types: the second provides for five pitches which are characterised by their softening points. Other properties specified are specific gravity, "free carbon," ash, and distillate at 270° and 300°.

A number of papers have appeared on the subject of the determination of high-boiling constituents of coal tar. Two such papers refer to the determination of benzpyrene by fluorometric methods.[178] V. I. Chmelevski and I. J. Postovski have given methods for the estimation of anthracene, phenanthrene, carbazole, and acridine.[179]

A method of detecting contact of soil with coal gas has been developed by the Chemical Department of the South Metropolitan Gas Co.[180]; it depends on the presence in the soil of benzene or toluene derived from the gas. Air drawn through the soil is passed into a mixture of nitric and sulphuric acids; the nitrated compounds are extracted with butanone and are detected by the purple colour developed on shaking with aqueous potash. E. H. Green and E. A. Cox[181] have given a method for the determination of tar and bitumen in road materials, using methylene chloride as solvent; a considerable saving of time without undue loss of accuracy is claimed.

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[178] V. M. Bergolt and E. B. Kofman, *Biochimia*, 1945, **10**, 79; C., 1945, 251. A. Kling and M. Heros, *Compt. rend.*, 1941, **212**, 348; C., 1946, 18.

[179] *J. Appl. Chem. Russ.*, 1944, **17**, 463; C., 1945, 239.

[180] *Gas J.*, 1945, **246**, 532; C., 1945, 268.

[181] *J.S.C.I.*, 1946, **65**, 1; C., 1946, 82.

MINERAL OILS.

By W. W. Goulston, B.A., B.Sc., A.R.I.C., F.Inst.Pet.
The Shell Petroleum Co. Ltd.

Crude Oil.

The world production of crude oil and the consumption of petroleum products remain as high as at the peak period of the war. Military requirements for some years to come will remain much above the pre-war level, and reconstruction in war-devastated areas involves a heavy consumption of oil products.[1] In the past, Europe has been largely supplied from the Western hemisphere, owing to the cost of transporting oil through the Suez Canal. The construction of pipelines from the Middle East fields to the Mediterranean, and the extension of refineries at Haifa on the Mediterranean coast, will lead to the substantial supply of European requirements from the Middle East, where the production of crude oil is increasing rapidly.

The crude oils from the new oilfields in the Middle East, Bahrein Island and Saudi Arabia, have very similar properties and are usually batched together for treatment in the refinery. The two crude oils have the following properties[2] :

	Bahrein.	Saudi Arabia.
Specific gravity	0·859	0·851
Viscosity (Saybolt/100° F.)	58·5	42·7
Pour point (° F.)	+20°	+10°
Sulphur (% wt.)	2·21	1·75
Gasoline from crude ;		
Yield (% vol. of 437° F. E.P.)	37	37
Octane number	40	37
Residue from crude ;		
Yield (% vol.)	62	62
Specific gravity	0·934	0·904

Natural Gas.

In 1939 an extensive source of natural gas was discovered in south-west France ; this gas is almost pure methane, having a calorific value exceeding 1000 B.Th.U. per cu. ft. It emerges at a pressure of 150 atmospheres and the existing installations are capable of supplying 6·35 million cu. ft. daily. It is proposed to increase the capacity of the plant to 28 million cu. ft. daily, and the gas will be used as the raw material for a nitrogen-fixation plant to be erected near Toulouse.[3]

The consumption of liquefied petroleum gases (propane and butane) in the United States continues to increase at a rapid rate. The consumption in 1945 was 21·4% above that in 1944 and in 1946 the consumption was

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[1] C. O. Willson, *Oil and Gas J.*, 1946, **45**, *No.* 5, 65.
[2] *Ibid.*, 1945, **44**, *No.* 24, 110.
[3] *Chem. Trade J.*, 1946, **119**, 294.

1425 million gallons, an increase of 33% above that in 1945.[4] Some of the latest developments in the use of liquefied petroleum gas are in connexion with agriculture for the destruction of weeds by flame and for the promotion of growth and ripening of fruit.

The conversion of natural gas into gasoline using the Fischer–Tropsch process is being energetically developed[5] and it is claimed that the stage is being reached when this method of manufacturing gasoline is competitive with the production of gasoline from crude oil in the United States.[6] A large commercial plant is being constructed at Brownsville, Texas, for the production of petroleum products and chemicals from natural gas; the daily capacity of this plant is expected to be 6000 barrels of gasoline, 800 barrels of Diesel fuel, and 70,000 lb. of crude alcohol.[7]

The development of the Fischer-Tropsch process in the United States, particularly as applied to natural gas, has introduced a number of improvements which reduce the cost of the process.[8] Instead of the fixed bed of expensive cobalt–thoria catalyst used in Germany, a fluidised bed of cheap iron-type catalyst is used for the conversion of synthesis gas ($CO + H_2$) into hydrocarbons. A uniform temperature can be readily maintained under the turbulent conditions of the fluid bed and the amount of heat-transfer area required under these conditions is only about 5% of that necessary in the conventional fixed bed process. Of the hydrocarbons produced after the polymerisation of C_3 and C_4 olefines, 80% consist of gasoline of octane number 75—80 and the remainder is Diesel fuel of cetane number above 50; in addition, crude alcohols are obtained to the extent of about 10% of the hydrocarbon yield.[9]

PETROLEUM SUBSTITUTES.

Considerable development work on the use of methane as a fuel was carried out at the Imperial College during recent years.[10] It was found that the most suitable method for automobiles was to carry methane as a liquid in vacuum-jacketed tanks at approximately atmospheric pressure. The cost of liquid methane produced from coal gas was considerably higher than the cost of producing the equivalent quantity of gasoline from petroleum but was competitive with the cost of liquid fuels produced from coal by other methods.

In a report on the manufacture of aviation gasoline in Germany during the war period[11] it is stated that most of the components of aviation fuel were products obtained in the synthetic oil plants using the process of hydrogenating coal and coal tar. A peak production of approximately

[4] G. G. Oberfell and R. W. Thomas, *Oil and Gas J.*, 1946, **45**, *No.* 34, 146.

[5] *Ann. Repts.*, 1945, **30**, 67 : J. C. Lane, *Refiner*, 1946, **25**, *No.* 8, 87, *No.* 9, 97.

[6] R. P. Russell, *Chem. and Ind.*, 1947, 56.

[7] *Chem. Trade J.*, 1947, **120**, 129.

[8] R. P. Russell, *Chem. Eng. News*, 1947, **25**, 87.

[9] R. C. Alden, *Oil and Gas J.*, 1946, **45**, *No.* 27, 79.

[10] A. Egerton, *Nature*, 1946, **158**, 105; B., 1946, I, 284.

[11] *U.S. Naval Mission in Europe, Tech. Rept.* 145–45; *Oil and Gas J.*, 1946, **44**, *No.* 41, 92.

two million gallons per day of such fuels was reached in 1943. Alkylate was produced by the dehydrogenation of butane, followed by interaction with *iso*paraffins which were obtained from the same base by a vapour-phase isomerisation process using aluminium chloride as catalyst.

A description of the development of the Fischer–Tropsch process in Germany has been given by C. C. Hall.[12] The combined rated annual production of a total of nine plants was 740,000 tons of hydrocarbon products, but the maximum output obtained was 570,000 tons, that is, less than 8% of the total German oil production. It is estimated that the production of oil products by this process, under present-day British conditions, would cost between 2s. and 2s. 6d. per gallon.

It is recommended that the synthetic oil industry as such, in Germany, should not be revived as these plants are uneconomic, but there is a possibility that one or more of the Fischer–Tropsch plants may be started up for the production of synthetic non-edible fatty acids owing to the extreme shortage of this commodity in Germany for the manufacture of soap.[13]

Some experimental work has been done on the production of synthetic lubricating oils by the aluminium chloride polymerisation of some olefine fractions of the primary hydrocarbon product obtained in the Fischer–Tropsch synthesis carried out under atmospheric pressure in the presence of a cobalt catalyst[14]; the higher-boiling fractions gave a lower yield of lubricating oil of similar viscosity but the viscosity index was higher.

Of the four plants erected by the Australian Commonwealth Government for the production of alcohol from wheat,[15] only the plant in New South Wales, completed in 1943, actually came into use. It remained in operation for one year only and yielded a total of somewhat more than 2,500,000 gallons of alcohol during that period. The remaining plants were completed but were never put into operation. In consequence of the poor wheat crop, the scheme of producing alcohol from wheat has been abandoned and some other use is to be found for these idle plants.[16]

In the United States, most of the industrial alcohol produced is made by synthesis from petroleum gases; only about 20% is made from molasses; the cost of production of alcohol in the United States is about 12—15 cents per gallon when made from petroleum and is much higher when made from molasses.[17]

A claim has been made for the use, in internal-combustion engines, of a fuel consisting of a solution of ammonium nitrate in liquid anhydrous ammonia[18]; the use of such a fuel would need no outside source of oxygen and could therefore operate in the higher stratosphere or in submarines and in other situations where air intake is difficult.

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[12] *Chem. and Ind.*, 1947, 67; *J. Inst. Fuel*, 1947, **20**, 65.

[13] *Petrol. Times*, 1946, **50**, 1316.

[14] D. Gall, *J.S.C.I.*, 1946, **65**, 185; B., 1946, I, 402.

[15] *Ann. Repts.*, 1943, **28**, 62.

[16] *Petrol. Press Serv.*, 1946, **13**, *No.* 1, 16.

[17] *Chem. Trade J.*, 1946, **119**, 552.

[18] U.S.P. 2,393,594.

A white substitute for carbon black has been developed which is particularly suitable for the compounding of rubber. This material is obtained by burning ethyl silicate to a white, partly translucent powder. It behaves in the same way as carbon black in rubber compositions, giving additional strength together with tear- and abrasion-resistance; the use of this material makes it possible to produce finished rubber in any desired colour. At present, the cost of this substitute is higher than that of carbon black but it is expected that large-scale production will reduce the cost to a competitive level.[19]

REFINERY PLANT.

The construction of a submarine pipeline which involved numerous problems was carried out in the strait between Saudi Arabia and Bahrein Island.[20] The line, used for crude oil, is 17 miles long and 12 in. in diameter; it is protected, with a thick coating of a mixture of asbestos fibres, sand, and asphaltic bitumen, against corrosion from sea-water of high salt concentration and comparatively high temperature. To avoid rupture of the pipeline, a series of concrete supports were erected at the high points on the coral beds so as to keep the line clear of the coral.

Cathodic protection against corrosion of refinery plant and, particularly, of buried pipelines has been successfully applied for some years. The usual method involves the use of an anode of iron, copper, or carbon buried in the ground and supplying, from an outside source, a direct current along the pipeline to be protected. This type of protection is known as the "electrolytic" anode method.[21] In another method which is being used, known as the "galvanic" anode method, an anode metal is used which is sufficiently high in the electrochemical series that when coupled with iron it provides its own source of current, thereby eliminating the need for an outside source of power.[22] Zinc has been used for this purpose in the past but the use of magnesium is now being developed and has been found efficient for this application.[23]

It was found in plants used for the production of butadiene, under the conditions of the high temperature of 1300° F., used for the vapour-phase cracking of naphtha fractions obtained from Refugio Texas crude oil, that these vapours when passed through 18–8 type stainless steel tubes in a superheater caused intense corrosion of the tubes, which failed after only 120 hours in operation. Although the cause of the corrosion was not identified, a considerable improvement was obtained when certain sulphur compounds were present. The corrosion has been reduced to reasonable proportions by the injection of 0·3% of carbon disulphide into the feed naphthas.[24]

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[19] *World Petrol.*, 1946, **17**, *No.* 6, 86.

[20] R. Sneddon, *Petrol. Eng.*, 1946, **17**, *No.* 6, 131.

[21] D. Holsteyn, *ibid.*, *No.* 8, 154.

[22] J. R. James and R. L. Featherly, *Oil and Gas J.*, 1946, **45**, *No.* 22, 88.

[23] L. M. Oldt, *Nat. Petrol. News*, 1946, **38**, *No.* 10, 186R.

[24] E. Q. Camp, C. Phillips, and L. Gross, *ibid.*, 192R.

Petroleum refining capacity is being extended all over the world, particularly in the Middle East. The Haifa refinery has started on an extensive enlargement programme doubling the present capacity of four million tons of crude oil per annum. The additional crude oil will be made available on the completion of the new 16-in. pipeline from Kirkuk in Iraq to Haifa in Palestine. It is proposed to construct a catalytic cracking unit and a lubricating oil unit at this refinery.[25]

CRACKING.

The use of thermal cracking is still widespread in spite of the growing importance of catalytic cracking. Some of the recently-erected thermal cracking plants incorporate the "delayed coking" operation[26] in which the heated topped crude oil enters one of two insulated coking drums where it is reduced to coke; the removal of coke is carried out by a combination of boring tools and powerful hydraulic jets.[27] Apart from the production of gasoline and gas, the gas oil produced can be used as a feedstock for catalytic cracking plants.

Continuing the experimental work on the catalytic cracking of pure hydrocarbons,[28] it was found that under normal catalytic cracking conditions, olefines were isomerised by change in position of the double bond and by a change in the original configuration of the carbon skeleton. Pentenes were found to undergo branch-chain isomerisation much more readily than the butenes. Olefinic cracked gasolines when recracked over cracking catalysts produced less olefinic gasolines of higher lead-susceptibility. This is due to the formation of *iso*paraffins, and accounts for the high ratio of *iso*- to normal paraffins in gasoline produced by catalytic cracking.[29]

Owing to increasing demands in the United States for high-quality gasoline, the capacity for catalytic cracking is increasing steadily. It is estimated that the capacity at the end of 1946 was 1,200,000 barrels per day, or about 25% of the total intake of the refineries. Approximately 68,000 barrels per day of new capacity was erected during 1946 and 140,000 barrels per day of additional capacity is under construction.[30]

The use of bead catalysts[31] for catalytic cracking gives results superior to those obtained with pelleted clay catalysts.[32] In spite of the higher initial cost of the bead catalyst, the lower loss due to attrition, the higher initial activity, and the improved yield of gasoline of superior quality make the use of bead catalysts a distinct advantage. The bead catalyst

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[25] *World Petrol.*, 1946, **17**, *No.* 12, 92.

[26] R. B. Tuttle, *Oil and Gas J.*, 1946, **44**, *No.* 48, 109.

[27] A. L. Foster, *ibid.*, **45**, *No.* 18, 74; B., 1947, I, 12.

[28] *Ann. Repts.*, 1945, **30**, 70.

[29] H. H. Voge, G. M. Good, and B. S. Greensfelder, *Ind. Eng. Chem.*, 1946, **38**, 1033; B., 1947, II, 93.

[30] R. P. Russell, *Chem. Eng. News*, 1947, **25**, 86.

[31] *Ann. Repts.*, 1943, **28**, 64.

[32] L. P. Evans, *Oil and Gas J.*, 1946, **44**, *No.* 47, 167; B., 1946, I, 319.

is manufactured by allowing a stream of a mixture of aluminium hydroxide and sulphuric acid, in the form of a hydrogel, together with a solution of sodium silicate, to flow over a fluted distributing cone and then through a 7-ft. column of light mineral oil above a 3-ft. column of water. In the water layer the hydrogel breaks into individual droplets averaging $\frac{1}{8}$ in. in diameter; after a series of washing operations, the beads are dried and shrink to one eleventh of their original size. Finished beads average about 3 mm. in diameter and are spheroidal in shape: they consist approximately of SiO_2 89·5%, Al_2O_3 10%, water 0·5%.[33] A catalytic cracking plant specially designed to use a new type of micro-spheroidal catalyst has been erected at Houston, Texas, having a capacity of more than 20,000 barrels of charging stock daily.[34]

GENERAL REFINING.

Particular attention has been given in recent years to the treatment of high-sulphur crude oils such as those from West Texas. Of a number of processes available, one method is to treat the distillate with aluminosilicate cracking catalyst or with zinc oxide-type catalyst A second method is to use a solvent-extraction process with a solvent such as anhydrous hydrofluoric acid. The application of this solvent is restricted to virgin stocks owing to its action as an alkylating and polymerising agent in the presence of olefines.[35]

The catalytic refining of catalytically cracked gasoline is carried out by a process known as "polytreating": this process employs temperatures ranging from 400° to 560 F. and a pressure of about 600 lb. per sq. in., and yields gasoline of a low olefine content and an increased lead-susceptibility.[36]

Alkylates which have been produced by reactions in the presence of Friedel-Crafts type catalysts (aluminium chloride) are liable to contain excessive quantities of chlorine in the form of organic chlorine derivatives. The lead-susceptibility of the alkylates is lowered by the presence of these chlorine compounds, which can be removed effectively by passing the vaporised product over Porocel at 700° F. and washing the condensed vapours with caustic soda solution; this treatment also reduces the tendency to gum formation.[37]

A new group of non-corrosive selective oil-refining solvents has been developed during the war and has recently been disclosed. These solvents are known as "sulpholanes" and are derivatives of tetramethylene sulphone (thiophan 1 : 1-dioxide). A semi-commercial plant has been completed for the manufacture of dimethylsulpholane in California.[38] The starting material for the production of the sulpholanes is diacetone

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[33] R. W. Porter, *Chem. Met. Eng.*, 1946, **53**, *No.* 4, 94.
[34] *Petrol. Eng.*, 1946, **17**, *No.* 13, 256.
[35] E. J. Scafe, *Refiner*, 1946, **25**, *No.* 9, 87.
[36] V. Haensel and V. N. Ipatieff, *Ind. Eng. Chem.*, 1946, **38**, 1045; B., 1947, I, 123.
[37] R. G. Haldeman and W. A. Pardee, *ibid.*, 242; B., 1946, II, 230.
[38] *Chem. Engineering*, 1946, **53**, *No.* 10, 116.

alcohol, which is converted into hexylene glycol and dehydrated to methylpentadiene; the latter is then treated with sulphur dioxide to produce dimethylsulpholene, which, on hydrogenation, yields dimethylsulpholane. The sulpholanes are used as selective solvents for liquid–vapour and liquid–liquid extraction processes. They are used for separating aromatics from paraffins, naphthenes, and olefines and also to desulphurise petroleum fractions. They can be easily removed from many mixtures by a simple water wash. They have the disadvantage, however, of being stable only below 240° c.; at higher temperatures sulphur dioxide is slowly liberated.

Investigation of recent German technical progress has revealed a number of new solvent-refining processes which were being developed during the war. The use of a substitute for propane for de-asphaltising residual fractions was being investigated and successful results were obtained with a solvent consisting of 90% of dioxan and 10% of formic acid[39]; this solvent mixture was used in equal proportions with the oil and the process was carried out at 5° c.

The use of hydrofluoric acid was developed for desulphurising petroleum fractions including gasoline[40] and antimony trichloride was used for the extraction of aromatic and naphthenic fractions (Mirasol process).[41] It was also found that hydrazine derivatives were particularly good as solvents for dewaxing oil.[42]

Motor Spirit.

In order to obtain adequate supplies of 100-octane aviation fuel it was found desirable to isolate certain hydrocarbons from petroleum fractions using a process of superfractionation, that is, fractional distillation on an extended scale involving the use of series of columns, each 12 ft. in diameter, having a total of 552 bubble-trays. By this means, 315,000 gallons per day of refined *iso*hexane and *iso*heptane were produced, amounting to 35% of the daily output of 100-octane aviation fuel from one particular refinery.[43]

Another hydrocarbon which was produced for use as a component in high-octane aviation fuel was di*iso*propyl (2 : 3-dimethylbutane); this was made mainly by the alkylation reaction of ethylene and *iso*butane in the presence of an aluminium chloride catalyst.[44] In the absence of catalysts and at high temperatures and pressures, neohexane (2 : 2-dimethylbutane) was formed.

The supply of suitable fuel for gas turbines for aircraft is a problem

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[39] *Combined Intelligence Objectives Sub-Commee., File* XXXII–94, 135.

[40] *Ibid.*, 136.

[41] *Ibid.*, 39.

[42] *Ibid.*, 134.

[43] S. F. Birch, P. Docksey, and J. H. Dove, *J. Inst. Petroleum*, 1946, **32**, 167; B., 1946, I, 259.

[44] R. C. Alden, F. E. Frey, H. T. Hepp, and L. A. McReynolds, *Oil and Gas J.*, 1946, **44**, *No.* 40, 70.

which will loom large in the immediate future.[45] The fuel being used at present is a kerosine of the paraffin-base type with a distillation range of 150—300° C.; the freezing point is about —40° C. However, the supplies of kerosine are limited and it will be necessary to look for a fuel which is more plentiful when gas turbines are used on an extensive scale. Gas oil is also a possible fuel, although the freezing point of —40° C. may be difficult to achieve. Low-octane gasoline is another possible fuel which would be more plentiful than either kerosine or gas oil. The solution to this problem is mainly a supply question and will probably be met by some compromise between the fuels which can be made available and the best results in service. It is of interest to note, in this connexion, that in propeller-driven aircraft, weight is always of the greatest importance and space for fuel is readily available in the wings. In the case of high-speed jet-propelled planes, however, the wings are thin and allow no space for fuel; on this account, the emphasis in the latter case may shift from weight to space, that is, the fuel should have a high calorific content per gallon rather than per pound.[46]

It has been demonstrated by test flights using aviation gasoline charged with air and also with nitrogen that one of the causes of vapour lock in aircraft engines, at altitudes between 8000 and 12,000 ft. and in the early stages of the flight, is the presence of dissolved air in the gasoline[47]; a method which has been developed to overcome this difficulty is to install a submerged centrifugal pump in the bottom of the fuel tank to supplement the feed pump.

During the war, extensive use was made of gelled gasoline for filling incendiary bombs and for flame-throwers. The thickening agent used for this purpose, known as "napalm," is an aluminium soap derived from a combinatiin of acids of the types exemplified by lauric acid and by naphthenic or oleic acid.[48] A type of gelled gasoline, known as "Fras Fuel," which improved the range of flame-throwers was developed in the United Kingdom and large quantities were manufactured in this country.[49]

A method has been proposed for treating leaded gasoline so as to make it suitable for a cooking fuel or for cleaning fluid and other purposes; the leaded gasoline is treated with stannic chloride, resulting in an insoluble mixture of lead diethyl chloride and tin diethyl chloride which can be removed after agitation with water.[50]

LUBRICATING OILS.

Synthetic lubricating oils of good quality are being produced in the U.S.A. by an undisclosed process, from natural gas as a starting point;

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[45] F. R. Banks, *J. Roy. Aero. Soc.*, 1947, **51**, 51.

[46] A. G. Cattaneo, *Automotive and Aviation Ind.*, 1945, **93**, *No.* 12, 30.

[47] W. A. Craig, *Petrol. Eng.*, 1946, **18**, *No.* 1, 278.

[48] L. F. Fieser, G. C. Harris, E. B. Hershberg, M. Morgana, F. C. Novello, and S. T. Putnam, *Ind. Eng. Chem.*, 1946, **38**, 768; B., 1946, I, 387.

[49] B. M. Cawley, *Petroleum*, 1946, **9**, 56; B., 1946, I, 162.

[50] *Oil and Gas J.*, 1946, **44**, *No.* 52, 142; U.S.P. 2,390,988.

these lubricants are marketed under the name of "Prestone" but are more expensive than ordinary petroleum lubricants.[51]

The production of synthetic lubricating oils was developed extensively in Germany. A good grade of lubricating oil was manufactured by the polymerisation of ethylene and also by the condensation of the ethylene polymer with petroleum or with coal-tar distillates.[52]

The present standard quality of transformer oil will probably be revised in the near future on the lines recommended in a symposium on transformer oil held by the Institute of Petroleum.[53] The grades A and B should be replaced by one grade approximating to the present B grade, which is giving satisfactory service, but the specification should include a limit for acidity after the oxidation test. It was the general opinion that the present British Standards Institution sludge test has a number of drawbacks and should be revised or a more suitable test should be substituted.

An examination of the oxidation behaviour of fractions of a lubricating oil stock was carried out in order to obtain information on the susceptibility to oxidation of the various types of hydrocarbons present in petroleum lubricating oils. It was found that the development of acidity can be taken generally as a measure of the breakdown of the side-chains, whereas increase of viscosity gives a rough indication of condensation. Naphthenes were found to be the most resistant to oxidation, paraffins tended to form acidic compounds without much condensation or increase in viscosity, whereas aromatic compounds were susceptible to the formation of condensation products which increased the viscosity.[54]

Resistance to oxidation is achieved by the addition of suitable agents in small proportions. For use in turbine oils and transformer oils an additive which renders the oil highly resistant to oxidation and gum or sludge formation is 2 : 4-dimethyl-6-*tert.*-octylphenol used in the proportions of 0·05—2% by weight.[55] It has been found that the use of oxidation inhibitors in turbine oils prevents the formation of surface-active type of compounds which are good protectors against rust formation and therefore it is desirable to add rust-preventives in addition to antioxidants.[56]

A detailed study of the causes of corrosion of bearings[57] showed that in laboratory corrosion tests babbitt alloys were the most resistant to corrosion whilst cadmium alloys were attacked to the greatest extent. Under engine operating conditions cadmium–silver alloys showed the greatest corrosion and copper–lead alloys were most resistant. Corrosion can be

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[51] J. C. Kratzer, D. H. Green, and D. B. Williams, *Nat. Petrol. News*, 1946, **38**, *No.* 6, 135R.

[52] H. Schildwachter, *Refiner*, 1946, **25**, *No.* 3, 109.

[53] *J. Inst. Petroleum*, 1946, **32**, 355; cf. B., 1946, I, 402.

[54] S. F. Kapff, J. R. Bowman, and A. Lowry, *J. Inst. Petroleum*, 1945, **31**, 453; B., 1946, I, 162.

[55] Shell Development Co., and D. B. Luten, jun., B.P. 572,012; B., 1946, I, 60.

[56] A. A. Neff and G. H. S. Snyder, *World Petrol.*, 1946, **17**, *No.* 8, 94.

[57] H. H. Zuidema, *Oil and Gas J.*, 1946, **44**, *No.* 41, 100; *No.* 42, 151; *No.* 43, 66; B., 1946, I, 340.

reduced by the addition of a small proportion of certain metals such as zinc or indium. The conclusions drawn from these investigations are that the principal means of controlling corrosion of bearings are : (*a*) use of new types of bearings, *e.g.*, sandwich type or indium-treated bearings ; (*b*) operation of engines at lower temperatures ; (*c*) selection of suitable lubricants, *i.e.*, those not very susceptible to oxidation and the formation of corrosive oxidation products : (*d*) use of suitable inhibitors.

FUEL OIL.

The generation of smoke for smoke screens and for other purposes in war and peace generally involves the use of petroleum products which are low in cost and form screens of good opacity and permanence.[58] Post-war applications of smoke screens are the protection of maturing crops against frosts, light visible smokes, and the formation of fogs in cinema films.

The tendency to smoke of organic compounds was investigated by the use of a lamp in which the flame-height could be measured from about 9 to 450 mm. It was found that increasing tendency to smoke for hydrocarbons was in the order : paraffins, naphthenes, olefines, and aromatic compounds. In general, a compact molecule was found to give a smoky flame. Increased oxygen content of an organic compound resulted in decreased smoking tendency, compounds such as methyl acetate giving a high flame without smoking.[59]

The use of catalytically cracked distillates for fuel for domestic heating is becoming widespread in the United States.[60] This type of fuel contains a relatively high proportion of aromatic compounds but by suitably modifying the design of pot burners, the fuel does not give trouble due to smoking or carbon deposits.[61] A new design of head for an oil burner of the "pressure-gun" type has been proposed for obtaining best results from this type of fuel oil ; in this new burner head, the introduction of secondary air makes it possible to obtain good combustion when using only 5—10% of excess air instead of the much higher proportion used with the usual design of burner.[62]

Owing to the shortage of coal in the United Kingdom, the Government have encouraged the use of oil instead of coal wherever this can be done. To assist in this conversion, the duty of 1d. per gallon on gas oil and fuel oil has been removed.[63] As a result of this situation, a large number of locomotives are being converted from coal to fuel oil.[64]

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[58] H. A. Levy, *Chem. Industries*, 1946, **58**, 980; B., 1946, I, 316.

[59] A. E. Clark, T. G. Hunter, and F. H. Garner, *J. Inst. Petroleum*, 1946, **32**, 627.

[60] *Ann. Repts.*, 1945, **30**, 73.

[61] S. R. Cauley and H. R. Linden, *Oil and Gas J.*, 1946, **45**, *No.* 14, 80.

[62] *Chem. Industires*, 1946, **58**, 1004.

[63] *Petrol. Times*, 1946, **50**, 995.

[64] *Ibid.*, 1102.

A new type of streamlined Diesel-electric locomotive of 6000 horsepower has been constructed in the United States; it is more powerful than any other heavy-duty locomotive now in operation. Six other locomotives of this type are now under construction and they are designed to give economical operation with a potential speed ranging up to 120 miles per hour.[65]

Relatively thick fuel, having a viscosity of 1500 seconds Redwood at 100° F., has been successfully used in marine Diesel engines, for normal operation on long voyages. This fuel was used on the tanker, M.V. *Auricula*, the only precaution taken being that the fuel was passed through a suitable system of centrifuges and clarified to remove any solids in suspension.[66]

SPECIAL PRODUCTS.

The chemical industry based on raw materials derived from petroleum is expanding rapidly both in the United States and in the United Kingdom.[67] An extensive development is taking place in the separation of isolated hydrocarbons in the pure state; for example, *cyclo*hexane is being produced and is used as a base for the manufacture of nylon.[68]

During the last five years the United States Bureau of Mines plants have produced over 370 million cu. ft. of helium,[69] and at the present time it can be produced at a cost of less than one cent per cu. ft. As the present production of helium from natural gas is more than the demand, a number of industrial applications are being developed. Originally the gas was used as a non-inflammable inflating agent for airships and balloons. At the present time it is used, mixed with oxygen, in connexion with the method of treating divers after deep-sea diving and it is being developed in medical practice for the treatment of respiratory ailments. It is also being used to improve the method of welding light metals such as aluminium and magnesium.[70]

A plant is being erected in the United Kingdom for the conversion of naphtha or gas oil into a liquid containing about 95% of aromatic hydrocarbons[71]; in the process to be used, known as the Catarole process, the petroleum fraction is passed through a tube packed with a suitable catalyst, such as metallic copper, at a temperature of 630—680° C. at atmospheric pressure.

The manufacture of acetylene from natural gas was developed in Germany during the war.[72] The method, known as the "Arc" process, consists in passing the purified natural gas through an iron arc, when a gas

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[65] *Science News Letter*, 1946, **50**, 199.
[66] *Petrol Times*, 1946, **50**, 1126.
[67] F. E. Smith, *J. Roy. Soc. Arts*, 1945, **45**, 566; B., 1946, I, 54.
[68] B. H. Weil, *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 121.
[69] *Petrol. Eng.*, 1946, **17**, 146.
[70] *Chem. Trade J.*, 1946, **118**, 102.
[71] *Petroleum*, 1946, **9**, 252.
[72] *Chem. Trade J.*, 1946, **118**, 103; B., 1946, I, 315.

is obtained containing carbon monoxide 0·9, oxygen 0·2, acetylene 16·8, ethylene 3·9, paraffins (mostly methane) 24·9, hydrogen 50·7, and nitrogen 2·5%; after suitable treatment, acetylene of 95—96% purity is obtained. As the amount of ethylene present in the arc gases was insufficient for the production of synthetic rubber, part of the acetylene was hydrogenated to ethylene. This reaction is carried out at 200° C. using a 50% excess of hydrogen at atmospheric pressure in the presence of a palladium-on-silica gel catalyst containing 0·01% of palladium.

Among some of the new plants being constructed for the manufacture of chemicals from petroleum may be mentiined one for the production of ethylene glycol at Sarnia in Canada,[73] the first of its kind in that country, and another for the production of glycerin at Houston in Texas,[74] where the process to be used will be the one developed by E. C. Williams about ten years ago.[75]

The four principal methods used for the production of oxygen derivatives of hydrocarbons from natural gas or refinery gases are: (1) direct oxidation; (2) dehydrogenation followed by oxidation or hydration; (3) oxidation to carbon monoxide and hydrogen (Fischer–Tropsch process) and hydrogenation of the carbon monoxide; (4) chlorination followed by hydrolysis.[76] The first commercial plant using the direct oxidation method was erected in 1936 for the production of formaldehyde used in the resin and plastics industry.

A method developed in Germany for the production of oxygen derivatives of hydrocarbons, known as the "OXO" process, consists of interaction of olefines with water-gas in the presence of a Fischer–Tropsch catalyst, to produce aldehydes. This process is applied to polymerised olefines to produce aldehydes of high molecular weight which are then converted into alcohols, carboxylic acids, and esters.[77]

As a substitute for tin in the plating of steel for can manufacture, it has been proposed to use a solid polymer of ethylene which can be applied in the form of a solution in xylene.[78] The coating is 0·001 in. in thickness and when baked on, it is flexible enough to withstand the distortion encountered during the manufacture of cans, and has high resistance to both acids and abrasion.

A useful by-product of petroleum is the vanadium present in some types of crude oil, particularly in that from Venezuela.[79] During the war the production of vanadium pentoxide from this source was of great value for the manufacture of alloy steels, particularly in view of the loss of an important source of tungsten from the Far East.

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[73] *Chem. Industries*, 1946, **58**, 1048.

[74] *Oil and Gas J.*, 1946, **45**, *No.* 31, 130.

[75] *Ann. Repts.*, 1938, **23**, 120.

[76] J. C. Walker and H. L. Malakoff, *Oil and Gas J.*, 1946, **45**, *No.* 33, 59.

[77] C. I. Kelly, *Petrol. Times*, 1946, **50**, 751.

[78] U.S.P. 2,406,039.

[79] *Chem. Trade J.*, 1946, **119**, 488.

ANALYSIS AND TESTING.

The seventh edition of "Standard Methods for Testing Petroleum and its Products" was published by the Institute of Petroleum in 1946. A number of methods have been amended and the specificatiins for hydrometers and thermometers have been modified. Among the new methods is the estimation of the percentage of sulphur as carbon disulphide in petroleum and a test for coagulation of bitumen when a bituminous emulsion is subjected to low temperatures.

The report of Committee D2 of the American Society for Testing Materials contains a number of proposals for amendments of Standard tests and for new tests.[80] It is recommended that the method for estimating carbon residue (Conradson), D189, shall have a note added, pointing out that the Ramsbottom test (D524) is to be preferred. The method for determination of aromatics in mixtures with naphthenes and paraffins by silica gel adsorption has been approved for publication and recommendation. The Committee has submitted for publication, for information, a proposed method for determining the foaming characteristics of viscous petroleum oils which is applicable to lubricating, hydraulic, and other viscous oils; the method consists of measuring the volume and stability of foam produced when air is blown through a diffuser stone into oil at room and at elevated temperatures.

In the estimation of the char value of kerosine it has been shown that the only variable in this test which may affect the result to any great extent is the quality of the wick[81]; it is, therefore, recommended that the wick, before use, be extracted successively with water, alcohol, and light petroleum in order to obtain good resproducibility in the char value.

A method has been proposed for the determination of the binder content of bituminous mixtures, which is rapid enough for plant control and sufficiently accurate for routine analysis.[82] The soluble binder is extracted from the mixture with methylene chloride, the solvent is distilled off under reduced pressure from an aliquot portion of the solution, and the residue is weighed. The time required for the method varies from 30 to 90 minutes, according to the type of bituminous mixture. This method gives good agreement with determinations by the British Standard methods.

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[80] *A.S.T.M. Bull.*, 1946, *No.* 139, 64.

[81] F. W. H. Matthews and W. H. Thomas, *J. Inst. Petroleum*, 1946, **32**, 269: C., 1946, 158.

[82] E. H. Green and E. A. Cox, *J.S.C.I.*, 1946, **65**, 1; C., 1946, 82.

INTERMEDIATES AND DYES.

By R. Fraser Thomson, M.A., D.Sc., A. H. Knight, B.Sc., A.R.I.C., and J. D. Rose, B.A., B.Sc.,

Imperial Chemical Industries Ltd. (*Dyestuffs Division*).

During the year under review, the volume of publication has increased slightly. Although a large proportion of the dye patents bear dates early in the war period, there is distinct growth in intermediates and, as in the last few years, this growth is particularly noticeable in the aliphatic division.

It is interesting on this occasion to compare the knowledge with which the reader of patent scripts had to be content in pre-war days with authentic information derived from actual process development within the chemical industry itself. This is exemplified by the official intelligence reports on the German chemical industries, and the opportunity is taken on this occasion to survey the section of this vast field of the greatest interest for the present report, namely, developments by the I.G. Farbenindustrie from acetylene. The distinguished German chemist J. W. Reppe is closely associated with these developments.[1]

There are many signs of post-war development in our own organic chemical industries. Thus Imperial Chemical Industries have announced[2] that they are to develop a large site on Teesside—the Wilton estate—especially, in the first instance, for heavy organic chemicals. Shortly after this, the Dyestuffs Division of the same company announced[3] a £9,000,000 expansion of its existing manufacturing plants, including £1,000,000 for expansion of its research and evaluation departments. Announcements of other firms make it clear that a vast drive is being made in this country for increased production of organic chemicals.

It is too early since the war-time curtailment of publication to discuss output statistics in dyestuffs manufacture, but it may be noted that exports of dyes in 1946 exceeded those of 1938 :

Exports of Synthetic Dyestuffs (Tons).

1938.	1945.	1946.
3981.	4690.	9307.

Aliphatic Intermediates.

Nitrated Hydrocarbons.

In this field development continues, both in the preparation of nitro-derivatives, and in the study of their reactions. Their applications as industrial solvents appear to possess considerable significance.

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[1] M. H. Bigelow, *Chem. Corps. J., Jan.*, 1947. Cf. *Chem. Trade J.*, 1947, **120**, 187.
[2] *Chem. Trade J.*, 1945, **117**, 674.
[3] *The Times, May 5th*, 1946.

Commercial Solvents Corporation[4] nitrate alkanes in the gas phase, diluted with steam, with nitric acid in low concentration at about 390° ; propylene in this way gives a 40% conversion into nitropropane. Imperial Chemical Industries[5] pass gaseous alkanes and nitric acid over a silicate glass containing arsenic, antimony, or lead as catalyst, after which the nitro-compounds may be extracted and the gases recycled ; the catalysts aid conversion and lessen oxidation and explosion risks. The same firm[6] employ nitrogen peroxide in the gas phase with an aluminium catalyst, giving a 9% nitration yield, while nearly 3% is completely oxidised. According to the same firm,[7] ethylene yields $\alpha\beta$-dinitroethane and β-nitroethyl nitrate when nitrated with liquid nitrogen peroxide at −10°, under pressure, and after recovering the excess of peroxide, diluting with water : the former product is a solid crystalline substance, m.p. 40°, b.p. 135°/5 mm. Commercial Solvents Corporation[8] use aqueous nitric acid in a liquid-phase nitration at about 150° in presence of a reducing catalyst such as sulphur, carbon, or the nitrated hydrocarbon ; normal heptane so treated gives a 52% yield of nitrated hydrocarbons.

β-Nitroethanol can be obtained from $\alpha\beta$-dinitroethane (see ref. 7), according to Imperial Chemical Industries,[9] by pouring the oily reaction product into methanol.

The Purdue Research Foundation[10] describe unsaturated nitro-alcohols, obtained by adding an unsaturated aldehyde to a mixture of nitromethane, methanol, and potassium carbonate ; the mixture is neutralised and yields, *e.g.*, α-nitropent-γ-en-β-ol, $CHMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$, from β-methacraldehyde.

The reactions of saturated or unsaturated nitrated hydrocarbons yield some interesting results. Imperial Chemical Industries have six cases in this section. Nitroethylenes or their homologues, or the corresponding nitroethanol esters, react with sodium bisulphite[11] to give the corresponding nitrosulphonates : $OX{\cdot}CRR'{\cdot}CHR''{\cdot}NO_2 \rightarrow SO_3Na{\cdot}CRR'{\cdot}CHR''{\cdot}NO_2$ where R, R′, and R″ represent hydrogen or hydrocarbon radicals and X is alkyl. The same commencing materials, on interaction with a Grignard reagent,[12] attach the organic group (R″) of the latter to the β-carbon, yielding the substituted nitroethanes $CRR'R''{\cdot}CHR'''{\cdot}NO_2$. R″ may belong to a wide range of plain or substituted alkyl, *cyclo*alkyl, or aryl groups. β-Nitroethyl ethers[13] result from the interaction of nitroethylene or nitroethyl nitrate with alcohols at the boiling point of the latter.

[4] U.S.P. 2,327,964 ; B., 1945, II, 366.
[5] B.P. 575,733, 578,044 ; B., 1946, II, 233, 360.
[6] B.P. 576,129 ; B., 1946, II, 233.
[7] B.P. 572,949 ; B., 1946, II, 71.
[8] U.S.P. 2,332,491 ; B., 1946, II, 233.
[9] B.P. 575,604, 575,618 ; B., 1946, II, 233.
[10] U.S.P. 2,332,482 ; B., 1946, II, 234.
[11] B.P. 571,157 ; B., 1945, II, 329.
[12] B.P. 571,804 ; B., 1946, II, 3.
[13] B.P. 573,872 ; B., 1946, II, 111.

Nitroethylene itself is capable of polymerisation. It is formed at room temperature from αβ-dinitroethane or nitroethyl nitrate[14] in 80% yield. It may then be polymerised by means of alcoholic potash, or αβ-dinitroethane in a solvent may be converted and polymerised in one operation[15] by means of alkali carbonate or ammonia. When β-nitroethyl nitrate is the starting material,[16] a water-miscible solvent is used with the same reagents.

Halogen Derivatives.

In the preparation of vinyl chloride, an intermediate of considerable importance, usually from acetylene and hydrochloric acid with a mercuric chloride catalyst, a number of patents are concerned with minor variations of the catalyst.

Thus the mercuric chloride adsorbed on carbon suffers loss by volatilisation during the reaction, and Distillers Co. Ltd.[17] replace or prevent this by a pre-passage of the acetylene–hydrochloric acid gas stream over pellets of mercuric chloride kept at 60°. In another case,[18] the same firm suspend the catalyst in a hydrocarbon or chlorinated hydrocarbon solvent, such as paraffin. E. I. Du Pont de Nemours & Co.[19] use a calomel catalyst at 250°, on a carbon carrier. E. Schaeffer[20] describes a porous carrier impregnated with an alkaline-earth chloride. As an alternative to the acetylene process, vinyl chloride is obtained by Distillers Co. Ltd.[21] by dehydrochlorination of αβ-dichloroethane at a high temperature, the resulting gases being cooled and washed with a solvent such as xylene or liquid vinyl chloride; the hydrochloric acid passes on and may be combined with acetylene by the conventional process.

The normal mercuric chloride catalyst is readily poisoned by sulphur in the acetylene. Imperial Chemical Industries[22] describe how it may be regenerated by passing in chlorine gas at 100—120°.

The halogenation of olefines, retaining the double bond, has in general to be carried out in oxidising conditions. E. I. Du Pont de Nemours & Co.[23] treat the olefine with the halogen in presence of oxygen and a copper oxidation catalyst. Imperial Chemical Industries[24] find that αγ-dienes or 2 : 5-dihydrothiophen 1 : 1-dioxide react with chlorine set free by polychloro-methanes or -ethanes in presence of a peroxide, an iron catalyst, and a polyhydroxybenzene; thus αααε-tetrachloropent-γ-ene is obtained from 2 : 5-dihydrothiophen 1 : 1-dioxide and carbon tetrachloride.

[14] B.P. 572,803; B., 1946, II, 30.
[15] B.P. 572,891; B., 1946, II, 30.
[16] B.P. 573,785; B., 1946, II, 72.
[17] B.P. 573,561; B., 1946, II, 73.
[18] B.P. 575,381; B., 1946, II, 191.
[19] B.P. 573,670; B., 1946, II, 73.
[20] U.S.P. 2,338,459; B., 1946, II, 316.
[21] B.P. 573,594; B., 1946, II, 73.
[22] B.P. 576,099; B., 1946, II, 233.
[23] U.S.P. 2,327,174; B., 1945, II, 330.
[24] B.P. 570,869; B., 1945, II, 330.

Dehydrochlorination of saturated alkyl halides is also a source of halogenated olefines. Thus Distillers Co. Ltd.[25] heat the halides in presence of small amounts of halogen and oxygen; when, however, the alkyl halide contains the grouping ·CHCl·CHCl·, as in αβ-dichloroethane or ααββ-tetrachloroethane, oxygen alone is necessary to produce vinyl chloride and trichloroethylene, respectively. E. I. Du Pont de Nemours & Co.[26] describe two methods for producing trichloroethylene. In the first case, acetylene is chlorinated to yield tetrachloroethane of 95% purity, and this is dehydrochlorinated by heat at 450° without a catalyst; in the other, the tetrachloroethane is fractionated and the pure material heated in presence of a barium chloride catalyst. This gives essentially pure trichloroethylene, while the first method gives material which requires distillation. Imperial Chemical Industries[27] prepare αα-dichloroethylene by a slightly different procedure. Vinyl chloride with excess of chlorine in presence of a Friedel–Crafts catalyst yields ααβ-trichloroethane; this is used as solvent in a continuous process, and the product is treated continuously with excess of caustic soda solution and the resulting αα-dichloroethylene distilled off. Standard Oil Development Co.[28] prepare chloro*iso*olefines by dehydrohalogenation of halogenated pentanes of the type βγ-dichloro-γ-methylbutane to give a mixture of γ-chloro-β-methylbut-α-ene and γ-chloro-β-methylbut-β-ene: $CMe_2Cl{\cdot}CHMeCl \rightarrow CMe_2Cl{\cdot}CH{:}CH_2 + CMeCl{:}CMe_2$.

Normal addition of halogen to the double bond yields saturated polyhalogen compounds. P. J. Thurnam and J. Downing[29] thus convert vinyl chloride into ααβ-trichloroethane. E. I. Du Pont de Nemours & Co.[30] obtain a range of dihalogenated esters by cold addition of chlorine to substituted acrylic esters $CH_2{:}CR{\cdot}CO_2R'$ (R, R′ = hydrogen or alkyl). Monsanto Chemical Co.,[31] by addition of halogen to vinyl acetate in solution in methyl or ethyl alcohol, obtain αβ-dihalogenated ethyl acetates, which readily lose halogen acid to give the corresponding β-halogenoacetals on slight warming. Commercial Solvents Corporation[32] condense an α-chloroketone with an aliphatic aldehyde, so yielding α-chloro-β-hydroxyketones; a good yield of methyl αα-dichloro-β-hydroxyethyl ketone is thus obtained from αα-dichloroacetone and formaldehyde. Again, according to Universal Oil Products Co.,[33] ethylene or propylene may be condensed readily with alkyl halides in presence of Friedel–Crafts type of metal halide catalysts, especially bismuth trichloride, to give higher alkyl halides, many examples being quoted.

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[25] B.P. 573,532, 573,599; B., 1946, II, 71, 72.
[26] B.P. 575,530, 575,559; B., 1946, II, 191.
[27] B.P. 577,876; B., 1946, II, 316.
[28] U.S.P. 2,332,778; B., 1946, II, 233.
[29] B.P. 571,370; B., 1945, II, 360.
[30] U.S.P. 2,195,712; B., 1945, II, 362.
[31] U.S.P. 2,330,570; B., 1946, II, 32.
[32] U.S.P. 2,330,179; B., 1946, II, 34.
[33] B.P. 573,376; B., 1946, II, 71.

There is increasing interest in organic fluorine derivatives. Imperial Chemical Industries[34] exchange one chlorine in a halogenated methane, or in a tetrachloroethane or higher homologue having three chlorines attached to one carbon atom, by heating with anhydrous hydrofluoric acid under pressure; thus carbon tetrachloride yields trichlorofluoromethane, and many higher homologues are described, including olefinic compounds such as βγγ-trichloro-ααα-trifluoroprop-β-ene. E. I. Du Pont de Nemours[35] similarly treat ααβ-trichloroethylene, giving αβ-dichloro-αα-difluoroethane. Imperial Chemical Industries[36] describe the oxidation of the above-mentioned chlorofluoroalkenes $CF_2X{\cdot}CY{:}CYZ$, where X is halogen or hydrogen and Y and Z are chlorine or hydrogen, by alkaline permanganate: thus βγγ-trichloro-ααα-trifluoroprop-β-ene yields trifluoroacetic acid, and similarly difluoroacetic acid can be obtained from βγ-dichloro-αα-difluoroprop-β-ene in excellent yields. Kinetic Chemicals Inc.[37] treat trifluoroalkyl halides with sodium methoxide in alcoholic solution under pressure to give trifluorodialkyl ethers, such as βββ-trifluorodiethyl ether from α-chloro-βββ-trifluoroethane.

Aldehydes and Ketones.

The reaction of olefines with carbon monoxide and hydrogen (the OXO process), using a metal of group VIII as catalyst with a metal oxide activator, is described by O. Roelen[38]; the products are aldehydes and ketones. Thus ethylene over a cobalt-thorium catalyst at 100°/100 atm. gives 40% of propaldehyde, 20% of diethyl ketone, and 40% of higher-boiling oxygenated products. In the commercial process developed in Germany,[39] C_{11-17} olefines from the Fischer-Tropsch process are treated with water-gas and a suspended cobalt-thorium magnesium catalyst, giving straight-chain aldehydes and ketones which on reduction over Raney nickel yield the corresponding alcohols. The Du Pont Co.,[40] by interaction of acetylene and its homologues with carboxylic acid chlorides and a Friedel-Crafts catalyst, obtain olefinic ketones as the main products: $CR{:}CR' + R''{\cdot}COCl \rightarrow CRCl{:}CR'{\cdot}COR''$, where R etc. are saturated alkyls of low molecular weight.

The preparation of acraldehyde has attracted several workers. Imperial Chemical Industries obtain it[41] together with ethylene by thermal decomposition of 2 : 3-dihydropyran, the use of a silica catalyst being optional; similarly 5-chloro-2 : 3-dihydropyran[42] gives α-chloroacraldehyde. Distillers Co. Ltd.[43] obtain acraldehyde from formaldehyde and acetaldehyde

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[34] B.P. 576,189–90; B., 1946, II, 233.

[35] B.P. 575,756; B., 1946, II, II, 233.

[36] B.P. 577,481; B., 1946, II, 275.

[37] U.S.P. 2,336,921; B., 1946, II, 317.

[38] U.S.P. 2,327,066; B., 1945, II, 331.

[39] R. L. Hasche and R. H. Boundy, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXVII–18; B., 1946, II, 151.

[40] U.S.P. 2,194,704; B., 1945, II, 331.

[41] B.P. 573,507; B., 1946, II, 71.

[42] B.P. 578,071; B., 1946, II, 362.

[43] B.P. 573,573; B., 1946, II, 77.

in the vapour phase over a catalyst of sodium silicate or silica gel. E. I. Du Pont de Nemours & Co.[44] absorb propylene in aqueous mercuric sulphate and heat at moderate temperatures to give acraldehyde. The Acrolein Corporation[45] work similarly in three towers, two being absorbers and one a stripping tower. Shell Development Co.[46] treat non-tertiary vinyl halides with acids; thus β-chlorobut-β-ene with sulphuric acid of 84% at 28° gives a good yield of methyl ethyl ketone.

Distillers Co. Ltd.[47] describe the oxidation of the acraldehyde type $CHR:CH\cdot CHO$ below 50° with an osmic or chromic or vanadic oxide catalyst, to give both the hydroxy-aldehyde $OH\cdot CHR\cdot CH(OH)\cdot CHO$ and the acrylic acid $CHR:CH\cdot CO_2H$.

*iso*Propyl alcohol readily gives acetone in presence of a hydrogen acceptor; thus the Du Pont Co.[48] obtain good yields of acetone and *cyclo*hexane from a mixture of 3 mols. of *iso*propyl alcohol and 1 mol. of benzene, over a nickel catalyst on a reduced copper and magnesium oxide support Shell Development Co.[49] show that the oxidation of olefines with oxygen in presence of hydrobromic acid gives carboxylic acids, ketones, and peroxides at about 250°. Propylene, oxygen, and hydrobromic acid (2 : 2 : 1) yield 18·5% of acids (mainly acrylic). 5·3% of bromoacetone, and 18·5% of allyl bromide. The oxidation of a typical branched-chain paraffin, *iso*butane, at 150—200° with oxygen in presence of hydrobromic acid gives, according to the same Company,[50] 42% of di*tert*.-butyl peroxide, 39% of *tert*.-butanol, 7% of propaldehyde, 7% of recovered *iso*butane, and 5% of other oxygenated compounds. The same company[51] show that in the oxidation of hydrocarbons in the vapour phase at 350—450 to give aldehydes and ketones, the formation of peroxides and carboxylic acids is discouraged by treating the reacting gas stream with a porous silicon carbide catalyst, with a deposit of an easily oxidisable metal such as silver, cobalt, iron, copper, nickel, or vanadium.

Carboxylic Acids and their Derivatives.

The "carboxylation" of acetylene discovered by J. W. Reppe is referred to later (cf. ref. 75) as a new synthesis of acrylic acid and its esters from acetylene, carbon monoxide, and water or alcohols, nickel carbonyl being used as the carrier for the carbon monoxide.

The synthesis of other unsaturated carboxylic acids is still under active investigation, and the products are mostly of interest for polymerisation. E. I. Du Pont de Nemours & Co.[52] describe a modernised process for the

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[44] U.S.P. 2,197,258; B., 1946, II, 32.
[45] U.S.P. 2,334,091; B., 1946, II, 275.
[46] B.P. 572,963; B., 1946, II, 77.
[47] B.P. 573,722; B., 1946, II, 76.
[48] U.S.P. 2,204,978; B., 1946, II, 193.
[49] B.P. 576,255; B., 1946, II, 235.
[50] B.P., 577,841; B. 1946, II, 317.
[51] B.P. 576,060; B., 1946, II, 235.
[52] U.S.P. 2,194,363; B., 1945, II, 331.

preparation of propiolic acids; acetylene or one of its homologues is treated with sodamide in liquid ammonia solution, yielding sodium acetylide; the ammonia is then replaced by an aromatic hydrocarbon and the product is carbonated under pressure. The resulting propiolic acid, on hydrogenation[53] in solution with a nickel catalyst, gives a 90% yield of propionic acid, the remainder being chiefly adipic acid. Oxalyl chloride is widely useful in carboxylating saturated or unsaturated hydrocarbons, as described by the same firm,[54] and is used in presence of actinic light or benzoyl peroxide. The same firm[55] describe the reaction of furfuraldehyde or its derivatives with substituted acetic acids $CH_2R{\cdot}CO_2R'$ (R is alkyl, aryl, 2-furyl, or alkoxy; R′ is alkyl or *cyclo*-alkyl), yielding esters of β-2-furylacrylic acids. Wingfoot Corporation[56] prepare a series of keto-esters of α-alkylacrylic acids by condensing metal salts of the latter with primary or secondary halogenated ketones; thus sodium methacrylate and chloroacetone yield acetylmethyl methacrylate, $CH_2{:}CMe{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}COMe$. Another interesting series of esters are the methylenemalonates, $CH_2{:}C(CO_2R)_2$, prepared by the General Electric Co.[57] by condensing formaldehyde with dialkyl malonates in alkaline solution.

Keto-acids are prepared, according to G. West,[58] by condensation of alkyl vinyl ketones with a class of reagents $CR{\cdot}CH_2R'$, where R is N, $O{\cdot}NH_2$, or CO_2Alkyl, and R′ is CN, acyl, aryl, or CO_2Alkyl, in presence of metallic sodium; thus methyl vinyl ketone, sodium, and ethyl cyanoacetate yield ethyl 5-cyano-2 : 8-diketononane-5-carboxylate. Acrylonitrile readily adds twice, as described in Resinous Products & Chemical Co.,[59] to each methylene group *ortho* to carbonyl in *cyclo*-pentanone, -hexanone, and -heptanone, and the products hydrolyse to tetra-β-carboxyethyl substitution products. L. W. Butz[60] shows that substances containing the divinylacetylene skeleton add two molecules of maleic anhydride by diene addition in absence of solvent; thus divinylacetylene itself gives 1 : 5-dimethyl-2 : 3 : 4 : 6 : 7 : 8-hexahydronaphthalene-3 : 4 : 7 : 8-tetracarboxylic dianhydride.

E. I. Du Pont de Nemours & Co.[61] describe the dehydrohalogenation of α-chloro*iso*butyric esters with zinc or zinc chloride, yielding α-alkylacrylic esters. Wingfoot Corporation[62] have described a large series of substituted acrylic esters, $CH_2{:}CX{\cdot}CO_2R$ (X = halogen, R = alkyl etc.), which are obtained either by removal of two halogen atoms from trihalogenated esters $CH_2X{\cdot}CX_2{\cdot}CO_2R$ by a finely-divided metal in alcohol

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[53] U.S.P. 2,194,362; B., 1945, II, 331.
[54] U.S.P. 2,326,228–9; B., 1945, II, 335.
[55] B.P. 569,529; B., 1945, II, 335.
[56] B.P. 571,560; B., 1945, II, 362.
[57] U.S.P. 2,330,033; B., 1945, II, 362.
[58] U.S.P. 2,328,370; B., 1945, II, 363.
[59] U.S.P. 2,329,432; B., 1946, II, 5.
[60] U.S.P. 2,329,979; B., 1946, II, 38.
[61] U.S.P. 2,199,774; B., 1946, II, 75.
[62] B.P. 573,596–7, 573,624–5; B., 1946, II, 75.

solution or by dehydrochlorinating the dihalogenated esters $CH_2Cl{\cdot}CHCl{\cdot}CO_2R$; when R is tetrahydrofurfuryl, dehydrohalogenation is effected by heating with dimethylaniline.

Carbide and Carbon Chemicals Corporation[63] synthesise unsaturated acids from keten and ketones CORR′ where R, R′ may be alkyl or alicylic groups, and so obtain, for instance, dialkylacrylic and β-alkylcinnamic acids.

E. I. Du Pont de Nemours & Co.[64] describe the oxidation of *cyclo*hexylamine by nitric acid in the liquid phase, and Imperial Chemical Industries[65] the use of a mixed copper–vanadium catalyst in the oxidation of *cyclo*hexanone, all processes yielding adipic acid, the latter giving the high yield of 89%. I.G. Farbenind.[66] oxidise with nitric acid *cyclo*hex-4-ene having at 1, 2, or both a CR substituent which can lead to a carboxyl group on oxidation, and so obtain butanepolycarboxylic acids, *cyclo*hexenecarboxylic acids, and substituted adipic acids depending on the intermediate chosen for oxidation.

E. I. Du Pont de Nemours & Co.[67] describe acetals $CHMe(O{\cdot}CH_2{\cdot}CO_2R)_2$, where R is alkyl, aryl, or a heterocyclic group, obtained by interaction of acetylene, in presence of a special boron trifluoride–methanol–mercuric oxide complex catalyst, with glycollic esters $OH{\cdot}CH_2{\cdot}CO_2R$; thus methyl glycollate and acetylene yield di(carbomethoxymethyl) acetal (R = Me).

German Developments from Acetylene.

By J. D. Rose.

The past year has seen the publication, in the form of reports from the British Intelligence Objectives Sub-Committee (B.I.O.S.) and Combined Intelligence Objectives Sub-Committee (C.I.O.S.), of a large number of reports on German research and industry. Many of these, particularly reports on the I.G. Farbenindustrie factories of Ludwigshafen and Gendorf, have dealt with the application of acetylene to the synthesis of organic intermediates of industrial value.

The I.G. synthesis of butadiene from acetylene via acetaldehyde, acetaldol, and butane-1 : 3-diol is well known. An alternative route was developed by I.G., and a 30,000 tons per year plant erected at Ludwigshafen for the manufacture of butadiene from acetylene and formaldehyde via but-2-yne-1 : 4-diol.[68] Aqueous formaldehyde and acetylene are passed co-current over a copper–bismuth acetylide catalyst at 5 atmospheres pressure and 90—110°. The 35—40% aqueous butynediol solution is hydrogenated over a nickel–cobalt–manganese catalyst, yielding an aqueous solution of butane-1 : 4-diol, which is de-

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[63] B.P. 570,839 ; B., 1945, II, 330.
[64] U.S.P. 2,196,357 ; B., 1946, II, 32.
[65] B.P. 572,260 ; B., 1946, II, 32.
[66] U.S.P. 2,203,628 ; B., 1946, II, 154.
[67] B.P. 576,027 ; B., 1946, II, 318.
[68] I.G., B.P. 508,062 ; B., 1939, 913.

hydrated in the liquid phase with phosphoric acid at 280°/100 atmospheres to tetrahydrofuran, vapour-phase dehydration of which affords butadiene. Major features of this plant are the safety precautions[69] developed jointly by I.G. and the Chemische Technische Reichsanstalt for the safe handling of acetylene in bulk under pressure.

A minor by-product in the acetylene–formaldehyde reaction is propargyl alcohol, the formation of which is largely suppressed by excess of formaldehyde, and favoured by carrying out the reaction in tetrahydrofuran solution. Dehydration of aqueous solutions of propargyl alcohol is carried out by azeotropic distillation with benzene or dimethyltetrahydrofuran[70] and oxidation of propargyl alcohol with air in the presence of cuprous chloride and ammonium chloride gives high yields of hexa-2 : 4-diyne-1 : 6-diol, which on hydrogenation yields hexane-1 : 6-diol.

Although the manufacture of butadiene by the but-2-yne-1 : 4-diol route had no economic advantage over the normal route (via acetaldol), it was adopted by I.G. for large-scale production at Ludwigshafen on account of the versatility of but-2-yne-1 : 4-diol as a raw material in the manufacture of organic intermediates, particularly for plastics.[69] This is illustrated by the following syntheses[71]: tetrahydrofuran and hydrochloric acid give 1 : 4-dichlorobutane, convertible by sodium cyanide into adiponitrile and thence, by hydrolysis, into adipic acid. Interaction of acetylene and acetaldehyde gives a mixture of but-3-yne-2-ol and hex-3-yne-2 : 5-diol; the former, with formaldehyde yields pent-2-yne-1 : 4-diol. Hex-3-yne-2 : 5-diol and pent-2-yne-1 : 4-diol, by hydrogenation and dehydration, followed by ring opening with hydrochloric acid, treatment with cyanide, and hydrolysis, give respectively α-methyl- and αα′-dimethyl-adipic acids. Reduction of the nitriles gives methyl-substituted hexamethylenediamines.

Oxidation of tetrahydrofuran with nitric acid affords succinic acid, and catalytic dehydrogenation of butane-1 : 4-diol gives γ-butyrolactone, converted by cyanide into 3-cyanopropane-1-carboxylic acid and thence by hydrolysis into glutaric acid, or by hydrogenation into pentamethylenediamine. Oxidation of succinic acid with chlorine yields maleic anhydride, and intermolecular decarboxylation gives γ-ketopimelic acid (3-ketopentane-1 : 5-dicarboxylic acid). γ-Butyrolactone and aqueous sodium hydroxide at 180—200° give sodium 3-hydroxypropane-1-carboxylate, which loses water in the presence of alumina to yield "oxy-dibutyric acid" (3 : 3′-dicarboxydipropyl ether). The sulphur analogue "thiodibutyric acid" (3 : 3′-dicarboxydipropyl sulphide) is similarly formed from γ-butyrolactone and sodium sulphide, and on oxidation with chlorine gives the corresponding sulphone. Hydration of but-2-yne-1 : 4-diol in the presence of mercury salts gives hydroxymethyl 2-hydroxyethyl

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[69] C. J. S. Appleyard and J. F. C. Gartshore, *B.I.O.S.*, *Final Rept.* 367, *Item* 22.
[70] J. D. Rose and J. W. Fisher, *ibid.*, *Final Rept.* 357, *Item* 22; B., 1946, II, 311
[71] J. D. Rose, *ibid.*, *Final Rept.* 350, *Item* 22; B., 1946, II, 311.

ketone, which on catalytic hydrogenation affords butane-1 : 2 : 4-triol, a glycerol substitute.

Interaction of ammonia and γ-butyrolactone results in the formation of pyrrolidone, which with acetylene under pressure in the presence of alkalis affords *N*-vinylpyrrolidone.[72] This substance is polymerised in aqueous solutions, using hydrogen peroxide as catalyst and ammonia or amines as buffers, giving polyvinylpyrrolidones ("Kollidones"), polymers soluble in water and common organic solvents. A 3·5% aqueous solutions of polyvinylpyrrolidone containing small quantitites of inorganic salts and buffered to pH 6 was sold by I.G. as "Periston," a synthetic blood plasma substitute.

An interesting series of products has been reported[73] from acetylene and ammonia or amines. Acetylene, heated with ammonia and some complex inorganic salts such as $Co(NH_3)_6Cl_2$, or alkyl vinyl ethers heated with, *e.g.*, copper phosphate, gives 2-methyl-5-ethylpyridine ; the reaction is postulated as proceeding via the hypothetical vinylamine, $CH_2{:}CH{\cdot}NH_2$. With primary and secondary amines *N*-sustituted 2-aminobut-3-ynes are formed, *e.g.*, 2-diethylaminobut-3-yne from diethylamine, acetylene, and cuprous chloride. Trimethylamine and water, or trimethylamine hydrochloride, and acetylene at 60° under pressure give respectively trimethylvinylammonium hydroxide (neurine) and trimethylvinylammonium chloride.

An elegant synthesis of adipic acid[74] by direct carbonylation of tetrahydrofuran with carbon monoxide was developed by I.G. during the war, but owing to technical difficulties, concerned chiefly with finding a suitable constructional material, was never developed beyond the pilot-plant stage. Nickel iodide is used as catalyst and nickel carbonyl as carbon monoxide carrier ; the reaction is carried out at 270°/200 atmospheres. The steel converter was platinum-lined, and yields of 80% of adipic acid were obtained, with 15% of valeric acid and 5% of valerolactone as by-products.

A remarkably facile synthesis of acrylic esters was discovered by the Ludwigshafen workers.[75] Acetylene is passed into a mixture of alcohol and hydrochloric acid to which nickel carbonyl is added ; the reaction, represented by the overall equation $4C_2H_2 + Ni(CO)_4 + 4EtOH + 2HCl = 4CH_2{:}CH{\cdot}CO_2Et + NiCl_2 + H_2$, proceeds exothermically and rapidly, giving high yields of the ester. The nickel chloride solution, after addition of sufficient ammonia to form $Ni(NH_3)_6Cl_2$, is reconverted into nickel carbonyl by reaction with carbon monoxide at 170°/200 atm.[76]

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[72] J. D. Rose, *B.I.O.S., Final Rept.* 354, *Item* 22 ; B., 1946, II, 314. Cf. Fikentscher and Herrle, *Mod. Plastics*, 1945, **23**, *No.* 3, 157 ; B., 1946, II, 109.

[73] J. D. Rose, *B.I.O.S. Final Rept.* 359, *Item* 22 ; B., 1946, II, 313.

[74] J. F. C. Gartshore, J. W. Fisher, and J. D. Rose, *ibid.*, *Final Rept.* 351, *Item* 22 ; B., 1946, II, 311.

[75] *Idem, ibid.*, *Final Rept.* 358, *Item* 22 ; B., 1946, II, 311.

[76] J. W. Fisher, *ibid.*, *Final Rept.* 371, *Item* 22 ; B., 1946, I, 368.

Several reports have been published[77,78] describing the normal mercury-catalysed hydration of acetylene to acetaldehyde; a novel method, avoiding the use of mercury, was devised by the I.G. at Ludwigshafen.[79] Acetylene and methyl alcohol in presence of potassium hydroxide at 160°/16 atm. give methyl vinyl ether, which is hydrolysed by 0·25% sulphuric acid to acetaldehyde and methyl alcohol, the former being purified by distillation and the latter recycled to the primary operation. It is claimed that this eliminated the expense of the valuable mercury lost in the normal hydration operation, and gave a product which, being free from residual traces of mercury, was more suitable for many industrial operations than acetaldehyde produced by the orthodox method.

A war-time development in the I.G., particularly in the Schkopau and Anorgana (Gendorf) factories, was the production of ethylene by the partial hydrogenation of acetylene over a nickel catalyst.[77,80] The formation of vinyl chloride from acetylene and hydrochloric acid (mercuric chloride catalyst),[77] and of acrylonitrile from acetylene and hydrocyanic acid, have also been described.[81]

One final subject deserves mention in this account of I.G. research and development work on acetylene chemistry, viz., the polymerisation of acetylene to *cyclo*polyolefines. Polymerisation of acetylene in tetrahydrofuran solution, using a nickel cyanide catalyst and either ethylene oxide or calcium carbide, yields a complex mixture of products the major component of which is *cyclo*octa-1 : 3 : 5 : 7-tetraene.[82] Minor components are hydrocarbons $C_{10}H_{10}$ and $C_{12}H_{12}$—tentatively described by J. W. Reppe,[83] on clearly inadequate evidence, as *cyclo*deca-1 : 3 : 5 : 7 : 9-pentaene and *cyclo*dodeca-1 : 3 : 5 : 7 : 9 : 11-hexaene (a structure denied by Reppe's co-workers; see ref. 82), and azulene. The function of the ethylene oxide or calcium carbide is probably that of a dehydrant, since the polymerisation succeeds in their absence provided all reactants are carefully dried. The yield of *cyclo*octatetraene is 80% when the polymerisation is carried out at 80° and 15 atm. acetylene pressure for 24—36 hours. The chemistry of *cyclo*octatetraene has been comprehensively explored[83]; one of its most interesting features is its ability to react as if it existed in three separate forms, viz., (*a*) as an eight-ring compound (**I**), (*b*) as *dicyclo*-[0 : 2 : 4]-octa-2 : 4 : 7-triene (**II**), and (*c*) as 1 : 2 : 4 : 5-dimethylene*cyclo*hexa-2 : 5-diene (**III**).

Examples of reactions of type (*a*) are catalytic partial hydrogenation to *cyclo*octene (oxidised by nitric acid to suberic acid) and complete

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[77] W. S. Calcott, *C.I.O.S.*, 1945, *Item* 22, *File* XXII–20; B., 1946, II, 310.

[78] W. L. Wood, *B.I.O.S.*, *Final Rept.* 75, *Item* 22; B., 1946, II, 312.

[79] J. W. Fisher, *ibid.*, *Final Rept.* 370, *Item* 22; B., 1946, II, 311.

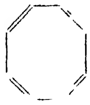
[80] J. F. C. Gartshore, C. J. S. Appleyard, and J. W. Fisher, *ibid.*, *Final Rept.* 360, *Item* 22; B., 1946, II, 309.

[81] A. Cambron, *ibid.*, *Final Rept.* 92, *Item* 22; B., 1946, II, 312. F. J. Curtis and M. F. Fogler, *C.I.O.S.*, 1945, *Item* 22, *File* XXIII–25; B., 1946, II, 312.

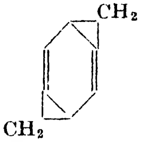
[82] J. D. Rose, C. J. S. Appleyard, J. F. C. Gartshore, and J. W. Fisher, *B.I.O.S.*, *Final Rept.* 352, *Item* 22; B., 1946, II, 312.

[83] Reppe, *ibid.*, *Final Rept.* 137, *Item* 22; A., 1946, II, 497.

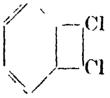
hydrogenation to *cyclo*octane. Examples of type (*b*) are the formation of the dichloride (IV), and of the Diels–Alder adducts with benzoquinone and acetylenedicarboxylic ester; the structures of these compounds have been proved. Oxidation of (I) causes aromatisation of type (*c*); thus hypochlorite or chromic acid gives terephthalaldehyde or terephthalic acid. The manufacture of *cyclo*octatetraene in I.G. had not proceeded beyond a large laboratory scale when the war ended, and the investigations on its chemical properties had been confined to classical organic chemical research rather than an attempted industrial exploitation.


(I)


(II)



(III)



(IV)

Nitriles.

The industrial importance of acrylonitrile is leading to a very considerable development of aliphatic nitriles, both saturated and unsaturated, and all the usual synthetical methods are being utilised.

Wingfoot Corporation[84] treat α-halogeno-ketones with hydrocyanic acid and a basic catalyst (alkali cyanide) and acetic anhydride or acetyl chloride; the resulting β-halogeno-α-acyloxynitriles readily lose acetic acid to yield unsaturated halogeno-nitriles. Similarly[85] the substituted halogen acrylonitriles $CRR'{:}CX{\cdot}CH$, where R, R′ are H, alkyl, or halogen and X is alkyl or halogenoalkyl, are obtained by loss of acid from the corresponding α-acryloxypropionitriles. The monobromoacrylonitriles and β-bromo-α-methylacrylonitriles[86] are also of interest; for instance, α-bromoacrylonitrile is prepared by distilling αβ-dibromopropionitrile or by heating it with bases.

The same firm[87] dehydrohalogenate the nitriles $CCl_3{\cdot}CHR{\cdot}CN$ (R is hydrogen, alkyl, or chloroalkyl) or $CHCl_2{\cdot}CHR{\cdot}CN$ or $CH_2Cl{\cdot}CR'Cl{\cdot}CN$ (R′ is hydrogen, alkyl, or halogen) to give the halogeno-acrylonitriles $CR'Cl{:}CX{\cdot}CN$, where X is hydrogen, chlorine, or alkyl and R′ is hydrogen or chlorine. For example αββ-trichloropropionitrile yields αβ-dichloroacrylonitrile. By distilling the same intermediate[88] with a tertiary amine boiling above 200° it is possible to prepare αβ-dichloroacrylonitrile.

Shell Development Co.[89] prepare α-methacrylonitrile by treating the corresponding alkylamine with oxygen in presence of an oxidation catalyst of silver or its alloys at about 570°.

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[84] B.P. 569,524; B., 1945, II, 332.
[85] Wingfoot Corp., B.P. 570,616; B., 1945, II, 332.
[86] *Idem*, U.S.P. 2,326,095; B., 1945, II, 332.
[87] B.P. 571,750; B., 1945, II, 364.
[88] B.P. 570,835; B., 1945, II, 332.
[89] U.S.P. 2,328,984; B., 1946, II, 35.

Wingfoot Corporation[90] also prepare $\alpha\alpha\beta$-trichloropropionitrile by passing chlorine into acrylonitrile, β-chloro- or $\alpha\beta$-dichloro propionitrile. Alkoxypropionitriles are prepared[91] by adding alcohol to acrylonitriles, 'in presence of an alkali metal or tertiary amines. On the other hand[92] the di- and tri-chloropropionitriles $CH_2Cl{\cdot}CXCl{\cdot}CN$, where X is Cl or Me, can be treated with alkali alkoxides ROH under varied conditions to yield $CHCl{:}CX{\cdot}CN$, $OR{\cdot}CH{:}CX{\cdot}CN$, $OR{\cdot}CH_2{\cdot}CX(OR){\cdot}CN$, or $OR{\cdot}CH_2{\cdot}C(OR)_2{\cdot}CN$, R being methyl, ethyl, or other alkyl group. Acrylonitrile is readily hydrogenated[93] to propionitrile in presence of Raney nickel, at moderate temperature and pressure, and the reaction is exothermic.

American Cyanamid Co.[94] describe two methods for the preparation of chloroacetonitrile. In the first, hydroxyacetonitrile is treated with an inorganic acid chloride in presence of a tertiary base. The method is superior to the conventional one from chloroacetamide and phosphorus pentachloride, as separation by distillation is easy; the yield obtained is 85% of theory. The second alternative is a 60% yield obtained by treating a cooled aqueous solution of aminoacetonitrile hydrochloride with a deficiency of nitrosyl chloride, the product being extracted with ether.

E. I. Du Pont de Nemours & Co.[95] show that, in the preparation of acrylonitrile by the combination of acetylene and hydrocyanic acid over a sodium cyanide catalyst on an active carbon carrier, the condensate from the reaction is liable to decompose by secondary reactions unless kept acid, for instance, by sodium dihydrogen phosphate.

Röhm & Haas Co.[96] describe the preparation of nitriles by passing a mixture of saturated primary alcohols and ammonia gas at 300—400° over reduced copper or silver catalysts, or preferably a mixture of both dispersed on alumina, zirconia, thoria, or a rare-earth oxide; propionitrile is thus obtained from *iso*butyl alcohol.

E. I. Du Pont de Nemours & Co.[97] claim the interaction of hydrocyanic acid with esters of unsaturated alcohols in presence of an alkaline catalyst, giving nitrile esters; thus acrylic acid, potassium acetate, and hydrocyanic acid, kept at 50° for four days, yield lactonitrile formate. The same firm describe other condensations of acrylonitrile, for instance, with cyanohydrins and an alkaline catalyst to yield $\alpha\beta$-dicyano-ethers[98]: $CH_2{:}CH{\cdot}CN + OH{\cdot}CHMe{\cdot}CN \rightarrow CN{\cdot}[CH_2]_2{\cdot}O{\cdot}CH_2{\cdot}CHMe{\cdot}CN$, and with aldehydes[99] to give aldehydo-nitriles; thus acetaldehyde yields both γ-cyanobutaldehyde

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[90] B.P. 572,298; B., 1946, II, 34.
[91] B.P. 572,101; B., 1946, II, 35.
[92] B.P. 573,563; B., 1946, II, 77.
[93] U.S.P. 2,334,140; B., 1946, II, 276.
[94] U.S.P. 2,331,681–2; B., 1946, II, 34.
[95] B.P. 573,456; B., 1946, II, 78.
[96] U.S.P. 2,337,421–2; B., 1946, II, 319.
[97] B.P. 573,627; B., 1946, II, 78. *Cf.* B.P. 570,042; B., 1945, II, 295.
[98] U.S.P. 2,333,782; B., 1946, II, 276.
[99] B.P. 576,427; B., 1946, II 276.

and γ-formylpimelonitrile by the two possible modes of addition to the double bond.

Adiponitrile, the important nylon intermediate, is obtained by the same firm[100] in a continuous process by passing adipic acid and excess of ammonia over a boron phosphate catalyst at 350—450°.

AROMATIC INTERMEDIATES.

Solvay Process Co.[101] describe the preparation of phenols by the oxidation of benzene and toluene in the vapour phase with oxygen in vessels coated with boric oxide. On the other hand, Shell Development Co.[102] gently oxidise toluene and ethylbenzene in presence of hydrobromic acid as explosion retarder, and obtain benzyl alcohol and acetophenone respectively.

Howards & Sons Ltd.[103] describe a modified process for preparing thymol from *m*-cresol, giving a higher yield of thymol than previous methods.

In the oxidation of naphthalene to phthalic anhydride, Allied Chemical & Dye Corporation[104] use steam as a carrier gas in the evaporation of the naphthalene, the limits being between ½ and 2 parts of steam per part of naphthalene. There is some prospect that supplies of *o*-xylene will become available from petroleum sources in the U.S.A. at prices sufficiently attractive to compete with naphthalene for oxidation to phthalic anhydride. Allied Chemical & Dye Corporation[105] describe one method of isolating pure *o*-xylene from "drip oil" by azeotropic distillation, chlorination, and fractional distillation, the first two steps removing the non-aromatics and olefines respectively.

N. W. France and M. W. Keibler[106] have studied the controlled oxidation of bituminous coals with oxygen in presence of caustic soda at 200—300° under pressure, followed by acidification of the filtered alkaline solution; a 60% yield is obtained of a mixture, mainly of benzene-tri- and -tetracarboxylic acids of average molecular weight 250.

Some of the selective weed killers now coming into prominence are based on 2 : 4-dichlorophenoxyacetic acid or its derivatives, where one chlorine may be replaced by methyl. Six patents[107] by Imperial Chemical Industries in this field deal with details of preparative methods; according to one of these, phenol is chlorinated below 90° to a setting point of 34° and fractionation then gives a 90—95% yield of pure 2 : 4-dichlorophenol. Again the cheaper mixed cresols may be monochlorinated and pure 4-chloro-*o*-cresol can be isolated from the product. Pure *p*-cresol yields

[100] U.S.P. 2,200,734; B., 1946, II, 112.
[101] U.S.P. 2,328,920; B., 1945, II, 366.
[102] B.P. 578,608; B., 1946, II, 365.
[103] B.P. 571,137; B., 1945, II, 366.
[104] U.S.P. 2,329,638; B., 1945, II, 365.
[105] U.S.P. 2,332,370; B., 1946, II, 237.
[106] *Chem. Industries*, 1946, **58**, 580; B., 1946, II, 231.
[107] B.P. 573,475-9, 573,510; B., 1946 II, 79.

2-chloro-*p*-cresol. The various phenols are condensed with chloroacetic acid in excess of alkali.

The same firm also describe[108] the preparation of 2 : 4 : 5-*trichlorophenyl-acetic* acid, commencing with 2 : 4 : 5-trichloro-1-chloromethylbenzene, which is treated with an alkali cyanide and hydrolysed with caustic soda. Another acid is of the phenylenediacetic acid[109] type, containing one to three chlorine atoms, obtained by treating the appropriate *p*-di(chloromethyl)benzene with alkali cyanide, followed by hydrolysis with caustic soda.

Imperial Chemical Industries[110] describe the preparation of iminomethylbenzyl cyanides CN·CHPh·CH NH ; these are formed in two steps by first treating formylbenzyl cyanides, CN·CHPh·CHO, with liquid ammonia at low temperature, giving an additive compound, probably $CN{\cdot}CHPh{\cdot}CH(NH_2){\cdot}ONH_4$, which readily splits off water and ammonia on heating in a solvent.

G. W. Gladden and W. W. Cocker[111] obtain chloroimides by chlorinating an aqueous suspension, which may include a wetting agent, of an acylarylamine in presence of an alkali carbonate or bicarbonate to maintain the pH at 7—9 ; thus 2 : 4-dichlorobenzamide is chlorinated until the m.p. is 86°, yielding 2 : 4-dichlorobenzchloroimide.

E. I. Du Pont de Nemours & Co.[112] describe a series of azo-dye intermediates, suitable for colour-couplers in photography ; the feature is the introduction of a polyamide chain of 14 to 36 carbons as the anti-diffusion grouping for the successive layers of the emulsion in the colour film. Thus dimethyl adipate and hexamethylenediamine are heated to form the amide $[CH_2]_6(NH{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2Me)_2$; this is then heated with *m*-aminophenol, which replaces the methyl ester groups. This product in the silver halide emulsion yields blue images on development with diethyl-*p*-phenylenediamine. For the magenta image, hexamethylenediamine is treated with methyl *N*-*m*-(5-keto-3-methyl-1-pyrazyl)phenyladipamate. The yellow is obtained, for example, by first coupling diazotised aniline with methyl phenyladipamate, which is then heated with hexamethylenediamine to replace the remaining methyl group, and is then reduced to a diamine, $[CH_2]_6(NH{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4\text{-}NH_2\text{-}p)_2$, which is condensed with ethyl acetoacetate.

General Aniline & Film Corporation[113] describe a series of dye intermediates having a long-chain alkyl group R with at least nine carbon atoms ; these are made by interaction of the corresponding acid chloride R·COCl with dialkyl sodiomalonates, and the resulting product is treated with an amine, for instance a hydrazine. Thus diethyl sodiomalonate

[108] B.P. 573,377 ; B., 1946, II, 80.
[109] B.P. 574,477 ; B., 1946, II, 113.
[110] B.P. 570,528 ; B., 1945, II, 334.
[111] B.P. 575,382 ; B., 1946, II, 194.
[112] U.S.P. 2,330,291 ; B., 1946, II, 37.
[113] U.S.P. 2,200,306 ; B., 1946, II, 81.

and heptadecyl chloride are caused to interact and phenylhydrazine-*m*-carboxylic acid is then added; the product is 1-(*m*-carboxyphenyl)-3-heptadecylpyrazolone.

Naphthalene derivatives are described in a number of cases. E. J. Cross[114] describes in detail sodium 2-hydroxy-3-carboxynaphthalene-6-sulphonate, which exists in two crystalline forms; one with two molecules of water of crystallisation is yellow, and the other with only one molecule is colourless. The author corrects the orientation wrongly given in B.P. 499,742[115] as the 5-sulphonate. On heating, the salt first becomes anhydrous at 150° and by caustic potash fusion at 280—290° yields 2 : 6-dihydroxy-3-naphthoic acid; the latter when sulphonated yields the 6- and 8-sulphonic acids. General Aniline & Film Corporation[116] boil 4-chloro-5-nitro-1-chloromethylnaphthalene with sodium sulphite and then reduce to the amino-compound, which is transformed by 10% sulphuric acid into 4-chloro-5-hydroxy-1-sulphomethylnaphthalene.

Considerable attention is still paid to the preparation of sulphones and their derivatives. J. R. Geigy A.-G.[117] condense *p*-nitrobenzene-sulphenyl chloride with mono- or di-alkylated arylcarboxylamides, oxidise the products to sulphones, and then reduce to the amino-compounds. The same firm[118] condense naphthasultone with a carboxyl or sulphonyl halide in presence of aluminium chloride in an inert solvent and then subject the product to hydrolysis or ammonolysis. Thus naphthasultone 4-methyl ketone, from naphthasultone and acetyl chloride, heated with 30% caustic soda yields 4-acetyl-1-naphthol-8-sulphonic acid or with 25% ammonia gives the ammonium salt and the sulphonamide. American Cyanamid Co.[119] obtain 2 · 4-diaminodiphenyl sulphone by interaction of a *p*-arylaminobenzenesulphonic acid with an *o*-halogenonitrobenzene, reduction of the nitro-group, and hydrolysis. The same firm[120] prepare 4:4′-derivatives of 2-carboxydiphenyl sulphones, for instance, by the following method. Potassium acetanilide-*p*-sulphinate is condensed with ethyl 2-chloro-5-nitrobenzoate in presence of copper powder and iodine, yileding the nitro-sulphone, which is reduced by iron and acetic acid to 4-amino-4′-acetamido-2-carbethoxydiphenyl sulphone, and this is hydrolysed by hydrochloric acid to the 4 : 4′-diamino-ester.

Manchester Oxide Co. Ltd.[121] describe the preparation of *p*-arylamino-benzenesulphenamides by two methods: either a di-*p*-acylaminobenzene disulphide is converted into *p*-acylaminobenzenesulphenyl chloride by

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[114] *J. Soc. Dyers & Col.*, 1946, **62**, 150, B., 1946, II, 271.
[115] B., 1939, 356.
[116] U.S.P. 2,199,568; B., 1946, II, 80.
[117] B.P. 575,811; B., 1946, II, 238.
[118] B.P. 575,285; B., 1946, II, 238.
[119] U.S.P. 2,336,445; B., 1946, II, 364.
[120] U.S.P. 2,336,210; B., 1946, II, 366.
[121] B.P. 569,604; B., 1945, II, 334.

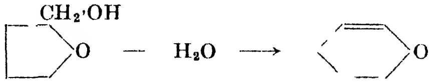
means of chlorine in ethyl acetate solution, or a disulphide[122] having a carbamic ester grouping in the *p*-position is treated with chlorine in, for instance, chloroform solution; the intermediate sulphenyl chloride is treated with ammonia to yield the sulphenamide.

HETEROCYCLIC INTERMEDIATES.

The chemistry of the related heterocyclic systems based on furan and pyran continues to attract considerable investigation. These two series of compounds promise to acquire commercial interest and the uses of the various available types both as solvents and as chemical reagents are making good progress. The present seems a convenient time to review this field, particularly directed to the pyran compounds and their derivatives.

E. I. Du Pont de Nemours & Co.[123] describe the use of quicklime or hydrated lime as catalyst for the preparation of furan from furfuraldehyde, in place of the usual nickel[124], in another case,[125] steam and furfuraldehyde vapour are passed over a chromite of zinc, manganese, nickel, cobalt, iron, cadmium, or tin at 425°. Revertex Ltd.[126] by heating tetrahydrofurfuryl alcohol in presence of a reduced copper–cobalt catalyst and preferably also hydrogen, obtain 2 . 3-dihydro- and tetrahydro-furan, in the proportion of 2 : 5 parts. Eastman Kodak Co.[127] hydrogenate furfuraldoxime in alcoholic solution with a nickel or cobalt catalyst to give 2-furfurylamine (at 90—100°) and tetrahydro-2-furfurylamine (at 150°).

The main source of pyran derivatives is the dehydration of tetrahydrofurfuryl alcohol,[128] giving 2 : 3-dihydropyran :



This may be carried out, as by the original author,[128] by passage over alumina, or as modified[129] by Imperial Chemical Industries, over a boron phosphate catalyst.

2 : 3-Dihydropyran is a very reactive substance and takes part in a rich array of transformations. When passed over silica chips at 500—550°[130] it decomposes to ethylene and acraldehyde. It polymerises[131] with Friedel–Crafts catalysts and is readily hydrogenated[132] to tetrahydropyran.

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[122] B.P. 570,528; B., 1945, II, 334.

[123] U.S.P. 2,337,027, B., 1946, II, 324.

[124] Cf. *Ann Repts.*, 1944, **29**, ref. 31.

[125] B.P. 575,362; B., 1946, II, 196.

[126] B.P. 576,533; B., 1946, II, 324.

[127] U.S.P. 2,338,655; B., 1946, II, 324.

[128] Cf. *Org. Syntheses*, **23**, 25; Paul, *Bull Soc. chim.*, 1933, [iv], **53**, 1492.

[129] B.P. 547,334; B., 1942, II, 396.

[130] J. G. Bremner, D. G. Jones, and S. Beaumont, *J.C.S.*, 1946, 1018; A., 1947 II, 000.

[131] B.P. 558,106; B., 1944, II, 84.

[132] B.P. 565,175; B., 1945, II, 52.

Tetrahydropyran takes part in a number of reactions. The ring is opened by acid chlorides to yield ω-chloroamyl esters $Cl{\cdot}[CH_2]_5{\cdot}O{\cdot}CO{\cdot}R$. With oxygen it gives δ-valerolactone,[133] using as catalyst an oxide or salt of cerium, cobalt, lead, manganese, or copper. With ammonia it gives piperidine[134] and it is readily chlorinated[135] to give a mono-, di-, tri-, and tetra-chlorotetrahydropyran. Halogen acid[136] dehydrates it and opens the ring to give $\alpha\varepsilon$-dihalogenopentane. The latter reacts with alkali cyanide to yield pimelonitrile, which is hydrogenated to heptamethylene-1 : 7-diamine.

2 : 3-Dihydropyran adds the elements of water by means of mineral acid, giving δ-hydroxyvaleraldehyde or di-2 : 2′-tetrahydropyryl ether.[137] The former can be hydrogenated[138] to pentane-$\alpha\varepsilon$-diol, and the latter then again oxidised to δ-valerolactone.[139] Again, δ-hydroxyvalerolactone is oxidised by nitric acid[140] to glutaric acid.

With hydroxy-compounds, the behaviour of 2 : 3-dihydropyran is again olefinic in character. Alcohol yields tetrahydropyryl ethyl ether, tetrahydrofurfuryl alcohol yields tetrahydropyryl tetrahydrofurfuryl ether, and ethylene glycol reacts at both ends of the molecule to give the di-2-tetrahydropyryl ether. These ethers resemble acetals and are unstable to acids.

The 2 : 3-dihalogeno-derivatives of tetrahydropyran are produced by addition of free halogen to 2 : 3-dihydropyran.[141] The 2-chlorine is more reactive than the 3- and hence yields 3-chloro-2-cyanotetrahydropyran with copper cyanide; dehydrochlorination then occurs on heating with pyridine, giving 6-cyano-2 : 3-dihydropyran, and the corresponding pyroic acid on saponification. Similarly, 2 : 3-dichlorotetrahydropyran reacts with aniline only at the 2-chlorine, giving 5-chloro-6-anilinotetrahydropyran. Again, if 2 : 3-dichlorotetrahydropyran be dehydrochlorinated, it yields 5-chloro-2 : 3-dihydropyran. When heated, 5-chloro-2 : 3-dihydropyran yields α-chloroacraldehyde.[142] It adds chlorine[141] to yield 2 : 3 : 3-trichlorotetrahydropyran ; in the latter compound the 2-chlorine atom is still the most reactive. Aqueous chlorination of 5-chloro-2 : 3-dihydropyran yields 3 : 3-dichloro-2-hydroxytetrahydropyran. The great reactivity of the 5-position is shown even in 5-chloro-2 : 3-dihydropyran by the fact that it will accept hydrogen from 3-chloro-2-hydroxytetrahydropyran with the formation of 3 : 3′-dichloro-2 : 2′-ditetrahydropyryl ether. Again, 2 : 3-dihydropyran

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[133] B.P. 572,752 ; B., 1946, II, 32.

[134] G.P. 706,693.

[135] B.P. 571,265 ; B., 1945, II, 367.

[136] C. L. Wilson, *J.C.S.*, 1945, 48; A. 1945, II, 123. Cf. *Org. Syntheses*, **23**, 67.

[137] L. E. Schniepp and H. H. Geller, *J. Amer. Chem. Soc.*, 1946, **68**, 1646; A., 1947, II, 81.

[138] I.C.I., B.P. 576,087 ; B., 1946, II, 234.

[139] I.C.I., B.P. 583,344 ; B., 1947, II, 100.

[140] I.C.I., B.P. 576,098 ; B., 1946, II, 235.

[141] I.C.I., B.P. 571,265–6 ; B., 1945, II, 367.

[142] I.C.I., B.P. 578,071 ; B., 1946, II, 362.

adds halogen acids to yield 2-halogenotetrahydropyrans; these react with copper cyanide to give 2-cyanotetrahydropyran. Hypochlorous acid addition[143] gives 3-chloro-2-hydroxytetrahydropyran, while phosgene reacts to yield 2 : 3-dihydro-5-pyroyl chloride and the corresponding pyroic acid.[144]

AZO-DYES.

BY A. H. KNIGHT.

The main directions of research on azo-dyes by dye manufacturing firms, as revealed by the patent specifications which are considered in this review, continues to be towards new direct cotton dyes and dyes for cellulose acetate. It must be recognised, however, that much of the work surveyed in this section was done before or in the early days of the recent war. In the field of direct dyes the emphasis is still on the provision of structures, based on known intermediates, which lend themselves to after-treatments, either by formaldehyde or diazotisation and development to increase washing-fastness, or by coppering to improve both washing-fastness and light-fastness, rather than the use of new intermediates. However, the use by Society of Chemical Industry in Basle of 3 : 3′-dihydroxybenzidine as a tetrazo-component is of particular interest, since it permits the building up of a wide variety of structures which, unlike those from its already widely used dimethyl ether, viz., dianisidine, can be coppered on the fibre to give true copper complexes of *oo*′-dihydroxyazo- or *o*-hydroxy-*o*′-carboxyazo-compounds.

The conspicuous features of the patenting on dyes for cellulose acetate are the numerous specifications by Eastman Kodak Co. and the diversity of coupling components employed by that firm. Of particular interest is the extent to which heterocyclic structures are being incorporated in such coupling components. Whilst wide ranges of shades can be produced by suitable choice of components, it would seem that much of the effort of this firm is still being directed to the provision of dyes for this fibre which yield violet and blue shades, especially such as are resistant to "burnt gas fumes." Attention is still being given by some manufacturers to the search for new water-soluble dyes for acetate rayon, and, as remarked in last year's survey, provision for both dispersed-insoluble and water-soluble types is often made in the same patent specification.

Very few developments have taken place in azo-dyes for wool and leather, or in the fields of azoic dyes and azo-pigments.

General.

J. S. P. Blumberger[145] has discussed the effects of steric hindrance or resonance in vicinally substituted azo-dyes derived from 1-naphthylamine-4 : 8- and -6 : 8-disulphonic acids, such substitution often resulting in a considerable hypsochromic effect on shade. A similar effect on

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[143] I.C.I., B.P. 570,160.

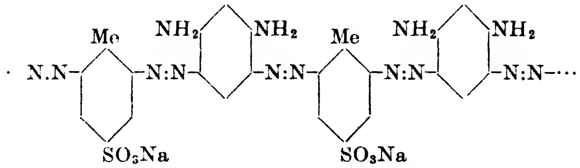
[144] I.C.I., B.P. 570,974; B., 1945, II, 367.

[145] *Rec. trav. chim.*, 1944, **63**, 127; A., 1946, II, 80.

shade is produced by substituting certain sodium azo-β-naphtholsulphonates with $-SO_3Na$ close to the azo-link as compared with analogues having no such $-SO_3Na$ group. Steric comparisons are made between *p*-nitrobenzeneazodimethyl-*o*-toluidine and the analogous dimethylaniline compound. The steric hindrance of resonance of *o*-substituted derivatives of diphenyl and of certain azo-dyes from benzidine which are unable to dye vegetable fibres directly is also discussed.

(Mme.) P. Ramart-Lucas[146] has made some general observations on the determination of the structure of acyl derivatives of hydroxyazo-dyes such as hydroxyazobenzenes and similar substances. For this purpose chemical methods are impossible on account of the ease with which these substances undergo intramolecular change, but spectroscopic methods are valid. The conclusions reached are that the acyl derivatives examined are definitely esters of azophenol, but the structure of the parent compounds cannot be deduced from that of their acetates. Comparisons of the absorption spectra of the *O*-acyl derivatives with those of the azo-hydrocarbon of the same series and the compounds having methyl in place of *O*-acyl are also discussed.

P. Ruggli and R. Fischer[147] have cast doubts on the validity of the structural formula commonly assigned to Toluylene Brown G on account of the supposed presence of a 10-membered heterocyclic ring which cannot be regarded as a stable arrangement. The chromatogram of Toluylene Brown G is very similar to that of the dye of constitution:



so that a similar chain-like structure is assigned to the technical product. Since all substantive dyes hitherto investigated are polydispersed, not only the degree of aggregation of the colloid anions, but also the chain-length, is probably indefinite. The authors, however, consider that the molecular weight lies within moderate limits.

The same authors have discussed the evidence afforded by the application of reduction methods to certain disazo-dyes from *m*-phenylenediamine for the positions of coupling to the latter under specified coupling conditions. When 1 mol. of *m*-phenylenediamine is coupled with 2 mols. of diazotised sulphanilic acid, first in mineral acid, then in sodium carbonate, and finally in caustic alkali medium, formation of 1 : 3 : 4 : 6-tetra-aminobenzene on reduction of the product indicates that coupling has occurred in the 4 : 6-positions in the *m*-phenylenediamine and there is no indication of an isomeric disazo-dye. Coupling in the 4 : 6-positions has also been shown to occur by a similar procedure for the tetrakisazo-dye

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[146] *Bull. Soc. chim.*, 1944, [v], **11**, 75; A., 1946, II, 21. Cf. A., 1944, II, 192.
[147] *Helv. Chim. Acta*, 1945, **28**, 445; B., 1946, II, 197.

obtained by coupling 1 mol. of benzidine with 2 mols. of *m*-phenylenediamine, and then coupling the product with 2 mols. of diazotised sulphanilic acid. In the case of the tetrakisazo-dye obtained by coupling 1 mol. of diazotised sulphanilic acid with 1 mol. of *m*-phenylenediamine and then coupling 2 mols. of the resulting monoazo-dye with 1 mol. of tetrazotised benzidine, the evidence indicates that coupling with the *m*-phenylenediamine has occurred in the 2 : 4-positions.[148]

P. Nawiasky, F. Ebersole, and J. Werner[149] have drawn attention to the dangerous nature of the reaction between diazonium compounds and sodium sulphide or hydrogen sulphide; various conditions under which explosion is likely to occur are stated, with special reference to the reactions of diazotised 4-chloro-*o*-toluidine.

E. I. Du Pont de Nemours & Co. claim improved yields of amino-dye by reducing the tetrakisazo-combination (*p*-nitroaniline-*o*-sulphonic acid $\rightarrow$ mixed Cleve's acid)$_2$ $\rightrightarrows$ di-*J*-acid [di-(7-sulpho-5-hydroxy-2-naphthyl)-amine] in 10—30% sodium chloride solution with sodium hydrosulphide at 80—85°; the major part of the nitro-compound and the amino-compound remain in suspension during reduction and side-reactions are thus diminished.[150]

Support for the views of Voroschcov[151] on the structure of the bisulphite derivatives of azo-dyes is afforded by experiments by V. N. Ufimtzev[152] on the sulphonation of hydrazobenzene with chlorosulphonic acid in pyridine at ordinary temperature to give the *N*-sulphonic acid, which is stable to alkalis, rearranged by acids to benzidine-*N*-sulphonic acid, and oxidised by ferric chloride to azobenzene.

O. Süs[153] has obtained conclusive evidence that the formation of dyes by the action of light on diazo-anhydrides from *o*-amino-phenols and -naphthols is due to coupling between undecomposed diazo-compound and *cyclo*pentadienecarboxylic acid derivatives which have been formed. H. H. Hodgson and D. E. Hathway[154] have investigated the decomposition of 3-nitronaphthalene-1-diazonium chloride by sodium sulphite and sodium acetate and discussed the mechanisms of these decompositions; the former reagent gives almost entirely 3 : 3′-dinitro-1 : 1′-azonaphthalene whilst the latter gives mainly 3 : 3′-dinitronaphthalene-1′ : 2-azo-1-naphthol.

S. Rangaswami and K. R. Rao[155] have examined the coupling behaviour of 5-hydroxy-7-methyl- and -4 : 7-dimethyl-coumarins and 7-hydroxy-5-methylcoumarin with diazotised *p*-nitroaniline (1 and slightly more than 2 mols.) at 0°. They suggest why these compounds give mixtures

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[148] *Helv. Chim. Acta.*, 1945, **28**, 1270; A., 1946, II, 18.
[149] *Chem Eng. News*, 1945, **23**, 1247; A., 1945, I, 312.
[150] U.S.P. 2,199,576; B., 1946, II, 158.
[151] *J. Amer. Chem. Soc.*, 1936, **58**, 2327; A., 1937, II, 13.
[152] *J. Gen. Chem. Russ.*, 1940, **10**, 1757; A., 1946, II, 134.
[153] *Annalen*, 1944, **556**, 65, 85; A., 1946, II, 195, 196.
[154] *J.C.S.*, 1945, 451; A., 1945, II, 316.
[155] *Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 14; A., 1944, II, 270.

of mono- and dis-azo-compounds and never only disazo-compounds even when excess of diazo-compound was used.

J. S. Salkind and Z. I. Cheifetz,[156] in investigating azo-dyes of the phenanthrene series, state that the depth of coloration obtained by coupling with diazonium salts varies in the order 2-phenanthrol > β-naphthol > 3-phenanthrol whilst 3-phenanthrylamine occupies an intermediate position as a diazo-component between α- and β-naphthylamine; melting points of some azo-compounds from these components are given.

C. Pfizer & Co.[157] describe the coupling of diazonium salts of the benzene series with tetra-acetyl-4 : 5-dimethyl-*d*-ribamine, in solvents containing little or no water, to give azo-compounds which can subsequently be deacetylated.

Azo Dyes for Wool and Leather.

In continuation of their investigations on the use of halogenoacylphenylenediamine derivatives as diazo-components for acid dyes for animal fibres,[158] Imperial Chemical Industries have described further disazo-dyes yielding dyeings on wool of good fastness to washing, milling, and light of the pattern : A (acid) → 1-amino-8-naphthol-3 : 6- or -4 : 6-disulphonic acid ← (alkaline) A′, A being an amine of the benzene or naphthalene series carrying at least one SO_3H or $SO_2{\cdot}NH_2$ group (the latter may be substituted) and A′ a *m*- or *p*-amino-monochloro- or -monobromo-acylanilide, the remaining hydrogen of the acylamino-group being optionally substituted by alkyl (C_1—C_6), aryl, or aralkyl and the phenyl of the anilide residue by Me, OMe, or SO_3H.[159]

J. R. Geigy A.-G.[160] prepare new chromable monoazo-dyes, particularly suitable for application to wool by the single-bath chroming process, by coupling diazotised 4-nitro-2-aminophenol-6-sulphonic acid with a phenol carrying in the 2-position a *tert.*-alkyl (C_1—C_8) or *cyclo*alkyl group and in the 4-position an alkyl (C_1—C_8) or *cyclo*alkyl group, the 5-position being optionally substituted by methyl; the 2-*tert.*-high alkyl group is said to give improved potting- and (in part) light-fastness in comparison with analogous chromed dyes of B.P. 325,208 and 450,127. The unchromed shades are orange to brown and those of the chromed dyes olive-brown to brown-olive.

Complex chromium compounds which dye leather generally in green shades fast to washing and acids have been made by General Aniline & Film Corporation[161] from azo-dyes formed by coupling diazotised nitro-*o*-aminophenols with 1-amino-8-naphthols substituted by NO_2 and SO_3H groups in 7 : 5-, 7 : 4-, or 5 : 7-positions respectively.

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[156] *J. Gen. Chem. Russ.*, 1945, **15**, 368; B., 1946, II, 366.
[157] U.S.P. 2,332,666; B., 1946, II, 281.
[158] Cf. *Ann. Repts.*, 1942, **27**, 85; 1943, **28**, 73; 1944, **29**, 78.
[159] B.P. 570,972; B., 1945, II, 368.
[160] B.P. 576,306; B., 1946, II, 280.
[161] U.S.P. 2,198,701; B., 1946, II, 40.

Copper-containing disazo-dyes obtained by coupling to resorcinol firstly a diazotised *o*-amino-phenol- or -naphthol-sulphonic acid and secondly an aryldiazonium compound free from sulphonic acid groups, at least one of the diazo-components being linked to a phenyl nucleus by an atom or grouping of non-basic character, *e.g.*, $-SO_2-$, $-SO_2\cdot NEt-$, $-O\cdot SO_2-$, –O–, –CO–, –CO·NH–, and coppering have been described by J. R. Geigy A.-G.[162]; alternatively the copper may be introduced after the first coupling. The dyes yield various shades of brown on wool and silk of good fastness to washing and water and excellent fastness to light. Their particularly good exhaustion properties on silk and superior fastness properties to those of dyes hitherto proposed are attributed to the use of a diazo-component containing the above type of non-basic linking atom or group for two phenyl nuclei.

Dyes for Cotton.

J. R. Geigy A.-G.[163] have described blue, green-blue, and grey trisazo-dyes, having better light-fastness than known comparable dyes, for diazotising and developing on the fibre to give dyeings within the same shade range. These are of the type : *p*-acylamido- or nitro-benzenesulphonic acid → M → M′ → aroyl-J-acid, finally hydrolysed or the nitro-group reduced (M = 1 : 6- or 1 : 7-Cleve's acid, a mixture thereof, or a 1-amino-2-alkoxynaphthalene-6- or -7-sulphonic acid, M′ = M or a 2 : 5-dialkoxyaniline). Surprisingly, it was found that, when a *p*-acylamidodiazobenzenesulphonic acid is used as the first component saponification of the diacylated dye obtained after the third coupling results in the splitting off of the acyl group in the starting component only. As an example, the hydrolysed dye *p*-aminoacetanilide-2-sulphonic acid → mixed Cleve's acid → 2 : 5-dimethoxyaniline → benzoyl-J-acid diazotised and developed with β-naphthol gives a green-blue dyeing.

E. I. Du Pont de Nemours & Co. have further extended their researches on polyazo-dyes, based on resorcinol as a twice-coupling component, for after-treatment on the fibre with formaldehyde. In one specification[164] they describe dyes of the pattern : resorcinol or certain 5-substituted derivatives ← *m*- or *p*-phenylenediamine → M → M′ → a naphtholsulphonic acid (M and M′ = α-naphthylamine which may have alkyl and/or alkoxy-groups in the 2 : 3-positions and not more than two of the groups alkyl, alkoxy, CO_2H, or SO_3H in the 5-, 6-, 7-, 8-positions). The dye : resorcinol ← *p*-phenylenediamine → 1 : 6-Cleve's acid → 1 : 6-Cleve's acid → 1-naphthol-5-sulphonic acid (oxy-L-acid) gives blue shades on viscose which are made faster to washing by after-treatment with formaldehyde. Provision is also made for converting the dyes into metallic complexes. In a second specification[165] the pattern is : (resorcinol or a 5-substituted derivative) ← *D* → (alkaline) aminonaphtholsulphonic

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[162] B.P. 577,673 ; B., 1946, II, 367.
[163] B.P. 575,423 ; B., 1946, II, 198.
[164] U.S.P. 2,204,229 ; B., 1946, II, 157.
[165] U.S.P. 2,204,230 ; B., 1946, II, 157.

acid → *m*-phenylenediamine ← *D* → (resorcinol etc.), where *D* = a diamine $NH_2R{\cdot}B{\cdot}R{\cdot}NH_2$, R being phenyl and B = O, S, NH, NH·CO·NH, CH:CH, N:N, azoxy, $[CH_2]_n$, etc. A typical example is: resorcinol ← 4 : 4′-diaminoazobenzene → (alkaline) 2-amino-8-naphthol-3 : 6-disulphonic acid → *m*-phenylenediamine ← 4 : 4′-diaminoazobenzene → resorcinol, which gives brown shades on viscose, made faster to washing by after-treatment with aqueous formaldehyde. In the same field, Society of Chemical Industry in Basle[166] have patented trisazo-dyes of the pattern : A → M → J- or gamma-acid → resorcinol or *m*-aminophenol; A and M are both benzenoid and free from OH, CO_2H, and SO_3H groups. In addition to formaldehyde after-treatment which improves wet-fastness, the dyes can be developed with diazotised aromatic amines, resulting in even better wet-fastness. For example, the combination : aniline → *o*-anisidine → gamma-acid → resorcinol, yields olive-brown shades on cotton when developed with diazotised *p*-nitroaniline.

In the field of metallisable dyes for cotton Sandoz Ltd.[167] have claimed the manufacture of metallic complexes of certain trisazo-dyes which yield blue, grey, green, and olive shades of very good fastness to washing and light on cotton, linen, and viscose, for which they have very good affinity; they can also be used for dyeing leather. Methods of making the starting disazo-compounds, which may already contain metal, are also described. A typical example is: 1-amino-2-naphthol-4-sulphonic acid → *m*-aminophenol → 1 : 6-Cleve's acid → phenyl-J-acid (coppered) which gives bright blue shades.[168]

Tetrazotised 3 : 3′-dihydroxybenzidine is used by Society of Chemical Industry in Basle[169] for metallisable tris- and poly-azo-dyes from coupling compounds which couple more than once, such as di-J-acid, the urea of J-acid, and pyrazolones substituted by an aryl residue capable of coupling such as a hydroxynaphthalene residue. In coupling the tetrazotised 3 : 3′-dihydroxybenzidine it is often desirable to use a medium containing ammonia or an alkali hydroxide to ensure completion of coupling. The examples supplied suggest that the dyes are mainly for after-coppering on the fibre to produce thereon metal complexes which, if dianisidine (3 : 3′-dimethoxybenzidine) were used as tetrazo-component, could only be satisfactorily produced in substance. However, the value of the soluble copper complexes, prepared in substance, of the metal-free dyes having a low order of affinity for the fibre is stressed, whilst those metal complexes of sparing solubility can be used to colour resins, lacquers, spinning masses, etc. A typical example is 3 : 3′-dihydroxybenzidine ⇉ (di-J-acid ← 2-aminophenol-4-sulphonamide)$_2$ which gives fast blue shades on cotton on after-coppering by the single-bath or two-bath processes.

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[166] B.P. 573,025; B., 1946, II, 82.
[167] B.P. 571,334; B., 1945, II, 368.
[168] Swiss P. 222,797.
[169] B.P. 572,852; B., 1946, II, 82.

E. I. Du Pont de Nemours & Co.[170] have prepared unsymmetrical copper-containing disazo-dyes yielding clear blue shades of excellent light-fastness on cotton and viscose; this light-fastness is retained when the dyeings on viscose are submitted to a crease-resisting process by treatment with a resinous condensation product such as one from urea and formaldehyde. The parent dyes are of the type : H-, K, 2R- (2-amino-8-naphthol-3 : 6-disulphonic), or 2S- (1-amino-8-naphthol-2 : 4-disulphonic) acid ← dianisidine → a disulphonated α- or β-naphthol coupling *o*- to the OH-group, the SO_3H being in a pair of the 3-, 6-, 7-, 8-positions, not adjacent to one another and with at least one of the 2- and 3-positions so occupied, and the coppering is effected in aqueous solution.

Additional examples of self-coupling dyes are described by General Aniline & Film Corporation[171]; they consist of red to blue-black monoazo-dyes, of very good fastness properties, obtained by coupling a 4-nitro- or -acylamido-aniline with certain naphthol- or chloronaphthol-sulphonyl derivatives of J-acid or its *N*-methyl or -phenyl derivatives and reducing the nitro-group or hydrolysing the acyl group.

Imperial Chemical Industries[172] have prepared ternary sulphonium salts of 4 : 4′-dibenzthiazyl(2)-azobenzenes containing two alkylthiol or two aralkyl- or alkyl-thiolmethyl groups and optionally one or more halogen, alkyl, or alkoxy (all alkyls of C_1—C_4) attached to Ar, in $\cdot CH_2\cdot S\cdot CH_2Ar$, by heating the latter with a dialkyl sulphate. The products dye cotton from a mildly alkaline bath in bright yellow shades as fast to washing, open soda-boiling, and soda ash treatment as dyeings of Caledon Yellow G (Colour Index No. 1118) and of good fastness to light. The same firm have also made other yellow azo-dyes of similar fastness consisting of quaternary ammonium salts of 4 : 4′-dibenzthiazyl(2)-azobenzene by heating with a *tert.* amine, especially pyridine or tetramethylthiourea, the azobenzene directly substituted by at least one chloromethyl group and containing one or more alkyl or alkoxy-groups of C_1—C_4.[173]

Azoic Dyes.

5-Halogeno-2-aminodiphenyls are used by American Aniline Products Inc.[174] as diazo-components for yellow combinations on cotton from bisacetoacetoamides of benzidine and *o*-tolidine. E. I. Du Pont de Nemours & Co.[175] employ monoazo-compounds, made by coupling diazotised amines of the benzene series of general formulæ 2 : 6 : 3 : 4 : 5 : 1-$C_6X_2Y_3\cdot NH_2$ or 1 : 2 : 3 : 4 : 5 : 6-$NO_2\cdot C_6Y_4\cdot NH_2$, where $X = H$, Cl, NO_2, Me, Et, OMe, or OEt, and $Y = NO_2$ or H, in acid medium with amino-naphthols, especially 1-amino-7-naphthol, as coupling components for

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[170] B.P. 575,437; B., 1945, II, 198.
[171] U.S.P. 2,205,481; B., 1946, II, 240.
[172] B.P. 576,234; B., 1946, II, 240.
[173] B.P. 576,270; B., 1946, II, 281.
[174] U.S.P. 2,331,812; B., 1946, II, 82.
[175] U.S.P. 2,200,949; B., 1946, II, 198.

azoic colours. They give dark shades; *e.g.*, 5-nitro-2-anisidine → (acid) 1-amino-7-naphthol. This would appear to be an extension of the investigations leading to U.S.P. 2,193,996–8.[176]

Guanidine derivatives solubilised by carboxy-[177] and sulpho-groups[178] are used by American Cyanamid Co. as stabilisers in the preparation of triazens from diazo- or tetrazo-compounds having a polynuclear residue, for use in azoic printing compositions; for example, tetrazotised dianisidine is combined alkaline with $NH_2{\cdot}C(:NH){\cdot}NH{\cdot}CH_2{\cdot}CO_2K$ (2 mols.) and the triazen mixed with 2-hydroxy-3-naphthoic-*o*-anisidide to give a blue printing composition. In another specification[179] the same firm make triazens from diazotised 2 : 5-substituted anilines, wherein the specified substituents are selected from halogen, NO_2, alkyl, CF_3, aryloxy, or alkoxy, and the above carboxylated guanidines or others of the general formula $NH_2{\cdot}C(:NH){\cdot}NA_2$, where A = H, aryl, aralkyl, alkyl, alicyclic, or heterocyclic incapable of coupling and substituted by 1—3 carboxyl or sulpho-groups. For example, a printing composition is made as in ref. 177 with the triazen 4-chloro-*o*-toluidine → $NH_2{\cdot}C(:NH){\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$. In a third specification[180] the triazens are those made from the tetrazodiphenyls of ref. 177 combined with the guanidine derivatives of ref. 179.

Messrs. Kuhlmann[181] prepare triazens by coupling the diazo-compounds of ice-colour bases, including those having negative substituents, with salts of 5-sulpho-2-*cyclo*alkylaminobenzoic acids; the diazo-compounds are regenerated by the action of dilute acids at low temperature and are used to print fabrics with ice-colours.

National Aniline & Chemical Co.[182] describe the use of soluble salts of alkyl or aralkyl esters of polyhydric inorganic acids as stabilisers for aromatic nitrosoamines (diazotates) or of dyeing or printing compositions prepared from them, such as the Rapid Fast Colours.

Water-soluble coupling components are made by General Aniline & Film Corporation[183] by acetylating monoarylamides of polynuclear aromatic *o*-hydroxy-carboxylic acids at both OH and NH with acyl groups carrying CO_2H, SO_3H, or quaternary NH_4 and partly hydrolysing so as to convert the *O*-acyl group back into OH.

Azo-Dyes for Cellulose Acetate.

Of the twenty patents in this section coming under review, sixteen are by the Eastman Kodak Co. and all these relate to monoazo-dyes. In many cases the essential chemical features of their inventions reside in the coupling components employed. They frequently use the

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[176] B., 1945, II, 298; *Ann. Repts.*, 1945, **3**, 87, refs. 61 and 62.

[177] U.S.P. 2,205,663; B., 1946, II, 240.

[178] U.S.P. 2,200,926; B., 1946, II, 194.

[179] U.S.P. 2,205,795; B., 1946, II, 240.

[180] U.S.P. 2,205,796; B., 1946, II, 240.

[181] Comp. Nat. de Mat. Col. et Manuf. de Prod. Chim. du Nord Réunies Etabl. Kuhlmann, B.P. 576,619; B., 1946, II, 322.

[182] U.S.P. 2,205,417; B., 1946, II, 194.

[183] U.S.P. 2,331,415; B., 1946, II, 80.

traditional unsulphonated diazo-components for azo-dyes for cellulose acetate such as nitroanilines (especially *p*-nitro-) containing substituents such as halogen and nitro in *ortho*-positions to the amino-group and 2-aminobenzthiazoles.

2-Amino-benz- or -naphth-oxazoles are used as diazo-components for a variety of coupling components, *e.g.*, 2-aminobenzoxazole → 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione gives greenish-yellow shades and 6-nitro-2-aminobenzoxazole → *N*-ethyl-*N*-β-hydroxyethylcresidine gives bluish-red shades.[184]

Nitroanilines containing at least one –CO·NRR′ group, where R and R′ = H, Ph, alkyl, allyl, or *cyclo*hexyl, and optionally halogen, nitro, alkyl, alkoxy, or $-SO_2 \cdot NRR'$, are diazotised and coupled with phenols or arylamines Ar·NR″R‴, where R″ and R‴ = H, benzyl, or alkyl, or form a morpholine ring, *e.g.*, 5-bromo-3-nitro-6-aminobenzamide → *p*-cresol.[185] 3 : 5-Dinitro-2-aminophenol is used as diazo-component for aryl, heterocyclic, or acetoacetarylamide coupling components. Thus, diazotised 3 : 5-dinitro-2-aminophenol coupled with barbituric acid gives a greenish-yellow and with *N*-*n*-butyl-*N*-β-sulphoethyl-*m*-toluidine gives a water-soluble violet.[186] Nitroanilines containing an –SR group (R = H, alkyl, or hydroxyalkyl) are also used as diazo-components; *e.g.*, 3-nitro-4-aminophenylthiol → *N*-βγ-dihydroxypropylaniline gives red shades.[187]

New coupling components employed by this firm include *m*-aminobenzyl alcohols which may be *N*-substituted by alkyl, hydroxyalkyl, etc.; *e.g.*, *o*-chloro-*p*-nitroaniline → *N*-ethyl-*N*-β-hydroxyethyl-*m*-aminobenzyl alcohol yields rubine shades.[188] Phenmorpholines which may be *N*-substituted by alkyl or hydroxyalkyl or in the nucleus by alkyl or halogen are coupled to a wide variety of diazo-components to give a range of shades; *e.g.*, *p*-nitroaniline → 6-chlorophenmorpholine gives orange-red and 5-nitro-1 : 4-naphthionic acid → 2-methylphenmorpholine gives rubine shades.[189] Yellow dyes are obtained by coupling diazotised amines of the benzene, naphthalene, or benzthiazole series free from nuclear SO_3H groups with *cyclo*homotetronic acid which may be substituted at 5- or 6-positions by alkyl, aralkyl, etc.[190]

Red to violet dyes, including water-soluble sulphuric and phosphoric ester dyes, are obtained by coupling diazotised benzenoid amines, especially *p*-nitroanilines, with 1-alkylindoles which may be substituted at positions 2 and/or 3[191] and blue shades from naphthindole derivatives.[192] Thus, *p*-nitroaniline → 3-methyl-1-β-hydroxyethylindole gives red and

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[184] U.S.P. 2,193,037; B., 1946, II, 7.
[185] U.S.P. 2,200,205; B., 1946, II, 157.
[186] U.S.P. 2,313,738; B., 1946, II, 40.
[187] U.S.P. 2,200,206; B., 1946, II, 157.
[188] U.S.P. 2,196,221; B., 1946, II, 7.
[189] U.S.P. 2,196,222; B., 1946, II, 7.
[190] U.S.P. 2,196,745; B., 1946, II, 7.
[191] U.S.P. 2,196,757; B., 1946, II, 7.
[192] U.S.P. 2,198,002; B., 1946, II, 40.

→ 6-hydroxynaphthindole blue shades whilst 6-chloro-2 : 4-dinitroaniline → 3-phenyl-1-β-hydroxyethylindole sulphuric ester gives violet shades and → sodium salt of 6 : 7-dihydroxy-3-methyl-1-β-phenylphosphatoethylnaphthindole greenish-blue shades. 1 : 2 : 3 : 4-Tetrahydro-1 : 10- and -1 : 7-phenanthrolines having H, Ph, CH_2Ph, alkyl, or allyl attached to the N and OH, which may be esterified with sulphuric or a phosphorus acid, CO·Alkyl or alkoxy *meta* to N in the reduced ring, are used as coupling components for a similar range of diazo-components to give yellow to blue dyes; *e.g.*, *o*-chloroaniline → 3-hydroxy-1 : 2 : 3 : 4-tetrahydro-1 : 10-phenanthroline gives yellow shades and 2 : 4-dinitroaniline → ammonium salt of 3-sulphato-1-β-methoxyethyl-1 : 2 : 3 : 4-tetrahydro-1 : 7-phenanthroline gives blue shades.[193]

Secondary and tertiary arylamines containing a tetrahydrofurfuryl group attached to the nitrogen atom either directly or through an aliphatic link are used as coupling components for a variety of shades; thus *o*-chloroaniline → *N*-tetrahydrofurfurylmethyl-*m*-toluidine gives yellow shades and 2 : 4-dinitroaniline → *N*-tetrahydrofurfurylmethyl-3 : 5-dimethoxyaniline gives red shades.[194] Greenish-yellow shades are provided by dyes from diazotised benzenoid amines and ethylenemalonamide having at positions 2 and 3 H or alkyl and at position 1 and/or 4 H, aryl, aralkyl, alkyl, or furyl.[195]

O-Acyl derivatives of $ArN[CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH]_2$ (Ar = phenyl or naphthyl) are used by the same firm as coupling components for red to blue dyes, the diazo-components being *p*-nitroanilines optionally substituted in one *o*-position by halogen and in the other by nitro, *e.g.*, *p*-nitroaniline → 1-*NN*-di-(βγ-dihydroxypropyl)amino-5-naphthol acetylated gives blue shades[196] [cf. dyes of U.S.P. 2,183,999 (Eastman Kodak Co.),[197] in which only one OH group of a 1-*N*-βγ-dihydroxypropylaminonaphthalene is esterified, *e.g.*, by acetyl]. A wide shade range is also provided by dyes from certain 3-aminodiphenyl ethers, the amino-group of which may be substituted by alkyl, allyl, *cyclo*alkyl, or a heterocyclic residue; *e.g.*, *o*-chloroaniline → 3-*N*-ethyl-*N*-βγ-dihydroxypropylaminodiphenyl ether gives yellow shades and 6-chloro-2 : 4-dinitroaniline → 3-*NN*-di-(β-hydroxyethyl)aminodiphenyl ether violet shades.[198]

Diazo-components of general formula $NH_2{\cdot}R{\cdot}PR'R''(X)_n$, where R is benzenoid, X = O or S, n = 0 or 1, R′ and R″ each represent an amino-group or one substituted by alkyl, hydroxyalkyl, alkyloxyalkyl, acetyl, *cyclo*hexyl, aminopyridyl, etc., or a group OZ where Z = H, alkyl, phenyl, or an alkali-forming metal, are used with coupling components of the benzene, naphthalene, or heterocyclic series to give in

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[193] U.S.P. 2,196,776; B., 1946, II, 7.
[194] U.S.P. 2,199,987; B., 1946, II, 157.
[195] U.S.P. 2,200,204; B., 1946, II, 157.
[196] U.S.P. 2,336,275; B., 1946, II, 280.
[197] *Ann. Repts.*, 1945, **30**, 89; B., 1945, II, 265.
[198] U.S.P. 2,204,607; B., 1946, II, 197.

general greenish-yellow dyes, *e.g.*, *p*-aminobenzenephosphonamide → *p*-cresol.[199] Amino-coupling components of the benzene or naphthalene series, having as *N*-substituents alkylene phosphoric (and analogous thiophosphoric) ester groups $-[CH_2]_n{\cdot}O{\cdot}PO(OAlkyl){\cdot}OR$, where R is H or a cation giving solubility in water, are used with a wide range of diazo-components to give water-soluble yellow to blue dyes devoid of SO_3H and CO_2H groups; *e.g.*, 6-bromo-2 : 4-dinitroaniline → 1-*N*-*n*-propyl-*N*-β-hydroxyethylaminonaphthalene phosphoric ester gives blue shades.[200]

Continuing their investigations on water-soluble azo-dyes containing hydroxyalkyl sulphuric ester groups, Imperial Chemical Industries[201] have described new red dyes from diazotised *p*-nitroaniline and sulphuric esters of *N*-alkyl- (C_1—C_8) -*N*-monohydroxy-straight-chain-alkyl- (C_2—C_6) -anilines wherein the sum of the C atoms in the alkyl and hydroxyalkyl groups is greater than 6 and less than 11 and which may optionally carry in one *m*-position halogen or a methyl or alkoxy (C_1— C_4) group; these dyes have superior affinity for acetate rayon from dilute dyebath liquors, such as are used in dyeing with winch machines, than have the dyes of corresponding shade known from B.P. 181,750 and 237,739.[202]

Water-insoluble fluorescent dyes for cellulose acetate have been prepared by British Celanese Ltd.[203] by partly reducing *o*-nitromonoazo-dyes free from SO_3H groups, either in substance or on the fibre, by means of an alkali or ammonium formaldehydesulphoxylate; reduction occurs without splitting the azo-group. Thus, partial reduction of 6-chloro-2 : 4-dinitroaniline → *N*-acetyl-*N'N'*-di-(β-hydroxyethyl)-*m*-phenylenediamine yields a yellow shade with a blue-green fluorescence.

Azo-Lakes and Pigments.

Grey and violet pigments of pure tone, fast to light, and non-bleeding in organic solvents, which are copper complexes of monohydroxyazo-compounds, have been obtained by Interchemical Corporation[204] by coppering disazo-compounds of the type: benzidine, diaminobenzophenone, diaminodiphenyl ether, or diaminodiphenylalkane (with up to 3 substituents in the aryl nuclei) $\rightrightarrows$ (2-hydroxy-3-naphthoic acid)$_2$; *e.g.*, the copper complex of the dye from dianisidine is a bluish-grey pigment and of that from 3 : 3'-dichlorobenzidine is a reddish-grey one. A complementary specification[205] provides for analogous copper complex pigments derived from diamines of the above type but containing phenyl substituents; thus, diphenylbenzidine $\rightrightarrows$ 2-hydroxy-3-naphthoic acid)$_2$

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[199] U.S.P. 2,200,543; B., 1946, II, 197.
[200] U.S.P. 2,328,570; B., 1946, II, 8.
[201] B.P. 575,342; B., 1946, II, 197.
[202] Cf. *Ann. Repts.*, 1925, **10**, 176; B., 1925, 754.
[203] B.P. 574,882; B., 1946, II, 158.
[204] U.S.P. 2,335,535; B., 1946, II, 327.
[205] U.S.P. 2,335,539; B., 1946, II, 327.

coppered gives a reddish-purple pigment. Monoazo-pigments of various shades of brown described by the same firm are obtained by coppering combinations such as *p*-nitroaniline → and *m*-nitro-*p*-toluidine → 2-hydroxy-3-naphthoic acid[206] whilst others covering various shades are obtained by coppering analogous monoazo-compounds for which aryl- or aralkyl-substituted anilines are used as diazo-components; *e.g.*, *o*-aminodiphenyl → 2-hydroxy-3-naphthoic acid.[207]

o-Hydroxycarboxyarylamides of carbazole, dibenzfuran, and diphenylene sulphide are used by General Aniline & Film Corporation[208] as coupling components for a wide range of specified diazo-components to give brown pigments easily soluble in organic solvents and suitable for colouring lacquers and plastic masses; *e g.*, 3-amino-6-methoxybenz-*N*-*n*-butylanilide → 2-hydroxycarbazole-3-carboxyl-*p*-chlorophenylamide.

ANTHRAQUINONE DYES

Wool Dyes.

W. Hentrich and H. J. Engelbrecht[209] describe wool blues of the Ultra type (in general 1-amino-4-arylaminoanthraquinone-2-sulphonic acids) in which the 4-substituent is supplied by an acylarylamine $NH_2 \cdot R \cdot CO \cdot R'$, where R is a benzene residue optionally substituted by halogen, hydroxyl, or alkyl, and having the NH_2 *meta* to the carbonyl, while R′ is an alkyl of not more than C_4. The usual two methods of synthesis in this series are described, the sulphonic acid group being either present at the beginning, or inserted later by heating the corresponding 2-halogeno-derivative with sulphites in a high-boiling solvent such as phenol. General Aniline & Film Corporation[210] employ an amine of the type $NH_2 \cdot C_6H_4 \cdot X \cdot NRR'$, X being alkylene and R, R′ alkyl groups, and in addition to the 2-sulphonic acid groups present in the above anthraquinone intermediate, one to three more sulphonic acid groups are introduced; typical amines are *N*-*m*-aminobenzyl-*N*-methyl-*N*-β-sulphoethylamine, *p*-aminobenzyl-dimethylamine-, -morpholine, or -piperidine.

E. I. Du Pont de Nemours & Co.[211] have prepared a series of anthraquinone wool dyes containing the trifluoromethyl group by appropriate methods. Thus 2 : 4-dibromo-1-aminoanthraquinone is condensed with *m*-trifluoromethylaniline and sulphonated in the phenyl residue, giving a fast level-dyeing blue. The same amine may be condensed with other anthraquinone intermediates, *e.g.*, 4-bromo-1-amino-2-methyl- to yield a reddish-blue, 2 : 4-dibromo-1-hydroxy- to yield a violet, or 4-bromo-1-methylamino-anthraquinone to yield a blue and 4-bromo-1 : 9-*N*-methylanthrapyridone to give a red dye, all after sulphonation.

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[206] U.S.P. 2,335,537; B., 1946, II, 327.
[207] U.S.P. 2,335,538; B., 1946, II, 327.
[208] U.S.P. 2,204,958; B., 1946, II, 198.
[209] U.S.P. 2,335,412; B., 1946, II, 281.
[210] U.S.P. 2,333,137; B., 1946, II, 328.
[211] U.S.P. 2,333,402; B., 1946, II, 328.

The same firm[212] describe brown chromable anthraquinone wool dyes, obtained by disulphonating 2-arylamino-1 : 4-dihydroxy- or 2 : 4-diarylamino-1-hydroxy-anthraquinones or their halogen-substituted derivatives with oleum so that one sulphonic acid group enters the anthraquinone nucleus.

Sulphonated polyanthrimides have attracted further attention by the same firm. Thus[213] dianilinodianthrimides having methyl in the phenyl residues and NO_2 or NH_2 in the anthraquinone nucleus are described. Examples are prepared by condensing 4 . 4′-dinitro-1 : 1′-dianthrimide with *p*-xylidine, and sulphonating the product with oleum, or 4 · 4′-dibromo-5 : 5′-dinitro-1 : 1′-dianthrimide is condensed with *p*-toluidine, the product reduced or not as desired, and sulphonated with oleum, grey shades are obtained. The same firm[214] have extended the work to sulphonic acids of diarylaminotrianthrimides, which are also greys, and are prepared by similar methods.

Cellulose Acetate Rayon Dyes.

The search for fume-fast blues is still going on. Thus E. I. Du Pont de Nemours & Co.[215] describe derivatives of 1-hydroxyanthraquinone having, in the 4-position, the grouping $\cdot NH\cdot R\cdot CH_2\cdot X$, where R is a benzene residue and X may be CN, NHAr, or OMe, the dyes are of the Alizarine trisole type, but a feature is fastness to gas fumes. The method of preparation is the normal one from a mixture of quinizarin and leucoquinizarin (4 : 1) in presence of aqueous or alcoholic boric acid and the necessary amine. Similar dyes described by the same firm[216] have as the 4-substituent the grouping $\cdot NH\cdot Ar\cdot OR$, when R is $\cdot CH_2\cdot CO_2H$, $[CH_2]_2\cdot OH$, $\cdot CH_2\cdot CO_2Me$, or $\cdot CH_2\cdot CO_2Et$.

Eastman Kodak Co.[217] prepare blue water-soluble dyes by esterifying 1-amino-4-hydroxyalkylaminoanthraquinones with monoalkylorthophosphoryl chlorides; examples specially mentioned are the products from 1-ethylamino-4-β-hydroxyethylaminoanthraquinone and *n*-butyl orthophosphoryl chloride ($POCl_2\cdot OBu$) and the corresponding *n*-propyl derivative ($POCl_2\cdot OPr$).

The same firm[218] describe certain derivatives of 1-amino-4-tetrahydrofurfurylaminoanthraquinone which have the grouping $\cdot[CH_2]_n\cdot SO_3H$ ($n = 2$ or more) attached to the 1-nitrogen : they are obtained by heating leucoquinizarin with tetrahydrofurfurylamine and the necessary sulphoalkylamine and oxidising the leuco-dye with aqueous borax.

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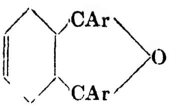
[212] U.S.P. 2,204,748; B., 1946, II, 198.
[213] U.S.P. 2,332,779; B., 1946, II, 281.
[214] U.S.P. 2,335,643; B., 1946, II, 281.
[215] U.S.P. 2,335,680; B., 1946, II, 282.
[216] U.S.P. 2,333,384; B., 1946, II, 328.
[217] U.S.P. 2,326,047; B., 1945, II, 337.
[218] U.S.P. 2,337,566; B., 1946, II, 327.

Wax and Oil Colourants.



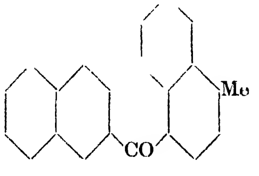
E. I. Du Pont de Nemours & Co.[219] condense butadiene or its derivatives with *s*-diaroylethylenes and dehydrate the resulting 4 : 5-diaroyl*cyclo*hexenes to 1 : 3-diaryl-4 : 7-dihydro*iso*benzfurans (see annexed formula). The products are fluorescent colours for mineral oil.

General Aniline & Film Corporation[220] condense polynuclear ketones of 4—6 fused rings, or their derivatives containing chlorine or amino-groups, with anhydrous halides (of zinc, beryllium, or aluminium) in presence of cyclic hydrocarbons or their chlorine derivatives boiling above 150° ; thus, for example, diphenyl, benzanthrone, and aluminium chloride are heated at 230°, and the product is extracted with benzene ; it colours oils dark red with a blue-green fluorescence.

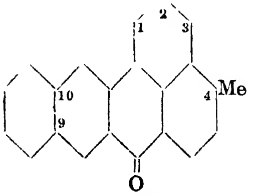
American Cyanamid Co.[221] note that the blue 1 : 4-di-(*n*-amylamino)-anthraquinone is more soluble in petrol than its analogues ; it is prepared by the normal method from leucoquinizarin.

Vat Dyes.

G. D. Buckley[222] has discovered a facile oxidative ring-closure which occurs when certain Friedel–Crafts reactions for the formation of 1 : 2′-dinaphthyl ketones are allowed excess of aluminium chloride, operating in the cold in the classical solvent, carbon disulphide. Thus *β*-naphthoyl chloride and 1-methylnaphthalene react with 1 mol. of aluminium chloride to give the normal product, 4-methyl-1 : 2′-dinaphthyl ketone (**I**), but with 2 mols. or more give a 70% yield of 4-methyl-9 : 10-benz-7-benzanthrone (**II**).



(I)



(II)

(**I**) is only slowly converted into (**II**) by aluminium chloride and hence is not an intermediate in the reaction concerned. *β*-Naphthoyl chloride may be replaced by 2-phenanthroyl chloride, but benzoyl chloride, α-naphthoyl chloride, and 3-phenanthroyl chloride give only ketones of the usual type. The benzanthrone formation is also prevented if the 1-alkylnaphthalene is replaced by naphthalene, 2-methylnaphthalene, bromonaphthalene, or 8-methylquinoline. A little of the benzanthrone analogue is formed from *β*-naphthoyl chloride and 1-ethylanthracene. No hydrogen is evolved by the ring-closure.

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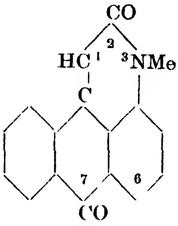
[219] U.S.P. 2,325,727 ; B., 1945, II, 335.
[220] U.S.P. 2,205,763 ; B., 1946, II, 241.
[221] U.S.P. 2,205,191 ; B., 1946, II, 367.
[222] *J.C.S.*, 1945, 561, 564 ; A., 1945, II, 404.

C. F. H. Allen and C. V. Wilson[223] contribute an interesting study of the substitution of 3-methylanthrapyridone (III) by halogen and nitro-groups. Chlorine readily enters the 1-position, and NO_2 most readily at 6. Substantial differences in reactivity exist between the 3-methyl- and the unsubstituted anthrapyridone, and the same applies to the parent materials, 1-methylamino- and 1-amino-anthraquinone, respectively.



(III)

The chlorination of indanthrone under certain conditions yields a dichloroindanthrone with fastness properties nearly equal to that of 3 : 3′-dichloroindanthrone prepared by the synthetic route from 3-chloro-2-aminoanthraquinone. For this purpose, E. I. Du Pont de Nemours & Co.[224] use nitrobenzene as solvent, an iron catalyst, and iodine as carrier; chlorination proceeds at normal temperature.

The same firm[225] have described new bluish-grey vat dyes obtained by first condensing a 3-halogeno- or a 3 : 9-dihalogeno-benzanthrone with heteronuclear-substituted aminoanthrones, such as 5-amino-1 : 9-anthrapyrimidine, 5-amino-1 : 9-*iso*thiazoleanthrone, 4-amino-*N*-methyl-1 : 9-anthrapyridone, or 5-amino-*N*-methyl-1 : 9-pyrazoleanthrone; the condensation products are then fused with alcoholic potash to yield the dyes, by formation of a new pyridine ring. In the case of the 3 : 9-dihalogenobenzanthrone, the procedure and products may be varied by interaction with a mixture of one of the above amines and a primary amine.

The same firm[226] describe pyridiazines obtained by the action of hydrazine on diphthaloylacridones containing an alkoxy, phenoxy, or ethylthiol grouping. Thus the methoxydiphthaloylacridone obtained by ring-closing 1-(2′-methoxy-5′-*o*-carboxybenzoylanilino)anthraquinone-2-carboxylic acid yields a greenish-grey dye with a red-violet vat.

The same firm[227] have prepared new arylaminoanthrapyridones by condensing 4-amino-*N*-methyl-1 : 9-anthrapyridine with mixed 6- and 7-bromo-2-*p*-chlorphenylanthraquinones; the condensation takes place first with the bromine, but by increasing the proportion of the amino-

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[223] *J. Org. Chem.*, 1946, **10**, 594; A., 1946, II, 343.
[224] U.S.P. 2,205,418; B., 1946, II, 241.
[225] U.S.P. 2,203,416; B., 1946, II, 115.
[226] U.S.P. 2,334,892; B., 1946, II, 328.
[227] U.S.P. 2,204,741–2; B., 1946, II, 367.

methylpyridone used, the chlorine also reacts. The dyes are fast bluish-reds. The halogenated intermediate is prepared by condensing 4-bromophthalic anhydride (prepared by brominating phthalic acid in *o*-dichlorobenzene solution at 120--175° until evolution of water ceases) with 4-chlorodiphenyl in presence of aluminium chloride, and ring-closing with sulphuric acid.

New carbazole browns are described by the same firm[228] starting with 1 : 6-dichloroanthraquinone ; this is condensed with 1 mol. of an α-aminoanthraquinone and ring-closed to a chlorodiphthaloylcarbazole, which is subsequently condensed with a second molecule of the same or a different α-aminoanthraquinone. Alternatively, 2 mols. of an α-aminoanthraquinone may be used at first and only mild ring-closure applied so that the resulting product is only closed in the α-position ; it is probably different from that of the first method. The dyes are red-browns.

The well-known yellow, 1 : 2 : 5 : 6-anthraquinone-C′-diphenylthiazole, has stimulated the same firm[229] to investigation of some of its more complex derivatives. Thus 2 : 6-diamino-1 : 5-dithiolanthraquinone or one of its substituted derivatives, especially the 3 : 7-dihalogeno-derivatives (1 mol.), is condensed with 1-aminoanthraquinone-2-aldehyde or its 4-halogeno-derivatives (2 mols.) in sulphuric acid solution. Alternatively, the same products result when the alkali salts of the same thiols are condensed with 1-aminoanthraquinone-2-carboxyl chloride in an organic solvent, followed by ring-closure in sulphuric acid, or by replacing the 1-aminoanthraquinone-2-aldehyde by the corresponding 1-aminoanthraquinone-2-phenylazomethines ; dyes of various shades are obtained, for instance, burgundy, blue-violet, and bluish-red. The conversion of aminodibenzanthrone into a direct black vat dye in substance has also been exemplified by this firm[230] by fusing with caustic alkali in presence of oxidising agents such as potassium chlorate or nitrate or sodium nitrite.

PHTHALOCYANINES.

The Harmon Colour Works Inc.[231] prepare fine-textured phthalocyanine pigments, capable of forming stable uniform dispersions in paint, lacquer, or varnish vehicles, by incorporating aluminium benzoate, or sodium benzoate and aluminium sulphate, in the wet pigment paste and drying the mixture. E. I. Du Pont de Nemours & Co.[232] find that increased strength and brilliance of shade is conferred on phthalocyanines, as well as anthraquinone and thioindigo vat dyes, by dilution of a sulphuric acid solution of the pigment with water in a state of turbulent flow.

[228] U.S.P. 2,203,227 ; B., 1946, II, 115.
[229] U.S.P. 2,335,698 ; B., 1946, II, 282.
[230] U.S.P. 2,334,891 ; B., 1946, II, 327.
[231] U.S.P. 2,327,472 ; B., 1945, II, 390.
[232] U.S.P. 2,334,812 ; B., 1946, II, 282.

MISCELLANEOUS DYES.

E. I. Du Pont de Nemours & Co.[233] describe blue to green sulphur dyes, obtained by thionating leucoindiphenols $1:x:4\text{-}OH\cdot C_6H_4X\cdot NH\cdot C_{10}H_6\cdot NR\cdot[CH_2]_n\cdot SO_3H\text{-}1:4$, where R is hydrogen, ethyl, butyl, phenyl, tolyl, or xylyl, n is 2 or 4, and X is hydrogen or halogen; the thionating agent is sodium polysulphide in water, aqueous alcohol, or ethylene glycol methyl ether, with or without the addition of copper.

The same firm have two patents[234] on dioxazine dyes. The amino-compounds obtained by condensing chloranil, 2 : 5-dichloro-benzo- or -tolu-quinone, or their analogues with aminoanilino-benztriazoles or -pyrazoles are ring-closed to bisoxazole dyes, and then sulphonated; the products have affinity for both wool and cotton and are used to dye unions. Thus chloranil and 5-(4′-amino-2′-sulphoanilino)-1-methyl-benztriazole give after condensation and sulphonation a blue dye. The necessary benztriazole derivatives are prepared by condensing 1-chloro-4-nitrobenzene-2-sulphonic acid with aminobenz-iminazoles, -thiazoles, or -oxazoles, which may have aryl or alkyl attached to N, and NH, NAryl, NAlkyl, O, or S at 2.

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[233] U.S.P. 2,335,381, B., 1946, II, 282.
[234] U.S.P. 2,336,521, 2,336,664: B., 1946, II, 328.

FIBRES, TEXTILES, AND CELLULOSE.

THE PROTEIN FIBRES.

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In a world which politically is still confused and turbulent, and where progress is hampered by the inevitable adversities which follow a major war, there are hopeful signs of a return to more normal conditions in an increasing interest in those branches of pure and applied science not connected with warfare. The growing recognition of the significance of studies on fibres was evident at the Dyers and Colourists Symposium on Fibrous Proteins and at the Annual Conference of the Textile Institute—the first full-scale Institute conference to be held since 1939—and accounts of the proceedings are important additions to the literature. No less valuable are the reports on German industry and research, for not only do they describe new work of high quality, but also they often provide useful accounts of well-established processes, details of which have been omitted from the standard technical monographs.

The Properties and Production of Protein Fibres.

Silk.—The structural unit of all textile fibres is the chain or linear polymer molecule, and lateral forces between these chains largely determine fibre strength. In the crystalline parts of silk, the chains are fully extended peptides with small side-chains, and consequently there is high lateral adhesion; according to K. H. Meyer[1] the "molar cohesion" is more than one million calories. In the more amorphous regions, where the chains possibly carry longer side-chains, *e.g.*, tyrosine residues, lateral adhesion is reduced. As in other fibres, the more highly organised parts of the fibre are linked with, and run into, the amorphous regions. The considerable lateral adhesion of the extended chains and the high degree of crystallisation and orientation account for the comparatively high strength of silk, while its poor recovery from extension is explained in terms of the lack of covalent linkings between the chains.[2,3]

More detailed information about the nature of the chain molecule is provided by F. O. Howitt and D. Coleman,[4] who have approached the problem from the chemical rather than from the physical angle. They give the most reliable values for the weight (in g.) of the various amino-acids obtained from 100 g. of dry fibroin as glycine 43·80, alanine 26·40,

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[1] "Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, 1942, p. 452.

[2] D. Entwistle, *J. Soc. Dyers and Col.*, 1946, **62**, 261; B., 1947, II, 9.

[3] C. Diamond, *J. Roy Soc. Arts*, 1946, **94**, 382; B., 1946, II, 282.

[4] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 144; B., 1947, II, 110.

serine 12·60, tyrosine 10·60, valine 3·20, glutamic acid 2·03, aspartic acid 2·0, proline 1·50, phenylalanine 1·50, threonine 1·50, *iso*leucine 1·37, arginine 1·05, lysine 0·88, leucine 0·80, histidine 0·47; fibroin does not contain amide-nitrogen and the mean residue weight (obtained by three different methods) is 78. Dissolution of silk in cupriethylenediamine solution followed by addition of acetic acid until the pH is about 8 and subsequent dialysis yields dispersed and water-soluble forms of fibroin which are not substantially modified. This conversion of fibroin into a water-soluble form is considered to be due to combination of cupriethylenediamine with imino-groups of the long chains; the hydrogen bonds between adjacent chains are broken down, and if neutralisation is delayed the chains coil or fold on themselves probably at places in the chain that are rich in tyrosine and proline. When the copper is removed by means of acetic acid the folded chains are free to link up with each other through ·CO and NH: groups which are now available. The molecular weight of the soluble protein as determined by osmotic pressure measurements is between 30,000 and 33,000. Films made from the soluble fibroin by evaporation (in vacuum over phosphorus pentoxide) of a thin layer of the aqueous solution on a clean mercury surface can be stretched, both stretched and unstretched films giving a β photograph. The stretched film is very much more robust, is insoluble in water, and is strongly birefringent when examined under crossed Nicols. These results arise presumably from an unfolding of folded molecules in the soluble fibroin and subsequent alignment of the chains: insolubilisation of natural silk by the silk worm is probably a similar process. Digestion of a clear solution of fibroin with trypsin results in the separation of a substance of molecular weight 8000—10,000 (approximately one third that of the parent fibroin), free from proline, and containing less than 1% of tyrosine. It must be concluded from this observation that the Bergmann-Niemann[5] hypothesis, which would imply that of the 420—430 amino-acid residues in the silk fibroin unit, the four proline and the 20 tyrosine residues are regularly spaced along the chain, does not apply to fibroin. It would appear that in fibroin all the proline and most of tyrosine are concentrated in regions of the chain about one third and two thirds along the length of the chain, and this is supported by the isolation of a peptide (serylprolyltyrosylproline) from fibroin hydrolysates.

The isoelectric point of the water-soluble fibroin (determined by the gold sol method) is pH 3·2,[6] a value which is considerably lower than those obtained by T. H. Morton[7] using ion-exchange methods. It is well known that the precise value of the isoelectric point depends on the ionic strength of the solution in which the determination is carried out, and values in 0·01M-, 0·1M-, and M-sodium chloride solutions are 4·74, 4·55, and

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[5] *J. Biol. Chem.*, 1938, **122**, 577; A., 1938, III, 210.

[6] C. J. Cadwallader and F. O. Howitt, *Trans. Faraday Soc.*, 1946, **42**, 642; A., 1947, I, 88.

[7] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 153; A., 1947, I, 52.

4·45, respectively. A similar figure (pH 4·35) was obtained by S. M. Neale and R. H. Peters[8] using the streaming potential technique in presence of mixtures of sodium chloride and hydrochloric acid which were 0·001N. with respect to the chloride ion.

Nylon.—The main chains in nylon, like those in silk, are fully extended and have short side-chains, which allow close packing. The usual melt-spinning process yields a thread containing disorganised chain molecules which is consequently highly extensible—extensibility at break is of the order of 300%.[9] When the fibre is cold-drawn its tensile strength increases to 4·6—5·1 g. per denier and its extensibility falls to 16—21%; these changes are due to orientation and alignment of micelles. There is ready flow in the random (undrawn) state but hydrogen-bonding forces supply sufficient drag between the chains to prevent slippage. The permanence of the cold-drawn fibre is said to be due to crystallisation which takes place while the fibre is under tension.[2]

Most commercial nylon is made from *cyclo*hexanol (made by hydrogenating phenol[10]) from which adipic acid and hexamethylenediamine are obtained.[11] Adipic acid may also be prepared[12] by the action of carbon monoxide on tetrahydrofuran at 270°/200 atm. in presence of nickel iodide as a catalyst and nickel carbonyl as a carbon monoxide carrier. If 0·005– 0·05% by weight of titanium oxide is incorporated in the fibre the number of breakages during cold-drawing is reduced[13] without delustring of the fibre; incorporation of larger amounts of oxide (0·1—5%) or other finely-divided pigment, however, delustres the fibre.[14] Heating the dry filaments under tension (400% extension) in a dry state in an inert medium (kerosene) strengthens them, by increasing the degree of orientation.[15] Lower water adsorption and greater stiffness, heat-stability, and resistance to fatigue are obtained[16] by treating with a one-stage alkali phenol-formaldehyde resin, washing, and heating until the resin is fully condensed. The interesting fact that the nylon fibre shows no hysteresis between adsorption and desorption of water is probably associated with the absence of side-chains in the chain molecule. At low R.H. undrawn nylon has a similar moisture content to drawn nylon,[9] which supports the view that drawing nylon results mainly in the alignment of disoriented micelles rather than in the formation of micelles by the alignment of molecules. Moreover, the heat of adsorption of water by oriented nylon is less than the corresponding value for the undrawn

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[8] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 159; cf. A., 1946, I, 388.

[9] J. B. Speakman and A. K. Saville, *J. Text. Inst.*, 1946, **37**, P271; B., 1947, II, 10.

[10] G. L. Clark, *Brit. Intelligence Objectives Sub-Commee.*, 1945, *Final Rept.* 743, *Item* 22

[11] J. W. Fisher, *ibid.*, *Final Rept.* 368, *Item* 22; B., 1946, II, 312.

[12] J. F. C. Gartshore, J. W. Fisher, and J. D. Rose, *ibid.*, *Final Rept.* 351, *Item* 22; B., 1946, II, 311.

[13] Imperial Chem. Industries, B.P. 576,647; B., 1946, II, 417.

[14] E. I. Du Pont de Nemours & Co., U.S.P. 2,205,722; B., 1946, II, 206.

[15] *Idem*, B.P. 573,081; B., 1946, II, 97.

[16] Imperial Chem. Industries, B.P. 576,102; B., 1946, I, 299.

fibres at high regains, but the reverse is true at low regains. Nylon swells in water much less than wool, but like wool it shows a much greater increase in diameter as the R.H. rises from 60% to 100% than when it changes from 0% to 60%. Longitudinal swelling is much less than lateral, indicating that the crystallites in nylon are long and thin; the average thickness is of the order of 112 A. The high crystallinity and the cohesion between the hydrophobic sections of the main chains are no doubt responsible for the rigidity of dry nylon being approximately three times that of nylon in saturated air (the rigidity of wool is increased 15 times by transferring it from saturated air to a dry atmosphere). As would be expected from its chemical constitution, the elastic properties of nylon are more or less independent of pH from pH 1 to pH 10·7.[9]

The starting material for the German product Perlon L is again *cyclo*hexanol, which is dehydrogenated over a zinc–iron catalyst at 420° and atmospheric pressure to yield *cyclo*hexanone[3, 17]; an oxime prepared from this by interaction with hydroxylamine sulphate at 70° is treated with sulphuric acid to form hexolactam, which polymerises when it is heated under pressure in presence of carbon dioxide. Filaments for ordinary textile uses and for brush making are prepared from the polymer by techniques similar to the usual melt-spinning. To facilitate stretching the hexolactam is spun with 5—6% of the monomer still present and the yarn is subsequently washed to remove this. The fibre has a tenacity of 5—6 g. per denier and an elongation of 20%.[17]

The properties of more complex polyamides are determined by the nature of their long chain units and the ability to pack together which is largely controlled by the size of the side-chains. A fibre of increased toughness and of tenancity greater than 4·5 g. per denier is produced[18] by melt-spinning a mixture of polyhexamethylene sebacate (5—10%) and polyhexamethylene adipimide. Another type of polymer is obtained[19] by heating hexamethylenediamine and γ-thiopimelic acid in a closed vessel under carefully controlled conditions, and wool-like fibres result[20] from condensation of $R(CH_2{\cdot}NH_2)_2$ and $R'(CH_2{\cdot}CO_2H)_2$ (where R and R′ are bivalent hydrocarbon radicals of at least 2 C) followed by suitable cold-drawing and permanent crimping.

Polyurethanes are a new and interesting addition to the synthetic fibres related to the proteins. Perlon U,[21] the most important of these, is made by condensing tetramethylene glycol and hexamethylenedicarbimide (prepared from hexamethylenediamine and phosgene in chlorobenzene solution); the fibre is spun at 195—200° under conditions which are carefully controlled to avoid converting the glycol or the polyurethane into tetrahydrofuran. As compared with those of Perlon L,

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[17] R. H. Boundy and R. L. Hasche, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXVI–53.

[18] E. I. Du Pont de Nemours & Co., B.P. 574,956; B., 1946, II, 163.

[19] *Idem*, B.P. 571,708; B., 1946, II, 11.

[20] *Idem*, U.S.P. 2,197,896; B., 1946, II, 11.

[21] G. P. Hoff and D. B. Wicker, *Field Information Agency, Technical, Final Rept*, 37.

the fibres (m.p. 178°) are stiffer and less sensitive to acids and water; they have a moisture regain approximately one third that of nylon, a lower tenacity than nylon (4·0—4·5 g. per denier), and are more suitable than is nylon for making brushes. Drawing is rather difficult because crystallisation occurs more rapidly than in nylon. Some of the defects of Perlon U might arise from its comparatively low molecular weight of 15,000 as compared with 18,000—23,000 for nylon, but this will probably be increased as a result of future work.

Wool.—Since the side-chains in wool are bulkier than those in silk and nylon, close packing of the main chains is difficult and the comparatively weak hydrogen-bonding forces result in a lower fibre strength. Moreover, the chains are regularly folded, at least in the more highly organised regions, so that wool is easily extended, while its power of recovery from large extensions is made possible by covalent cystine linkings. A. J. P. Martin's[22] study of the products of partial hydrolysis of wool is of great assistance in elucidating the precise arrangement of individual amino-acids comprising the chains. Wool is hydrolysed until the average chain length is about two amino-acid units and then, after removal of the hydrolysing acid, is separated by ionophoresis[23] into fractions which are examined chromatographically.[24]

Only the fraction carrying a nett negative charge has so far been examined, but 17 dipeptides involving aspartic and glutamic acids have been isolated from this fraction and identified. According to Martin,[22] the existence of such a large number of dipeptides disproves the Bergmann–Niemann[5] hypothesis and the presence of a number of polar–polar dipeptides, *e.g.*, glutamylglutamic and aspartylglutamic acids, after partial hydrolysis, is difficult to reconcile with W. T. Astbury's view[25] that amino-acid residues in the polypeptide chains of keratin are alternately polar and non-polar.

It is probable that the folded chains of α-keratin are capable of further folding once the more resistant side-chains have been broken, for animal fibres exhibit the phenomenon of supercontraction.[26] This occurs when stretched fibres are relaxed in dilute caustic soda solution, in water at various temperatures, or in steam, and then released in the same media. The *X*-ray photograph of fibres so contracted is either of the normal α type or of the partly disoriented *β* form, and the supercontraction is due to changes in the amorphous parts of the fibre, but the type of chain folding which takes place is governed still by considerations of internal energy[27] and is not of a random nature like that in rubber or in denatured proteins.

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[22] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 1; B., 1947, II, 109.

[23] R. Consden, A. H. Gordon, and A. J. P. Martin, *Biochem. J.*, 1946, **40**, 33; C., 1946, 198.

[24] *Idem, ibid.*, 1944, **38**, 224; C., 1945, 193.

[25] "Advances in Enzymology," 1943, **3**, 63.

[26] C. S. Whewell and H. J. Woods, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 50; B., 1947, II, 47.

[27] H. J. Woods, *Nature*, 1946, **157**, 229; *J. Colloid Sci.*, 1946, **1**, 407; A., 1947, I, 74.

In view of its importance in other connexions, the supercontraction which takes place when extended fibres are steamed for two minutes and then released in steam has received special attention. J. B. Speakman[28] has suggested that it occurs as a consequence of hydrolytic fission of disulphide linkings, which is promoted by the strained condition, for unstretched fibres treated similarly do not supercontract. H. Phillips,[29] however, who has shown that disulphide linkings in extended and unextended fibres react to the same extent when boiled in an alkaline buffer solution, believes that the strained hydrogen bonds between the chains are broken when the fibre is steamed.

Chemical treatment of unstretched fibres will cause them to contrac and apparently they do so if disulphide linkings are broken. Thus treatment under appropriate conditions with sodium bisulphite, caustic soda, sodium sulphide, potassium cyanide, silver sulphate,[28] or chlorine[30] will produce supercontraction, but if the disulphide linkings are first converted into more stable bonds, *e.g.*, by immersing the fibres in 0·1N-caustic soda solution for 10 hours, supercontraction is prevented.[26] Contraction in sodium bisulphite solution must differ in some way from that of stretched fibres, for the *X*-ray photograph of hair which has been boiled in sodium bisulphite solution shows the presence of highly disoriented chains with the β configuration even when the contraction is limited to 12% ; in severely treated fibres the photograph resembles that of a denatured protein. The *X*-ray photograph of fibres treated with caustic soda is comparatively unaltered when they are subsequently boiled in sodium bisulphite solution.[26]

The reaction between wool and sodium bisulphite is more complex[31] than was originally believed, for the total cystine in wool may be divided into four subfractions *A*, *B*, *C*, and *D* of differing chemical reactivity. *A* yields labile cysteine and *S*-cysteinesulphonate side-chains with sodium bisulphite solution, *B* yields water-stable cysteine and *S*-cysteinesulphonate side-chains, *C* is inert, and *D* decomposes only in hot sodium bisulphite solution, yielding combined α-aminoacrylic acid. H. Phillips[29,31] has examined the contraction which results when the various types of disulphide linkings are broken, and believes that the breaking of type *A* linkings is a necessary condition for supercontraction so that the fibre can swell through the salt linkings. Breaking of linkings of the *A* type seems to have a more profound effect on the physical properties of the fibres than breaking of *B* type linkings, for while fibres in which both types of linkings are broken supercontract readily, fission of type *B* alone does not result in shrinkage. In Phillips' view, supercontraction takes place only when the grids of the main chains of α-keratin have been separated and so made

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[28] *Nature*, 1933, **132**, 930 ; A., 1934, 203.

[29] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 39 ; B., 1947, II, 109.

[30] J. L. Stoves, *ibid.*, 58 ; B., 1947, II, 46.

[31] E. G. H. Carter, W. R. Middlebrook, and H. Phillips, *J. Soc. Dyers and Col.*, 1946, **62**, 203 ; B., 1946, II, 454.

free to coil. Weakening of cohesive forces by localised swelling and hydration or fission of linkings of types *A* and *B* are not sufficient, for supercontraction does not occur without agitation caused by an increase in temperature or by powerful swelling. In this connexion it is interesting to record that fibres supercontract in solutions of formamide[32] or phenol[33] at high temperatures, and also when heated at temperatures of about 120°.[34] Although keratin fibres do not supercontract in formic acid they become rubbery,[35] and it is significant that the rubber-like properties are due not to entropy effects in the backbone, but to the tendency of mutual attractions between side-chains to hold the fibre in a firm configuration—a state of affairs which is reflected in the absence of thermo-elastic effects. These findings are in agreement with those of H. J. Woods, who has given a preliminary account[27] of an investigation in which the contributions of changes in entropy and free energy are analysed.

The importance of main chains is also emphasised[26] by the contraction which occurs when fibres are immersed in ammoniacal solutions of copper hydroxide. Copper is absorbed and attractive forces are set up between the metal atoms and appropriate groups (probably :NH) in the main chains. There is an accompanying progressive weakening of the α photograph, which disappears completely at 30% supercontraction. The outstanding feature of this phenomenon is that when the copper is removed, *e.g.*, by acid treatment, the fibre returns to its original length and the α photograph returns. Relaxed fibres contract more quickly than do normal fibres, but show the same rate of recovery on removal of copper.

The phenomenon of set is closely related to that of supercontraction; the first stage in setting is considered by J. B. Speakman[36] to be fission of disulphide linkings, and this is followed by the formation of new linkings probably of the ·S·NH· type. This type of linking is also thought to be formed by interaction of free amino-groups and *S*-cysteinesulphonate residues when extended fibres are set by boiling in aqueous solutions of sodium bisulphite. It might be expected, therefore, that *S*-cysteinesulphonate residues would react with monomethylamine added to the setting medium, in which case subsequent acid hydrolysis of the wool would liberate monomethylamine. On carrying out this experiment, however, H. Phillips[29] and his colleagues were unable to detect any methylamine, and this fact, coupled with his finding that set may be obtained in fibres in which disulphide linkings of types *A* and *B* remain broken, has led Phillips to the view that reversible (hydrogen) bonds exist between the peptide grids. These must be intact before set can be realised and are strained by the act of stretching so that they are easily

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[32] E. Elöd and H. Zahn, *Kolloid Z.*, 1944, **108**, 94.

[33] H. Zahn, *Private communication.*

[34] E. Elod, H. Nowotny, and H. Zahn, *Textilber.*, 1944, **25**, 73.

[35] D. J. Lloyd, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 24; B., 1947, II, 46.

[36] *J. Soc. Dyers and Col.*, 1936, **52**, 335; B., 1936, 1033.

broken when stretched fibres are steamed. Under conditions of setting, their fission is followed by molecular readjustment or slippage and finally by their re-formation. They are disrupted by swelling initiated by the salt linkings, which is modified by the presence of intact disulphide or lanthionine linkings. Contrary to this view is the observation[37] that stretched fibres cannot be set by immersion in concentrated solutions of weak acids, followed by washing and drying, for under these conditions the hydrogen bonds should be broken and given an opportunity to re-form. As a result of an examination of the effect of urea solutions on fibrous proteins which yield the β X-ray photograph, K. M. Rudall[38] is also of the opinion that hydrogen bonding is of importance in setting. When supercontracted epidermis is treated with 50% aqueous urea solution, the xβ photograph is changed to the normal α. Transformation from the β photograph to the normal α is also observed when a wool fibre which has been extended 70% and set in boiling water for 5 minutes is immersed in saturated urea solution for 48 hours ; if the time of setting is increased to 30 minutes, the change is less complete. Rudall suggests that the setting of the β-keratin is due to locking of main chains by close fitting in the backbone direction ; since, however, the set released by urea is undoubtedly temporary set, the theory does not apply to the phenomenon of true permanent set.

Main chains are of particular importance in determining water absorption, the :CO groups being water-attracting.[39] According to G. A. Gilbert[40] there are defects in all the current theories[41] put forward to account for the water adsorption of textiles, and the familiar view that water absorbed by fibres is under considerable pressure is questioned by P. H. Hermans.[42] R. M. Barrer,[43] however, postulates sorption of water molecules on a limited number of sites in accordance with the Langmuir isotherm and a simultaneous but independent process of sorption by mixing of water and polymer chains, comparable, for example, with the imbibition of acetone by rubber. Although views on the mechanism of water absorption are many and varied, results of carefully planned experiments are lacking and until these are obtained, progress must remain slow and unsatisfactory.

In the light of our present knowledge the chemical reactivity of fibres appears to be concerned largely with side-chains, although possibly their importance in this respect is over-emphasised on account of the lack of suitable technique for breakdown of main chains. Alkalis convert the

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[37] J. B. Speakman, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 47.

[38] *Ibid.*, 15 ; A., 1947, III, 143.

[39] A. B. D. Cassie, *ibid.*, 86 ; B., 1947, II, 45.

[40] *Ibid.*, 96 ; B., 1947, II, 46.

[41] F. T. Pierce, *J. Text. Inst.*, 1929, **20**, T133 ; A., 1929, 1141. A. B. D. Cassie, *Trans. Faraday Soc.*, 1945, **41**, 450, 458 ; A., 1946, I, 19. S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309 ; A., 1938, I, 190.

[42] "Contributions to the Physics of Cellulose," Elsevier Publishing Co., Inc., 1946 ; *J. Polymer Sci.*, 1946, **1**, 149, 156, 162 ; B., 1946, II, 369.

[43] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 93 ; cf. B., 1947, II, 53.

cystine fraction ($A + B$) into lanthionine[29]—the presence of this acid in the treated fibres has been demonstrated[44] by partition chromatography—and subfraction A reacts more rapidly than B. Fractions C and D are converted by alkali into combined α-aminoacrylic acid, C reacting more slowly than D. Some cross-linking may also occur between the hydrolytic products of disulphide linkings and free amino-groups to yield linkings of the ·CH:N· type,[30] but although measurements of the supercontraction of alkali-treated fibres under various conditions support the presence of these linkings, it has not been demonstrated by analysis. According to A. Schöberl[45] the protein removed from wool by the action of an excess of 25% aqueous ammonia contains 4·5—5% of sulphur, probably present in the form of a thioether or in an oxidised form, but little cystine. When wool is treated with thiolacetic acid at pH 4·5 and 35°, subfractions A and B are reduced and again show different reactivities; in the reduced wool[29] A yields djenkolic acid with formaldehyde and reacts with methylene dibromide, while B is inert to the latter reagent and yields thiazolidine-4-carboxylic acid with formaldehyde. Subfractions C and D are reduced much more slowly under the same conditions. Using the reaction with calcium thioglycollate which causes reduction of disulphide linkings, M. Harris[46] has shown that when these ruptured linkings are subsequently methylated with methyl iodide to prevent them from reforming, the loss in cystine content is roughly proportional to the load required to stretch the wet fibres 25% of their original length. Similar changes have very little effect on the dry load unless a large number of cross-linkings are broken. Thus in the dry fibre secondary forces are very much more important than cross-linkings. The reaction between formaldehyde and wool is complex and is determined largely by conditions of temperature and pH, but apparently subfraction C is involved.[29] Oxidising agents probably attack the disulphide linking, and hydrogen peroxide also destroys amino-groups.[30] Some cysteic acid is produced during chlorination.[44] It is suggested[29,31] that the different reactivities of the sulphur linkings in wool arise from differences in their amino-acid environment; the more reactive fraction $A + B$ may be cross-linking main chains separated by polar side-chains and fraction ($C + D$) main chains separated by non-polar side-chains. The relative proportions of the various fractions may be altered.[47] For example, esterification of the free carboxyl groups of combined glutamic and aspartic acids does not affect the magnitude of the bisulphite-reactive fraction $A + B$, but causes the cysteine and S-cysteinesulphonate groups produced from A to become stable to rinsing in water like those produced from B.

Many reactions are affected by the morphological characteristics of the

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[44] R. Consden, A. H. Gordon, and A. J. P. Martin, *Biochem. J.*, 1946, **40**, 580; A. 1946, III, 564.

[45] *Biochem. Z.*, 1942, **313**, 214; B., 1945, II, 368.

[46] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 203; B., 1947, II, 46.

[47] H. Lindley and H. Phillips, *Biochem. J.*, 1947, **41**, 34.

fibre. When transverse sections of fibres from Kolinsky are treated for 2 hours with 5% caustic soda solution the cuticle is partly disintegrated whilst the cortex is completely dissolved [30] Medulla cells of fibres from Kolinsky, hares, and horses all resist the action of alkali and do not contain cystine. Similarly, when transverse sections of Kolinsky fibres are treated with Millon's reagent the medulla is deeply stained, but only a pink coloration develops in the cortex and cuticle. The action of dyes and of trypsin is equally selective, and there is clearly a great deal yet to learn about the various structural parts of animal fibres. Microscopic work of a very high order has been carried out by H. Reumuth,[48] who has prepared many photographs illustrating the structural complexity of wool and other animal fibres. The electron microscope is particularly useful in studies of this type and the results of preliminary investigations by E. H. Mercer,[49] and by E. Elod and H. Zahn,[50] are full of promise, as are those[51] on the distribution of heavy metal sulphides in fibres and their components. Of special interest is the finding by E. Lehmann[52] of an epidermal membrane of considerable mechanical strength under the scale layer of wool fibres.

Regenerated Protein Fibres.—M. Harris and A. E. Brown[46] consider that synthetic protein fibres are structurally more closely related to wool than to silk, because they are in general made from materials built up of amino-acids with bulky side-chains The molecules of globular proteins from which most regenerated protein fibres have been produced are approximately spherical and yield solutions of low viscosity. On denaturation there is an increase in viscosity, and the simultaneous development of streaming birefringence indicates an elongation of the molecule.[2] The solution of denatured protein is usually extruded into an acid bath containing a high concentration of sodium sulphate. Very little orientation is produced by stretching at this stage because of the ease with which the swollen fibres dissipate stress and hence it is advantageous to treat the fibres with a neutral aldehyde before stretching. Further stabilisation against the action of alkalis and hot liquids is also given by treatment with cross-linking agents.

The particular conditions employed in practice vary widely. Urea and dilute alkaline solutions have been used[53] to produce spinning dope from arachin (protein from peanuts), casein, and soya bean; C. B. Croston, C. D. Evans, and A. K. Smith[54] have suggested a process of frothing followed by aëration for zein solutions, and H. P. Lundgren[55] employs

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[48] *Klepzig's Textil-Z.*, 1942, *No.* 13/14, 288.

[49] *Austral. J. Exp. Biol.*, 1946, **24**, 147, 175; A., 1946, III, 927; B., 1947, II, 46.

[50] *Textilber.*, 1943, **24**, 157.

[51] E. Elöd, H. Nowotny, and H. Zahn, *Ber.*, 1941, **74**, [*B*], 1759; B., 1946, II, 42.

[52] *Kolloid Z.*, 1944, **108**, 6; B., 1946, II, 368.

[53] R. H. K. Thomson, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 173; B., 1947, II, 47.

[54] *Ind. Eng. Chem.*, 1945, **37**, 1194; B., 1946, II, 159.

[55] *Text. Res.*, 1945, **15**, 335.

detergents, *e.g.*, long-chain alkylsulphonates, in the preparation of spinning solutions from albumin and from chicken feather keratin. Dilute solutions containing protein and detergent cannot be used for rayon production for on dehydration with acetone the protein is precipitated from dilute solutions in a flocculent form; dehydration of concentrated solutions yields a fibrous protein as is revealed by electron microscopical examination. It is believed that a complex is formed by interaction between the basic groups of the protein and an ionic detergent, and that additional detergent is bound by non-polar forces. In the manufacture of fibres from egg white or from chicken feathers dispersed in 1% sodium bisulphite solution at pH 6·5, 40 parts by weight of protein are mixed with 40—60 parts of detergent (Nacconal NRSF—commercial alkylbenzenesulphonate) and the spinning solution contains 19—21% of solids and has a viscosity of 100—150 poises. The solutions are spun into a saturated solution of magnesium sulphate to which sulphuric acid is added to adjust the pH to 1—2. By suitable stretching during washing after precipitation a high degree of orientation is introduced and the fibres give a good *X*-ray photograph of the β type.

Accurate control of conditions is essential[53] in the production of all types of protein rayon, and modifications of technique continue to appear. Thus the freshly prepared solution of peanut protein in aqueous caustic soda solution of concentration not less than 0·8% but less than the optimum for fibre spinning at ordinary temperatures is stored[56] at 35—60° until it has attained a maximum viscosity and is then cooled to room temperature before spinning. Any tendency of protein solutions to gel is avoided[57] by dissolving the protein at pH 11—11·5 and precipitating at the isoelectric point before dispersing in dilute alkaline solutions at pH 8—8·5. In the production of Sarelon—an American fibre from peanut protein—it has been found[58] advantageous to add dibutyl tartrate, diglycol laurate, and oil to the spinning solution. Sugar[59] may be a component of spinning solutions of soya-bean protein, and satisfactory fibres are produced[60] from a mixture of this protein dispersed in an alkaline solution of compounds $RO{\cdot}SO_2M$ (R = alkyl, M = metal, *e.g.*, sodium or zinc) with 5—25 parts of viscose. An aqueous solution containing 13·0—16·5% of zein, caustic soda, formaldehyde, and urea is aged[54] for 72 hours prior to spinning into a bath containing sulphuric acid, acetic acid, and zinc sulphate. The German protein fibre, Marena, used in brush manufacture is made[61] from waste hides and skin, whilst fish protein may be prepared[62] for fibre production by heating fish at 60° for

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[56] Imperial Chem. Industries, B.P. 573,375 ; B., 1946, II, 43.

[57] *Idem*, B.P. 574,984 ; B., 1946, II, 204.

[58] A. L. Merrifield and A. F. Pornes, *Text. Res.*, 1946, **16**, 369.

[59] Showa Sangyo Kabushiki Kaisha, U.S.P. 2,198,538 ; B., 1946, II, 11.

[60] Tubize Chatillon Corp., U.S.P. 2,333,527 ; B., 1946, II, 249.

[61] K. S. Markley, *Field Information Agency, Technical, Final Rept.* 365.

[62] P. Laroso and A. C. Burton, *Brit. Intelligence Objectives Sub-Commee.*, 1945, *Final Rept.* 90; B., 1946, III, 178.

1 hour in 0·5% acetic acid solution and then soaking in 90% ethyl alcohol; the protein is then treated with carbon disulphide and dissolved in viscose solution.

Protein fibres may also be prepared by the dry-spinning technique, *e.g.*, from a solution[63] of zein, urea, and formaldehyde in ethylene formal and methyl alcohol, and in this method homogenisation in a drum mill[64] fitted with stainless steel beating rods followed by filtering under pressure and de-aëration is claimed[65] to be advantageous when carried out at 40—60°. Fire-resistant casein fibres are produced[66] when sodium silicate is added to the usual casein dope and the mixture is extruded into an acid bath containing acetic acid and calcium chloride, thereby forming calcium silicate in the fibres.

Wet strength and resistance to attack by hot liquids may be improved by treatment[67] of the fibres with chromium, zinc, cadmium, or mercury compounds, usually basic salts; the water imbibition is also decreased and *X*-ray photographs of treated casein fibres suggest that the metal is in the main attached to the side-chains, although there is some adsorption of cadmium and zinc compounds in fibre interstices. Zinc is preferred to other metals as it does not colour the fibre. An alternative technique consists[68] in treating dry fibres with a gaseous hardening agent such as formaldehyde vapour, neutralising, stretching at 35—65°, and then giving a second hardening treatment in a liquid, *e.g.*, an alkaline solution of chrome alum. R. Signer[69] also hardens fibres with a gaseous reagent, by applying a suitable cross-linking agent dissolved in an organic solvent, or by adding compounds such as polyoxymethylene or hexamethylenetetramine to the spinning solution and forming an effective cross-linking agent by subsequent heating. Another procedure suggested by this author[70] is to treat dry-spun casein fibres at 18—20° with gaseous aldehydes in an atmosphere of 33—66% R.H., *e.g.*, by use of 38% aqueous formaldehyde which is saturated with sodium chloride or mixed with 20% of its weight of fused calcium chloride. Immersion of relaxed fibres insolubilised by acid formaldehyde in concentrated aqueous formaldehyde solution of pH 9—10 for 30—45 minutes also causes[71] an increase in strength. Acetylation of synthetic protein fibres is claimed to improve their properties and is made use of in the production of Aralac. Although it is customary to measure the effectiveness of hardening treatments by direct determinations of wet strength and solubility, the new spreading

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[63] Celanese Corp. of America, U.S.P. 2,331,434; B., 1946, II, 45.

[64] R. Signer, B.P. 573, 888; B., 1946, II, 86.

[65] *Idem*, B.P. 573,865; B., 1946, II, 118.

[66] S. P. Gould and E. O. Whittier, U.S.P. 2,204,336; B., 1946, II, 118.

[67] F. Happey and R. L. Wormell, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 160; B., 1947, II, 47. Courtaulds Ltd., B.P. 573,015; B., 1946, II, 43.

[68] R. Signer, B.P. 570,572; B., 1945, II, 341.

[69] B.P. 573,432; B., 1946, II, 86.

[70] B.P. 576,007; B., 1946, II, 249.

[71] Imperial Chem. Industries, B.P. 579,588; B., 1946, II, 417.

technique of L. Maaskant[72] should be useful for obtaining more accurate figures.

THE TECHNOLOGY OF PROTEIN FIBRES.

Scouring.—Most fabrics need scouring but the process should result in the least possible adverse modification of desirable properties of the fabric. For this reason some workers favour scouring wool fabrics at pH 7 with synthetic detergents. Prior to the war the most common impurities in wool fabrics were neutral fatty oils and fatty acids added to facilitate spinning and combing, but shortage of natural fats has led to an increased interest in the use of mineral oils, which are available in large quantities and also have the advantage of being stable to oxidation when exposed in thin films to air ; moreover they are not liable to spontaneous heating,[73] and in this connexion a new form of Mackey tester[74] in which the metal cylinder is replaced by a spiral of lead-free glass and the cotton by rayon staple is of interest. The main disadvantage of the use of mineral oil as a lubricant for wool is the difficulty of its subsequent removal, which arises from its high interfacial tension against detergent solutions and its high adhesion for wool. These are attributed by J. B. Speakman[75] to the non-polar character of mineral oil, and he has put forward the view that blending a suitable polar compound with mineral oil would increase the ease of removal. This is confirmed by the relative ease with which a blend of 7% of oleyl alcohol and 93% of mineral oil is removed by the ordinary scouring technique. Oleyl alcohol is not, however, wholly acceptable and the search for an ideal polar compound continues. According to A. C. Goodings and H. B. Marshall[76] a mineral oil (η^{38} 50—250 sec. Saybolt) which contains 5—20% of the product obtained by partial esterification of polyhydric alcohols with naphthenic acid, *e.g.*, glycerol mononaphthenate, is readily removed. Other monoglycerides, *e.g.*, that of oleic acid, are also effective[77] in facilitating removal of mineral oil, as is addition of an Emulphor (a condensation product of oleic acid with ethylene oxide[78]). Two oils containing this reagent have been used in Germany[79] throughout the war, viz., one, containing 10% of Emulphor, for rag pulling and another, containing 30% of Emulphor, for spinning, and both of these are removed by scouring in 5% sodium carbonate solution. Polar compounds also assist[80] in the removal of chlorinated paraffins. Mixtures of hydrocarbons and sulphonated hydrocarbons have

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[72] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 105 ; B., 1947, II, 47.

[73] B. R. Vickers & Sons Ltd., *Hosiery Times*, 1946, **19**, *No.* 203, 35.

[74] S. Schmidt-Nielsen and L. Eikeland, *Kgl. Norske Videnskab. Selskab. Forh.*, 1942, **15**, 127.

[75] *Trans. Faraday Soc.*, 1933, **29**, 358 ; B., 1933, 298.

[76] U.S.P. 2,336,087 ; B., 1946, II, 247.

[77] A. C. Goodings and H. B. Marshall, *Canad. Text. J.*, 1945, **62**, *No.* 24, 44.

[78] W. Baird, *Brit. Intelligence Objectives Sub-Commee*, 1945, *Final Rept.* 421, *Item* 22.

[79] C. B. Brown, *ibid.*, *Final Rept.* 418, *Item* 22.

[80] Imperial Chem. Industries, B.P. 574,828 ; B., 1946, II, 163.

been suggested[81] as wool lubricants, and they have the added advantage of being able to facilitate subsequent milling. Higher fatty acid esters of an ether condensation product of ethylene oxide with a polyhydric alcohol or sugar are also useful as textile lubricants.[82]

Certain fabrics which become distorted during scouring and dyeing are set[83] before scouring by winding on to a roller and boiling in water or in slightly alkaline solutions. Unless this process is carefully controlled, considerable damage will result and if the desired degree of set can be obtained at pH 6 it is advisable to maintain the pH in this region.[84] Many nylon fabrics, particularly hose, also require setting,[85] but this does not take place on simply boiling in water or in solutions of caustic soda, borax, sodium bisulphite, or sodium sulphite; it is necessary to treat the fabrics with wet steam at 115—126° for about 5 minutes.[85]

Felting of Wool and Related Fibres.—Wool and animal hairs are distinguished from other fibres by their ability to felt, which forms the basis of the felt industry and of many typical wool finishes. A summary of present-day views on this complex process presented by M. R. Freney[86] shows that in spite of considerable progress it is as yet imperfectly understood. Scaliness or, more precisely, scale effectiveness, the elastic properties of the fibres, and the freedom of movement of the fibres have been recognised as important factors determining the ease of felting, but M. R. Freney, K. R. Deane, and J. R. Anderson[87] have suggested that the tendency of wool fibres to twist especially on being transferred from an atmosphere of ordinary R.H. to one of saturated air may also play a part. Ability of fibres to curl is also considered[88,89] to promote felting.

The felting of wool becomes a source of trouble in the production of dimensionally stable wool fabrics. Simple relaxation shrinkage can be prevented by careful control of finishing procedure, but chemical treatment is necessary to prevent felting.[90] Wet chlorination is still popular and has the advantages of being cheap and requiring no special apparatus, although often it results in uneven treatment as revealed by the Kiton Red[91,92] or indigo-carmine test. The Wool Industry Research Association dry chlorination with chlorine gas and the papain process are more satisfactory as they are more easily controlled. The latter process has given rise to the "perzyme" finish[90] in which fabric is treated with hydrogen peroxide before treatment with papain, and to the "chlorzyme"

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[81] E. I. Du Pont de Nemours & Co., U.S.P. 2,387,510.

[82] Amer. Viscose Corp., B.P. 575,531; B., 1946, II, 204.

[83] *Dyer*, 1946, **95**, 305, 355.

[84] C. S. Whewell and D. M. Bee, *J. Soc. Dyers and Col.*, 1946, **62**, 178; B., 1946, II, 335.

[85] E. B. Abbott, *Text. Manufr.*, 1946, **72**, 207.

[86] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 178; B., 1947, II, 54.

[87] *Nature*, 1946, **157**, 664; B., 1947, II, 78.

[88] G. Berg, *Textilber.*, 1944, **25**, 110, 145, 183, 221; B., 1946, II, 200.

[89] M. Harris, *Amer. Dyestuff Rep.*, 1945, **34**, 72.

[90] H. Phillips, *J. Text. Inst.*, 1945, **37**, P302; B., 1947, II, 9.

[91] E. G. H. Carter and R. Consden, *ibid.*, 1946, **37**, T227.

[92] W. L. Semple, *ibid.*, T260.

finish which refers to dry-chlorinated wool after-treated with papain. The fibres so produced are without scales and are soft with a silk-like gloss; they make excellent filling for quilts and cushions. Alkalis dissolved in various solvents[93,94] and sulphuryl chloride[95] in white spirit have also been used commercially during the war for making knitted fabrics unshrinkable, while patent protection has been secured for processes involving treatment with fluorine,[96] stannous salts either alone[97] or followed by alkaline hypochlorites, or by nitrogen-containing compounds such as nitrogen trichloride,[98] various oxidising agents, *e.g.*, acid potassium permanganate,[99] or hydrogen peroxide,[100] reducing agents including sodium sulphide,[101] and thio-alcohols.[102]

All the above processes reduce the effectiveness of the scale in promoting unidirectional fibre movement, but detailed study reveals differences in their mode of action. M. Lipson and P. Howard,[103] for example, have measured coefficients of friction (μ_2 with and μ_1 against the scales) between a cylinder of horn and wool fibres subjected to various non-shrink processes. Treatment with sulphuryl chloride in carbon tetrachloride solution, caustic potash in alcohol, aqueous bromine or chlorine, or chlorine dissolved in carbon tetrachloride decreases the directional frictional effect (D.F.E.), *i.e.*, $(\mu_1 - \mu_2)/(\mu_1 + \mu_2)$, and this is also reduced when the horn is treated with the reagents and the fibres are left untreated. The actual values of μ_1 and μ_2 are of importance: μ_2 is increased by the treatment with halogens and sulphuryl chloride, but alcoholic alkali causes both μ_1 and μ_2 to increase. The D.F.E. has been ascribed[104] to the ratchet-like surface of the wool fibres and to a particular[105] chemical composition of the surface; both properties are no doubt important, but the results of the above experiment are considered to emphasise the part played by surface orientation. E. H. Mercer[106] believes that chemical bonding occurs between acid and basic groups of the peptide chains of different fibres in contact and that the D.F.E. is due to these linkings being more easily sheared in one direction than in the other; increases in the values of μ_1 and μ_2 are attributed to an increased number of free active surface groups. The significance of the part played by the gross structure is illustrated by the fact[107] that the D.F.E. is not reduced when fibres are

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[93] Tootal Broadhurst Lee Co., B.P. 538,396; B., 1941, II, 385.

[94] M. R. Freney and M. Lipson, *Counc. Sci. Ind. Res. Austral.*, 1940, *Pamph.* 94, 7, 25; B., 1940, 434.

[95] A. J. Hall, W. N. Hicking, and S. J. Pentecost, B.P. 464,505; B., 1938, 1150.

[96] Wolsey Ltd., B.P. 578,499; B., 1946, II, 420.

[97] Tootal Broadhurst Lee Co., B.P. 541,965; B., 1942, II, 109.

[98] Stevensons (Dyers), Ltd., B.P. 570,582; B., 1945, II, 344.

[99] Wolsey Ltd., B.P. 586,020.

[100] Bleachers' Assoc., B.P. 553,923; B., 1943, II, 286.

[101] *Idem*, B.P. 539,057; B., 1941, II, 385.

[102] E. I. Du Pont de Nemours & Co., B.P. 572,041; B., 1946, II, 50.

[103] *J. Soc. Dyers and Col.*, 1946, **62**, 29; B., 1946, II, 123.

[104] J. B. Speakman, *J. Text. Inst.*, 1941, **32**, T83; B., 1941, II, 376.

[105] A. J. P. Martin, *J. Soc. Dyers and Col.*, 1944, **60**, 325; B., 1945, II, 76.

[106] *J. Counc. Sci. Ind. Res., Australia*, 1945, **18**, 188; B., 1946, II, 41.

[107] H. M. S. Thomson and J. B. Speakman, *Nature*, 1946, **157**, 804; B., 1947, II, 7.

coated with a thin film (0·03 μ. thick) of silver or gold even though the chemical character of the surface layer has been completely altered, but is reduced when the film is made sufficiently thick to cover the gross imbrications. The precise action of the scales in promoting shrinkage is not clear, but K. M. Rudall[108] suggests that soft rubber-like outer edges on the scales determine fibre movement. Non-shrink treatments may remove these without causing general damage to the scales as a whole and electron photomicrographs of the scales of fibres treated with alcoholic potash confirm[109] this view. This softening of the extremities of the scales is probably due to attack of disulphide linkings and has given rise to the generalisation[110] that any reagent which can break these linkings and is incapable of forming new cross-linkings between main chains will, if applied under such conditions that its action is restricted to the surface, make wool fabrics unshrinkable. Further support of this view is provided by the results of an investigation on the action of fluorine on wool[111]; under suitable conditions (dry fluorine on dry wool) fabrics are made unshrinkable by treatment with 0·5—1% of fluorine and purely chemical evidence is given in favour of a simple reaction in accordance with the equation·

$$R{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}R' + 7F_2 \rightarrow R{\cdot}CH_2F + 2SF_6 + R'{\cdot}CH_2F$$
$$(R \text{ and } R' = \text{peptide chains}).$$

10—25% aqueous hydrogen fluoride also produces[111] some reduction in felting which is attributed to attack on main chains. It is interesting that knitted fabrics treated with fluorine or with acid solutions of potassium permanganate do not shrink when milled in alkaline solutions, although they shrink on acid milling.[112] Moreover, there are corresponding changes in the D.F.E. measured by the violin bow method. No satisfactory explanation of this phenomenon has yet been offered, but it is possible[113] that differences in swelling of the degraded protein in the acid and alkaline media play a part. Further, under conditions employed by P. Alexander,[112] treatments with alkaline sodium hypochlorite solutions, aqueous bromine, or bromine in carbon tetrachloride confer complete resistance to alkali milling but only partial resistance to acid milling, whereas chlorine gas, solutions of chlorine in carbon tetrachloride or in water, sulphuryl chloride, and alcoholic potash produce complete resistance to both acid and alkali milling.

Resin-treated wool fabrics are often unshrinkable either because of reduced scaliness due to masking of the scales by a film of resin or of

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[108] *Private communication*, quoted by J. B. Speakman, N. H. Chamberlain, and J. Menkart, *J. Text. Inst.*, 1945, **36**, T91; C., 1946, 88.

[109] E. H. Mercer and A. L. G. Rees, *Nature*, 1946, **157**, 589.

[110] J. B. Speakman, *J. Roy. Soc. Arts*, 1945, **93**, 603; B., 1946, II, 8.

[111] R. F. Hudson and P. Alexander, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 193; B., 1947, II, 54.

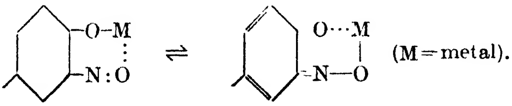
[112] P. Alexander, *ibid.*, 199; B., 1947, II, 54.

[113] J. B. Speakman, *ibid.*, 202.

modified elastic properties due to internal deposition of resin. When dicarbimides[114] are applied to a fabric under conditions which yield unshrinkability some of the carbimide is converted into a diamine which copolymerises with the unchanged dicarbimide, forming a surface film over the scales. Alternate treatments with dicarbimide and diamine give better results, as does application of 5% by weight of a mixture of dicarbimide and diamine from solution in benzene, followed by baking for 1 hour at 100°.

Deposition of polymers in wool to modify elastic properties may be carried out successfully by treatment with dispersions of monomers in presence of catalysts. For example, cloth is made unshrinkable[115] by immersing in 0·2% ferrous sulphate solution, squeezing, drying, and treating with an aqueous solution of methyl methacrylate containing hydrogen peroxide for 1—2 hours at 95—100°. Impregnation with non-polymerised alkylated melamine-formaldehyde resins[116] followed by baking also reduces the shrinkage of wool fabrics. In the Lanaset[117] treatment, a fabric is impregnated with a solution of methylated methylolmelamine and an acid catalyst, squeezed, dried, and baked at 140°, and 10% of polymer deposited within the fibres gives a high degree of unshrinkability. According to J. R. Dudley and J. E. Lynn,[118] fabrics containing sufficient urea resin to make them resistant to shrinking are stiff and boardy, phenol resins yield dark colours, guanidine resins are too difficult to make, thiourea and vulcanisable vinyl resins usually turn brown, and normal vinyl resins are difficult to apply with the necessary degree of control.

Dyeing.—Several new commercial colours have been made available[119] during the year under review and a new method[120] of obtaining fast shades on wool and silk has been evolved, which consists in forming coloured metal complexes in the fibres by treating them first with nitrites and then with metallic salts. The reaction takes place on the tyrosine residues with the formation of an *o*-nitroso-derivative which chelates with metal atoms to form a derivative of the following structure :



A variety of colours may also be produced by after-treatment with complex-forming compounds such as dimethylglyoxime. The proposed

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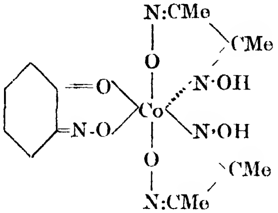
[114] T. Barr, C. W. Capp, and J. B. Speakman, *J. Soc. Dyers and Col.*, 1946, **62**, 338.
[115] M. Lipson and J. B. Speakman, *Nature*, 1946, **157**, 590.
[116] Amer. Cyanamid Co., U.S.P. 2,329,622 ; B., 1946, II, 168.
[117] J. E. Lynn, *Amer. Dyestuff Rep.*, 1944, **33**, 554 ; B., 1946, II, 166.
[118] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 215 ; B., 1947, II, 53.
[119] *J. Soc. Dyers and Col.*, 1946, **62**, 35, 53, 220, 294.
[120] B. Nilssen, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 142; B., 1947, II, 110.

mechanism of this reaction is illustrated by interaction of the cobalt metal residue with dimethylglyoxime yielding the compound :



The problem of the union between dyes and fibres has been attacked from several angles, involving measurement of the amount[121,122] and rate[123] of adsorption of dyes and dye acids by fibres at various pH values and temperatures, *X*-ray studies of dyed fibres,[124] and the study of the effect of dyeing on the elastic and setting properties of fibres.[125] The results of many of these investigations and of mathematical analyses[126,127] of the data indicate that combination of acid dyes with wool takes place by association of protons and dye anions with the NH_3^+ and COO^- of the salt linkings, the extent of combination at any particular pH value being dependent on the intrinsic affinities of the protons and the anions. Combination is probably stoicheiometric,[128] for the combining capacity of wool for colour acid is approximately the same as for hydrochloric acid, implying that all amino-groups in the fibre are accessible to the dye. According to *X*-ray examination of the dyed fibres, however, which does not reveal any distortion of the α photograph, dye does not enter into the crystalline part of the fibre, but since the setting properties of the dyed fibres are impaired it would appear that hydrogen ions penetrate into it. To reconcile these facts it is suggested[128] that as the hydrogen ions penetrate into the micelles they leave an equivalent number of dye anions on the micellar surface : this is probably accompanied by a subdivision of the micelles, for the swelling of wool fibres in anthraquinone-2-sulphonic acid at pH 1·08 is very much greater than in hydrochloric acid at the same pH value.

The rate of dyeing is intimately connected with diffusion characteristics, and this aspect of dyeing has been treated mathematically by R. M.

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[121] J. Steinhardt, C. H. Fuggitt, and M. Harris, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 293 ; B., 1941, II, 338 ; *ibid.*, 1942, **29**, 417, 425; B., 1944, II, 253, 254.

[122] F. L. Goodall and C. Hobday, *J. Soc. Dyers and Col.*, 1942, **58**, 36 ; B., 1942, II, 193.

[123] J. B. Speakman and S. G. Smith, *ibid.*, 1936, **52**, 121 ; B., 1936, 691.

[124] W. T. Astbury and J. A. T. Dawson, *ibid.*, 1938, **54**, 6 ; B., 1938, 502.

[125] G. H. Elliott and J. B. Speakman, *ibid.*, 1943, **59**, 124 ; B., 1943, II, 252.

[126] G. A. Gilbert and E. K. Rideal, *Proc. Roy. Soc.*, 1944, **182**, **A**, 335 ; A., 1944, II, 248.

[127] G. A. Gilbert, *ibid.*, **183**, **A**, 167 ; A., 1945, I, 223.

[128] J. B. Speakman and G. H. Elliott, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 116.

Barrer.[129] The precise amount of dye absorbed under practical dyeing conditions is affected by the type of fibre,[130] any chemical treatment which the fibre has undergone, and the nature of the dye. Determinations of titration curves with hydrochloric acid, affinities for Naphthalene Orange G, and isoionic points[131] show that wool damaged by alkali, hydrogen peroxide, or chlorine absorbs dye more rapidly than untreated wool, due to increased swelling promoted by fission of sulphur linkings; carbonising decreases the amount of dye absorbed by formation of cross-linkings of the sulphamide type with consequent reduction of the number of sites available for the dye. Stoved wool[132] dyes more slowly than unstoved, and treatment with formaldehyde, which reacts with amino-groups, reduces the rate of dyeing. The rate of dyeing of wool is increased as a result of treatment with hydrogen peroxide, although the amount of dye taken up is reduced by the fall in the number of free amino-groups. Impregnation with resins reduces the rate of dyeing, and an excellent resist against acid dyes may be obtained[133] by forming an acid polymer (polymethacrylic acid) within the wool fibres. The magnitude of the differences in dyeing properties between modified (by weathering, carbonising, or chlorinating) and normal wool depends[134] on the type and constitution of the dye, a fact of particular significance when choosing dyes for unions or for chemically treated fibres.

Investigation of the dyeing of wool with chrome dyes is complicated by the complexity of the reactions involved. At 0° chromic acid behaves[135] as a weak monobasic acid, the anions having a marked affinity for wool. When wool is boiled in potassium dichromate, $HCr_2O_7^-$ ions, combine with the wool; the pH value of the liquor consequently rises and there is attack on disulphide linkings. This gives rise to hydrogen sulphide and reducing groups which reduce the chromium in the bath and on the fibre to the tervalent state. Addition of ammonium sulphate to the bath keeps the pH value sufficiently low to prevent disulphide bond fission, and any oxidation of these linkings by direct attack of chromate ions may be minimised by chroming in presence of ammonium salts of easily reduced acids. The complex[136] formed on the fibre when wool is dyed with 4-chloro-2-aminophenol-6-sulphonic acid → β-naphthol, 3 : 4 : 6-trichloro-2-aminophenol → 1-benzamido-8-naphthol-4-sulphonic acid (alkaline coupled) (I), or Metachrome Brilliant Blue BL by the on-chrome or afterchrome processes have two molecules of dye associated

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[129] *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 108; B., 1947, II, 53.

[130] A. N. Patterson, *Rayon Text. Month.*, 1944, **25**, 465, 511, 567; B., 1946, II, 47.

[131] D. R. Lemin and T. Vickerstaff, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 129.

[132] R. H. Kienle, G. L. Royer, and H. R. McCleary, *Rayon Text. Month.*, 1945, **26**, 408, 482, 541; B., 1946, II, 121.

[133] M. Lipson and J. B. Speakman, *Nature*, 1946, **157**, 736.

[134] F. Townend and G. G. Simpson, *J. Soc. Dyers and Col.*, 1946, **62**, 47; B., 1946, II, 165.

[135] P. W. Carlene, F. M. Rowe, and J. B. Speakman, *ibid.*, 331.

[136] E. Race, F. M. Rowe, and J. B. Speakman, *ibid.*, 372.

with one atom of chromium. In the case of (I) the complex is probably a tribasic acid and combination appears to occur through amino-groups in the fibre and chromium and sulphonic groups in the complex.

Casein fibre (Fibrolane) has an affinity for those acid and mordant dyes used on wool, as well as for many which are usually applied to cellulosic fibres, *e.g.*, sulphur and vat colours, but C. P. Tattersfield[137] has emphasised many important differences in the practice of dyeing wool and Fibrolane. According to J. Boulton,[138] who has provided extensive data on the adsorption and fastness of many types of dye, the combination between nylon and dye is by attachment through salt linkings and through residual valencies. Direct colours are absorbed by nylon at a rate which is greatly increased by decrease in pH, and the presence of neutral salts increases the rate and degree of exhaustion from both acid and neutral baths. The dyed fibres show dichroism when examined in polarised light, and are not unduly degraded by exposure to light, although vat-dyed nylon is seriously damaged. Oxygen appears to be necessary for photodegradation but the dyes fade in presence or absence of oxygen. Protection against light-tendering is, however, obtained[139] by formation of a pyrocatechol–formaldehyde resin inside the fibres. The affinity of nylon for direct colours is increased[140] by impregnation with acid solutions of condensation products of cyanamide or its derivatives and formaldehyde, drying, and heating at 140° for 10 minutes, while fabrics of nylon and other fibres which contain amino-groups may be dyed[141] with acid dyes in presence of water-soluble carboxyl or sulphonic acids which have an affinity for the fibres.

Miscellaneous Chemical Treatments and Testing.—It is not possible in the space available to deal adequately with these topics and only the chief items are mentioned. Wool fabrics are made resistant[142] to attack by bacteria by impregnation with an ammoniacal solution of copper chromate containing Perminal PW, followed by rinsing in running water and drying at 60°, and they may be mothproofed by application of guanidine pentachlorophenoxide,[143] DDT,[144,145] Gammexane,[144] or 1 : 2 : 4-thiodiazole.[146] New finishes on nylon include waterproofing with any of the standard reagents followed by friction calendering at 100—170° which gives[147] the material a translucent finish, local delustring by printing with a solution

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[137] *Soc. Dyers and Col., Symp. Fibrous Proteins*, 1946, 167.
[138] *J. Soc. Dyers and Col.*, 1946, **62**, 65, 77 ; B., 1946, II, 205.
[139] E. I. Du Pont de Nemours & Co., B.P. 572,136.
[140] Courtaulds Ltd., B.P. 570,602 ; B., 1945, II, 343.
[141] Gen. Aniline & Film Corp., U.S.P. 2,325,972 ; B., 1945, II, 343.
[142] E. Race, *Soc. Dyers and Col. Symp. Fibrous Proteins*, 1946, 67; A., 1947, III, 174
[143] Amer. Cyanamid Co., U.S.P. 2,377,167.
[144] H. Wahl, *Chim. et Ind.*, 1945, **53**, 167 ; B., 1946, II, 282.
[145] F. L. Goodall, T. F. Gordon, and J. V. Summersgill, *J. Soc. Dyers and Col.*, 1946, **62**, 189 ; B., 1946, II, 419.
[146] E. I. Du Pont de Nemours & Co., B.P. 559,260; B., 1944, III, 91.
[147] Imperial Chem. Industries, B.P. 577,433 ; B., 1946, II, 336.

of a metallic inorganic salt (calcium chloride) in a lower fatty alcohol,[148] and crêping fabrics containing nylon and cellulose in a reagent which causes the cellulosic component to shrink but does not affect the nylon.[149]

Satisfactory cloth processing is possible only when control is adequate, and it is in this connexion that testing[150] methods find an important application. Various new techniques[91,92,151] for assessing damage in wool materials, resistance to abrasion,[152] and water-repellency[153] are useful additions to those methods already available and critical investigations on some of the well-known[154] tests, *e.g.*, resistance to abrasion,[155] are to be welcomed. The results of studies[156] of fundamental properties of fabrics should also help to emphasise the scientific aspects of cloth building and so facilitate the designing of cloths for special purposes.

Finally, mention should be made of the publication during the year of a great wealth of information on German auxiliary products[78,79,157] used in textile processing—wetting, emulsifying, and waterproofing agents, soap substitutes, reagents for dispersing lime soaps, finishes for rayon, etc. Many of these were familiar to British dyers and finishers before the war and patent specifications relating to their manufacture have been described in previous issues of these Reports,[158] but precise details of their composition and method of preparation have not until now been available.

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[148] Imperial Chem. Industries, B.P. 574,785 ; B., 1946, II, 168.

[149] Brit. Nylon Spinners, B.P. 576,050 ; B., 1946, II, 206.

[150] L. Fourt, B. A. Holgate, C. W. Schoffstall, F. M. Steadman, and A. M. Viditz-Ward, *Field Information Agency, Technical, Final Rept.* 466 ; W. Baird, C. B. Brown, and G. R. Perdue, *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 518, *Item* 22.

[151] E. Elod and H. Reutter, *Textilber.*, 1940, **21**, 346 ; C., 1946, 88. A. Schöberl, *Collegium*, 1941, 177 ; B., 1946, II, 83.

[152] F. R. Dean, *J. Text. Inst.*, 1946, **37**, P380. W. J. Hamburger, *Text. Res.*, 1945, **15**, 169. A. C. Walker and P. S. Holmstead, *ibid.*, 201.

[153] S. Baxter and A. B. D. Cassie, *J. Text. Inst.*, 1945, **36**, T67 ; C., 1946, 88.

[154] H. E. Wilde, *Rayon Text. Month.*, 1944, **25**, 466 ; C., 1946, 21. M. Nopitsch, *Textilber.*, 1944, **25**, 172, 207, 243, 276 ; C., 1946, 87. D. Frishman, R. L. Smith, and M. Harris, *Text. Res.*, 1946, **16**, 160.

[155] T. R. Dawson, *J. Rubber Res.*, 1946, **15**, 65 ; C., 1946, 166.

[156] W. H. Rees, *J. Text. Inst.*, 1946, **37**, P132 ; A. B. D. Cassie, *ibid.*, P154 ; W. H. Dutton, *ibid.*, P212 ; G. E. Collins, *ibid.*, P392; B., 1947, II, 8, 9.

[157] J. Avery and W. Burger, *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 710, *Item* 22. H. D. MacMurray and H. C. Raine, *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 364, *Item*, 22. E. Mather, *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 667, *Item* 22. G. D. Jackson, *Field Information Agency, Technical, Final Rept.* 556. W. A. M. Edwards and J. H. Clayton, *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 422, *Item* 22. D. Traill, *Field Information Agency, Technical, Final Rept.* 170. W. Baird, *Brit. Intelligence Objectives Sub-Commee., Final Repts.* 239, 259, 420, 478, *Item* 22. R. E. Richardson, J. G. Kern, R. L. Murray, and R. W. Sudhoff, *Combined Intelligence Objectives Sub-Commee., Item* 22, *File* XXVI–2 ; B., 1946, II, 447. G. R. Perdue, *Brit. Intelligence Objectives Sub-Commee., Final Repts.* 436, 547, *Item* 22. D. Traill and S. Brown, *Field Information Agency, Technical, Final Rept.* 486. R. J. Ozol and C. C. Chaffee, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXX–10 ; B., 1946, II, 447. J. G. Kern, R. L. Murray, and R. W. Sudhoff, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXVI–63 ; B., 1946, II, 448.

[158] *Ann. Repts.*, 1934, **19**, 212 ; 1935, **20**, 221 ; 1936, **21**, 217 ; 1937, **22**, 220 ; 1938, **23**, 212 ; 1939, **24**, 169.

CELLULOSE TEXTILE CHEMISTRY.

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The Structure and Constitution of Cellulosic Materials.

The fine structure of cellulose continues to attract the attention of many workers, principally in order to obtain a better understanding of the relationship between fibre structure and physical properties for the natural cellulosic fibres and the regenerated cellulose rayons.

The molecular orientation of cotton fibres in relation to their tensile properties has been investigated by R. Meredith,[1] using the physical approach through double refraction. Correlation was found between tensile strength, initial Young's modulus, and double refraction for many varieties of raw cotton fibre. The angles of the spiral fibrils calculated from the refractive indices ranged from 27° for fine Sea Island to 35° for coarse Indian cotton and values of initial Young's modulus were found to be inversely proportional to the fibre weight. Working with mature but undried cotton fibres, T. Kerr[2] has reported on the spiral structure of the outer layers in relation to the opposite spiral structure of the primary wall and the restrictions these layers impose on the fibres during swelling in cuprammonium solution. In a study, with E. Berkley,[3] of the *X*-ray patterns of undried fibres, he found no evidence of crystalline cellulose in fibres taken from the maturing boll, the characteristic pattern of native cellulose appeared partly on stretching but mainly on drying.

In a series of papers dealing with the density and refractivity of cellulosic fibres P. H. Hermans, D. Vermaas, and J. J. Hermans[4] have criticised the use of helium as a medium for density determinations and have used carbon tetrachloride and nitrobenzene in their work,[5] as these liquids do not penetrate dry cellulose at room temperature ; the techniques adopted for density and refractivity determinations on isotropic and oriented viscose rayon filaments are described.

L. M. Welch, W. E. Roseveare, and H. Mark[6] have developed a method for differentiating between highly oriented and unoriented rayons, as the former yield fibrils, which may be observed with the optical microscope, on being broken down with 70% nitric acid.

In the course of an electron-microscope investigation of mechanically degraded material, more pronounced fibrillation was observed by E. Husemann and A. Carnap[7] with cotton than with rayon fibres.

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[1] *J. Text. Inst.*, 1946, **37**, T205; B., 1947, II, 7.

[2] *Text. Res.*, 1946, **16**, 249.

[3] *Ind. Eng. Chem.*, 1946, **38**, 304; B., 1946, II, 241.

[4] *J. makromol. Chem.*, 1944, **1**, 247; A., 1946, I, 215.

[5] *J. Polymer Sci.*, 1946, **1**, 149; B., 1946, II, 369.

[6] *Ind. Eng. Chem.*, 1946, **38**, 580; B., 1946, II, 368.

[7] *J. makromol. Chem.*, 1944, **1**, 158; B., 1946, II, 83.

The crystallisation of bacterial cellulose films into threads of approximately 200 A. diameter has been reported by A. Frey-Wyssling and K. Muhlethaler[8] from observations under the electron microscope.

R. F. Nickerson and J. A. Habrle,[9] using the differential hydrolysis-oxidation procedure for determining the structural components of cellulose (recently improved by C. C. Conrad and A. G. Scroggie[10]), have estimated the proportion of amorphous material in scoured and mercerised cotton and high-tenacity viscose rayon as 3, 7, and 8% respectively. Calculation of the degree of hydration from the loss of regain capacity at 65% R H. and 70° F. on removal of the amorphous fraction indicates that this component is more hygroscopic than the crystalline material, 3·5—5·1 molecules of water being associated with each anhydroglucose unit. A transitional or mesomorphous fraction was also estimated and it resembled in its hygroscopic and hydrolytic behaviour the compact, highly resistant crystalline material rather than the amorphous cellulose.

True hydrate formation by cotton cellulose has been reported by P. H. Hermans and A. Weidinger.[11] From *X*-ray data hydrate I, having, a composition $C_6H_{10}O_5$,0·33 or 0·5H_2O, is obtained from mercerised cotton whilst hydrate II, which is formed by hydrolysis of alkali-cellulose and cellulose xanthate at 0° and is almost identical with the "water-cellulose" of Sakurada and Hutino, has a composition $C_6H_{10}O_5$,1·33 or 1·50H_2O. In obtaining these compositions the assumption has been made that the water content of the hydrate is proportional to the coefficient of dilatation of the crystal lattice. The crystalline part of mercerised cotton fibres forms hydrate I in the process of sorption, whereas native cotton cellulose does not. In the amorphous regions hydrates are always formed in the presence of sufficient moisture. The same authors[12] have found that the three-dimensional crystal lattice of either native or regenerated cellulose is destroyed by dry grinding ; recrystallisation occurs, however, on wetting with formation of hydrate I : computed from *X*-ray data, heats of wetting, and sorption ratios the proportion of amorphous material after recrystallisation is 67%.

The determination of the molecular weight of undegraded cellulose indirectly through viscosimetric measurements on cuprammonium solutions is still the subject of much research. Using extreme precautions to exclude oxygen from the fibres and the nitrogen atmosphere in which the viscosity determinations were made, O. P. Golova[13] has obtained values of the order 1·6 × 10^6. The suggestion is also made, in a paper with V. I. Ivanov,[14] that these results should be corrected for residual oxygen strongly held by the fibres, by graphical extrapolation to

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[8] *J. Polymer Sci.*, 1946, **1**, 172; C., 1946, 255.

[9] *Ind. Eng. Chem.*, 1946, **38**, 299; B., 1946, II, 242.

[10] *Ibid.*, 1945, **37**, 592; C., 1945, 240.

[11] *J. Colloid Sci.*, 1946, **1**, 185; A., 1946, I, 215.

[12] *J. Amer. Chem. Soc.*, 1946, **68**, 1138; A., 1946, II, 527.

[13] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **47**, 31; B., 1946, II, 9.

[14] *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 279; A., 1946, I, 12.

zero oxygen content; this procedure gave a molecular weight value of at least $2{\cdot}43 \times 10^6$, which considerably exceeds the high values obtained in the sedimentation experiments of Gralén and Svedberg.

The Baker equation, $\eta_r = (1 + pc)^n$, relating relative viscosity (η_r) with concentration (c), where p is a constant and n has an integral value between 6 and 10, has been found by F. Howlett, E. Martin, and J. Swan[15] to hold for cuprammonium solutions of viscose rayon. The constant K_m, of the Staudinger equation has been evaluated for cellulose in cuprammonium solution, using material derived from esters of known chain length. Applying Kraemer's value of K_m for secondary cellulose acetate in acetone solution, a K_m value of $2{\cdot}5 \times 10^{-4}$ was obtained indirectly for cellulose in cuprammonium. A rather higher value of $2{\cdot}8 \times 10^{-4}$ was obtained by direct dissolution of the secondary cellulose acetate in cuprammonium, the difference being caused by acetic acid liberated by hydrolysis. The molecular weight of cellulose has been determined by H. Sihtola[16] from the viscosity of solutions in 65% zinc chloride; in this way a K_m value of $18{\cdot}73 \times 10^{-4}$ was arrived at and the variation with temperature determined. It is suggested that an additive compound is formed between the zinc chloride and the cellulose, as hydrochloric acid can be added to the cellulose solution with heating at 60—80° without causing much change in activation energy or activation constant.

A most comprehensive study of cellulose nitrate has been made at Uppsala by I. Jullander, assisted by H. Mosiman and I. and S. Claesson.[17] From theoretical considerations it is shown that the weight-average molecular weight (M_w) or the Z-average of Lansing and Kraemer (M_z) can be obtained for multimolecular substances from diffusion experiments under specified conditions, while sedimentation velocity measurements allow number- (M_n), weight-, or Z-average molecular weights to be determined. Frequency distributions were calculated from the sedimentation diagrams and absolute values (M_n) determined by osmotic pressure measurements using an osmotic balance, in which an accurate weighing takes the place of the small inaccurate length measurements associated with the conventional osmometers when adapted to the determination of high molecular weights. The theoretical relationship, $M_n < M_w = M_v < M_z$, where M_v is the average derived from viscosity, which should apply to all multimolecular systems, held for the series of nitrocelluloses investigated. Adsorption analysis using activated charcoal indicated that fractionation occurred on a molecular weight basis and is independent of degree of esterification, a result which is in line with the behaviour of other cellulose esters. The refractive index increment (dn/dc), however, was found to be a function of the nitrogen content. The same team have studied, with consistometer and ultracentrifuge,

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[15] *J. Text. Inst.*, 1946, **37**, T77; B., 1946, II, 371.
[16] *Finnish Paper Timber J.*, 1944, **26**, 287; *Chem. Abs.*, 1946, 4879.
[17] *Arkiv Kemi, Min., Geol.*, 1945, **21**, **A**, *No.* 8; B., 1946, II, 9.

nitrocellulose gels formed by reactions with silicon and titanium tetrachlorides involving cross-linking of the cellulose ester chains.

Considerable caution has hitherto been exercised in applying to high polymers the Staudinger equation relating intrinsic viscosity to molecular weight, as this relationship was established in the first instance by cryoscopic and end-group determinations on low polymers. It has been shown by G. V. Schulz[18] to be valid for degrees of polymerisation between 61 and 1420. He used cellulose nitrate prepared from cotton cellulose degraded by oxygen in cuprammonium, and by phosphoric acid, and the molecular weights were derived from osmotic pressure and viscosity measurements. A linear relationship was obtained connecting intrinsic viscosity and degree of polymerisation.

The chemical homogeneity of nitrocelluloses has been investigated by G. Champetier and M. Foëx,[19] using X-ray diffraction technique, and they have found that whereas nitration in solution yields chemically homogeneous products, nitration with dry nitric acid vapour gives an X-ray diagram similar to that for a mixture of unchanged cellulose and cellulose trinitrate. Their results agree with the theory that with nitrating acids low in water content nitration proceeds more rapidly than diffusion into the crystallites, whilst with more dilute acids the rate of diffusion exceeds that of nitration and a homogeneous ester results.

A wide, comprehensive survey has been made of the literature relating to the fractionation of high polymers by L. H. Cragg and H. Hammerschlag.[20] This review is particularly complete concerning the fractionation of cellulose and cellulose esters and ethers by use of the ultracentrifuge and by the standard procedures of fractional precipitation and dissolution, and chromatographic adsorption.

Since the observations of Staudinger and Mohr that cellulose could be nitrated and denitrated without appreciable degradation, the direct fractionation of cellulose by precipitation from cuprammonium solution has not been widely used. Recently, O. A. Battista and W. A. Sisson[21] have reported the results of preliminary experiments in which cellulose in cuprammonium was fractionated with sodium potassium tartrate, acetone, and *n*-propyl alcohol as precipitants. The organic compounds possessed good resolving power on a molecular weight basis, but the tartrate caused separation without resolution of molecular weights. On fractionating cellulose from cuprammonium solutions below 0° the reverse-order precipitation reported by D. R. Morey and J. W. Tamblyn[22] was observed. These workers found excellent resolution of cellulose acetate butyrate from acetone solution with aqueous ethyl alcohol as precipitant, but with *iso*propyl ether as precipitant the fractions of lower

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[18] *J. makromol. Chem.*, 1943, **1**, 146; A., 1946, I, 86.

[19] *Bull. Soc. chim.*, 1941, [v], **8**, 115; A., 1945, I, 330.

[20] *Chem. Rev.*, 1946, **39**, 79.

[21] *J. Amer. Chem. Soc.*, 1946, **68**, 915; A., 1946, II, 478.

[22] *J. Physical Chem.*, 1946, **50**, 12; A., 1946, I, 154.

molecular weight were found to be less soluble than the higher ones and to precipitate first; this effect is associated with the use of *iso*propyl ether, as it occurs with solvents other than acetone.

The solubility and fractionation of secondary cellulose acetate has been the subject of a study by F. Howlett and A. R. Urquhart.[23] After reviewing suitable fractionation methods, the fractional dissolution procedure was adopted principally as it avoids the entrainment of material of low molecular weight by the fractions of higher molecular weight, which is an inherent drawback of fractional precipitation methods. The results of solubility determinations on secondary cellulose acetate rayons in a series of organic solvents with various diluents led to the choice of acetone as solvent and butyl acetate as diluent.

The molecular weights of several cellulose acetate fractions have been calculated by R. S. Stein and P. Doty[24] from turbidity dissymmetry and depolarisation measurements on acetone solutions. Their results show very close agreement with the molecular weight values obtained by viscosity and osmotic pressure methods in view of the effect on accuracy of even small amounts of suspended matter in an optical investigation of this type. The molecules were found to be rather extended up to molecular weights of 80,000, whilst at higher values the molecule tended to coil back on itself.

In an attempt to end the confusion which exists over the names and symbols for the various viscosity functions L. H. Cragg[25] has proposed a terminology which, if adopted, should achieve its purpose.

Dry cotton cellulose irradiated with ultra-violet light in an atmosphere of helium or nitrogen shows post-irradiation degradation when, after exposure, the material is stored in an oxygen atmosphere but not when stored in nitrogen. The hypothesis that this effect is caused by modification of the hydroxyl group adjacent to the glycosidic link to such an extent that it is attacked by oxygen has been shown to be untenable by E. Heuser and G. N. Chamberlin,[26] who have made experiments on cellulose triacetate in which, of course, this hydroxyl group is blocked. They found that the esterified cellulose exhibited the effect without deacetylation occurring and consequently it would seem that the hydroxyl groups are not primarily involved in the latent effect produced during irradiation. Irradiation by ultra-violet light in an oxygen atmosphere caused both extensive deacetylation and degradation. Working with cellulose acetate butyrate films, R. L. Tichenor[27] observed marked degradation but no appreciable change in acyl content.

The water-soluble degradation products formed by the air oxidation of cellulose in cuprammonium solution have been examined by V. I.

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[23] *J. Text. Inst.*, 1946, **37**, T89; B., 1946, II, 371.
[24] *J. Amer. Chem. Soc.*, 1946, **68**, 159; A., 1946, I, 176.
[25] *J. Colloid Sci.*, 1946, **1**, 261; A., 1946, I, 341.
[26] *J. Amer. Chem. Soc.*, 1946, **68**, 79; A., 1946, II, 371.
[27] *J. Polymer Sci.*, 1946, **1**, 217; B., 1946, II, 371.

Ivanov and E. D. Kaverzneva[28] and found to contain formic and acetic acids, carbon dioxide, and approximately 30% of uronic acid, indicating that the primary hydroxyl group is preferentially attacked. In a later paper[29] it is reported that monotriphenylmethylcellulose, in which only the primary hydroxyl group is substituted, resists oxidation by air in both cuprammonium and pyridine solutions.

The short-chain decomposition products of oxidation-hydrolysis reactions are generally too complex for isolation of the individual components to be effected, with the result that attention has been almost entirely directed towards the insoluble oxy- or hydro-celluloses which still retain the basic structure of the original fibre. Periodic acid is more specific towards cellulose than most oxidising agents, causing cleavage of the glucose ring by oxidation of the secondary hydroxyl groups to aldehyde without appreciable formation of carboxylic acid groups. Using this reagent in a two-stage oxidation, G. Jayme and S. Maris[30] have isolated in 97% yield a polymeric aldehyde, which, after hydrolysis, give 53% of glyoxalphenylosazone. By reduction of the aldehyde with hydrogen in alkaline solution in presence of a nickel catalyst they obtained up to 39% of optically inactive erythritol. The high yields of glyoxal and erythritol obtained provide strong evidence for the accepted theory of the mechanism of oxidation by periodate.

Methods for the determination of aldehyde groups by oxidation with alkaline hypoiodite solutions have been criticised by E. Pacsu,[31] who has shown that the reagent is unstable and not specific, and that the results are influenced considerably by small differences in experimental procedure, particularly in the analysis of the alkali-sensitive periodate oxycelluloses. Similar objections have been made to the hypobromite method[32] and evidence is produced to show that cellulose is attacked by this reagent to a degree approaching that obtained in wet combustion; the absence of breaks in the oxidation–time curve indicates that attack of the various groups proceeds simultaneously. R. A. Hiller and E. Pacsu[33] have proposed an alternative procedure involving the use of dilute solutions of acidified potassium permanganate, which they claim is selective in its oxidising action; the high rate of reaction and the low temperature at which the hydrocellulose is in contact with the reagent reduce acid degradation to a minimum. This method has been applied to a study of hydrocellulose,[34] and these workers have found that, in the early stages of acid attack, the reducing power of the cellulosic materials used decreases. On the basis of these results they have proposed a new structural formula for cellulose[34,35] in which the primary chains, consisting of

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[28] *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 492; B., 1946, II, 200.

[29] *Ibid.*, 603; A., 1946, II, 646.

[30] *Ber.*, 1944, **77**, [*B*], 383; *Chem. Abs.*, 1946, 5242.

[31] *Text. Res.* 1946, **16**, 105.

[32] *Ibid.*, 163.

[33] *Ibid.*, 318.

[34] *Ibid.*, 490.

[35] *Ibid.*, 243.

condensed β-glucopyranose units, are held together by secondary chains of open glucose units joined to one another and to the primary chains through semiacetal linkings. Such a hypothesis would, of course, explain the results obtained, but before the theory achieves widespread acceptance further work is obviously required to establish that the observed decrease in reducing power is not brought about by the oxidation and elimination of small amounts of non-cellulosic impurities in the materials employed. Support for the view that there are two types of linkings in the cellulose chain comes from the work of E. Husemann and A. Carnap,[36] who have detected in cotton and ramie weak links distributed at intervals of approximately 500 anhydroglucose units, which are hydrolysed at more than 100 times the rate of hydrolysis for the β-glycosidic link.

Rupture of the cellulose chain by addition of a molecule of an alcohol at the glycosidic linking (alcoholysis) yields products which are entirely different from hydrocellulose in their chemical properties, as R. E. Reeves, W. M. Schwartz, and J. E. Giddens[37] have shown. Modified celluloses, prepared by the action of methyl-alcoholic hydrochloric acid solutions on purified cotton linters, were stable to hot alkali and non-reducing in character, although possessing high cuprammonium fluidities and substantial alkoxyl contents. The low alkali-solubilities recorded support the view advanced by Davidson that the loss in weight suffered by hydrocelluloses in hot dilute alkali is a function of reactivity rather than solubility.

Measurement of the dissociation constants of the carboxyl and hydroxyl groups in cellulose presents difficulties which are not easily overcome. When the material is suspended in water the hydrogen-ion concentration gradient in the electric double layer increases towards the negatively charged groups and decreases towards the positively charged ones, making it difficult to establish a quantitative relationship between hydrogen-ion concentration and degree of dissociation for the various groups. This obstacle has been overcome by S. P. Saric and R. K. Schofield[38] by using suspensions of cellulose in an electrolyte concentration equal to that in the standard half cell, which eliminates junction potentials and confines the effect of the local hydrogen-ion concentrations to the immediate vicinity of the charged groups. With this modification they have found that for suspensions of a solid containing only one kind of buffer group operating within the range of 4—5 pH units the equation $\mathrm{pH} = \mathrm{p}K + \log a/(1 - a)$, which has the same form as the Henderson equation, should apply. The dissociation curves obtained with suspensions of fibre cellulose were of the Henderson type and pK values of 2·95 for the carboxyl group and 13·3 and 15·0 (approximate) for the first and second stages of dissociation of the hydroxyl groups in

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[36] *Naturwiss.*, 1944, **32**, 79; A., 1946, **I**, 133.
[37] *J. Amer. Chem. Soc.*, 1946, **68**, 1383.
[38] *Proc. Roy. Soc.*, 1946, **A**, **185**, 431.

starch and cellulose were derived. The hypothesis is advanced that the hydroxyl groups in order of decreasing dissociation occupy the 2, 3, and 6 positions.

The adsorption by cellulose of lead and thallium from dilute solutions of their salts has been studied by J. G. Gavoret.[39] Cation adsorption at a given pH at first increases with concentration, then falls to a minimum value, and afterwards increases regularly. This anomalous adsorption observed at low concentrations is attributed to preferential adsorption of water. At a given concentration adsorption of lead increases from zero with pH over the range 2·7—6·6, while anion adsorption does not occur. The conductivities of dilute salt solutions are lowered by addition of cellulose and the maximum decrease is observed at pH 2·6, the point of minimum swelling of the cellulose. In this treatise, which has only recently become available, the authoress has discussed these results in the light of current theories of adsorption and cellulose structure.

The catalytic effects of ferrous hydroxide on the hypochlorite oxidation of cellulose have been found to resemble those of active leuco-vat dyes in that the rise in copper number and cuprammonium fluidity is related by a linear curve to the oxygen consumed. These results have been reported by G. M. Nabar and H. A. Turner,[40] who observed that the green ferrous hydroxide complex is more active than the white, and that hydrous ferric oxide has practically no catalytic action. The literature relating to the catalytic oxidation of cellulose in the presence of iron compounds has been usefully summarised by H. A. Turner.[41]

Methods for differentiating hydrocellulose and the various types of oxycellulose have engaged the attention of chemists for many years, and although the search for a relatively simple scheme for diagnosing the cause of damage in a cellulosic textile fabric still continues, it is gratifying to reflect that much of our knowledge of cellulose chemistry has sprung from the endeavours of the chemist to develop such methods. A summary of the qualitative tests available for the detection of carboxyl, carbonyl, and free aldehyde groups in oxycelluloses and the aldehyde group in semiacetal linking which occurs in both hydro- and oxy-celluloses has been compiled by E. Geiger and P. Künzler[42] with full experimental details of their application. In a second paper[43] it is shown that by pretreatment of a chemically tendered fabric with cold aqueous phenylhydrazine-*p*-sulphonic acid at pH 1 followed by immersion in aqueous solutions of various metallic salts, of which alkaline auric chloride and ferric sulphate–potassium ferricyanide were found to be the most satisfactory, it is possible to differentiate between oxycellulose and hydrocellulose; the former reduces the metals or causes colour changes, whilst the latter is without action. Hydrocelluloses also give positive results

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[39] *Thesis, Paris,* 1939; A., 1945, I, 334.

[40] *J. Soc. Dyers and Col.,* 1945, **61**, 258; B., 1946, II, 9.

[41] *Ibid.,* 255.

[42] *Helv. Chim. Acta,* 1945, **28**, 283; B., 1946, II, 200.

[43] *Ibid.,* 1159; B., 1946, II, 116.

following a treatment with a buffer solution at pH 8·5. The quantitative determination of aldehyde groups in semiacetal linking has been investigated by the same workers,[44] who have suggested a method in which primary amines or other bases are condensed with the aldehyde groups; the picrates of the substituted bases are then formed and the picric acid liberated from them by decomposition with dilute sodium hydroxide solution is measured colorimetrically.

B. Meesook and C. B. Purves[45] have found the calcium acetate method to be preferred to the silver *o*-nitrophenoxide method of Sookne and Harris for the estimation of carboxyl groups in reducing oxycelluloses; the latter method gave sharper end-points and more accurate results with materials of low carboxyl content, but the reagent was liable to be reduced to metallic silver by reducing groups. Using the calcium acetate and hydroxylamine hydrochloride methods for the determination of carboxyl and carbonyl groups in a series of chromic acid oxycelluloses, practically all the oxygen consumed was accounted for; the discrepancies observed were probably due to retention of chromium by the carboxyl groups. Reoxidation of the oxycellulose by chlorous acid, which is assumed to oxidise aldehyde groups to carboxyl and to leave ketone groups unaffected, enabled the carbonyl content to be subdivided into ketone and aldehyde group contents.

A method for the determination of uronic acids has been described by R. M. McCready, H. A. Swenson, and W. D. Maclay[46]; the apparatus employed for the absorption, and estimation by titration, of the evolved carbon dioxide incorporates several ingenious ideas.

E. Heuser[47] has reviewed and discussed the published work relating to cross-linkings in cellulose and their practical application in reducing the swelling and increasing the wet strength of cellulosic rayons.

An interesting use of nitrogen peroxide oxycellulose as a cation absorber has been reported[48]; absorption of sodium ions from sodium chloride solution by the glucuronic acid groups is claimed to be nearly quantitative.

BAST FIBRES.

Jute fibre which has been treated with 30% sodium hydroxide solution, washed, and air-dried has been found by S. C. Sirkar and N. N. Saha[49] to give an *X*-ray diffraction pattern differing from those of the recognised cellulose hydrates; the treated material resembles coarse wool in its physical properties.

Using the experimental methods of Urquhart and Williams, W. G. Macmillan, R. R. Mukherjee, and M. K. Sen[50] have determined the absorption

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[44] *Helv. Chim. Acta*, 1945, **28**, 1638; C., 1946, 21.
[45] *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 223; B., 1947, II, 49; C., 1947, 13.
[46] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 290; C., 1946, 161.
[47] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 21; B., 1946, II, 160.
[48] *Chem. Eng. News*, 1946, **24**, 703.
[49] *Nature*, 1946, **157**, 839; B., 1947, II, 11.
[50] *J. Text. Inst.*, 1946, **37**, T13; B., 1946 II, 241.

isotherms for tossa and white jute; their results confirm earlier work by Powrie and Speakman. A loss of hygroscopicity, which was restored on re-wetting, was observed on heating at 110° and was attributed to an increase in crystallinity. Jute was found to have a greater heat of wetting than cotton and a higher compression factor for the absorbed water; the latter was almost as high as for wool and suggests that bonds other than hydrogen bonds are involved in the absorption process. The greater hygroscopicity of jute as compared with cotton, it is suggested, is caused by groups in the lignin and hemicellulose which possess a stronger affinity for water than cellulosic hydroxyl groups. Tossa jute was found to be more hygroscopic than white jute.

A series of important papers have been published by J. B. A. Stroink, H. J. Bendel, and D. A. Beerens[51] on the subject of the cottonising of flax. Hydrolysis of the intercellular layer by a pancreatic diastase preparation containing some proteolytic enzyme followed by chlorination in acid solution gave a product containing a higher proportion of fibres with staple lengths in the optimum region than did hydrolysis by means of a caustic soda pressure boil in presence of sodium hydrosulphite. Chemical processes bring about degradation of the primary cellulose structure before the intercellular layer has been dissolved and disruption of the cross-linking between fibre bundles effected; this results in an undesirable increase in irregularity of fibre length. Sodium hydrosulphite exerts a protective action against reduction in chain length during the alkali boil but the effect decreases with increasing kier pressure.

Exploratory work has been carried out by H. B. Hanson[52] on the yield and properties of fibres from several species of common weeds.

Apparatus for the decortication of bast fibres has been protected[53] and a patent[54] has been taken out covering the application of dry-cleaning methods to jute to facilitate subsequent dyeing operations.

RAYONS.

Viscose Rayon.—The effects of pre-swelling treatments and variations in the relative proportions of cellulose, sodium hydroxide, and carbon disulphide on the viscosity of the xanthation products have been studied by G. Jayme and J. Wellm,[55] who found that accurate estimations of degree of polymerisation can be obtained directly from viscosity measurements on bleached wood-pulp xanthate solutions provided that they are made at approximately equal velocity gradients, but less accurate results were obtained with unbleached wood-pulp xanthates. The changes occurring during the ripening of viscose syrup have been followed by P. C. Scherer[56] by measuring the extension at break of a syrup thread

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[51] *Textilber.*, 1944, **25**, 181, 217, 253; B., 1946, II, 199.
[52] *Iowa State Coll. J. Sci.*, 1946, **20**, 365; B., 1946, II, 368.
[53] J. Thomson, B.P. 572,666; B., 1946, II, 47.
[54] Lumsden & Mackenzie Ltd., and C. Garrett, B.P. 571,799; B. 1945 II 377.
[55] *Kolloid Z.*, 1944, **108**, 20; B., 1946, II, 370.
[56] *Rayon Text. Month.*, 1945, **26**, 69; B., 1946, II, 117.

removed by a bar withdrawn at constant speed from the viscose; the recorded extensions are related to the viscosity of the syrup and increase with time of ripening until gel formation occurs. The various factors involved in the ripening and coagulation of xanthate solutions have been investigated empirically by R. Prince and J. Seiberlich[57] by examination of the shrinkage pattern of viscose films cast on glass. None of the films showed stress patterns when viewed in transmitted polarised light, indicating that the patterns actually represent the resultants of the shrinkage stresses. Degree of shrinkage and decrease in film thickness were related directly to the Hottenroth number of the viscose and inversely to the precipitating bath temperature.

Flow birefringence measurements have been made on ripening viscose by R. Signer and W. Meyer.[58] In the early stages of the process the decrease in flow birefringence due to the shortening of chains by oxidative degradation is masked by an increase in birefringence brought about by hydrolysis of the dithiocarbonate groups After about four days, the oxidative degradation comes to an end and, although the orientation angle continues to decrease, the birefringence increases at each of several velocity gradients, a result which is explained by the increasing anisotropy of the individual particles in solution. On the assumption that the γ value (number of xanthate groups per hundred glucose units) and the birefringence are in linear relationship, it has been possible to calculate the increase in flow birefringence in the first four days of ripening.

The dispersion of cellulose by cellulose xanthate prepared from wood pulp of high α-cellulose content has been the subject of a paper by P. C. Scherer[59], expressed on the weight of cellulose xanthate it was found that a maximum of 12% of viscose rayon and smaller amounts of α-cellulose could be dispersed, indicating the possibility that in the xanthation process certain of the molecules may be completely esterified while others are only partly or not xanthated. In a second paper[60] Scherer has shown that the dispersive power of cellulose xanthate decreases with time and is related to the decreasing sulphur content of the xanthate.

The fine structure of rayon filament has recently received considerable attention and the question has arisen whether or not high-stretch spinning results in increased crystallinity as well as greater orientation in planes containing the fibre axis. The results of accessibility determinations made by E. L. Lovell and O. Goldschmid,[61] using a simplified Nickerson hydrolysis–oxidation procedure, indicate that the degree of crystallinity is determined primarily in the process of coagulation and regeneration and that the effect of stretching is small. Etch figures obtained by hydrolysis with 2·33N-hydrochloric acid at 100° for 45 minutes show up micellar

[57] *J. Physical Chem.*, 1946, **50**, 222; B., 1946, II, 370.
[58] *Helv. Chim. Acta*, 1945, **28**, 325, A., 1946, I, 155.
[59] *Rayon Text. Month.*, 1946, **27**, 22, B., 1946, II, 242.
[60] *Ibid.*, 409; B., 1947, II, 49.
[61] *Ind. Eng. Chem.*, 1946, **38**, 811; B., 1946, II, 415.

orientation by longitudinal and transverse splitting which occurs when the hydrolysed material is subjected to slight pressure on the microscope slide. Examination under polarised light revealed that although viscose rayons regenerated without stretching possessed uniformity of crystallite orientation, the crystalline structure is present in such material as in high-tenacity tyre cord rayons. The subject of viscose rayon structure has been approached from a different angle by E. Elöd and H. G. Frohlich,[62] who have devised an ingenious technique for determining variations in the radial density of fibres. The fibres are acetylated for different times and the acetylated coatings dissolved away; the density and swelling properties of the fibre cores are then determined by established procedures. Whereas the natural cellulosic fibres, and fibres regenerated in the Muller bath process, increase in density from the centre outwards, some rayons, including the Lanusa type, show uniform density. Degree of swelling in water was generally inversely proportional to the mean density of the fibres and repeated drying was found to bring about structural changes resulting in decreased swelling.

Patents covering the production of stable, aqueous solutions of cellulose with sodium zincate[63] and with pyrrolidinium hydroxide[64] have been granted, whilst the continuous spinning of cellulose from solutions in strong mineral acids has also been protected.[65] The continuous production of viscose from sodium cellulose xanthate compressed into the form of strip has been patented by British Cellophane Ltd.[66] Sodium hydroxide solution is fed into the apparatus along with the cellulose xanthate, and viscose is drawn off continuously; in this way formation of air bubbles in the viscose is minimised. The incorporation of anion-active agents of the alkylarylsulphonate type prior to the shredding of the soda-cellulose pulp has been claimed[67] to decrease shredding time, and to reduce apparent density of the shredded material and the amount of carbon disulphide required for subsequent xanthation; the main effect of such additions, however, is to increase the rate of filtration of the viscose by assisting the production of a uniform product free from highly swollen, partly xanthated fibres.

Two patents have been granted for improving the strength of viscose yarn by modification of the spinning process. In the first of these,[68] after coagulation and washing, the yarn passes through an alkaline swelling liquor containing sodium sulphate in which the stretching takes place. In the second[69] the yarn is stretched in a hot sulphuric acid solution following the coagulating bath. Regenerated cellulose of low sulphur

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[62] *Text. Res.*, 1946, **16**, 432.

[63] S. M. Edelstein, B.P. 573,767; B., 1946, II, 87.

[64] O. Hecht and E. Gassenmeier, U.S.P. 2,339,012; B., 1946, II, 333.

[65] H. Fink, G. Rath, and R. Hofstadt, U.S.P. 2,334,615; B., 1946, II, 248.

[66] B.P. 571,502; B., 1945, II, 374.

[67] Rayonier, Inc., B.P. 573,775; B., 1946, II, 87.

[68] H. Fink and G. Plepp, U.S.P. 2,327,516; B., 1945, II, 372.

[69] G. I. Thurmond and E. Brenner, Assrs. to Amer. Enka Corp., U.S.P. 2,328,307; B., 1945, II, 374.

content has been claimed[70] to be produced by treating with desulphurising agents followed by a wash in a dilute solution of non-oxidising mineral acid at 80—100°.

A highly crimped set and wool-like characteristics result from the treatment of highly twisted filament yarn, wound on perforated bobbins, with powerful swelling agents such as caustic alkalis, zinc chloride, or sulphuric acid followed by washing and reversal of the twist.[71]

The application to viscose staple fibre of antistatic compositions containing *cyclo*hexyldialkylamine salts of sulphated long-chain aliphatic alcohols in mineral oils has also been patented.[72]

Cuprammonium Rayon.—The production of cuprammonium rayon by I.G. Farbenindustrie at Dormagen has been described by R. S. Krausen[73] and some interesting developments are recorded. High recovery (93%) of copper from alkaline solutions containing the tetrammine complex is obtained by using ion-exchange resins containing active sulphonic acid groups. Spinning takes place in a stream of water and the filament is cut into staple fibre before complete removal of the copper, a procedure which results in a crinkled fibre. Yarns of high elasticity and moisture-resistance are obtained, it is reported, by spinning into 20% sodium hydroxide solutions and impregnating, after washing, with a solution containing urea, formaldehyde, and ammonium nitrate.

Industrial Rayon Corporation[74] have patented a cuprammonium spinning solution in which the ratio of ammonia to cellulose falls between the limits of 0·5 and 0·8 to 1 and the ratio of copper hydroxide to cellulose is approximately 0·6 to 1. Dissolution of the cellulose is effected preferably at 0°. The cupric hydroxide may be formed *in situ* from basic copper sulphate by addition of an alkaline hydroxide and the solution diluted before spinning provided that the ammonia to cellulose ratio is maintained.

Cellulose Esters and Ethers.—In a valuable addition to the published knowledge concerning the rôle of sulphuric acid in cellulose acetate production C. J. Malm, L. J. Tanghe, and B. C. Laird[75] have shown that combination of the acid with cellulose before the acetic anhydride is added is small but that quantitative combination (7% on the weight of cellulose) occurs during the intermediate stage of acetylation; there is then a gradual replacement of sulphate by acetyl groups. The sulphur content of acetylated material falls sharply on hydrolysis with water, although rapid addition of water at low temperatures favours the retention of small amounts of combined sulphur, at the completion of esterification

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[70] Brit. Cellophane, Ltd., B.P. 577,657, B., 1946, II, 334.

[71] Heberlein & Co. A.-G., B.P. 572,140; B., 1946, II, 43.

[72] W. T. Jackson and W. G. Faw, Assrs. to Eastman Kodak Co., U.S.P. 2,197,930; B., 1946, II, 43.

[73] *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XIX-5; B., 1946, II, 371.

[74] S. Gulbrandsen, N. S. Sernis, and G. T. Trant (Assrs.), U.S.P. 2 36,481; B., 1946, II, 285.

[75] *Ind. Eng. Chem.*, 1946, **38**, 77, B., 1946, II, 161.

the combined sulphur content was roughly proportional to the concentration of sulphuric acid used. L. Clément and C. Rivière[76] have found that high concentrations of sulphuric acid increase the rate of saponification during ripening whilst low concentrations yield secondary cellulose acetates insoluble in acetone. These workers have also investigated the effects of duration of pretreatment on cuprammonium viscosity, and of acetic anhydride concentration on the extent and rate of acetylation, and have discussed their results in relation to the kinetics of the acetylation reaction.

The methods used by I.G. Farbenindustrie in the production of cellulose acetate rayon have been outlined by R. S. Krausén in a report to which reference has already been made.[73] A method whereby the excess of acetic acid is reduced from 600 to 100% on the weight of cellulose by using methylene chloride as the solvent, and 1% sulphuric acid as catalyst, is described. In this process the heat of reaction is dissipated by vaporising the solvent, which is condensed and returned as reflux; the resulting accurate temperature control allows the processing of larger batches than are possible with the standard procedure. Viscose staple fibre was acetylated without dissolution of the resulting acetate by the use of acetic anhydride solutions in carbon tetrachloride, although the main drawback to the method would appear to be connected with the use of large quantities of zinc chloride up to 30% on the weight of cellulose—in the form of a suspension in the acetylation solution; the advantage of the process lies in the retention by the acetate of the crinkly nature imposed on the staple fibre in its method of production.

A continuous esterification process which avoids the accumulation of impurities in the esterification bath has been patented.[77] Staple fibre sliver is impregnated with potassium acetate solution and then with the organic acid anhydride; esterification takes place in a current of hot air at 100—110° and occupies about 3 minutes. The difficulties of temperature control in such a sequence of operations will be obvious, and may result in a very variable product.

The formation of cellulose esters by reactions with acetic, chloroacetic, formic, and nitric acids and acetic anhydride in the vapour phase under various conditions of temperature, pressure, and concentration has been studied by G. Champetier and M. Foex,[78] who concluded that the acids are reacting in their monomeric form under these conditions. A. Sippel[79] has investigated the tension-spinning of cellulose acetate in acetone solution into rapidly moving water, and from measurements of rate of loss of solvent has developed a mathematical theory of the process.

Attention is still focussed on the development of esterification catalysts if the number of patents granted is to be regarded as a reliable indication.

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[76] *Bull. Soc. chim.*, 1942, [v], **9**, 494; B., 1946, II, 10.

[77] Soc. Chem. Ind in Basle, B.P. 577,103; B., 1946, II, 285.

[78] *Bull. Soc. chim.*, 1942, [v], **9**, 711; B., 1945, II, 370.

[79] *Z. Elektrochem.*, 1944, **50**, 152; B., 1946, II, 117.

British Celanese Ltd. have patented[80] a method for the production of cellulose mixed esters of the acetate propionate type, using mineral acids such as perchloric acid as catalysts, whilst the esterification of cellulose alkyl ethers with stearic anhydride in the presence of metallic halides such as stannous, zinc, or ferric chloride has been protected[81]; it is claimed that derivatives of low moisture regain and good water-resistance are produced. The use of boron compounds, exemplified by boric acid and borax, as catalysts in the preparation of aralkyl esters of cellulose, *e.g.*, benzylcellulose, has been the subject of yet another patent.[82]

Means whereby the stability to heat of ethylcellulose may be improved have been covered[83] and the stabilisation of cellulose esters which have been prepared in presence of sulphuric acid by treatment with dilute acid solutions containing complex sulphated long-chain secondary alcohols has been reported.[84]

The production of high-tenacity filaments from pigmented cellulose ester dopes by stretch-spinning in steam has been patented[85]; the spinning process may be followed by saponification to obtain a regenerated cellulose filament of equal or higher tenacity.

The formation of thin filaments of cellulose esters by spinning the semi-fluid material without the use of solvents or plasticisers within the temperature range 220—295° is an important advance[86]; the specific viscosity of the melt is controlled by careful timing of the heat-treatment, part of which may be carried out in the absence of air to minimise the risk of degradation.

The use of electrostatic fields in disrupting extruded cellulose acetate into fibres has been patented by Eastman Kodak Co.[87] and the claim is made that the fibres retain sufficient charge to attach themselves to previously formed fibres when a spinneret of dielectric material is used.

Modification of alkaline saponification baths by the inclusion of formaldehyde and salts which repress swelling has been claimed[88] to enable cellulose ester fibres and films to be converted into regenerated cellulose products without loss in strength, whilst the incorporation of triethanolamine esters into conditioning oil emulsions, it is suggested,[89] improves the knitting properties of cellulose acetate yarns and filaments.

Other Rayons.—The development of alkali-resistant alginate yarns and fabrics shows no sign of relaxing although the patents taken out recently are more concerned with devices for handling the material than with the

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[80] Brit. Celanese Ltd., B.P. 578,504; B., 1946, II, 377.

[81] J. W. Fisher, B.P. 571,572; B., 1945, II, 373.

[82] K. Meinel, Assr. to Hercules Powder Co., U.S.P. 2,205,487; B., 1946, II, 204.

[83] J. H. Sharphouse and J. Downing, B.P. 580,359; B., 1946, II, 458.

[84] Brit. Celanese Ltd., B.P. 577,963; B., 1946, II, 334.

[85] *Idem*, B.P. 577,718; B., 1946, II, 375.

[86] L. N. Bent, Assr. to Hercules Powder Co., U.S.P. 2,336,159; B., 1946, II, 248.

[87] H. R. Childs (Assr.), U.S.P. 2,338,570; B., 1946, II, 375.

[88] Brit. Celanese Ltd., B.P. 580,433; B., 1946, II, 458.

[89] J. B. Dickey and J. B. Normington, Assrs. to Eastman Kodak Co., U.S.P. 2,333,770; B., 1946, II, 248.

chemical reactions themselves. J. B. Speakman, N. H. Chamberlain, and Cefoil Ltd.[90] have protected methods of treating alginate fabrics with basic chromium or beryllium salts, or with formaldehyde either as vapour or in ammonium chloride solution ; the sodium alginate is generally converted into alginic acid by treatment with hydrochloric acid before application of the metallic salt solutions. A second patent from the same source[91] deals with the formation of methylene cross-linkings by treatment of alginate filament, after coagulation in hot calcium chloride or sulphuric acid solution, with formaldehyde or other aldehyde solutions at room temperature. The difficulty of washing and drying alginate yarn in cake form owing to high shrinkage has been overcome by processing in single thread form—a method not favourable to high rates of production and low cost.

The partial formation of insoluble metallic alginates in the coagulating bath followed by completion of the reaction in neutral solution is a sequence of wet treatments in a continuous process patented by Courtaulds Ltd.[92] ; thread-advancing devices capable of holding up to 60 ft. of thread are used to give fairly prolonged contact with the washing and metallic salt solutions which are sprayed on to the yarn.

A. Johnson and J. B. Speakman[93] have reviewed the uses of transient calcium alginate rayon yarns in the manufacture of crêpes, pile and furnishing fabrics, and fabrics composed of twistless yarns. Their use does not entail extra finishing operations since the alginate material, although insoluble in water, is removed in the normal alkaline scouring processes.

SIZING.

There is little to report in this field, but reference should be made to a general study of rayon warp-sizing materials by G. B. Frankenberg, A. M. Sookne, and M. Harris.[94] Sizing efficiency as measured by the loom stoppages resulting from warp breakage and the amount of fibre shedding was related to deformability and hardness of the size film and stiffness of the resulting cloth. Of the synthetic resin sizing agents examined, sodium cellulose glycollate gave better performance than medium-viscosity, thin-boiling corn starch, but methylcellulose and sodium polyacrylate compared unfavourably with starch sizes. The addition of 15% of sodium polyacrylate to corn starch resulted in an improvement in size efficiency. The adhesive power of common sizing agents was measured by the strength of the bonds between cloth and viscose or cellulose acetate films. Most starch and synthetic resin products gave good bond strengths with viscose films but sodium polyacrylate and a polyacrylate ester product were the only sizing agents examined

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[90] B.P. 573,058; B., 1946, II, 45.
[91] B.P. 572,798; B., 1946, II, 45.
[92] With H. J. Hegan, B.P. 571,657; B., 1945, II, 372.
[93] *J. Soc. Dyers and Col.*, 1946, **62**, 97; B., 1946, II, 242.
[94] *Rayon Text. Month.*, 1945, **26**, 165, 227, 285; B., 1946, II, 117.

which adhered at all strongly to cellulose acetate films. The use of acrylate polymers of various types in the sizing of cellulose esters has been patented by British Celanese Ltd.,[95] who have, in the same specification, protected the use of low-molecular ethylene oxide polymers; these synthetic resin sizes may be applied in hank or warp sizing and can be used very conveniently during down-twisting in winding.

SCOURING AND BLEACHING.

The hydrolysis of soluble starch to dextrins and maltose by the α- and β-amylases has been investigated by K. Myrbäck and N. O. Johansson,[96] who have concluded that the affinity of β-amylase for the substrate remains practically constant throughout the hydrolysis to maltose. On the other hand, α-amylase brings about the hydrolysis in two stages, the first of which results in the formation of dextrins of low molecular weight, while the second, which involves the conversion of dextrins into maltose, is characterised by low affinity between enzyme and substrate. The desizing efficiency of an enzyme product, it has been suggested,[97] is related to its starch-liquefying power and should be measured by viscosity changes or by the rate at which the starch–iodine colour is destroyed. The need for removing alkaline-earth compounds, which act as enzyme inactivators, before desizing finished cloths is stressed by L. Mayer[98] in a survey of the methods for using vegetable and mould diastases and pancreatic and bacterial amylases in textile processes.

The speed and mechanism of the removal of unsaponifiable oils from various fibres by sodium lauryl sulphate solutions have been studied under the microscope by W. Kling[99]; oily products were found to be retained more strongly by cuprammonium than by viscose rayon.

A comparison on the large scale of the conventional kier boil–hypochlorite bleach with the double-boil hydrogen peroxide bleach has been made by J. H. Kettering and R. M. Kraemer,[100] who found, after an exhaustive examination of the resulting products, that the slight advantages afforded by the peroxide bleach did not justify the extra labour and cost involved. D. Butterworth[101] has reported improvements in "J" box construction and briefly indicates the advantages of the continuous peroxide bleaching process over the intermittent kier boil, without, however, comparing the qualities of the products.

E. Scheller[102] has investigated the stabilisation of hydrogen peroxide solutions at elevated temperatures and pH 7 by means of pyrophosphates and magnesium silicate; the action of these substances is attributed to

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[95] B P. 572,884; B., 1946, II, 49.

[96] *Arkiv Kemi, Min., Geol.*, 1945, **20**, **A**, *No.* 6; A., 1946, III, 225.

[97] *Silk and Rayon*, 1946, **20**, 1112.

[98] *Textilber.*, 1940, **21**, 176; B., 1946, II, 167.

[99] *Ibid.*, 1944, **25**, 198; B., 1946, II, 158.

[100] *Amer. Dyestuff Rep.*, 1946, **35**, 285.

[101] *Rayon Text. Month.*, 1946, **27**, 320.

[102] *Textilber.*, 1944, **25**, 234; B., 1946, II, 165.

the formation of stable additive compounds which limit the amount of free hydrogen peroxide in the bath and to their effectiveness in reacting with positive catalysts. Working with more strongly alkaline conditions, R. Kuchinka[103] has found that phosphates give incomplete stabilisation and this leads to severe degradation in flax bleaching; sodium metasilicate stabilisers are to be preferred with boiling peroxide solutions containing sodium hydroxide. The causes of chemical damage during bleaching have been discussed by E. Klenk,[104] who has considered the catalytic effects of iron, manganese, and copper in the bleaching process.

G. Holst[105] reports a value of 0·75 volt for the oxidation potential of sodium chlorite at pH 5 compared with 1·05 volts for sodium hypochlorite solution at pH 9.

Mathieson Alkali Works[106] have patented the use of buffered chlorite solutions containing persulphates or aldehydes in the bleaching of cellulose acetate materials, whilst E. Klenk[107] has shown that whereas persulphates are suitable for the oxidation of sulphur and vat dyeings, their bleaching action on cellulosic materials, particularly at high temperatures, may be accompanied by severe degradation.

DYEING.

From a study of the dichroic behaviour of various classes of dyes T. H. Morton[108] has put forward a molecular theory of dyeing. All direct dyes, vat dyes in the leuco-form, and some insoluble azo- and acid dyes on ramie exhibit positive dichroism, indicating that the long axes of the dye molecules are oriented parallel to the axes of the cellulose chains, to which they are probably held by secondary valency forces; direct dye micelles, however, show negative dichroism so that, if the colloidal theory of dyeing is accepted, it is also necessary to accept that the elongated micelle is absorbed in a position oriented perpendicular to the fibre axis. This theory is difficult to reconcile with what is known of the fine structure of cellulose, and Morton has put forward his theory to explain the dichroic behaviour. The dye solution is considered to contain particles ranging in size from large aggregates to single molecules; these latter are absorbed by the cellulose fibre and migrate through the capillary pore system in a thermally activated diffusion process. Molecules are re-formed from the larger dye aggregates to take their place, and the process continues until equilibrium is reached. The fact that vat dye molecules exhibit dichroism in the leuco-form but not in the oxidised state is taken to indicate that these dyes are retained within the fibre by virtue of their insolubility rather than by combination with the cellulose.

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[103] *Texilber.*, 1944, **25**, 167, 202; B., 1946, II, 164.

[104] *Kolloid Z.*, 1944, **108**, 10; B., 1946, II, 380.

[105] *Svensk Papperstidn.*, 1945, **48**, 23; *Chem. Abs.*, 1945, 3194.

[106] Assees. of C. A. Hampel, B.P. 576,909–10; B., 1946, II, 288.

[107] *Textilber.*, 1944, **25**, 351; *Chem. Abs.*, 1946, 4891.

[108] *J. Soc. Dyers and Col.*, 1946, **62**, 272; B., 1947, II, 16.

The equilibrium absorption of Chrysophenine G by cellulose sheet has been studied by H. F. Willis, J. O. Warwicker, H. A. Standing, and A. R. Urquhart,[109] who have developed a theory of dyeing based on the preferential attraction between dye anions and active centres in the cellulose; the energy released in dyeing supports the view that two hydrogen bonds are formed per absorbed dye molecule. From measurements of diffusion coefficients in aqueous solution, and in solutions of various electrolytes, F. H. Holmes and H. A. Standing[110] have found this dye to be only slightly, and Direct Fast Orange SE to be appreciably, aggregated in the presence of excess of electrolyte, while from conductivity data they have concluded that, on the assumption that the micelles do not contain a high proportion of cations, neither of the above direct dyes nor Chlorazol Sky Blue FF can be aggregated to any marked extent in salt-free aqueous solutions.

Measurements of rate of dyeing made by D. R. Lemin, E. J. Vickers, and T. Vickerstaff[111] on a very wide range of direct dyes under conditions which simulate normal dyeing practice have led these workers to conclude that the behaviour of binary combinations, due to interaction of dye molecules and other causes, is not that which would be predicted from the behaviour of the individual dyes and that rate of migration is of more importance than rate of dyeing. A method of defining salt controllability is put forward and in conjunction with data for rate of migration a classification has been made indicating the most suitable methods of application of the many dyestuffs examined. The conclusions drawn from this work have been strongly criticised by J. Boulton.[112]

Differences in optical properties of the fibre and in dye penetration are held by R. W. Jacoby[113] to be the cause of the darker shades obtained with mercerised goods dyed under the same conditions as unmercerised material; there is no evidence for the theory that mercerisation increases the affinity of the cellulose for direct dyes.

A. I. Sokolov and A. M. Frolova[114] have found that dyeings obtained with a number of substantive dyes, including those of the Coprantin series, possessed increased washing- and light-fastness when mordanted in two stages with a dicyanodiamide–formaldehyde condensation product and copper acetate.

The relationship between the structure and colour of indigo and indanthrone has been discussed by H. H. Hodgson[115] from the viewpoint of the modern resonance theory and it has been concluded that the colour is caused by the interaction of the nitrogen and oxygen atoms. In all resonance forms the nitrogen atom is positively charged, and

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[109] *Trans. Faraday Soc.*, 1945, **41**, 506; B., 1946, II, 14.
[110] *Ibid.*, 542, 568; B., 1946, II, 14.
[111] *J. Soc. Dyers and Col.*, 1946, **62**, 132; B., 1946, II, 287.
[112] *Ibid.*, 285; B., 1947, II, 16.
[113] *Amer. Dyestuff Rep.*, 1946, **35**, 56; B., 1946, II, 380.
[114] *Tekstil'naya Prom.*, 1946, **6**, *No.* 6, 33; *Chem. Abs.*, 1946, 5923.
[115] *J. Soc. Dyers and Col.*, 1946, **62**, 176; B., 1946, II, 326.

replacement of the NH group by S or O makes resonance more difficult as these atoms have less affinity for the positive charge than nitrogen, with the result that the colour is changed from blue in indigo to red and orange respectively.

The formation of peroxide groups during the reoxidation by air or sodium hypochlorite of the leuco-forms of anthraquinone and a series of commercial vat dyes has been observed by W. Atherton and H. A. Turner[116]; one peroxide group was formed per reduced quinone group, and while this reaction is considered to be an essential step in the tendering of cellulose by active vat dyes, it does not determine the degree of activity. An indication of this activity is obtained by Y. M. Waly, J. M. Preston, F. Scholefield, and H. A. Turner[117] by determining the characteristic potential of the vat dye on cellulose in the oxidised and leuco-forms, in the dark and when illuminated; inactive dyes show no significant change in value but with active dyes the potential becomes more negative on illumination and the change is greater the more active the dye. By determining the characteristic potential at various pH values the authors have shown that the activity of dyes under conditions of processing and storage may be determined. The tendering of cellulose by vat dyes has also been investigated by J. Brear and H. A. Turner,[118] who used a repeating cycle of reduction and oxidation operations to obtain pronounced cuprammonium fluidity increments: tendering was observed with all the 21 dyes examined, the maximum effect occurring when the oxidation process was carried out in the region of pH 11·6.

In the field of practical dyeing S. Burgess[119] has studied the vat dyeing of viscose rayon hanks with the aid of a simple strike test which also indicates the levelling power of the dye; the strike index is correlated with exhaustion speed for the slow, intermediate, and rapidly exhausting dyes and dyeing methods best suited to the bulk dyeing of viscose rayon hanks are indicated. Vat dyes which give level shades in the pigment padding process have been listed by A. B. Cox,[120] who has discussed the application of the process to the dyeing of viscose cake. The new process comprises the circulation of the unreduced dye dispersions through the cake, with gradual addition of sodium chloride to effect deposition of the dye, and reduction; the dyeings are then developed with sodium hypochlorite.

The advantages of the continuous pigment-pad process for piece dyeing have been discussed by G. F. Womble,[121] P. L. Meunier,[122] and A. E. Hirst[123]; it is an essential feature of the process that the volume

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[116] *J. Soc. Dyers and Col.*, 1946, **62**, 108; B., 1946, II, 250.
[117] *Ibid.*, 1945, **61**, 245; B., 1946, II, 14.
[118] *Ibid.*, 273; B., 1946, II, 47.
[119] *Ibid.*, 1946, **62**, 41; B., 1946, II, 166.
[120] *Ibid.*, 45; B., 1946, II, 166.
[121] *Rayon Text. Month.*, 1946, **27**, 316; B., 1947, II, 53.
[122] *Textile Manuf.*, 1946, **72**, 99.
[123] *Cotton (U.S.)*, 1945, **109**, 101.

of reducing liquor is kept as small as possible to avoid removal and subsequent redeposition of dispersed dye particles. Plant designed to work with low liquor ratios has been patented[124]; the fabric is treated with the reducing solution and held between a rubber blanket and a rotating heated drum while dyeing with the leuco-compound takes place.

The use of buffered sodium chlorite solutions in the oxidation of vat and sulphur colours,[125] patented by Mathieson Alkali Works,[126] is a suitable application for this non-degrading oxidising agent.

The treatment of cellulosic material with condensation products of aliphatic amines and water-soluble polyamides in formaldehyde solution has been claimed[127] to increase its affinity for acid dyes, whilst methods for increasing the washing-fastness of dyed textiles which have been covered by patents include those based on the after-treatment of dyeings with compounds such as *NN'N''*-tri(methoxymethyl)melamine.[128] Similar products have also been claimed[129] to improve the fastness to burnt gas fumes of aminoanthraquinone dyes on cellulose acetate, whilst the difficulty of applying such substances in sufficient quantity on account of their low water-solubility has led to the application of cyanamide solutions containing an acid catalyst in order to obtain the same improvements in fastness[130]; the rather prolonged heat-treatment required to bring about polymerisation is the disadvantage of this type of treatment.

British Celanese Ltd.[131] have claimed that dyeings of unusual brilliance are obtained on cellulose acetate in dyebaths containing direct dyes, approximately 65% of ethyl alcohol, and 1—8% of an organic acid such as formic or acetic acid.

Cellulose acetate material of acetic acid yield greater than 59% may be swollen in acetic acid and fixed in this state by treatment with alkali or alkaline-earth metal salts (*e.g.*, 20% sodium chloride or 5% sodium acetate); in this condition it is claimed[132] that the material can be dyed in full shades or, if the reagents are applied locally, patterned effects may be obtained.

Application of ammonium soaps to one side of an acetate fabric followed by removal of ammonia by heating and saponification on the reverse side enables the fabric to be dyed with direct and acetate dyes in the production of two-shade dyeings.[133]

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[124] J. Welch & Sons Ltd., and C. Newton, B.P. 571,325; B., 1945, II, 376.

[125] *Silk and Rayon*, 1946, **20**, 985.

[126] Assees. of G. P. Vincent and A. L. Dubeau, B.P. 576,296; B., 1946, II, 288.

[127] O. Grimm and H. Rauch, Assrs. to Rohm & Haas Co., U.S.P. 2,328,900; B., 1945, II, 376.

[128] E. I. Du Pont de Nemours & Co., B.P. 573,790; B., 1946, II, 124.

[129] H. C. Olpin and S. A. Gibson, B.P. 569,557; B., 1945, II, 376.

[130] H. Dreyfus, B.P. 571,056; B., 1945, II, 376.

[131] B.P. 576,927; B., 1946, II, 288.

[132] R. Schnegg, U.S.P. 2,328,682; B., 1945, II, 377.

[133] A. Mellor and R. J. Mann, B.P. 570,880; B., 1945, II, 343

Cyanamide–formaldehyde condensates applied to calcium, chromium, or beryllium alginate material increase its affinity to direct, acid, and mordant dyes.[134]

Much useful information concerning the dyeing and printing of Celanese and Fortisan fabrics is contained in a paper by A. Mellor.[135] The subjects covered include the pre-crêping and embossing of Celanese, saponification preparatory to discharge printing, and dyeing by the solvent process. Methods are suggested for increasing the affinity of Fortisan towards dyes, and suitable printing techniques, which closely follow those for cotton, have been outlined.

PRINTING.

The complex systems which are termed printing pastes do not lend themselves readily to scientific study but progress continues to be made in determining the various factors involved in the production of high-quality prints. In investigating some of these factors, R. W. Jacoby[136] has shown that the particles of several commercial vat dyes carry negative charges and that the addition of electrolytes carrying opposite charges to pastes made from them leads to agglomeration, as also does the action of some thickeners in preventing hydration of the dye particles; he has recommended adding sodium phosphate, which carries a negative charge, to overcome the first effect and hydration of the dye in water before mixing in the paste, to minimise the second. The application of acid dyes to cellulosic fibres by printing and steaming has been studied by W. Meitner,[137] who has outlined the conditions under which the particle size of the dye particle is reduced by the influence of steam and urea, enabling penetration of the fibre to take place; he has classified a series of acid dyes with respect to particle size and suggests methods for increasing the range of dyes suitable for rayon printing.

The factors governing the selection of acid dyes and thickening agents for use in the screen printing of rayon have been briefly surveyed,[138] whilst practical details and recipes are given by R. C. Geering.[139]

American Cyanamid Co.[140] have patented methods whereby leuco-vat dyes, or diazo-compounds stabilised against coupling, are mixed with thickeners and dried under vacuum at temperatures below that at which irreversible hydration occurs, giving powders which may be converted into printing pastes by addition of water. The use of plasticised urea-modified melamine–formaldehyde condensates in emulsion form in printing

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[134] Courtaulds Ltd., C. C. Wilcock, and H. Hampson, B.P. 572,778; B., 1946, II, 49.

[135] *J. Soc. Dyers and Col.*, 1946, **62**, 168; B., 1946, II, 335.

[136] *Amer. Dyestuff Rep.*, 1946, **35**, 3; B., 1946, II, 380.

[137] *I.C.I. Dyestuffs Div.. Technol. Monog.* 2; B., 1945, II, 342.

[138] *Silk J. and Rayon World*, 1946, **21**, 34.

[139] *Rayon Text. Month.*, 1946, **27**, 89; B., 1946, II, 250.

[140] M. L. Crossley, R. H. Kienle, and C. A. Amick (Assrs.), U.S.P. 2,196,958; B., 1945, II, 377.

pastes has been patented[141] and constitutes an important step in improving the wash-fastness of prints, whilst E. I. Du Pont de Nemours & Co.[142] have patented the incorporation of a wide variety of synthetic resins in alkaline printing pastes.

FINISHING.

Although interest in finishing as assessed by the patent literature has never been so keen, relatively few finishes have been developed which form an integral part of the fibre structure, and there is little to report in the way of scientific investigations of finishing processes.

In a discussion of the application of linear polymers and thermosetting condensates to textiles, C. D. Weston[143] has related chemical structure to physical properties and has shown how some of these properties are conveyed to the finished cloth. K. P. Monroe[144] has contrasted the effects on rigidity, resilience, and dimensional stability of the surface application of melamine–formaldehyde precondensates with those obtained by thorough penetration of the fabric, whilst C. S. Marvel[145] has supplied some much-needed information on the mechanism of polymerisation of the urea–formaldehyde resins.

Patents taken out by Imperial Chemical Industries Ltd.[146] cover the application of resin finishes in monomeric form from the vapour phase; the polymerisation catalyst is applied to the fabric along with oxygen acceptors, and surface coatings are built up on the fabric by treating with the vapours of a methacrylic or vinyl ester, or with styrene.

Permanent finishes obtained by impregnation with "catalytically activated" solutions of cellulose in caustic soda have been dealt with by D. M. Martin,[147] and C. B. Hollabaugh[148] has usefully reviewed the literature relating to the application of carboxymethylcellulose in finishing.

Polythene, after being rendered friable by modification, can now be obtained in the form of aqueous dispersions suitable for the production of permanent finishes.[149]

Water-repellent finishes based on the treatment of cellulosic material with the vapours or solutions of organo-silicon halides have been patented[150] and represent a new departure from previous trends in this

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[141] C. T. Douglas, A. Hill, W. Todd, and Imperial Chem. Industries, B.P. 573,558; B., 1946, II, 89.

[142] C. F. Miller (Assr.), U.S.P. 2,336,365; B., 1946, II, 288.

[143] *J. Text. Inst.*, 1946, **35**, P25.

[144] *Amer. Dyestuff Rep.*, 1946, **35**, 13; B., 1946, II, 381.

[145] *J. Amer. Chem. Soc*, 1946, **68**, 1681; A., 1947, II, 110.

[146] With J. B. Speakman and T. Barr, B.P. 570,883; B., 1945, II, 343. With W. C. S. G. Jarrett and E. E. Walker, B.P. 572,959; B., 1946, II, 46.

[147] *Text. Rec.*, 1945, **63**, *Sept.*, 59; *Oct.*, 60.

[148] *Ind. Eng. Chem.*, 1945, **37**, 943; B., 1946, II, 117.

[149] C. F. Flint, R. B. F. F. Clarke, and Imperial Chem. Industries Ltd., B.P. 572,695; B., 1946, II, 55.

[150] British Thomson-Houston Co., B.P. 575,675–6; B., 1946, II, 207. B.P. 572,740; B., 1946, II, 50.

field; compounds such as trimethylsilicon chloride, while having the advantages of low molecular weight and high reactivity, are liable, on hydrolysis, to cause degradation of cellulose with surface deposition of silica.

The production of water-repellent finishes by application of acid solutions of urea– or guanidine–formaldehyde condensation products has been protected[151] and compositions containing waxes and zirconium oxychloride with oleyl alcohol–formaldehyde condensates as emulsifying agents have been patented.[152]

German developments in water-resistant finishes, including the Persistols and the trifunctional 2 : 4 : 6-triethyleneimino-1 : 3 : 5-triazine compound have been well reviewed by R. A. Pingree,[153] whilst J. B. Rust[154] has patented the application of the reaction product obtained by heating together formaldehyde, an alkyl nitrile (below C_9), a tertiary amine, and an alkyl chloride (above C_9); the composition is applied to the fibre in aqueous solution and is rendered insoluble by a baking treatment at 120—170°. It is a distinct advantage for the intermediate compounds to be applied from solution rather than in emulsion form.

Fireproofing compositions containing ferric, antimony, and tin oxides with casein have been patented[155]; the casein is made insoluble by an after-treatment with formaldehyde and the resulting finish is claimed to be resistant to washing and weathering.

Several important developments have taken place recently in methods for reducing the swelling, and therefore the shrinkage, of rayon fabrics. H. F. Creegan[156] has discussed the application of urea– and melamine–formaldehyde condensates for this purpose and describes a new process termed "Definizing" in which the rayon fabric is treated with a protective agent (of undisclosed composition) and then with 40% sodium hydroxide at 80—100° F. for 5—30 seconds; the reaction is stopped by rapid neutralisation of the alkali in sulphuric acid or sodium bicarbonate solutions, and a high degree of dimensional stability is obtained in the finished fabric. Another permanent finish, involving treatment with glyoxal solutions in the presence of an acid catalyst, has been reported by J. Epelberg[157]; like "Definizing," it is free from the defect of chlorine retention which occurs with urea– and melamine formaldehyde finishes during subsequent hypochlorite bleaching.

The action of the aluminium chloride catalyst in the formaldehyde treatment of spun rayon has been investigated by A. Schaeffer,[158] whilst

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[151] J. R. Geigy A.-G., B.P. 571,919; B., 1946, II, 49.

[152] A. Doser, O. Bayer, and K. Hintzmann, Assrs. to Gen. Aniline & Film Corp., U.S.P. 2,328,431; B., 1945, II, 377.

[153] *Amer. Dyestuff Rep.*, 1946, **35**, 124: B., 1946, II, 381.

[154] Assr. to Montclair Research Corp., U.S.P. 2,333,623; B., 1946, II, 289.

[155] L. A. Jordan and L. A. O'Neill, B.P. 573,471; B., 1946, II, 90.

[156] *Amer. Dyestuff Rep.*, 1946, **35**, 514.

[157] *Ibid.*, 355; B., 1947, II, 48.

[158] *Textilber.*, 1944, **25**, 400; *Chem. Abs.*, 1946, 4220.

the practical drawbacks of formaldehyde treatments in general are reviewed in a recent Courtauld patent[159] covering further modifications of this type of process. Another patent from the same source[160] claims that the crease-resistance of spun rayon is improved by impregnation with an aldehyde resin precondensate, ammonium thiocyanate, and sodium hexametaphosphate followed by low-temperature drying and baking at 140°.

The application of organic dicarbimides and dithiocarbimides to rayon has been claimed[161] to improve the wet tensile strength and resilience, and to effect a decrease in swelling, whilst abietic acid derivatives containing a tricyclic hydroaromatic condensed nucleus have been applied to cotton materials to improve tensile strength properties.[162]

Condensation products of polyamines with long-chain fatty acids have been suggested[163] for use in producing suede finishes on yarns and knitted fabrics, and the application of synthetic resin dispersions in obtaining delustred rayon has also received attention.[164] D. H. Powers[165] has reported the use of aqueous dispersions of colloidal silica in increasing yarn friction and thereby reducing slippage in rayon fabrics, whilst the employment of the usual highly complex organic derivatives for this purpose has also been patented.[166]

In spite of the war-time importance of the subject, little has been published about the effects of standard dyeing and finishing treatments on the rate of chemical degradation of cellulose textiles during weathering. A. K. Haynes[167] has reported on the tendering of dyed fabrics under several types of climatic conditions and found that azoic colours increase the rate of degradation relative to an undyed bleached control whereas vat dyes produce little change and sulphur, diazo-, and light-fast direct colours, in general, exert a protective action ; chemical tendering was not related to the degree of fading observed.

E. Race, F. M. Rowe, and J. B. Speakman[168] have confirmed that insoluble chromium and chromium plus iron compounds, as formed in mineral khaki dyeing, increase the resistance of cotton cellulose to degradation during weathering, but find that this protective action is lost if copper compounds are also applied ; under certain alkaline conditions of treatment the presence of copper leads to accelerated degradation and

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[159] Courtaulds Ltd., C. M. Whittaker, C. C. Wilcock, W. Armfield, and H. W. Best-Gordon, B.P. 575,964 ; B., 1946, II, 206.

[160] Courtaulds Ltd. and C. M. Whittaker, B.P. 579,709 ; B., 1946, II, 461.

[161] E. I. Du Pont de Nemours & Co., W. E. Hanford, and D. F. Holmes, B.P. 571,975 ; B., 1946, II, 46.

[162] United States Rubber Co., B.P. 571,358 ; B., 1945, II, 378.

[163] J. Katz, Assr. to Warwick Chem. Co., U.S.P. 2,201,041 ; B., 1946, II, 124.

[164] R. G. Bartlett, A. H. Lord, C. A. Norris, and Imperial Chem. Industries, B.P. 577,313 ; B., 1946, II, 336.

[165] *Rayon Text. Month.*, 1945, **26**, 347.

[166] Soc. Chem. Ind. in Basle, B.P. 574,644 ; B., 1946, II, 168.

[167] *Amer. Dyestuff Rep.*, 1946, **35**, 29 ; B., 1946, II, 380.

[168] *J. Soc. Dyers and Col.*, 1946, **62**, 9, 19 ; B., 1946, II, 121.

copper compounds were found to be rapidly leached out during weathering in an industrial atmosphere. C. H. Bayley and M. W. Weatherburn[169] have observed a high rate of loss of copper from copper naphthenate rot-proofed fabrics during exposure, but found that this type of copper compound did not materially affect the rate of tendering, although the proofed fabrics, after a leaching test, were less able to withstand microbiological attack under conditions of soil burial.

A rot-proof finish depending on the treatment with acid solutions of iron, chromium, or copper salts of fabric impregnated with hydroxymethylcellulose has been patented[170] whilst the effects of partial acetylation of cotton on resistance to microbiological attack have been reported by C. F. Goldthwait, J. McLaren, and S. T. Voorhies, jun.,[171] who found that acetyl contents of 20—30% gave high resistance to attack in soil burial tests.

The effects of substituent groups on the toxicity of a number of basic dyes to the spores of *Fusarium culmorum* have been determined by W. M. Dion and K. A. Lord,[172] and J. W. Appling and B. F. Shema[173] have reported the acclimatisation of bacteria to sodium pentachlorophenoxide. The cause of acid tendering in rubber-lined fire hose has been traced by A. C. Thaysen and H. J. Bunker[174] to the action of sulphur-oxidising bacteria.

Imperial Chemical Industries[175] have patented the use of zinc dimethyldithiocarbamate for increasing the resistance of textiles to microbiological attack.

In an informative paper by F. L. Goodall, T. F. Gorton, and J. V. Summersgill[176] the preparation, properties, and textile applications of DDT are described; although relatively few insect pests attack cellulose, damage when it occurs is generally severe.

The subject of synthetic resin coatings is one in which considerable progress is being made. Cellulose ester and ether coatings are liable to develop tackiness and are not resistant to the action of organic solvents. In a recent patent[177] these disadvantages are claimed to be overcome by incorporating lower alkyl ethers of dimethylolurea into the mix; polymerisatiȯn is effected by curing and the process may be accelerated by using a phthalic anhydride catalyst. The incorporation of 25—35% of aluminium naphthenate brings about an increase in the softening range of

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[169] *Amer. Dyestuff Rep.*, 1945, **34**, 457; *Canad. J. Res.*, 1946, **24**, **F**, 193; B., 1946, II, 329.

[170] Sylvania Industrial Corp., B.P. 574,814; B., 1946, II, 168.

[171] *Text. World*, 1946, **96**, 115.

[172] *Ann. Appl. Biol.*, 1944, **31**, 221.

[173] *Paper Trade J.*, 1943, **117**, *TAPPI Sect.*, 157; B., 1946, II, 203.

[174] *Nature*, 1945, **155**, 322; B., 1946, II, 395.

[175] With W. Baird, J. G. Evans, and J. R. F. Jackson, B.P. 574,408; B., 1946, II, 125.

[176] *J. Soc. Dyers and Col.*, 1946, **62**, 189; C., 1946, 254.

[177] E. I. Du Pont de Nemours & Co., B.P. 572,906; B., 1946, II, 97.

low-molecular polythene polymers and enables a more satisfactory control of consistency to be obtained.[178]

The formation of polyvinyl acetal *in situ* on textile fabrics in the production of flexible, water-resistant coatings and linen-like or organdie finishes is a new development contained in a Calico Printers' Association patent.[179] By modification of polyvinyl acetal and butyral resins with monohydric alcohol–urea–formaldehyde condensates (which probably react to form cross-links between the free hydroxyl groups in the polymer chains) coatings which remain flexible over a wide temperature range are obtained.[180] High resistance to flexural and abrasive action is claimed[181] for finishes obtained by coating with a synthetic linear polyamide and overlaying with the reaction product of a polycarbimide and a polyester amide, the latter having an ester content above 50%.

Permanent finishes on rayon and cotton obtained by treatment with sodium zincate solutions of substantially unmodified cellulose, followed by precipitation of the cellulose, are claimed[182] to give increased stiffness and reduced slippage and shrinkage, whilst methods for obtaining metallic coatings with good adhesive properties have also been patented.[183]

ANALYSIS AND TESTING METHODS.

Reference has already been made to developments under this heading which have specific application; those dealt with here are of a more general character.

The "skin effect" observed with some types of viscose rayon has been studied by F. F. Morehead and W. A. Sisson,[184] who have developed an improved staining technique with basic dyes and applied it in determining the effect of spinning conditions on skin formation.

A procedure for estimating combined carbon disulphide in viscose solutions has been described by H. L. Barthelemy and L. Williams.[185] The method depends on the quantitative transformation of sulphur compounds (with the exception of sulphate-sulphur), in the presence of sodium zincate, into zinc sulphide, which is then estimated iodometrically; by-product sulphur is estimated in the filtrate following precipitation of the sodium cellulose xanthate, and the combined sulphur is obtained by difference. Full experimental details for the determination of non-sulphate sulphur in viscose sheet and filament are contained in a British Cellophane Ltd. patent specification.[186] On digestion of the viscose with

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[178] C. Dunbar, C. D. Weston, and Imperial Chem. Industries, B.P. 573,834; B., 1946, II, 89.

[179] With L. A. Lantz and A. Schofield, B.P. 573,574; B., 1946, II, 89.

[180] E. I. Du Pont de Nemours & Co., B.P. 572,206; B., 1946, II, 57.

[181] R. E. Christ and W. E. Hanford, Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,333,917; B., 1946, II, 251.

[182] S. M. Edelstein, B.P. 573,768; B., 1946, II, 89.

[183] Callender–Suchy Developments Ltd. and C. T. Suchy, B.P. 572,071; B., 1946, II, 15.

[184] *Text. Res.*, 1945, **15**, 443.

[185] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 624; C., 1946, 21.

[186] B.P. 577,657; B., 1946, II, 334.

sulphuric acid and aluminium foil carbon disulphide and hydrogen sulphide are evolved and absorbed in alcoholic potash and alkaline cadmium hydroxide respectively; these sulphur compounds are then determined by standard methods.

Reference has already been made to the problem of chlorine retention during bleaching by resin-treated rayon fabrics. W. Stump[187] has proposed a simple accelerated ageing test for assessing the ultimate damage which may result from this cause.

A Society of Dyers and Colourists' committee[188] have standardised tests for measuring the levelling power and salt-controllability of direct dyes and have classified many dyes on the basis of these tests, whilst J. Lenoir[189] has utilised the principles of chromatographic adsorption to determine the homogeneity of commercial dyes.

There is no doubt that, in the past, too much reliance has been placed on the results of biological tests bearing little or no relation to service conditions in assessing the efficiency of rot-proofing agents. The American Association of Textile Chemists and Colourists[190] have put forward testing methods of much wider scope for determining initial mildew-resistance and the permanence of such resistance during the storage and use of rot-proofed textiles.

S. Gottlieb and P. B. Marsh[191] have applied the reagent 4-amino-antipyrine to the colorimetric determination of phenolic fungicides in textiles whilst E. T. Illing and W. H. Stephenson[192] describe methods of analysis for DDT which are rather more specific than the one suggested in a paper to which reference has already been made.[176]

Anti-swelling finishes on rayon generally result in a reduction of the affinity of the cellulose for direct dyes. Making use of this property, F. Dittmar[193] has shown that dyeings with Sirius Light Blue following a pre-swelling treatment in 8—18% aqueous sodium hydroxide may be used to indicate the presence and uniformity of this type of finish.

Chemical tests having a specific application are to be preferred in identifying resin finishes, but the staining technique is useful in sorting tests, or where chemical tests are not available. Qualitative tests of both types have been described by F. P. Brennan,[194] who found that polyvinyl and polyacryl resins are deeply stained by Celleton Fast Yellow RRA (confirming an observation made by H. Rath[195]), whilst cellulose ether finishes possess high affinity (at room temperature) for Solantine Blue 4GL. The identification of nitrogen-containing synthetic

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[187] *Amer. Dyestuff Rep.*, 1946, **35**, P177.
[188] *J. Soc. Dyers and Col.*, 1946, **62**, 280; B., 1947, II, 16.
[189] *Bull. Soc. chim.*, 1942, [v], **9**, 475; C., 1946, 240.
[190] *Amer. Dyestuff Rep.*, 1946, **35**, 274.
[191] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 16; C., 1946, 118.
[192] *Analyst*, 1946, **71**, 310; C., 1946, 251.
[193] *Textilber.*, 1944, **25**, 205; C., 1946, 88.
[194] *Rayon Text. Month.*, 1944, **25**, 339; C., 1946, 23.
[195] *Textilber.*, 1940, **21**, 175; C., 1946, 89.

resins has been investigated by C. P. A. Kappelmeier[196] but some of the proposed tests require more material than is generally available in the examination of textile finishes.

A refinement to the method of measuring chemical degradation of cellulose by the fluidity of solutions in cuprammonium has been proposed by C. M. Conrad and V. W. Tripp,[197] who have derived equations whereby the observed fluidity value, obtained with a single-discharge viscometer and a specified cuprammonium reagent, may be corrected to a standard velocity gradient.

High-frequency electrical heating has been applied by Marconi Instruments Ltd.[198] to the rapid determination of moisture contents; the sample may be weighed during drying and automatic warning given when the fall in power consumption indicates that the process has reached completion.

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[196] *Paint Tech.*, 1946, **11**, 7; C., 1946, 171.
[197] *Text. Res.*, 1946, **16**, 275.
[198] With W. B. Bartley, B.P. 569,889; C., 1945, 291.

PULP AND PAPER.

By JULIUS GRANT, M.Sc., Ph.D., F.R.I.C.

CONDITIONS in the industry during the past year have shown a disappointingly slow return to "normal." Wood pulp from Sweden has not come up to expectations in quantity, owing to the shortage of coal in that country and to the necessity to burn wood in its stead. Little wood pulp was expected from Finland and Norway, so that there have been no great disappointments here. Added to this is the falling off in collections of waste paper, despite the renewal of propaganda, and the critical domestic coal supply position.

The return of esparto grass, after nearly six years, has, however, been a welcome relief, although the quantities received are only some 50% of the pre-war figures. A brighter side of the picture is also presented by the maintenance of imports of wood pulp from Canada and, indeed, it seems that it must be in this direction that we must look for our principal source of pulp supplies in the future. The easing of the labour position and of certain of the Paper Control regulations have also helped the paper maker, but on balance, it may be fairly stated that working conditions have continued very difficult—not only for the producer, but also for the consumer, who is still acutely aware of a paper shortage.

The latest reports from the newly-formed British Paper and Board Research Association record welcome signs of good progress in the alteration and equipping of the buildings recently acquired to house the laboratories, and the beginning of active investigations may shortly be expected. In common with the other industries, pulp and paper makers have sent teams to Germany to investigate mills in that country. Some of the reports have now been published (see especially, A. C. Hill and W. B. Campbell[1]). The general opinion (shared by most of the teams) is that no outstanding advances of a fundamental nature have been made in Germany during the war years. Many relatively minor, though useful, items of technical information have, however, been acquired, and the visits have doubtless been of value if only to establish the true position of the German industry.

PULPING METHODS.

Raw Materials.—Cotton linters has long been used for the manufacture of fine paper, but this has been the so-called "mill-run" or "second-cut" linters. W. H. Jones[2] now draws attention to the advantages of "first-cut" linters, which in the raw state has a mean fibre length of 6·3—7·1 mm.

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[1] *Brit. Intelligence Objectives Sub-Committee* [1946], *Final Repts.* 49, 51, 52, *Item* 22; B., 1946, II, 372, 373.

[2] *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 93; B., 1946, II, 457.

The linters must be processed, namely by mild digestion with 1·5—3·0% caustic soda at 30—40 lb. per sq. in. for 4 hours, followed by washing and bleaching. The result is an 80—85% yield of strong pulp, which is beaten lightly and used with 50% of sulphite wood pulp in a variety of fine and speciality papers. R. G. Lewis[3] discusses the utilisation of agricultural residues for pulp for paper and board in general, and deals with cereal straws, flax fibre, maize stalks, and bagasse, from the historical, chemical, and economic viewpoints.

Of the new raw materials investigated, special mention must be made of Malayan meranti wood (*Shorea* spp.), which, as E. L. Hill[4] has shown, has economic possibilities as a source of pulp for wrapping paper so long as the supplies of raw material are accessible. Digestion conditions are 5% of caustic soda for 5 hours at 155—165°, but the bleachability is then only moderate, and the paper is inferior to a good-grade kraft, although close in formation and hard. Milkweed plant (*Asclepias* spp.) was found by L. V. Forman and D. Niemeyer[5] to be more suitable than straw for corrugating board by reason of its high yield and good stiffness and tearing-resistance values. Here again, accessibility of supplies is likely to be the deciding factor. Rod-milling in the dry state, followed by screening, yielded 15% each of bast fibre and waste dust, and 70% of wood fibre.

An interesting paper on the chemical composition of wood barks, by G. H. Segall and C. B. Purves,[6] fills a gap in this branch of the literature of wood pulping, since it is shown that the "lignin" fraction (comprising 80% of the bark dust) includes amorphous phenolic complexes readily removable by the sulphite or alkaline process. Oxidation reactions produce lignin-free pulps, which, however, are not equal in quality or yield to those obtained from the wood. As general experience has shown, it is unlikely that bark can be an economic source of high-grade pulps, even if processed by suitably modified methods. In connexion with the subject of bark, attention should be drawn to a report by E. C. Shaw[7] on the recently-introduced method of removing bark from small logs by water jets operating at 650—800 lb. per sq. in. pressure. The volume of water required is, naturally, large (600 gallons per minute), and the initial cost of the plant is high, but the maintenance costs are low and the method is very efficient so long as a continuous supply of logs is delivered to the unit.

Sulphite Process.—A new attack on the problem of the reduction of the pitch content of sulphite pulp is recorded by O. Kress and P. E. Nethercut,[8] who accelerate the well-known effect of seasoning by aëration for 8 hours ; this also reduces the water content of the wood and so saves steam, while the resulting drop in temperature of 7—8° reduces the fire

[3] *Paper Mill News*, 1945, **68**, *No.* 7, 62 ; B., 1946, II, 332.
[4] *Bull. Imp. Inst.*, 1945, **43**, 265 ; B., 1946, II, 161.
[5] *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 95 ; B., 1945, II, 370.
[6] *Pulp and Paper Mag. Canada*, 1946, **47**, *No.* 3, 149 ; B., 1946, II, 243.
[7] *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 61.
[8] *Ibid.*, **122**, *TAPPI Sect.*, 289 ; B., 1946, II, 373.

risk. Improvements in the Tomlinson magnesium bisulphite cooking process are indicated by R. S. Hatch,[9] who records economies in steam requirements as compared with the use of the normal calcium-base liquor, and minimum loss of sulphur (if relatively pure chemical is used) and absorption of magnesium salts by the pulp. The method allows the use of a recovery system, and the loss of magnesium should not exceed 5%. The yellowing of sulphite pulp on heating is due principally to the carbohydrate constituents, the resins and lignin having relatively little influence according to H. W. Giertz.[10] The products formed are insoluble in water, but partly soluble in alkali. However, removal of the finest sieve fraction from the pulp increases its stability, although this effect is less marked with the soft-bleached sulphite pulps. Acidification after bleaching induces yellowing.

Yields from the sulphite process are discussed by J. C. W. Evans[11] in his summary of replies to a questionnaire from 38 Canadian mills. The values range from 41·7 to 51% (an exceptional claim is 58%). The yield decreases in the order: black spruce, white spruce, balsam, fir, jack pine, hemlock, and sawdust; it is raised by pre-saoking prior to and circulation of the liquor during cooking.

A report by E. G. Locke[12] summarises the present position of the yeast-producing section of the sulphite pulp industry in Germany. The liquor is neutralised with lime, and fermented in presence of mineral nutrients (ammonium salts and phosphates) at about 32° for 4·5 hours. The yeast sludge is then defoamed, dewatered on a vacuum filter, and finally dried in a spray dryer or two-drum rotary dryer, according as flake or powder is required for ultimate consumption by humans or cattle, respectively. A similar process is being developed in Florida, according to R. D. Walker, jun., and R. A. Morgen,[13] though for cattle and poultry food only. On the laboratory scale some 90% of the reducing sugars can be utilised in a 15-hour fermentation cycle, producing consistent yeast yields of up to 5% by volume; very little alcohol results. A point of interest is that the liquors from the sulphite pulping of southern pine differ in composition from those obtained from other woods, in that the percentage of bound sulphur is much higher, so that relatively little sulphur dioxide can be recovered by steaming. Such recovery is becoming an increasingly important economic factor in the sulphite process, and papers by A. G. Hellstrom[14] and by W. A. Sherman[15] describe some recent innovations in procedure. The former favours a tile-lined cement tower containing 10 ft. of Raschig ring packing and fed with raw calcium bisulphite acid, and he claims a 90% recovery from the relief gases. The latter prefers a

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[9] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 118; B., 1946, II, 242.

[10] *Svensk Papperstidn.*, 1945, **48**, 317; B., 1946, II, 202.

[11] *Pulp and Paper Mag. Canada*, 1946, **47**, *No.* 3, 55; B., 1946, II, 244.

[12] *Pacific Pulp & Paper Ind.*, 1946, **20**, *No.* 1, 20; B., 1946, II, 245.

[13] *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 63; B., 1946, III, 239.

[14] *Pulp and Paper Mag. Canada*, 1946, **47**, *No.* 3, 119; B., 1946, II, 244.

[15] *Paper Mill News*, 1946, **69**, *No.* 7, 38; B., 1946, II, 330.

slow blow-down, starting 2 hours before the usual time; this ensures a more even load on the recovery system, but it also has indirect benefits in that it improves the yield, colour, and cleanliness of the pulp, and reduces "liming" in the circulating system.

Alkaline Processes.—A patent due to R. S. Curry[16] provides for the manufacture of a semi-pulp by continuous digestion. The raw material (which may be straw or wood) is soaked in hot water or alkali, and fed continuously, with the liquor, through a rotating disintegrating machine so designed as to break up the plant structure by impact, without undue damage to the cellulose fibres; the product is then screened, and is ready for a final cook with caustic soda, after which it may be washed and bleached. J. H. Noble and J. P. Rich[17] discuss recent methods for the continuous washing of kraft wood pulp, and deal with layout, mechanical equipment, and control methods, maximum losses of 10, 15, and 20 lb. of chemical per ton being the objectives for soda, bleached sulphate, and board mills, respectively; the best results are to be expected with three-stage continuous vacuum filtration, and a reduction in the number of vacuum pumps, traps, and receivers minimises foaming tendencies and saves power.

V. Woodside[18] records that synthetic saltcake can be used successfully in kraft pulp manufacture, without increased corrosion effects, if it is added to the dissolving tank of an oscillating spray-type furnace; he gives analyses of the smelt and of the green and black liquors. E. A. Harper and N. V. Edmonson[19] report the results of 6 months' comparative trials of the direct and indirect cooking of sulphate pulp, and conclude that the latter is preferable where quality (including colour) is the main consideration, but that the incoming steam should be desuperheated to prevent carbonisation of liquor on the heater tubes. Carbon bricks have been suggested for lining the walls of kraft digesters. E. F. Tucker and L. C. Werking[20] confirm their resistance to attack by the liquor, and find also that their low heat-expansion renders them very resistant to thermal shock; moreover, they withstand abrasion and, of course, they do not contaminate the pulp with metallic impurities.

Testing Methods.—A rapid and simple test for residual lignin in pulp, suitable for the control of bleaching operations, comes from H. W. Giertz.[21] The pulp is dissolved in 76% sulphuric acid under standard conditions, and the intensity of the resulting brown colour measures the residual lignin; this is related to the whiteness of the final bleached pulp. O. P. Morgan[22] has investigated the application of the improved cupri-

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[16] B.P. 572,895; B., 1946, II, 46.
[17] *Paper Trade J.*, 1943, **117**, *TAPPI Sect.*, 219; B., 1946, II, 202.
[18] *Ibid.*, 1945, **121**, *TAPPI Sect.*, 212; B., 1946, II, 85.
[19] *Paper Mill News*, 1946, **69**, *No.* 7, 54; B., 1946, II, 330.
[20] *Paper Ind. & Paper World*, 1946, **28**, 60; B., 1946, II, 283.
[21] *Svensk Papperstidn.*, 1945, **48**, 485.
[22] *Pacific Pulp & Paper Ind.*, 1946, **20**, 56; B., 1946, II, 202.

ethylenediamine method for determining viscosity to bleached, ordnance-grade wood pulps ; he finds that the test is sensitive to changes in cooking conditions and in the nature of the wood, and that it has possibilities for controlling the quality of the unbleached pulps also. The determination of the caustic soda content of black liquor by ordinary titration involves the difficult problem of seeing the indicator end-point. W. V. Torrey and G. R. Nelson[23] overcome this by adding barium chloride and titrating to pH 8·25, using a glass electrode ; titration of the same sample to pH 2·40 gives the total alkali. Useful sorting tests for the identification of chemicals and non-paper-making fibres in rags are due to F. L. Simons[24] ; thus, any fabric which forms a molten lump on heating, is unaffected by a flame, or is dissolved or softened by a 40% solution of phenol in acetone is unsuitable for paper making.

New TAPPI methods include a sieve test for pulpwood chips (T 16 sm-45[25]) in which a standard vibrating mechanism is specified ; volumetric and gravimetric methods for the determination of water-soluble sulphates and chlorides in pulps (T 229 m-45[26]), the only special feature of which is the standardised conditions of extraction ; and a procedure for the bacteriological examination of pulp and slush stock (T 228 m-45[27]), in which an aqueous suspension of the disintegrated sample is grown in Difco dehydrated nutrient agar at 37° for 48 hours. The TAPPI method for the permangante number gives (according to R. Bourgon[28]) the most satisfactory results, and it correlates well with the Sieber number when laboratory sheets of pulp are used which are not pressed too hard or over-dried ; Bourgon also specifies more closely than does the official method the permissible variations in the volumes of reagents used, and in the temperatures and times of the operations.

PAPER MANUFACTURE.

Beater Operations.—A further contribution to the rapidly growing literature of continuous beating comes from D. M. Sutherland[29] in the form of a system which, it is claimed, is applicable to all paper-making fibres ; a single, rotating disc-type refiner is used for both beating and refining. Freeness is controlled by varying the inlet pulp pressure and by recirculation of the stuff through a unit or group of units in parallel (according to the size of the paper machine).

R. H. Cubberley[30] has obtained good results by the sizing of V-board and its liner stock with petroleum-base asphalt–water emulsions with a

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[23] *Paper Mill News*, 1945, **68**, *No.* 18, 94 ; C., 1945, 241.
[24] *Pulp and Paper Mag. Canada*, 1945, **46**, 694 ; C., 1946, 166.
[25] *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 106 ; C., 1945, 242.
[26] *Ibid.*, 1 ; C., 1945, 242.
[27] *Ibid.*, 31 ; C., 1946, 21.
[28] *Pulp and Paper Mag. Canada*, 1946, **47**, *No.* 3, 125 ; C., 1946, 167.
[29] *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 25 ; B., 1946, II, 372.
[30] *Ibid.*, 1945, **121**, *TAPPI Sect.*, 111 ; B., 1946, II, 11.

mineral colloid emulsifier ; they are better even than those obtained with the conventional sizes, and higher machine speeds (due to freedom from foam) and wet- and dry-bursting strengths, together with a 50% saving of alum, are claimed. C. and K. Singh[31] report good sizing results with a crude alkaline extract of groundnut cake ; unfortunately, for many purposes this material is uneconomical owing to the relatively large quantities required, although it can be used more profitably in admixture with rosin size

Two papers discuss the topical subject of melamine resins. One (by B. Ivarsson and B. Steenberg[32]) deals with the routine analysis of the dilute solutions (as added to the beater), a matter hitherto of some difficulty owing to the absence of good colour reactions, and to the unreliability of the Kjeldahl nitrogen determination (because of the stability of the triazole ring) ; a nephelometric method is proposed, the turbidity being produced by adding alkali under standardised conditions. The other paper (by F. A. Strovink[33]) deals with the technique of using the resin, which, it is stated, should be added to the stock as near the wire as possible. Of special interest, however, are the methods he gives for reclaiming "broke" containing the resin. Boiling at 15—40 lb. per sq. in. for 1—3 hours hydrolyses the resin, and treatment in a Hydrapulper or beater with alum at 82—83° completes the defibration.

The Paper Machine.—C. H. Pike[34] points out that a normal paper web has good electrical insulating properties, but that these can be improved by elimination of air and moisture so far as possible, and by impregnation : wood pulp (especially mixed with some manila pulp) is the most suitable furnish, the presence of the latter being particularly suitable for use with high voltages. Chlorinated benzene impregnants are frequently used, but they need to be stabilised (*e.g.*, with anthraquinone), and L. Egerton and D. A. McLean[35] have shown that stabilisers of this type do not appreciably affect the conductivity. In a new application of coating on the paper machine, Champion Paper & Fibre Co.[36] claim the use of a mixture of adhesive and pigment, the coated side of the paper being then pressed, while wet, against a liquid oil film (*e.g.*, deodorised kerosene) carried on a smooth roll ; when the coating has solidified the paper is dried in the usual way.

In a search for a substitute for locust bean flour, B. W. Rowland[37] found that guar (*Cyamoposis tetragonaloba* or *C. proraloides*), an Indian forage crop, yields a cheaper mucilage which, if added to the head box, slows the stock on the wire, but improves sheet strength and formation to a greater extent than can be attained when the same degree of slowness is

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[31] *Forest Res. Inst., Dehra Dun*, 1945, *Bull.* 126 ; B., 1946, II, 118.
[32] *Svensk Papperstidn.*, 1946, **49**, 1.
[33] *Paper Mill News*, 1945, **68**, *No.* 49, 28 ; B., 1946, II, 332.
[34] *Paper Maker*, 1946, **111**, TS 11 ; B., 1946, II, 162.
[35] *Ind. Eng. Chem.*, 1946, **38**, 512 ; B., 1946, II, 332.
[36] B.P. 575,254 ; B., 1946, II. 204.
[37] *Paper Maker*, 1945, **110**, TS 63 ; B., 1946, II, 85.

produced by mechanical refining; moreover, the web is free enough on the presses and dryers to allow an increase in speed of up to 10%.

The staff of the Research Laboratory of the Lindsay Wire Weaving Co.[38] have found that electrolytic corrosion of Fourdrinier wire seams is more common in summer than in winter, and that it is reduced by the inclusion of a brass weft in a bronze wire. Other factors which favour corrosion are: water having a high content of salts or organic matter, badly washed pulps containing bleach residues, and the use of an acid precipitant (*e.g.*, in the manufacture of high-wet-strength papers). An analogous problem is the mildewing of felts, and increases in life of over 20% have been obtained (by F. A. Soderberg[39]) by spraying new felts with a 1% solution of Preventol GD (dichlorodihydroxydiphenylmethane), followed by treatment with dilute acid to precipitate the substance on to the wool; this material is stable, non-toxic, and non-irritant. The rate of drying of paper on the machine has been studied by V. S. Burstein,[40] who attempts to relate the thermal insulating properties of the vapour layer between the paper web and the drying cylinder with the variation in its thickness as determined by the tensions on the web and on the felt. The drying rate increases proportionally with the temperature of the dryer until the free water in the sheet is at 100°. This usually corresponds with a dryer temperature of about 120°; thereafter the rate of increase is less. S. B. Applebaum[41] describes the Permutit reclaimer for white water, in which the liquid is agitated in an inverted-funnel-shaped compartment inside a cylindrical tank, from which it flows into the outer vessel; here the solid matter forms a suspended "blanket," 7—8 ft. thick, which acts as a filter for the incoming liquors, so that the thickened solids may be bled off for re-use as fast as they are formed. It is claimed that the fibre contents of white water containing 1—9 lb. of fibre per 1000 gallons may be reduced to 0·1 lb. per 1000 gallons.

As is pointed out by I. H. Andrews, R. S. Bledsoe, and S. A. Collicutt,[42] the properties of the wet sheet which control its behaviour on the suction couch of a paper machine are related to the adhesion between the sheet and the wire and to the ability of the sheet to withstand breakage when being removed from the wire. A method for making wet sheets under conditions which approach those operating at the suction couch was devised, and wet-strength and stretch tests indicated that, apart from the adhesion effect between the web and the wire, and so long as the freeness is constant, the usual dry-strength tests are a suitable guide to the wet strength of the web.

After-Processes.—G. W. Stanton and W. A. Henson[43] draw attention to the uses of Saran (polyvinyl chloride) resin latex for coating paper,

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[38] *Paper Ind. & Paper World*, 1946, **28**, 53; B., 1946, II, 284.
[39] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 281; B., 1946, II 331.
[40] *Ibid.*, 103; B., 1946, II, 246.
[41] *Ibid.*, 249; B., 1946, II, 374.
[42] *Pulp and Paper Mag. Canada*, 1945, **46**, 681; C., 1946, 89.
[43] *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 68; B., 1946, II, 416.

where resistance to oils, acids, alkalis, organic solvents, and water, together with gloss and heat-sealability, are required. The resin is applied as a colloidal dispersion in water, and full details of technique are given; most types of ordinary coating machine may be used, but festoon drying is desirable. The ordinary tub-sizing process may be modified to produce high-wet-strength papers, according to Wiggins, Teape & Co. (1919), Ltd., and S. R. H. Edge,[44] by the use of an aqueous solution containing approximately 5% of gelatin, 2·5% of urea, 1% of alum, and 6·25% of formalin. C. C. Kesler, J. E. Killinger, and E. T. Hjermstad[45] show that suitable treatment of corn starch with a urea–formaldehyde resin reduces film shrinkage to an extent which depends on the amount of resin present. The resulting product then produces good wax-tests, printability, and gloss, when used in clay paper-coating mixes; high strength, gloss, erasure properties, porosity, and oil absorption, when used as a tub-sizing medium; and improved wet- and dry-scuff-resistance when applied to paper as a calender size. Laminated, water-resistant, embossed wall-paper is made, according to L. C. Fleck,[46] by treating one side of each of two sheets of paper with a casein adhesive containing a small amount of phenol, and with a starch adhesive containing formalin and/or alum, respectively; the sheets are laminated together and embossed in one operation.

A paper by E. E. Thomas[47] is worthy of special note, because it deals with the fundamental principles governing the actions of calenders and supercalenders, a specialised subject hitherto somewhat neglected in the literature. The new types of American supercalenders described have protected anti-friction bearings, precision control of web tension, speed, and roll pressure, with hydraulic pressure application. They are up to 200 in. wide, with 10—12 rolls and a double finisher, and they may be used for coating at up to 1800 ft. per minute. In the same connexion, attention should be drawn to the studies of J. A. Van den Akker[48] on the rôle of shear effects in calendering; it is shown that pressure (without shear) will not produce the high finish and transparency desired for coated and glassine papers, respectively.

PAPER TESTING.

Strength Tests.—A number of new and revised TAPPI standard methods have been published. The flexural resistance and deflexion of fibreboard (T 469 sm-45[49]) are measured, on the Schopper tensile strength tester, by supporting the sample strip horizontally between a central cylindrical stirrup and a pair of similar stirrups resting on opposite sides of the paper, and attached to the upper and lower jaws of the instrument, respectively; the load and deflexion at the point of break or maximum

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[44] B.P. 578,541; B., 1946, II, 378.

[45] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 133; B., 1946, II, 246.

[46] U.S.P. 2,200,839; B., 1946, II, 120.

[47] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 235; B., 1946, II, 330.

[48] *Paper Ind. & Paper World*, 1946, **28**, 57; B., 1946, II, 285.

[49] *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 11; C., 1946, 90.

load are measured. The Clark instrument is adopted for measurements of the allied properties of rigidity, stiffness, and softness (T 451 m-44[50]). In the test for the compression-resistance of paper board (T 472 m-46[51]) the sample, in the form of a ring or tube, is mounted between two parallel platens which are brought together at a constant speed; the load at crushing is noted. It is well known that the resistance to tearing of a sheet of paper is different at the edge and after the tear is started. The familiar test for the latter is now supplemented by a standard test (T 470 m-45[52]) in which a strip is torn simultaneously, at opposite points on the edges, by means of a thin V-notched beam held in a stirrup fastened to a jaw of the tensile strength tester. In a new test for stiffness, due to E. Eftring,[53] a strip of the paper is clamped horizontally at one end, the remainder being supported on an edge 30 mm. distant, which is attached to one arm of a balance. The deviation (d mm.) is noted when the other arm is loaded with a known weight (w mg.), chosen according to the type of paper being tested. Then w/d gives the stiffness modulus.

Penetration and Sizing Tests.—The difficult problem of devising a standardised ink-line test for sizing has been attempted by M. O. Schur and R. M. Levy,[54] who use as a "pen" a brass frame supported on three wheels, one of which has a uniform circumferential slot, which is filled with standardised ink (methylene-blue in dilute phosphoric acid). This is drawn across the sheet at a known speed and under a known load. The spread of the resulting line (as compared with the width of the ink slot) is measured microscopically. Sheathing papers used under the external finish of the wall of a building, to provide extra resistance to the weather, should have wind- and water-resistance, strength, good water-vapour-permeability, and permanence; appropriate tests are described by J. D. Babbitt and J. Hyland.[55] In an isostatic method for determining the gas-permeability of paper described by D. W. Davis,[56] the sample is used to separate two chambers, through which the test gas and a "sweep" gas are passed, respectively, at the same pressure; the degree of permeation of the former, through the paper into the latter, may then be measured chemically. Thus, oxygen is used as the "sweep" gas for carbon dioxide, the latter being absorbed in ascarite and determined gravimetrically.

Printability tests involve measurements of the rate of penetration of printing ink into paper, and a photo-electric method of doing so in terms of time–light reflexion curves is described by A. Voet and J. S. Brand.[57] For most papers such curves are linear up to the saturation point, and they are similar in type for the same ink on various papers. Variations with

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[50] *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 197; C., 1946, 22.
[51] *Ibid.*, 1946, **122**, *TAPPI Sect.*, 137; C., 1946, 168.
[52] *Ibid.*, 1945, **121**, *TAPPI Sect.*, 179; C., 1946, 22.
[53] *Svensk Papperstidn.*, 1946, **49**, 169.
[54] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 121; C., 1946, 169.
[55] *Pulp and Paper Mag. Canada*, 1946, **47**, *No.* 5, 82; B., 1946, II, 284.
[56] *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 97; C., 1946, 256.
[57] *Ibid.*, **122**, *TAPPI Sect.*, 264; B., 1946, II, 374; C., 1946, 255.

temperature appear to depend on the corresponding variations in the viscosity of the pigment. In addition to the penetration, the coverage of the ink is important, and R. Buchdahl and M. F. Polglase[58] describe two novel methods for measuring it. A known amount of a soluble dye or of a radioactive material is added to the ink; the former is subsequently extracted from the print and determined colorimetrically; in the latter case the activity of the print is determined with a Geiger–Müller counter. Oil absorption is of importance in tests for mouldable paper products also. H. R. Alley[59] uses commercial Nujol for this purpose, and measures photoelectrically the reflectance of the opposite side of the sheet to that at which the oil is applied; tests for permanent and temporary distortion under pressure are also described, and "mouldability values" are obtained from the height of the bulge just prior to rupture in the Mullen bursting strength tester.

Chemical and Biological Methods.—Recommended modifications of the Libermann–Storch and Raspail qualitative tests for rosin in paper are contained in TAPPI method T 408 m-44.[60] The quantitative method recommended involves conversion of insoluble resinates into alcohol-soluble resins by treatment with a strong volatile acid under standard conditions (to minimise attack on the cellulose), extraction with ether, and correction for any unsaponifiable oils or waxes present. The method is, of course, unsuitable in presence of synthetic resins, and a scheme devised by J. H. Graff[61] meets this requirement so far as qualitative tests are concerned. Reagents used are iodine (for starch), biuret (glue), Raspail test (rosin), ammonium hexanitratocerate (polyvinyl alcohol), and Neocarmin W, Shirlastain, Colotex B, and Texchrome for the various synthetic resins.

A TAPPI method for testing analytical filter-papers (T 471 sm-46[62]) gives standardised versions of known methods for density, α-cellulose, pH, ash, and copper number. Filtration rate is determined by two-thirds filling the filter-cone with filtered water at 23°, allowing 20% to pass through, and timing the rate of passage of 50% of the remainder. Wet bursting strength is determined on a water-saturated pack of five circles. The TAPPI method (T 468 m-45[63]) for water-soluble chlorides and sulphites in paper is on the same lines as that used for wood pulp (*loc. cit.*[27]).

The larvæ of the cadelle and the adults of the lesser grain borer are used in the TAPPI method (T 473 sm-46[64]) for testing the insect-resistance of paper and paper products. The samples are used to cover shallow dishes containing the bait, or with complete packages these are filled

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[58] *Paper Mill News*, 1945, **68**, *No.* 34, 14; C., 1946, 22.

[59] *Paper Trade J.*, 1946, **122**, *No.* 25, 120; C., 1946, 168.

[60] *Ibid.*, *TAPPI Sect.*, 187; C., 1946, 169.

[61] *Ibid.*, 45; C., 1946, 169.

[62] *Ibid.*, 131; C., 1946, 169.

[63] *Ibid.*, 1945, **121**, *TAPPI Sect.*, 41; C., 1945, 242.

[64] *Ibid.*, 1946, **122**, *TAPPI Sect.*, 175; C., 1946, 168.

with infested wheat; the number of days required for complete penetration of the sample is noted. The TAPPI method for the bacteriological examination of paper (T 449 m-45[65]) is similar to that specified for pulp (*loc. cit.*[26]).

Miscellaneous.—F. W. Stocker and L. G. Durant[66] identify bleached sulphite and kraft fibres by staining a dry mount (prepared from a suspension in dilute acid) with Dupont Basic Orange 3RN in alcohol, followed (after blotting) with hydrochloric acid, blotting, Herzberg's stain, blotting, and an acidic solution of zinc and calcium chlorides. Pale tan to amber shades are obtained with bleached sulphite and blue shades with bleached kraft fibres; unbleached kraft fibres give an intermediate shade. The Institute of Paper Chemistry[67] has evolved a controlled relative humidity cabinet, in which specimens may be weighed without removal from the conditioned atmosphere; a selector device (operated from outside the cabinet) is used to deposit the cups to be weighed on a fork in the cabinet, but supported from the arm of a balance outside the cabinet.

The Printing and Allied Trades Research Association has released for general publication a valuable literature study (by V. G. W. Harrison[68]) on the subject of gloss and its measurement; the physical, psychological, and philosophical aspects of the subject are considered. G. A. H. Elton and G. Macdougall,[69] of the same Association, have given an account of their work on the evaluation of the surface area (roughness) of lithographic plates. One procedure is based on the peroxide decomposition method evolved by Clarke for the measurement of the specific surface areas of fibres; the other depends on the rate of loss of heat from the surface, and numerical agreement between the two methods is good. Specific surface volume is measured by a displacement method (*e.g.*, using water or oil); grain depth is assessed by polishing, cross-section, and profilometer methods.

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[65] *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 28; C., 1945, 241.

[66] *Pulp and Paper Mag. Canada*, 1946, **47**, *No.* 3, 123; C., 1946, 167.

[67] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 81; B., 1946, II, 203; C., 1946, 215.

[68] "Definition and Measurement of Gloss—A Survey of Published Literature" (London: PATRA), 1946.

[69] *J.S.C.I.*, 1946, **65**, 212; C., 1946, 315.

ACIDS, ALKALIS, AND SALTS.

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The difficulties facing the chemical industries in this country must exist to a greater or less degree in most of the countries of the world. Those chemical plants which were not damaged during the war have in general suffered from lack of maintenance, and considerable expenditure is necessary for repair and modernisation. In addition, the normal expansion of demand for basic chemicals must be overtaken. Scarcity of certain products amounts almost to famine. In view of the importance of heavy chemicals as raw materials to all other manufacturing industries it is essential that the greatest attention should be paid to the re-equipment of plants to make these products. Although work is continuing on new developments it is inevitable that the main effort must be directed towards increasing the output of existing products.

Shortages of fuel and construction materials are other factors which add to the feeling of frustration at the present time, but in the long run there is no doubt that these difficulties will be overcome.

Before the war the most important outlet for sulphuric acid was in the manufacture of superphosphate and ammonium sulphate and in wartime the production of these fertilisers expanded enormously. During the year under review the necessity of maintaining the output of agricultural products at a high level still persisted, with the result that the sulphuric acid industry has operated at its full capacity and Government plants have assisted private industry to supply a demand which could not otherwise have been met.

Experiments have been carried out under the supervision of the Building Research Station of the Department of Scientific and Industrial Research on the preparation of silicophosphates in a cement plant at Strood. Silicophosphates are made by calcining phosphate rock with soda ash and sand. The object of the experiments was to interest the manufacturers in this type of fertiliser containing citric-soluble phosphate, but until soda ash becomes more readily available there is little prospect of large-scale development of the process.

The limitations imposed on production of nitrogen in Germany and the relatively slow restoration of Continental plants to their pre-war output, due to the restricted supply of fuel, have contributed to the world shortage of fertiliser nitrogen. To some extent this has been met by the production of ammonium nitrate in wartime plants and its use as a fertiliser. It will probably be several years, however, before the nitrogen fertiliser industry is capable of supplying the full requirements of agriculture, particularly in view of the persistent fuel shortage and the delay in construction of new plants due to lack of other materials.

Reports on the examination of German chemical plants have appeared in increased numbers during the year and in general it may be said that the principal developments have been directly concerned with Germany's war effort. There are few major advances in established peace-time manufactures although some of the wartime developments may find application in these fields. One instance of this is the production of concentrated hydrogen peroxide used in connexion with the propulsion of rockets and other weapons where problems relating to stability and storage conditions have had to be overcome. Work on similar lines has been going on in countries outside Germany, but the pressure of wartime necessity brought this development to full-scale commercial production in Germany before this stage was reached elsewhere.

Plans for the use of gases from the cracking of hydrocarbon oils as raw materials for chemical manufacture have been announced by a number of companies in this country. This may be regarded as a major development.

Ammonia and Ammonium Salts.

The methods employed for the manufacture of the compressed hydrogen-nitrogen mixture required for ammonia synthesis are closely related to those used for large-scale hydrogen production. These are reviewed under "Industrial Gases," and this section deals only with the synthesis of ammonia.

With the ending of the war, and the consequent fall in demand for ammonia in explosives, considerable capacity for ammonia production has been made available for conversion to more peaceful uses. However, the total world demand for fertiliser nitrogen has been greatly in excess of the supply available during 1946. Grave concern has been expressed in the U.S.A.[1] about their supply of fertiliser nitrogen, and although the U.S.A. has capacity for synthesis of nitrogen compounds far beyond their present needs, most of the government-owned ammonia plants have been closed down, and it may be some time yet before these plants are restarted. Neutral countries who suffered a severe restriction of nitrogen supplies during the war continue to pursue plans for installing their own fixation plants: thus, Turkey[2] and Spain[3] have proposed extensive schemes, but in the latter country the companies concerned are handicapped because a considerable portion of their equipment had been ordered in Germany. The general impression recorded in the last annual Report, that German ammonia synthesis technique advanced but little during the war years, has been confirmed by the detailed reports of

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[1] *Chem. Eng. News*, 1946, **24**, 3180.
[2] *Chem. Age*, 1946, **55**, 615.
[3] *Chem. Trade J.*, 1946, **118**, 724.

the investigating teams, and the most recent German plant, that installed at Linz, appears to be of conventional design.[4]

R. J. Morley[5] has described German ammonia converters of the orthodox cooling-tube type; the Germans have also tried catalyst in the tubes and the cooling gas outside. R. M. Hunter[6] has given details of materials of construction. An attempt was made to employ multi-bed converters similar to those used in hydrogenation practice, with temperature control by the intermediate addition of cold gas, but this failed because of difficulties with corrosion of constructional materials.[5] It is therefore of interest that, according to J. A. Lee,[7] the Lake Charles plant in the U.S.A. employs twelve-bed ammonia converters, which suggests that these difficulties have been overcome and that intermediate or "quench" cooling is employed at 270 atm. pressure. The 16% ammonia obtained in the exit gas represents a reasonably good performance; constructional materials are not mentioned, however. Another American wartime plant, that at El Dorado, Arkansas, has been described[8]; again there is nothing particularly novel, but the method of preparation and the composition of two American ammonia catalysts are described. A very useful review of U.S.A. and Canadian ammonia plants has been published,[9] and detailed data on output, efficiency, and ammonia converter performance are recorded for the factories at Muscle Shoals (U.S.A.) and Welland (Canada).

A publication by J. S. Kazarnovski[10] of compressibility calculations on mixtures of hydrogen, nitrogen, and ammonia between 150° and 300° and 50 to 1000 atm. pressure will be of help in the theoretical treatment of ammonia converters, but the temperature range could with advantage have been extended.

The manufacture of ammonia catalyst in Germany has been described[5] and it is noteworthy that spent catalyst after re-fusion is said to be indistinguishable from new. However, perhaps the most significant item of German information relates to engineering rather than chemical technique, and it is their method of building up large pressure vessels from rolled strip of special section which is most interesting; it is described by R. W. Clarke.[11] A new procedure for rendering the catalyst for ammonia synthesis non-pyrophoric has been evolved by M. Temkin and V. M. Pishev,[12] and is the subject of a U.S.S.R. patent.[13] If, after reduction at 400°, the standard ammonia synthesis catalyst is allowed to

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[4] *Field Information Agency, Technical, No.* 481.
[5] *Combined Intelligence Objectives Sub-Commee., File* XXXII–107, *Item* 30.
[6] *Ibid.*, 1945, *File* XXIII–21, *Item* 22; B., 1947, I, 22.
[7] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 94; B., 1946, I, 129.
[8] *Petrol. Refiner*, 1946, **25**, *No.* 6, 245.
[9] *L'Ind. Chim.*, 1946, **347**, 95.
[10] *J. Phys. Chem. Russ.*, 1945, **19**, 314, 392.
[11] *Field Information Agency, Technical, No.* 577.
[12] *J. Phys. Chem. Russ.*, 1946, **20**, 151.
[13] U.S.S.R. Patent 64,607.

cool in a nitrogen-hydrogen mixture and then treated with a mixture of nitrogen, hydrogen, and 0·5—1% of air, it becomes covered with an oxygen or oxide film; when the catalyst is placed in the converter the passivating film wears off under the influence of the reducing conditions and temperature, and it is claimed that the activity of this catalyst is fully equal to that of a catalyst regenerated within a converter.

Some work has been reported on ammonium salts, mainly in connexion with ammonium sulphate. Consolidated Mining & Smelting Co. of Canada[14] describe an interesting method for the joint production of ammonium sulphate and sulphur from a solution containing ammonium thiosulphate, ammonium sulphite, and ammonium bisulphite. This solution is added continuously to an autoclave containing saturated ammonium sulphate solution and 10—50 g. of sulphuric acid per litre where, at 120—140° and 30—40 lb. per sq. in. pressure, autoxidation to ammonium sulphate and sulphur takes place; saturated ammonium sulphate is withdrawn continually, allowed to crystallise, and the mother-liquor returned to the autoclave, while liquid sulphur accumulates at the bottom of the vessel and is drawn off at intervals. Another novel development, in China, has been the production of ammonium sulphate from urine, by a base-exchange method; P. C. Yen[15] reports that 80% yields of ammonium sulphate, based on the nitrogen content of the urine, have been obtained.

In the production of by-product ammonium sulphate, E. V. Shulte[16] reports that a mixing type saturator has been developed, which provides a greater intimacy and a longer time of contact of the previously formed crystals with the supersaturated solution. He also describes the control of crystal size by variations of either the rate of circulation of liquor through the absorption zone or the superheat of the gas entering the saturator, and the production in this way of a comparatively free-flowing ammonium sulphate for fertilisers.

The recovery of ammonium thiosulphate and thiocyanate from liquors such as those obtained by evaporating spent ammonia gas washing solutions (thiocyanate/thiosulphate 1/0·8—1·5) has been described by J. A. Shaw.[17] In this process, an approximately equal volume of 95% ethyl alcohol is added to the liquor, forming two liquid phases, the upper predominantly alcoholic, and the lower predominantly aqueous; these layers are then separated and to each is added more alcohol to precipitate ammonium thiosulphate. The precipitate from the aqueous phase is washed to provide substantially pure ammonium thiosulphate; the alcohol is distilled from the alcoholic phase and ammonium thiocyanate can be recovered directly from the aqueous residue remaining after the distillation.

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[14] B.P. 571,212; B., 1945, I, 357.

[15] *J. Chinese Chem. Soc.*, 1945, **12**, 19; B., 1946, I, 290.

[16] *Blast Furn. Steel Plant*, 1946, **34**, 573, 625.

[17] U.S.P. 2,386,985.

Hydrazine.—During the war considerable progress was made in Germany in the manufacture of hydrazine hydrate for jet propulsion and rocket fuels. Two plants, one at Leverkusen and the other at Ludwigshafen, both owned by I.G. Farbenindustrie, have been described.[18,19] The German government are reported in these references to have built a much larger plant than either of these for the production of hydrazine hydrate at Gersthofen, but a description of this plant has not yet been reported.

The plant at Leverkusen[18] had a rated capacity of 60 tons of hydrazine hydrate a month. There were two distinct steps in the process. In the first step sodium hypochlorite solution, containing 12·7% of active chlorine, and ammonia solution of 20—25% concentration were caused to react in pressure equipment at 40—50 atm. to form hydrazine hydrate : $NaOCl + 2NH_3 = N_2H_4 + NaCl + H_2O$. Contrary to previous practice it was found that at this pressure no glue or gelatin was needed to act as an inhibitor to the decomposition of the hydrazine. The time of the solutions in the reaction coils, which were kept at 180°, was only a matter of a few seconds. This produced a crude 3% hydrazine hydrate solution containing 5—6% of sodium chloride and some caustic soda, in a yield of 70—75% based on the active chlorine in the hypochlorite solution. In the second part of the process, a standard evaporator was used for removing the sodium chloride and distilling over a solution of hydrazine hydrate. This solution was concentrated in two sets of distillation columns, the first producing 45% and the second 95 97% hydrazine hydrate solution.

The plant at Ludwigshafen,[19] which has been badly wrecked by bombs, produced hydrazine hydrate via hydrazine sulphate. Here, sodium hypochlorite, urea, and caustic soda were caused to react at 100°: $CO(NH_2)_2 + NaOCl + 2NaOH = N_2H_4 + NaCl + Na_2CO_3 + H_2O$; the hydrazine produced was precipitated as the sulphate by the addition of concentrated sulphuric acid; the sulphate, after filtration, was converted into the hydrate by means of caustic soda. Subsequent distillations gave 90—93% hydrazine hydrate solution in a yield of 40% based on the urea consumed. In both this and the Leverkusen plant the final distillation was carried out under a nitrogen atmosphere because of the extremely explosive nature of the product.

NITRIC ACID AND NITRATES.

Several developments have been discussed in the literature on the manufacture of nitric acid. The first of these relates to the use of oxygen in the conventional ammonia oxidation processes. The oxygen may be used either to enrich air or alone as in the Bamag direct process for concentrated nitric acid. Some aspects of these problems are discussed

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[18] *Combined Intelligence Objectives Sub-Commee.*, 1945, *File* XXII-18, *Item* 22; B., 1946, I, 290.

[19] *Brit. Intelligence Objectives Sub-Commee.*, 1945–46, *Final Rept.* 369, *Item* 22; B., 1946, I, 327.

by N. M. Shavoronkov,[20] who employs oxygen-enriched air of 27—29% oxygen content and adjusts the quantity to give about 5% of oxygen in the exhaust gases; he quotes experimental evidence for the increase in efficiency both of the conversion of ammonia into nitric oxide and of the subsequent absorption of the oxides of nitrogen. In spite of these benefits, he concludes that the direct process for the production of concentrated nitric acid is preferable and proposes recovery of tail gases by treatment with nitro-oleum. This process has been patented by L. J. Marcotte,[21] who arranges for the scrubbing of the gases with 20—60% oleum under conditions which lead to the production of a solid of composition $(SO_3)_2NO$, which is removed from the liquid by filtration through asbestos; the solid is subsequently decomposed and the sulphuric and nitric acids are recovered separately. A modification of existing processes to work with oxygen has been proposed by M. C. Sze and C. Wu,[22] who use an oxygen–ammonia mix of about 10% ammonia content, as in normal practice with air, thus avoiding the need for a diluent such as steam, to ensure safe conditions in the converter. Because of the very high oxygen content of the gases, the absorption section of the plant is much increased in efficiency and it is possible to achieve much more complete absorption than with air, since the tail gas contains 80—90% of oxygen. At the same time, more concentrated acid may be made and the exhaust gases, less a small purge to remove inerts, can be recycled because of the low concentration of oxides of nitrogen which can be maintained in the gases after the absorption plant. However, even with these benefits and the substantial saving of power over pressure plants, this process is economic only when low-priced by-product oxygen is available.

The arc process for the manufacture of nitric acid depended on the raising of a mixture of oxygen and nitrogen to a high temperature by passing the gases through an electric arc and then quenching the gases to stabilise the concentration of nitric oxide. This process is now used only to a very limited extent, but an editorial report of work at the University of Wisconsin[23] shows that, in a revised form, it may have a future. The special features of the new process are that the high temperature is achieved partly by heat exchange, in which a moving burden technique is utilised, and partly by the burning of fuel in the gas; by these means the energy requirements of the process are greatly reduced and the quenching is also much improved. The heat interchange in the process is covered by a patent by F. G. Cottrell[24] for the use of beds of granular ceramic material of specified surface/volume ratio for the quenching of the gases from the converter temperature of 2300° to the temperature of 1500°.

The principal interest in ammonium nitrate centres on its production

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[20] *Kislorod*, 1944, **4**, 27.

[21] Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,325,066; B., 1946, I, 98.

[22] *Chem. Eng.*, 1946, **53**, *No.* 8, 113; B., 1946, I, 406.

[23] *Chem. Industries*, 1946, **58**, 245.

[24] Can. Pat. 433,314.

in a form suitable for use as a fertiliser. A method of automatic control of a two-stage neutralisation process for the production of ammonium nitrate solution, using glass electrode pH meters, has been evolved by S. A. Harvey and P. R. Ewald,[25] and an improved continuous vacuum crystallisation process has been described by P. Miller and W. C. Saeman.[26] The latter process yields a rounded monocrystal with excellent mechanical strength which is eminently suitable for surface treatment to render the material comparatively non-caking and more resistant to moisture absorption. Suitable waterproofing agents and a criterion for determining their suitability are given by E. Fajans.[27] It has been found that when ammonium nitrate is granulated by spraying of a melt, the subsequent drying can cause weakening and disintegration of the granules; R. G. Datin[28] claims that this difficulty can be overcome by cooling the granules to a temperature below the 32° transition point and subsequently drying at about 100°; this procedure enables drying to be speeded up without weakening the granules.

An unusual method of obtaining nitrogen has been proposed by G. S. Ortner and J. N. Robinson[29] in which the tail gases from an ammonia oxidation plant are made to react with hydrogen over a copper catalyst to yield nitrogen for use in ammonia synthesis; the oxygen and nitrogen oxides in the gas are almost completely removed by this treatment. A modification of the normal nitric acid concentration processes in which indirect heating is employed for part of the denitration, so as to reduce the amount of sulphuric acid reconcentration required, is claimed by R. F. Peterson and P. G. Wrightsman[30]; complete denitration, however, is still effected by means of live steam.

PHOSPHATES.

The world shortage of phosphate rock continues despite the mining of the record quantity of 5,400,000 tons in the U.S.A. during 1945.[31] The planned production of 4,000,000 tons of phosphate rock in North Africa during 1945 fell behind schedule owing to lack of coal and an extreme drought which reduced the available hydroelectric power.[32] The first shipment of phosphate rock from Nauru and Ocean Islands for four years reached Australia and New Zealand during 1946. The estimated outputs of phosphate rock from Nauru during 1946 and 1947 are 200,000—275,000 and 500,000—650,000 respectively; it is hoped to produce at least the pre-war output of 1,000,000 tons in 1949, and plans have been made for an

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[25] *Instr.*, 1946, **19**, 500.
[26] 110th Meeting of Amer. Chem. Soc., *Sept.*, 1946.
[27] B.P. 575,617; B., 1946, I, 199.
[28] U.S.P. 2,382,298.
[29] *Chem. Industries*, 1945, **57**, 80; B., 1945, I, 357.
[30] U.S.P. 2,201,631; B., 1946, I, 17.
[31] *Chem. Eng. News*, 1946, **24**, 3181.
[32] *Fert. Feeding Stuffs J.*, 1946, **32**, 201.

annual production of 400,000 tons of phosphate rock at Ocean Island, which is twice the pre-war output.[33]

It was estimated that the production of phosphate rock in the U.S.A. during 1946 would be 6,049,000 tons, of which less than 10% would be sent abroad, although in pre-war years about one third of the United States output of phosphate rock was exported.[34] During 1945, about 4,000,000 tons of phosphate rock were used in the U.S.A. in the manufacture of 7,372,000 tons of normal superphosphate (basis 18% P_2O_5) and 251,000 tons of concentrated superphosphate (basis 45% P_2O_5). The production of normal superphosphate is expected to reach 8,333,000 tons during 1946 and the output of concentrated superphosphate will also increase. In addition, about 100,000 tons of fused phosphate of one kind or another will be made. The estimated consumption of phosphoric acid in the U.S.A. during 1946 is 1,339,000 tons (as P_2O_5), which is more than twice the average annual consumption during 1935–39 and represents an increase of 8% over the record quantity used in 1945. Capacity now exists in the U.S.A. to manufacture 12,000,000 tons of normal (18%) superphosphate and 500,000 tons of concentrated (45%) superphosphate.[31]

The average monthly production of superphosphate in the United Kingdom and Northern Ireland has shown a great increase from 38,900 tons in 1935 to 75,800 tons during 1945.[35] The annual Canadian production of N–P fertilisers (N 16, P_2O_5 20% ; and N 11, P_2O_5 48%) rose during the war years to 175,000 tons, of which 140,000 tons were exported. The world picture for 1946 nevertheless shows an estimated deficiency of 500,000 tons of fertiliser P_2O_5, which is equivalent to 2,500,000 tons of normal superphosphate.

There have been developments in the sulphuric and nitric acid methods of extraction of phosphate rock and further work has been done on kiln and furnace processes.

S. Nordengren[36] describes a new continuous process for the manufacture of superphosphate, in which phosphate rock and sulphuric acid are thoroughly mixed and discharged to a solidifying chamber ; in the mixing vessel, part of the phosphate rock reacts to form phosphoric acid, which converts the rest of the phosphate rock into monocalcium phosphate in the solidifying vessel and the mass matures in a chamber. The solidifying vessel is specially designed so that it does not destroy the porosity of the superphosphate passing through it ; the times of passage through the mixer, solidifying vessel, and maturing chamber are 2—5 seconds, 5—20 minutes, and 1—3 hours respectively. The rock is weighed and the acid measured automatically by an electrically operated

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[33] *Fert. Feeding Stuffs J.*, 1946, **32**, 369.
[34] *Ibid.*, 657.
[35] *Chem. Trade J.*, 1946, **118**, 338.
[36] *Chem. Age*, 1946, **54**, 691.

device and the power requirement is said to be low. The whole plant at Landskrona, Sweden, with an annual output of 220,000 metric tons, is operated by one man on shift.

Most of the other publications on phosphates describe German and American work. Several reports on phosphorus and phosphorus compounds have come out of Germany during the year. The manufacture of yellow phosphorus at Bitterfeld and Piesteritz by the reduction of phosphate rock in electric furnaces and the production from it of red phosphorus, phosphorus sesquisulphide, phosphorus tri-, penta-, and oxy-chlorides, and phosphoric acid are described by A. H. Loveless.[37] The Piesteritz plant, which produced a substantial proportion of the phosphorus made in Germany, contained four electric furnaces with a total capacity of 60 metric tons of phosphorus a day and a power requirement of 16,000 kw.-hr. per metric ton of phosphorus. The wet process for the production of phosphoric acid from phosphate rock and the subsequent preparation of mono-, di-, and tri-sodium phosphates, sodium hydrogen pyrophosphate, and sodium hexametaphosphate were also investigated.[38] The reports include diagrams illustrating the processes and the second gives some production costs.

A description of the plant used to produce phosphatic fertilisers at Leuna and Piesteritz is included in another report.[39] Granular fertilisers containing (*a*) N 16, P_2O_5 16, CaO 22%; (*b*) N 12, P_2O_5 12, K_2O 21·5, CaO 8%, were made by dissolving phosphate rock in nitric acid, cooling, removing the precipitated calcium nitrate tetrahydrate, neutralising with ammonia, and introducing slag or a potassium salt into the neutralised evaporated slurry; the resulting mixture was granulated in a screw conveyor. A new fertiliser called Leuna nitrophoska was being developed but had not yet reached the stage of commercial exploitation; it was made by dissolving phosphate rock in nitric acid (6·8—7 mols. of nitric acid per mol. of phosphorus pentoxide) and neutralising the resulting solution partly with lime and partly with ammonia, the exact proportion of the neutralising agents depending on the N/P ratio required in the finished fertiliser. A potassium salt could be added to the neutralised mixture before granulation. The product had undesirable hygroscopic properties but considerable improvement resulted if potassium sulphate was used as the source of potassium instead of potassium chloride.

In Holland the Dutch State Mines[40] have studied the four-component system $CaO–N_2O_5–P_2O_5–H_2O$ and have used the phase diagram obtained to develop a cyclic process for the production of dicalcium phosphate and calcium nitrate. Phosphate rock is added to the circulating acid solution, the temperature raised to 130°, and the resulting dicalcium phosphate filtered off; the filtrate is treated with nitric acid and cooled to

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[37] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 562.
[38] *Ibid.*, 256.
[39] *Field Information Agency, Technical, Final Rept.* 718.
[40] Belg. Pat. 447,737.

10—20°, when calcium nitrate tetrahydrate separates and is removed, the filtrate is heated, phosphate rock added, and the cycle of operations repeated. The process can be modified to produce monocalcium phosphate.

The Rhenania method of making the phosphoric acid in phosphate rock available as a plant food by calcining the rock with soda ash (22%) and sand (8%) in a rotary kiln has been described in detail by J. R. Hawes and F. M. Lea.[41] The development of a satisfactory process took 10—15 years but it is now possible to produce a fertiliser containing about 30% P_2O_5, of which 92—95% is soluble in citric acid or ammonium citrate. The Rhenania process requires careful control and experience in operation, but has been both technically and economically successful. The maximum annual output of one kiln converted from cement manufacture was 107,000 tons. A supplementary report[42] gives the production costs achieved in Germany and some of the analytical methods employed.

Work by the Metallgesellschaft A.-G. on the production of a phosphatic fertiliser by the calcination of a mixture of phosphate rock, sodium sulphate, and lignite in a reducing atmosphere at 800° has also been reported.[43] Satisfactory agricultural trials have been carried out in Germany on the product but the investigation has only reached the pilot-plant stage and further work will be needed before the process can be regarded as established. The replacement of sodium sulphate by potassium sulphate is said to be practicable and would permit the production of a P–K fertiliser. The disposal of kiln gases containing sulphur dioxide might present a problem, and the Metallgesellschaft A.-G. were undecided whether or not to develop the process to the full plant scale.

The production of silicophosphate in Great Britain ceased in 1946 owing to the reversion of the plant to its original use for cement manufacture. It is not known how far the manufacturing difficulties mentioned in last year's Report (p. 155) were overcome, but field tests on the product have been reported from which it is concluded that silicophosphate acts almost as rapidly as superphosphate over a wide range of soils and may be even more available than superphosphate on acid soils in wet regions.[44] Silicophosphate is particularly suitable for root crops and for re-seeding on phosphorus-deficient soils. On the other hand, silicophosphate acts less quickly than superphosphate or ammonium phosphate on dry soils and it is unlikely to be as useful as water-soluble fertilisers for spring cereals, especially in neutral or calcareous soils. It is of interest that the East African Industrial Research Board are working on a process somewhat similar to that developed in this country.[45] Considerable deposits of phosphate rock occur near Tororo in Uganda and the phosphoric acid

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[41] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 94; B., 1946, III, 214.

[42] *Ibid.*, 582.

[43] *Ibid.*, 107; B., 1946, III, 213.

[44] E. M. Crowther and F. M. Lea, *J. Min. Agric.*, 1946, **53**, 102; B., 1946, III, 168.

[45] *Third Ann. Rept.*, 1945, *E. African Ind. Res. Board.*

in this has been rendered available as a plant food by calcining the rock with soda ash from Lake Magadi, but without the addition of sand and steam as in the silicophosphate process. More than thirty tons of material have been made in a small rotary kiln.

The production of fused tricalcium phosphate by the defluorination of phosphate rock in a shaft furnace has been described in detail by the Tennessee Valley Authority.[46] An oil-fired shaft-furnace pilot plant was developed, the combustion of the oil providing the water vapour needed for adequate defluorination of the phosphate rock; the furnace charge contains 20—25% of silica. This pilot furnace was sufficiently successful to permit the construction of a demonstration unit containing two furnaces. The total designed capacity was 120 tons a day but an output of 150 tons a day was achieved. The molten phosphate tapped from the furnace was quenched and granulated by high-pressure water. The product resembled river sand in appearance and contained a maximum of 0·4% of fluorine. Fused tricalcium phosphate is neither water-soluble nor hygroscopic and can therefore be stored in the open and bagged in paper bags. Tests made on a wide variety of soils and crops showed it to be approximately equal to superphosphate for the same weight of total phosphoric acid content. Some material was remelted to reduce the fluorine content below 0·1% and then used as an animal feeding supplement. Tests by D. E. Williams, F. L. McLeod, E. Morrell, and F. P. Jones[47] on the addition of T.V.A. fused tricalcium phosphate containing 0·2—0·55% of fluorine as a phosphate carrier to the diet of rats have shown that fused tricalcium phosphate passing an 80-mesh sieve and containing not more than 0·3% of fluorine was virtually as effective as the control phosphate of the Osborne and Mendel salt mixture when evaluated by rat growth and body storage of phosphorus during a 90-day period. When judged by reproduction and lactation, the fused phosphate proved to be 75—93% as good as the salt mixture; this lower availability is possibly due to the presence of phosphorus in a less assimilable form than tricalcium phosphate rather than to the presence of fluorine in the tricalcium phosphate. E. J. Fox, W. L. Hill, K. D. Jacob, and D. S. Reynolds[48] have shown that superphosphate must be heated to 1000° to form tricalcium phosphate if the product is to be satisfactory as a phosphorus supplement in animal feeds; heating ordinary superphosphate to temperatures below 1000° removed most of the fluorine but produced calcium meta- and pyro-phosphates, which have a poor nutritive value.

A number of patents dealing with the production of phosphoric acid have been published. Norsk Hydro-Elektrisk Kvaelstofaktieselskab[49] claim a process in which raw phosphate is dissolved in hydrochloric or

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[46] T. P. Hignett and T N Hubbuch, *Ind. Eng Chem.*, 1946, **38**, 1208.

[47] *Ibid.*, 651; B., 1946, III, 201.

[48] *Ibid.*, 329; B., 1946, I, 229.

[49] Norw. Pat. 64,466; *Chem. Abs.*, 1946, 684.

nitric acid and the resulting acid solution is treated with a cation-exchange material containing hydrogen or alkali ions. The calcium is retained by the exchange material and a mixture of phosphoric and hydrochloric or nitric acids or a mixture of the alkali salts of these acids is obtained which is processed to give pure phosphoric acid or alkali phosphates. The exchange material can be regenerated by sea-water. M. Shoeld and the Davison Chemical Corporation[50] have patented a process for the production of phosphoric acid by leaching a bed of granular superphosphate with sulphuric acid; the phosphoric acid produced contains 40—50% P_2O_5 and is substantially free from calcium sulphate. In another process patented by J. H. Coleman and the Southern Phosphate Corporation[51] a phosphate complex with a CaO/P_2O_5 ratio between 1 : 1 and 1 : 2 is prepared by heating finely divided phosphate rock with 70% phosphoric acid at 175—240° until 75—90% of the moisture and 95—98% of the fluorine and other halogens have been removed; the resulting complex is digested for 1—2 hours with a mixture of sulphuric and phosphoric acids containing phosphoric acid (as 60% H_3PO_4) equivalent to about one and a half times the amount of P_2O_5 in the phosphate complex and enough sulphuric acid to precipitate all the calcium as calcium sulphate. Phosphoric acid containing 70—75% of H_3PO_4 and calcium sulphate in an easily filterable form are obtained. The "wet" and the furnace processes for making phosphoric acid have been compared by A. R. Maas,[52] who gives his reasons for preferring the furnace process; a description is given of some of the compounds which can be made from furnace acid and the recovery of vanadium from wet-process acid as phosphovanadic acid is also discussed.

I. Volfkovitsch and A. Loginova[53] have described the dissolution of apatite concentrates in hydrochloric acid and the subsequent processing of the solution to give sodium silicofluoride, rare-earth phosphates, and dicalcium phosphate. The Russian investigation of the system $CaSO_4$–P_2O_5–H_2O has continued and in the latest publication M. N. Schulgina[54] completes the study so far as the determination of the solubility relationships and stable solid phases are concerned, but the velocity of the transformation of one form of calcium sulphate into another remains to be investigated.

SULPHUR AND SULPHURIC ACID.

Sulphur.—Various methods of extracting sulphur from its ores have been reported. R. S. Siddiqui[55] finds that treatment of native sulphur in an autoclave with water and steam for 15 minutes at 35 lb. pressure or 10 minutes at 40 lb. is sufficient for extraction, though this method is not

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[50] U.S.P. 2,384,773; *Chem. Abs.*, 1946, 2595.
[51] U.S.P. 2,384,814; *Chem. Abs.*, 1946, 1978.
[52] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 112; B., 1946, I, 129.
[53] *J. Appl. Chem. Russ.*, 1944, **17**, 381; B., 1945, I, 356.
[54] *Ibid.*, 1945, **18**, 521.
[55] *J. Indian Chem. Soc., Ind. Ed.* 1945, **8**, 104; B., 1946, I, 265.

suitable for poor ores and earthy matter is not completely freed from sulphur; he also states that concentrated solutions of salts such as magnesium chloride which boil at a temperature above the melting point of sulphur can be successfully used. The powdered ore is mixed with the boiling solution; sulphur then separates in droplets which are converted into beads by diluting the hot solution with water.

J. K. Chowdhury and K. M. Hossain[56] use chlorine for the extraction of sulphur from iron pyrites. When dry chlorine is passed over heated pyrites the product consists of either sulphur or its chlorides. The residue depends on temperature and rate of flow of chlorine, though there is a certain limit up to which the reaction will give elementary sulphur and beyond which chlorination takes place, this so-called transition point is mainly a function of temperature, and the yield of sulphur also depends on the temperature and the chlorine flow.

A method of saving fuel in the recovery of sulphur from sulphur ore by melting has been described by W. R. Wade,[57] who heats a charge of sulphur in a retort until the sulphur melts and can be run off. The temperature is then raised and the sulphur vapour led into a bath of liquid sulphur so that, as the vapour condenses, a partial vacuum is set up.

Removal from sulphur of halides, for instance. sulphur chloride, can be effected, according to J. I. Jones and L. D. Richards (Assrs. to Dow Chemical Company),[58] by blowing the molten sulphur with dry or superheated steam, which decomposes the halides to form acidic vapours; these are swept from the sulphur without appreciable corrosion of the steel vessel.

Sulphuric Acid.—Sulphuric acid production continued at a very high rate throughout 1946, exceeding 160,000 tons a month in several months of the year according to the Monthly Digest of Statistics. Total production in the United Kingdom and Eire for 1946, expressed as 100%, was 1,379,194 tons of which 721,585 tons were made by the chamber process and 657,609 tons by the contact process.[59]

There is practically nothing to report on chamber acid. F. Perktold and P. M. Müller[60] have made an interesting study of the effect of nitric acid and nitrosulphuric acid, chlorine compounds, and alloying metals on the corrosion of lead by concentrated sulphuric acid. Nitrosulphuric acid increases the rate of corrosion considerably at the "critical temperature" (50—60°) for lead corrosion but there were no other marked effects. The results are confirmed by plant trials and experience in general, and many anomalies can be ascribed to the difficulty of assessing the effective temperature of a metal part in which a temperature gradient exists.

A method of recovering sulphur dioxide from the roasting of pyrites

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[56] *J. Indian Chem. Soc., Ind. Ed.*, 1945, **8**, 81; B., 1946, I, 265.
[57] U.S.P. 2.331,524; B., 1946, I, 23.
[58] U.S.P. 2,336,688; B., 1946, I, 234.
[59] *Chem. Trade J.*, 1947, **120**, 168.
[60] *Chem. Technik*, 1944, **17**, 1; B., 1946, I, 129.

has been claimed by R. F. Bacon and R. Fanelli,[61] who absorb sulphur dioxide in a solution of potassium, sodium, or ammonium tetraborate containing sufficient boric acid to saturate the solution at the temperature of liberation of sulphur dioxide ; absorption is carried out between 0° and 75° and regeneration of the sulphur dioxide at above 85°.

J. Cathala[62] states that gaseous mixtures containing not less than 15% sulphur dioxide and a deficiency of oxygen can be converted into sulphur trioxide over a contact catalyst at 450—800° if they are compressed to 3—9 atm. ; on cooling the reaction mixture to 0—25° a liquid comprising sulphur trioxide and excess of sulphur dioxide is obtained. The residual gases are scrubbed with liquid sulphur dioxide at 15 to remove the remaining sulphur trioxide, and residual sulphur dioxide is recovered by cooling to -40° and finally scrubbing with water.

The methods of production of contact sulphuric acid at the I.G. Farbenindustrie plants of Höchst and Ludwigshafen are described in detail by W. A. M. Edwards, J. H. Clayton, and A. Jackson.[63] The I.G. plants used a vanadium catalyst (6—8%) pelletted with kieselguhr and the converters were of the internal heat-exchange type with capacities up to 50 tons a day ; the process aimed at autothermic operation with gas containing 7—8% of sulphur dioxide.

Other information about catalysts for production of sulphur dioxide is contained in a patent specification by J. S. Streicher (Assr. to American Platinum Works),[64] who makes the catalyst by moistening dehydrated silica gel with a solution of platinum salt, which is dried at 60—100° and then slowly heated to above 600° to form platinum on the gel ; the platinised gel is then treated with a liquid containing a promoter agent such as arsenic pentoxide, vanadium pentoxide, chromium oxide, or iron oxide. The process is worked so that the loosely adhering promoter settles in the pores of the catalyst.

E. Utterback (Assr. to Socony–Vacuum Oil Co.)[65] has devised an apparatus for forming a sheath (iron or nickel) around aluminium–silica catalysts, perforating the metal sheath, and finally pelletting the sheathed catalyst.

G. F. Horsley and Imperial Chemical Industries Ltd.[66] state that platinum-containing catalysts for oxidising sulphur dioxide to sulphur trioxide are activated by treatment at a temperature below 20° with a solution obtained by the interaction of sulphur dioxide and metallic iron in presence of water ; pretreatment of the catalyst with dilute nitric acid improves the activation.

Catalysts which have been contaminated with carbon are stated by

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[61] U.S.P. 2,195,980 and 2,196,004 ; B., 1946, I, 98.

[62] B.P. 571,207 ; B., 1945, I, 358.

[63] *Brit. Intelligence Objectives Sub-Commee.*, 1945–46, *Final Rept.* 244, *Item* 22 ; B., 1946, I, 327.

[64] U.S.P. 2,200,522 ; B., 1946, I, 132.

[65] U.S.P. 2,331,521 ; B., 1946, I, 21.

[66] B.P. 573,961 ; B., 1946, I, 98.

J. N. Weiland (Assr. to Universal Oil Products Co.)[67] to be regenerated by passing heated oxygen-containing gas through them ; the products are burned with additional oxygen and with added fuel to produce a uniform high temperature, and oxygen is again added to part of those gases for use in the next or same catalyst undergoing regeneration.

A method of production of sulphur trioxide has been patented by E. I. Du Pont de Nemours & Co.[68] for use when the sulphur dioxide–oxygen mixture contains chlorine or nitrogen and has an oxygen content greater than the amount required for oxidation : the gases are heated at 400—500° with a fluid catalyst comprising an oxygen compound of vanadium and alkali sulphates melting below 700°. They also describe a process for obtaining liquid mixtures of sulphur dioxide and chlorine by heating sulphur trioxide and sodium chloride at above 450° ; the liquid mixtures first obtained are distilled at a pressure of, for example, 7 atm. to distil off an azeotrope, leaving a residue consisting mainly of sulphur dioxide, which is oxidised to sulphur trioxide and treated with more sodium chloride ; the azeotrope is then distilled at a higher pressure, for example, 20 atm., which leaves a residue consisting mainly of chlorine.

Another method of separating sulphur dioxide and chlorine mixtures is that of A. W. Hixson and R. Miller (Assrs. to Chemical Foundation, Inc.),[69] who bring the mixtures in contact with zirconium tetrachloride at −10° to 0°, so forming a compound of zirconium tetrachloride and sulphur dioxide and leaving chlorine ; the sulphur dioxide is regenerated by heating the complex at about 100°.

A method of producing a sulphur dioxide–air mixture suitable for conversion into sulphuric acid by the contact process has been described by B. Barnes and H. E. Broughton (Assrs. to Chemical Construction Corporation),[70] who heat, in a stream of air, a mixture of ferrous sulphate monohydrate, iron oxide, and about 3% of carbon which has been formed into ¼-in. briquettes ; the calcination must be rapid.

Huntington, Heberlein & Co., Ltd., E. D. Copley, and H. G. B. Marckwald[71] have described improvements in apparatus used for the concentration of sulphuric acid. They make the apparatus of a high-silicon cast iron and above the top bubbling tray place a dish for preheating the dilute feed liquor and condensing the necessary reflux ; no bubbling is effected in this tray but the aqueous vapour is passed up through annular spaces having a cylindrical surface for heat conduction to the liquor. After leaving the feed preheater the vapour passes through an entrainment separator.

Recovery of sulphuric acid from residual liquids such as are obtained in titanium salt hydrolysis can be effected, according to R. L. McCleary

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[67] U.S.P. 2,330,462 ; B., 1945, I, 388.
[68] B.P. 573,867–8 ; B., 1946, I, 98.
[69] U.S.P. 2,340,961 ; B., 1946, I, 292.
[70] U.S.P. 2,202,414 ; B., 1946, I, 23.
[71] B.P. 572,328 and 572,334 ; B., 1946, I, 61.

(Assr. to E. I. Du Pont de Nemours & Co.),[72] by treating the waste sulphuric acid and titanium and iron salts with sodium chloride, sulphate, chlorate, or phosphate; the solution is stirred vigorously and, after separating the resulting precipitate, an acid is left suitable for use in treating more ilmenite.

Another process for utilisation of the waste sulphuric acid content after ilmenite treatment is that of T. C. Oliver, R. D. Long, and L. H. Crosson (Assrs. to Charlotte Chemical Laboratories),[73] who treat the aqueous ferrous sulphate residue with an excess of aqueous ammonia to precipitate ferrous hydroxide and ammonium sulphate, which is separated and heated to 140° to render the iron insoluble in water; the ammonium sulphate is then leached out and may be recovered in a desirable form either directly or after further treatment.

Recovery of iron salts and acids from spent pickle liquors can be effected, according to N. Swindin,[74] by cooling the hot spent liquor in a tank in which some $FeSO_4,7H_2O$ separates; the overflow from this tank is preheated to strip any volatile acid such as hydrochloric acid and the preheated liquor is passed to a crystallising tank, where it is submitted to direct contact with hot gases to cause precipitation of partly dehydrated ferrous sulphate, leaving a hot concentrated sulphuric acid for re-use in the pickling process.

H. E. Keyes[75] has given operating data for a small commercial plant producing ferric sulphate by the catalytic liquid-phase oxidation of sulphur dioxide in the presence of ferrous sulphate; dilute sulphur dioxide and air are blown through porous aërators into a tank of ferrous sulphate solution, the sulphuric acid formed being continually neutralised with scrap iron. A modification of the process may be used to produce dilute sulphuric acid using ferrous sulphate or manganese sulphate as catalyst.

A. G. Edison (Assr. to E. I. Du Pont de Nemours & Co.)[76] produces ferric sulphate by treating a slurry of exsiccated ferrous sulphate in water at 65° with 96% sulphuric acid heated to 95°; the mixture is oxidised with 60% nitric acid during 1—15 hours, and it is recommended that the process should be carried out in an autoclave at 105—115 lb. per sq. in.

A method of producing anhydrite from waste sulphuric acid is that of R. W. Sullivan (Assr. to E. I. Du Pont de Nemours & Co.),[77] who adds to it sufficient milk of lime to neutralise 95% of the acid; the non-colloidal precipitate is collected and washed, and the press-cake added in portions at 90—100° to a colloidal suspension of calcium sulphate made by adding calcium hydroxide to sulphuric acid. The mixture is digested at 95—100°.

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[72] U.S.P. 2,192,687; B., 1946, I, 22.
[73] U.S.P. 2,333,672; B., 1946, I, 132.
[74] B.P. 575,776; B., 1946, I, 199.
[75] *Chem. Met. Eng.*, 1946, **53**, *No.* 5, 126; B., 1946, I, 264.
[76] U.S.P. 2,196,584; B., 1946, I, 21.
[77] U.S.P. 2,197,953; B., I, 1946, 96.

The free sulphuric acid in the mixture is approximately 1% and the calcium sulphate is obtained in a desirable form by filtering, washing, and calcining.

The production of sulphur compounds by two interesting applications of mercury cells, such as are used for brine electrolysis, is described by A. P. Lowes and Imperial Chemical Industries Limited[78] and by K. W. F. Dorph and Mathieson Alkali Works.[79] In the former, sodium sulphide is made by passing sodium polysulphide solution at 30—100° through a reaction vessel concurrent with sodium amalgam at 37—55°; the rates of flow are adjusted so that the reduction of polysulphide is completed as it leaves the vessel but the amalgam, on leaving, still contains a small amount of sodium. In the latter, sulphur dioxide and sodium amalgam are fed into a closed, corrosion-resistant vessel with means of cooling and stirring, in correct amounts to produce sodium hydrosulphite, water is introduced, and the mixture stirred while keeping the temperature down to 40—50°, the process is a continuous one and spent amalgam and sodium hydrosulphite are continuously drawn from the reaction zone.

HALOGENS.

Reports on improvements in chlorine production are concerned mainly with mercury cells and particularly with improvements to the cathodes. W. W. Gleave and Imperial Chemical Industries Ltd.[80] claim improved results by making the electrodes from porous carbon of which 35—45% of the pore space is impregnated with a resinous polymer of a lower alkyl ester of methacrylic acid or chloroacrylic acid; the ester is polymerised *in situ* in the carbon and the polymerising catalyst is incorporated in the ester used for impregnation.

B. W. Hirsh and Imperial Chemical Industries Ltd.[81] state that improved results are obtained in the electrolysis of alkali chloride solutions in a cell containing a horizontal graphite anode and a flowing mercury cathode at a temperature above 50°, with up to 0·02% of a wetting agent in the cell liquor. The wetting agent should not be rapidly decomposed under the conditions in the cell and should not cause appreciable frothing; for this purpose materials such as long-chain unsaturated fatty acids, sulphonated derivatives of fatty acids, soft soaps, and Turkey-red oil may be used.

W. C. Gardiner[82] points out, in a consideration of the basic principles of operation of mercury cells, that the main difficulties with the two-compartment mercury amalgam cell lie in the correct balance of the decomposition (or brine) cell and in the denuding (or caustic) cell.

In a diaphragm cell described by S. J. Burns, M. Chesterfield, J. A.

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[78] B.P. 577,034; B., 1946, I, 328.

[79] U.S.P. 2,204,476; B., 1946, I, 167.

[80] B.P. 574,870; B., 1946, I, 166.

[81] B.P. 572,950; B., 1946, I, 61.

[82] *Chem. Met. Eng.*, 1945, **52**, *No.* 7, 110. B., 1945, I, 356.

Flynn, and J. W. Ingersol (Assrs. to Hooker Electrochemical Co.),[83] foraminous cathodes or parts of the same cathode are covered with diaphragm material and interleaved with anodes; the cathode solution is contained in a tank which carries the cathode current and is closed at the top by the anode structures.

Electrolytic chlorine from a cell usually contains organic impurities. A method of removing these impurities by scrubbing the gas with liquid chlorine is disclosed by R. M. Hunter (Assr. to Dow Chemical Co.)[84]; the liquid chlorine is prevented from becoming too impure by removing from the scrubber a small proportion of the impure liquid, which is evaporated fractionally and returned to the feed.

In the production of caustic soda from diaphragm cells, the liquid from the cell usually contains about 9% of caustic soda and 13% of sodium chloride; the normal method of separation is in a triple-effect followed by a single finishing-effect salting evaporator. M. J. Kermer (Assr. to Buffalo Foundry & Machine Co.)[85] makes use of a non-salting concentration evaporator which is fed with enough steam to make sufficient vapour to heat both the first salting effect and the finishing effect; this evaporator is comparatively small as the feed is preheated to the boiling point by heat exchange.

Methods of production of chlorine other than by electrolysis have been claimed by F. W. de Jahn (Assr. to A. N. Mann),[86] who recovers chlorine from a mixture of hydrogen chloride and oxygen by passing it over a catalyst of copper and vanadium oxides, with or without various additions, at 385—435°; the effluent gas is scrubbed with sulphuric acid to remove water and passed over the catalyst at 400°. The reaction is not complete and the gaseous mixture of chlorine and unoxidised hydrogen chloride has to be scrubbed with water to remove the latter.

F. R. Balcar (Assr. to Air Reduction Co.)[87] describes a similar process using a copper–rare earth or copper–uranium catalyst controlled at temperatures such that any volatilised copper is condensed within the catalyst; the chlorine is washed with 25% hydrochloric acid to remove unchanged hydrogen chloride.

Methods for obtaining solid calcium hypochlorite have been the subject of patents by the Mathieson Alkali Works (Assees. of C. A. Hampel).[88] They prepare alkali hypochlorites by the reaction of the oxide, hydroxide, or basic hypochlorite with an alkyl hypochlorite vapour in presence of a small proportion of water; for instance, butyl hypochlorite is carried by a current of moist air through a tube containing calcium hydroxide at 25°, whereby 60% of the hydroxide is converted into the hypochlorite. The reaction can be carried out by mixing the hydroxide with water to a stiff

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[83] U.S.P. 2,330,404 and 2,330,415; B., 1945, I, 386.
[84] U.S.P. 2,199,797; B., 1946, I, 23.
[85] U.S.P. 2,330,221; B., 1945, I, 387.
[86] U.S.P. 2,330,114; B., 1946, I, 132.
[87] U.S.P. 2,204,172; B., 1946, I, 169.
[88] B.P. 570,962 and 570,992; B., 1945, I, 357.

paste, agitating it with the alkyl hypochlorite, removing the excess of the latter with the alcohol formed and water, and drying in a vacuum.

Production of a dustless calcium hypochlorite product is claimed in a series of patents by H. L. Robson (with H. D. Kaufmann, G. A. Petroe, and M. C. Taylor, Assrs. to Mathieson Alkali Works)[89] covering the treatment of dried calcium hypochlorite filter-cake. The filter-cake is removed by a doctor knife and formed into moist chips by means of rolls; these chips are screened to remove dust after drying in an inclined cylinder and the over-sized pieces are passed through rubber rolls. The cake is adjusted to contain 23—30% of water and dust is returned to and incorporated in the cake. A product is obtained containing sodium chloride, calcium hydroxide, calcium hypochlorite, etc. substantially free from dust and containing no binder other than water.

According to Mathieson Alkali Works (Assees. of C. A. Hampel and A. E. Soule)[90] chlorine dioxide is produced by adding an aqueous solution of alkali or alkaline-earth chlorate containing a water-soluble organic reducing agent, for example, aldehyde, carbohydrate, alcohol, or acid, to vigorously stirred sulphuric acid, the reactants being in the stoicheiometric proportions required to yield chlorine dioxide; a stream of nitrogen is passed through the reaction zone to remove the chlorine dioxide. In another process, C. A. Hampel and M. C. Taylor (Assrs. to Mathieson Alkali Works)[91] treat an alkali chlorite with an alkali persulphate at the correct pH or an alkali chlorate with an aldehyde, *e.g.*, paraformaldehyde, at pH not above 9.

Methods of producing substantially anhydrous hydrogen chloride from its aqueous solution have been mentioned by R. L. Comstock (Assr. to Bay Chemical Co.),[92] who passes the aqueous acid into a dehydrating tower, packed with anhydrous lump calcium chloride at a point about half way up. The heat of hydration raises the temperature to above 100° and is sufficient to drive hydrogen chloride gas containing less than 0·3% of water from the top of the tower; the water is removed at the bottom of the tower as calcium chloride solution and after dehydration the calcium chloride is returned to the process.

A method of purifying crude hydrochloric acid is that of J. W. Brown and D. P. Hill (Assrs. to E. I. Du Pont de Nemours & Co.),[93] who mix the acid with an oxidising agent and distil it under such conditions that the vapour contains water and hydrogen chloride in the proportions desired in the final acid; the vapours, which contain free chlorine, are passed upwards through activated charcoal before being condensed.

To prepare water-soluble chlorides, such as magnesium, zinc, and barium chlorides, from sea-water or brine, Ocean Salts (Products) Ltd.,

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[89] U.S.P. 2,195,754–7; B., 1945, I, 387.
[90] B.P. 575,173; B., 1946, I, 169.
[91] U.S.P. 2,323,593–4; B., 1946, I, 234.
[92] U.S.P. 2,321,282; B., 1945, I, 386.
[93] U.S.P. 2,196,246; B., 1945, I, 386.

B. A. Adams, and W. S. M. Whitehead[94] treat the sodium chloride solution with a copper base or basic salt and sulphur dioxide so as to form cuprous chloride; this is then treated with a base or basic salt of the required chloride, *e.g.*, barium hydroxide, to yield the metal chloride and a copper base or basic salt for re-use in the process.

Recovery of potassium chloride from potassium chloride brines has been described. E. P. Pearson (Assr. to American Potash & Chemical Corporation)[95] is concerned with its recovery from Searles Lake brine, which is concentrated at 93—116° and slowly cooled in crystallisers, producing crops of pure potassium chloride down to approximately 32°; further cooling produces a crop of potassium chloride and borax. These mixed salts are subjected to froth flotation in a cooled aqueous solution of both salts, when, with the right selective agent, the borax is floated; the agents suggested are oleic acid, xylene, turpentine, kerosene, or naphthenic acid. The borax float is added to the cold mother-liquor from the mixed crop, which is usually supersaturated with borax, and a large crop of borax crystals separates. The potassium chloride tailing is returned to the crystallisers.

A similar process of L. W. Ferris (Assr. to Bonneville Ltd.)[96] states that a potassium chloride concentrate obtained by flotation of ground potassium chloride–sodium chloride ores can be treated with just sufficient water to dissolve the sodium chloride completely, thus leaving relatively pure potassium chloride; the solution of sodium chloride which contains some potassium chloride is returned to the flotation process.

There is little to report on fluorine compounds. N. J. Wynne[97] states that fluorspar may be made suitable for metallurgical purposes by heat-treating fluorspar concentrate at 1100° so as to cause the particles to form agglomerates of the desired size without the use of bonding agents.

On the production of hydrofluoric acid a description of the plant at Stülln in Germany has been given by W. Archer, W. J. V. Ward, and O. S. Whitston.[98] The hydrofluoric acid from the retorts is condensed to give a 90% acid, which is worked up by batch distillation to anhydrous hydrofluoric acid. The most interesting part of this description is that which covers the production of fluorine and chlorine trifluoride; the latter is made by reaction of chlorine and fluorine in two stages: first to the chlorine monofluoride at 200° and then to the chlorine trifluoride at 260—280°, using nickel fluoride as a catalyst in pure nickel converters. Chlorine trifluoride is an extremely reactive liquid showing many of the properties of fluorine but, being a liquid, it is free from the difficulties of handling a liquefied gas.

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[94] B.P. 575,339; B., 1946, I, 199.

[95] U.S.P. 2,333,334; B., 1946, I, 61.

[96] U.S.P. 2,336,854; B., 1946, I, 232.

[97] B.P. 571,967; B., 1946, I, 19.

[98] *Brit. Intelligence Objectives Sub-Commee.* (1945–46), *Final Rept.* 261, *Item* 22; B., 1946, I, 327.

For the production of boron trifluoride, itself a useful catalyst, C. F. Swinehart (Assr. to Harshaw Chemical Co.)[99] has patented the compound $(NH_4)_2O,4BF_3$, which, on treatment with oleum, liberates boron trifluoride; the compound is prepared by evaporating a mixture of boric acid and ammonium hydrogen fluoride.

H. A. Depew[100] gives a warning about the handling of ammonium fluoride, which in dilute aqueous solution dissociates readily, forming free ammonia and ammonium hydrogen fluoride; this may lead to alkaline conditions and acid conditions in different parts of the same pipe. A combination of Karbate (impervious impregnated carbon) and silver is suggested as the best means of handling such material.

SODIUM COMPOUNDS.

Sea-water is generally regarded chemically as a source of sodium chloride and magnesia, but during the war the importance of making it potable has been of unusually high interest. Devices for installing in lifeboats for distilling sea-water have previously been described, but Permutit Ltd.[101] have approached the problem differently and patented a cation-exchange material containing exchangeable silver ions to remove chlorine ions and exchangeable barium ions to remove sulphate ions; products of this type are prepared by treating an organic or inorganic base, such as sulphonated coal or rosin or sodium aluminium silicate, with silver and barium salts. For lightness they may also be dehydrated.

Salt is made from sea-water in hot climates by solar evaporation. The solar salt works at Massawa, Eritrea, which produces about 100,000 tons of salt per annum, has recently been described[102]; the salt obtained at this works is not of very high quality as it contains up to about 1% of magnesium chloride, 2% of calcium sulphate, and 1% of insoluble matter. In non-tropical climates, salt is obtained from underground salt beds generally by flooding with water and pumping out the brine thus formed under controlled conditions. F. L. Bolton[103] has patented a means of producing such brine by establishing a pair of parallel tunnels in the salt bed; water is supplied to the upper part of one tunnel, and at a lower level brine flows to the other tunnel which acts as a sedimentation vessel; whether the method would have advantages depends on the form of the particular salt bed. Brines prepared from salt beds are generally impure, and contain small amounts of magnesium compounds, sulphates, etc. which are often objectionable. J. B. Pierce, jun. (Assr. to Standard Ultramarine Co.),[104] has patented a means of freeing brines from small proportions of sulphates by agitation at 15—60° with finely-divided barium carbonate; a suitable form of barium carbonate is obtained by treating aqueous barium

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[99] U.S.P. 2,196,907; B., 1946, I, 18.

[100] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 511; B., 1946, I, 229.

[101] B.P. 576,969 and 576,971; B., 1946, I, 329.

[102] *Pharm. J.*, 1946, **156**, 252; B., 1946, I, 229.

[103] U.S.P. 2,200,665; B., 1946, I, 18.

[104] U.S.P. 2,191,411; B., 1945, I, 357.

sulphide with carbon dioxide in a turbo-mixing apparatus, which gives a product having a particle size of less than 0·25 μ. Presumably the same effect can also be obtained by using the calculated equivalent of a soluble barium compound, but the use of barium carbonate may avoid the possibility of introducing barium into the brine.

Some lakes, which are fed by rivers of high dissolved solid content, and where rapid solar evaporation occurs, are a useful local source of sodium compounds. One such lake in India is the Lonar Lake, which has recently been examined by V. P. Pandit, M. S. Telang, and S. A. Saletore[105], it contains about 6000 tons of alkali, in the form of solid sodium sesquicarbonate (like most alkaline lakes), with some salt and insoluble matter, but it would be uneconomic to apply the usual recovery processes on this small amount. A simplified means has therefore been devised of extracting the alkali from this solid which merely involves dissolving it in water, filtering the solution, evaporating it to dryness, and calcining the solid to yield a sodium carbonate containing salt as its chief impurity.

I. E. Muskat (Assr. to Pittsburgh Plate Glass Co.)[106] has described methods of dehydrating caustic soda liquors. Such liquors are generally made either by electrolysis of brine or by causticisation of sodium carbonate solution, and they are readily concentrated although the final dehydration is difficult owing to the high temperature required. The process proposed is to treat liquor containing at least 50% of caustic soda with liquified ammonia or a methylamine. In one patent, the amount of ammonia is sufficient to precipitate solid caustic soda monohydrate and retain the impurities in solution. In the other patent, the treatment is carried out at 70—80° with several parts of ammonia per part of caustic soda, to give two liquid layers ; the top layer is removed and dehydrated, and the bottom layer is cooled and deposits fine, fluffy, anhydrous caustic soda. Although these methods are interesting and reveal an entirely different approach from those in commercial use, it is not clear whether they are commercially attractive because of the obvious difficulties of using liquified ammonia.

Two rarely used processes for making caustic soda which have recently been examined are the electrolysis of sodium carbonate in a diaphragm cell to give bicarbonate in the anolyte and hydroxide in the catholyte[107] and the fusion of sodium sulphate with ferric oxide. The latter process has been studied by J. E. Vilnjanski and E. I. Pinaevskaja,[108] who have shown that at 1450° the reaction readily yields sodium ferrite, but the lixiviation of this melt is difficult; either large amounts of wash water or repeated extraction must be used, and even then extraction is incomplete. They confirm the accepted conclusion that the process can only be of

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[105] *J. Sci. Ind. Res., India,* 1945, **4**, 16 ; B., 1945, I, 357.

[106] U.S.P. 2,325,339 and 2,196,593 ; B., 1946, I, 31, 18.

[107] H. L. Stewart, Assr. to Koppers Co., U.S.P. 2,340,254 ; B., 1946, I, 291.

[108] *J. Appl. Chem. Russ.*, 1944, **17**, 471 ; B., 1945, I, 356.

interest where large amounts of sodium sulphate and cheap fuel are available. The process has been patented in Russia by N. V. Morrin.[109] In most countries this process has long since been ousted by either electrolysis of sodium chloride or causticisation of sodium carbonate.

The principal publications on caustic soda and sodium carbonate have been three reports dealing with the methods used in Germany. One report[110] gives a detailed description of six ammonia-soda plants in Western and Southern Germany, in some of which caustic soda is also made by causticising the sodium carbonate. The total output of these plants was about 2400 tons of sodium carbonate and 200 tons of caustic soda a day, and most of the plants are still running or capable of being run. The American investigating team indicate that no technical information was found in Germany which would be any advance on current American practice. The second report[111] gives a detailed account of the electrolytic plant used for making caustic soda (40 tons a day), chlorine (35 tons a day), and hydrochloric acid by the Wolfen Works of I.G. Farbenindustrie; the plants were old and were not working in March, 1946. Development in Germany of processes for electrolysing sodium sulphate solution to give caustic soda and sulphuric acid is described in the third report,[112] but such work had not been developed to a manufacturing scale.

An interesting account has also been published of the development of part of the chemical industry in India, based on marine raw materials[113]; this covers the manufacture of salt from sea-water by solar evaporation, electrolytic caustic soda and chlorine made in diaphragm cells, sodium carbonate manufacture by the ammonia-soda process, as well as magnesia manufacture. Most of the development of this industry occurred before the war, however.

Caustic soda is generally sold as the fused, substantially anhydrous product. As it is used for most purposes in solution it is more economical for consumers near to the manufacturer to dispense with part of the evaporation and transport caustic soda as 44% or 75% liquor. The latter freezes at 62° and can be carried hot in nickel-clad thermally insulated tank wagons.[114] Such wagons are widely used in America but are not yet in general use in Britain. Any slight attack on the nickel may be minimised by immersing in the liquor an anode of material resistant to caustic soda, and making the nickel the cathode, while maintaining a cathode current density of 0·0005 amp. per square foot, according to the Solvay Process Co.[115] Other types of protective linings for steel tank cars are already well known, especially resins and cellulosic

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[109] Russ. P. 64,764.

[110] *Field Information Agency, Technical, Final Rept.* 430.

[111] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 680, *Item* 22.

[112] *Field Information Agency, Technical, Final Rept.* 429.

[113] *J. Sci. Ind. Res., India,* 1946, **5**, 121, 209.

[114] *Chem. Technik,* 1944, **17**, 6; B., 1946, I, 129.

[115] Can. P. 437,941.

materials. Another method[116] is to send granular 65—80% caustic soda in tank cars of ordinary steel; on arrival, the material is extracted by feeding water into the bottom of the tank car in a manner which avoids local rise of temperature or corrosion of the metal.

One interesting new use for caustic soda is as an agent for the removal of calcium sulphate scale from heat-exchange units. J. L. Wasco and F. N. Alquist[117] have shown that excellent removal of such scale is effected by treatment with 30—50% caustic soda solution at a temperature above 80°.

The manufacture and applications of sodium and potassium silicates have been reviewed by H. Lafuma,[118] who gives an itemised comparison of their consumptions in France in 1938 and 1941–43. These silicates have become more important as vehicles for paints, and as stabilising or aggregating agents for soils, and some developments are foreshadowed for silica sols obtained from these silicates either by partial neutralisation or by ionic exchange of hydrogen ion for the alkali metal ion. For example, silica sols have recently been examined in one form or another as tanning agents for white leather, as coagulants for suspended matter in water, and for modifying resins.

OTHER ALKALI METAL COMPOUNDS.

Searles Lake in California is best known for its production of sodium and potassium compounds, but during the extraction process lithium is concentrated as Li_2NaPO_4 in the sodium carbonate–sodium sulphate double salt which separates. Some years ago, this was regarded as a nuisance, but recently this concentrate (which represents one of the richest sources of lithium available) has been worked up further.[119] The method used is based on the slow rate of dissolution of this lithium sodium phosphate; the concentrate is leached in a small quantity of water, leaving the phosphate undissolved, and the phosphate is then floated with stove oil. The floated material is thickened and washed with hot water, and then dried to yield a crude lithium sodium phosphate containing 20% of lithium oxide.

Investigations have also been carried out by W. M. Sternberg, E. T. Hayes, and F. P. Williams[120] on the production of lithium chloride from spodumene, a lithium aluminium silicate. The process they used involved wet-grinding the spodumene with calcium carbonate and calcium sulphate, and then roasting at 1100° for 2—3 hours. This mixture was then leached with calcium chloride solution and at most 86% of the lithium was thereby extracted as chloride. Evaporation and fractional crystallisation left a solid residue containing the lithium chloride, which was then extracted by 2-ethylhexanol.

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[116] R. B. MacMullin, Assr. to Mathieson Alkali Works, U.S.P. 2,332,242; B., 1946, I, 61.

[117] *Ind. Eng. Chem.*, 1946, **38**, 394; B., 1946, I, 253.

[118] *Chim. et Ind.*, 1945, **54**, 235; B., 1946, I, 17.

[119] W. A. Gale, *Chem. Industries*, 1945, **57**, 442; B., 1946, I, 16.

[120] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3848; B., 1946, I, 264.

ALKALINE-EARTH COMPOUNDS.

An extensive study has been published by V. J. Azbe on the economical manufacture of high-quality lime.[121] In this work, which covers both vertical kilns and rotary kilns, he deals with the effect of impurities in the limestone on the fuel consumption and discusses the conditions in the burning zone, more especially when using oil or natural gas as the fuel. He also points out many reasons for poor performance of such kilns, and this publication may well repay careful study by manufacturers of lime. Calculations of fuel requirements in dry-feed and wet-feed limekilns can be based on formulæ deduced by R. Gibbs[122]; his formulæ take account of heat consumption by reaction, shell loss, and waste gas loss, and from them the optimum output and corresponding fuel consumption for a kiln of fixed dimensions can be calculated. One of the drawbacks to lime burning in rotary kilns is the large amount of dust evolved. An installation has been described by C. C. Porter, F. W. Bishop, and J. G. Liskow,[123] in which stack gases are passed through water which flows at the same rate as the gases; this gives a 50% sludge of predominantly calcium carbonate and 96—99% removal of the dust from the gases.

The German lime-burning industry has been described in a report[124] which shows that there is a wide variation throughout the industry in the types of equipment and extent of modernisation; the total annual output was 5½ million tons of lime and 1¼ million tons of burnt dolomite.

Few developments have been reported in the year under review in the field of finely-divided insoluble calcium compounds such as the carbonate, sulphate, and silicate, which are important as pigment extenders in paints and inks, and reinforcing agents or fillers in rubber and paper. In synthetic rubbers particularly it appears desirable to have special forms of fillers in order to give sufficient strength to the cured product.

It is reported by J. A. Merz[125] that Brazil is to work her vast deposits of magnesite, which average about 45% magnesium oxide, principally for the manufacture of basic refractories; it is not clear what process is to be employed, but many possible ones are available. Low-grade ore may first be concentrated by froth flotation, using a cationic flotation agent to produce a froth containing siliceous material, and then using an anionic agent to float the magnesium carbonate; such a process is described by H. A. Doerner and D. L. Harris.[126] The use of Canadian brucite for producing basic refractories has also been examined experimentally by M. F. Goudge and J. G. Phillips[127]; magnesia bricks were fired at various temperatures and tests of under-load refractoriness at 1450°

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[121] *Rock Products*, 1945, **48**, *No.* 8, 92; *No.* 9, 81; *No.* 10, 102; *No.* 11 95; **49**, *No.* 1, 113; *No.* 2, 90; B., 1946, I, 230. U.S.P. 2,199,384; B., 1946, I, 18.

[122] *Chem. Met. Eng.*, 1946, **53**, *No.* 4, 99; *No.* 5, 139; B., 1946, I, 264, 290.

[123] *Paper Trade J.*, 1946, **124**, *TAPPI Sect.*, 33.

[124] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 576, *Item* 22.

[125] *Rock Products*, 1945, **48**, *No.* 11, 92; B., 1946, I, 165.

[126] U.S.P. 2,205,923; B., 1946, I, 167.

[127] *Bull. Amer. Ceram. Soc.*, 1946, **25**, 87; B., 1946, I, 324.

and other data were obtained. The presence of small amounts of silica, lime, and ferric oxide only slightly affected the results, and the products were comparable with commercially available dead-burnt magnesites.

Several processes are available for separating the calcium carbonate from the magnesium carbonate in dolomite. The choice of process depends partly on local conditions but largely on the quality and physical form of product required. One known process involves partial calcination to give a mixture of calcium carbonate and magnesium oxide, dissolution of the latter in water as bicarbonate using carbon dioxide under pressure, filtering off the calcium carbonate, and boiling the solution to precipitate a basic magnesium carbonate. A variation of this process to yield a carbonate which is calcined to give heavy magnesium oxide has been described by W. H. MacIntire (Assr. to American Zinc, Lead & Smelting Co.),[128] who uses a 5—25% solution of a magnesium salt instead of water for dissolving the magnesium bicarbonate. In another method, described by C. M. Slansky (Assr. to Dow Chemical Co.),[129] the magnesium and calcium hydroxides in an aqueous suspension of calcined dolomite are separated by preferential dissolution of the calcium with a readily hydrolysable organic halogen compound; this halogen compound is recoverable by carbonation. Such compounds, however, are relatively expensive, and even small losses might make this process non-competitive.

Sea-water and other brines are another large source of magnesia, which is precipitated from them as hydroxide. The hydroxide is generally flocculent and difficult to filter or settle, and three patents have been published covering methods of precipitating the magnesium hydroxide as coarse, heavy particles. H. H. Chesny[130] has covered the method of gradually introducing the brine into a slurry of calcined dolomite with intimate mixing, so that the conversion of the calcium hydroxide part of the slurry into magnesium hydroxide precipitate by reaction with the dissolved magnesium salts is completed in about 15 hours; the presence of the slaked magnesia in the calcined dolomite slurry apparently assists considerably in weighting the precipitate and helping it to settle, but the conditions of mixing govern the purity, ease of settling, and amount of water which must be dried off the filtered precipitate. L. M. Clark, J. G. Robinson, and Imperial Chemical Industries Ltd.[131] have patented a means of avoiding the difficulties of separating flocculent magnesia, by growing it as coarse crystals; their method involves adding the brine and the source of hydroxyl ions to different points of a vigorously stirred suspension of brucite crystals, whereby high concentrations of magnesium ions in the vicinity of high concentrations of hydroxyl ions are avoided, and in this way the rate of precipitation does not exceed the rate at which crystal growth can occur. Crystals and aggregates of size exceeding 30 μ.

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[128] U.S.P. 2,328,286; B., 1946, I, 20.
[129] U.S.P. 2,338,876; B., 1946, I, 291.
[130] B.P. 571,467; B., 1946, I, 20.
[131] B.P. 571,276; B., 1946, I, 20.

can be obtained and filtration difficulties thereby overcome. The third method, which has been patented by W. H. Farnsworth and C. H. Martin (Assrs. to Morton Salt Co.),[132] involves precipitation of heavy, crystalline magnesium hydroxide by continuous addition of dry air-floated calcium hydroxide to a brine of high magnesium chloride content (8% $MgCl_2$) as the brine passes through a revolving disc mixer. The problems associated with the use of such magnesium-rich bitterns are very different from those involved with dilute brines such as sea-water. The same patentees have described a process[133] in which the brine is evaporated and salts are removed until a viscous mass containing the magnesium compounds is left; this mass is calcined at 700—850° to evolve hydrogen chloride, and magnesia is separated from the residue by leaching out the soluble chlorides.

One of the difficulties in making magnesium metal by electrolysing fused anhydrous magnesium chloride is the production of the anhydrous magnesium chloride, because in simple dehydration by heat the last traces of water cause hydrolysis to oxide or basic chloride, which is not merely useless but is also a nuisance in the electrolytic cell. Consolidated Mining & Smelting Co. of Canada have obtained two patents[134] for making fused magnesium chloride. In the first, materials containing magnesia such as calcined dolomite are heated to incipient fusion so as to form strong, porous, coherent pieces of magnesia of about 1 in. in size, and these are heated with chlorine in presence of coke at about 1100°. The second patent deals with the chlorination of the mixture of magnesia and coke in a vertical kiln, heated by a pair of vertical carbon resistance rods linked by a horizontal carbon bottom plate; chlorine is introduced at and molten magnesium chloride is run off from the bottom of the kiln, while unchanged coke etc. is withdrawn from a grate above the bottom outlet.

Little seems to have been published relating to barium compounds during the year. J. B. Pierce[135] has patented a method of converting barium carbonate into a free-flowing form by heating dry, precipitated barium carbonate at 400—450°. National Lead Co.[136] have patented a means of making barium aluminate by heating finely ground barium sulphate with alumina in a rotary kiln at 1400—1550°; it is possible to carry out part of this reaction under oxidising conditions, but at least mildly reducing conditions are needed to reduce the final barium sulphate content below 5%.

A report of a geological survey of barium minerals in England and Wales has recently been published by the Department of Scientific & Industrial Research.[137]

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[132] U.S.P. 2,191,650; B., 1945, I, 357.
[133] U.S.P. 2,191,651; B., 1945, I, 358.
[134] B.P. 572,662 and 574,771; B., 1946, I, 61, 167.
[135] U.S.P. 2,339,943; B., 1946, I, 291.
[136] B.P. 571,466; B., 1946, I, 19.
[137] *Wartime Pamphlet No.* 46.

ALUMINIUM COMPOUNDS.

Most of the literature on this subject during the year has been devoted to methods of extracting low-grade ores, or to minimising losses in extraction processes, this being one result of the general shortage of raw materials. Siliceous and ferruginous ores containing alumina occur more widely than bauxite of high alumina content. E. P. Flint, W. F. Clarke, E. S. Newman, L. Shartsis, D. L. Bishop, and L. S. Wells[138] have published the results of extraction experiments on clays and high-silica bauxites by existing methods. For the bauxites, alumina was first extracted with sodium hydroxide solution. For the recovery of alumina from clay, and from the residues from bauxite extractions which still contained some alumina, sintering with lime and annealing at 1300—1200° gave a powder which was readily extracted with sodium carbonate–sodium chloride solutions; when concentrated solutions of these sodium salts were used the extracts contained less silica, and the silica was largely removed by seeding with sodalite, after which the alumina was precipitated by carbon dioxide. H. Pederson, H. Ginsberg, and F. W. Wrigge[139] found that if the same materials were fused in an electric furnace in presence of coke as well as lime, pig iron or silicon iron was obtained with an aluminous slag; by slow cooling, a powdery slag consisting of CaO,Al_2O_3 with $5CaO,3Al_2O_3$ and $2CaO,SiO_2$ was obtained and the amount of gehlenite ($2CaO,Al_2O_3,SiO_2$) was minimised, and good extraction of the alumina by caustic soda solution was obtained. These low-grade ores require relatively large amounts of alkali for the extraction process, and J. M. Hall and S. J. Green[140] have investigated the recovery of soda from lime–soda sintering processes. The alumina is normally precipitated from its solution in aqueous caustic soda by treatment with carbon dioxide, leaving a solution containing sodium carbonate. Their tests showed that by straightforward evaporation and crystallisation, sodium carbonate monohydrate or decahydrate was obtained free from appreciable amounts of alumina. They studied the system Na_2CO_3–$NaOH$–Al_2O_3–H_2O, and also worked a small pilot plant on this recovery process.

In Germany, the shortage of alumina was so acute that power station boiler ashes containing 25—35% of alumina were used as raw material.[141] The process was essentially the same as for siliceous bauxites—burning with limestone in a rotary kiln at above 1300° in a reducing atmosphere to give a self-pulverising clinker. The method of extraction was varied, however, by the use of a dilute sodium carbonate solution instead of a concentrated sodium hydroxide solution, to give a solution containing 2—3 g. of Al_2O_3 per litre, which was carbonated in the usual way; the residue was suitable for cement manufacture, and two plants designed to

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[138] *J. Res. Nat. Bur. Stand.*, 1946, **36**, 63; B., 1946, I, 328.

[139] *Metall u. Erz*, 1944, **41**, 32; B., 1946, I, 16.

[140] *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 483; B., 1946, I, 94.

[141] *Brit. Intelligence Objectives Sub-Commee.*, 1945–46, *Final Rept.* 167, *Item* 22; B., 1946, I, 328.

produce 10,000 tons per annum were erected. The process was uneconomic for ashes containing less than 40% of alumina, but might well be applied to bauxites containing too much silica for use in the normal Bayer process.

Three other interesting methods of extracting alumina have been published. G. Antonoff,[142] who had previously shown that magnesium silicate can be split up by electrolysis, has patented the electrolysis of aluminium silicate in a diaphragm cell, using a suspension of the silicate in dilute hydrofluoric and sulphuric acids at 90° as the anolyte, and water as catholyte; he claims that electrolysis at 5 volts deposits aluminium hydroxide at the cathode. J. R. Callaham[143] has described a pilot plant producing 50 tons a day of alumina from clay by calcining it, and digesting with ammonium bisulphate to dissolve the alumina as an alum; the solution is filtered, reduced with sulphite, and the alum is recovered by crystallisation, and the process is completed by precipitating the alumina with ammonia and calcining it, and working up the mother-liquors for ammonium sulphate. The third method was devised by S. B. Thomas (Assr. to Shell Development Co.),[144] for concentrating bauxite; it involves heating ferruginous bauxite at 250—500° under mildly oxidising conditions (in carbon dioxide or steam) sufficient to convert ferrous compounds into magnetite but not into ferric oxide, and then using magnetic separation to give a concentrate relatively free from iron. None of these methods appears to be in use.

A German method[145] of making alumina in a form suitable for use as a rubber pigment involves careful addition of sodium carbonate solution to aluminium sulphate solution, and washing, drying, and grinding of the precipitate; the crystal size of the precipitate should not exceed about 1 μ., and probably this size is governed more by the conditions used for the precipitation and washing than by the reagents used.

Precipitated alumina gels are useful as adsorbents and as catalysts for polymerisation of unsaturated hydrocarbons. They may be precipitated, according to W. C. Davies and C. E. Hall,[146] from aluminium sulphate solution, sodium silicate solution, and enough ammonia to keep down the acidity of the mixture; on washing this precipitate, drying it at below 100°, crushing, and heating at about 250°, the product is obtained as hard lumps of high mechanical strength. The dried precipitate can also be aged by movement through a zone where it is heated to 50—100° by direct contact with air and steam, as shown in a patent granted to the Houdry Process Corporation.[147]

The process developed in Germany for making synthetic mica, a

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[142] B.P. 574,232; B., 1946, I, 131.

[143] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 108; B., 1946, I, 129.

[144] U.S.P. 2,322,674; B., 1946, I, 20.

[145] *Combined Intelligence Objectives Sub-Commee.*, 1945, *File* XXIII-19, *Item* 22; B., 1946, I, 265.

[146] B.P. 571,123; B., 1946, I, 21.

[147] B.P. 574,515; B., 1946, I, 168.

complex aluminosilicate, has been described.[148] It has only been used in the laboratory, but blocks up to 3½ in. in size have been made. The process involves cooling a suitable melt containing SiO_2 35—39, alumina and other tervalent metal oxides 12, bivalent metal oxides 29—35, and sodium and potassium fluorides and silicofluorides 20%. The cooling must be carefully controlled in the range 1270—1230°, with a magnetic field at right angles to the vertical axis of the graphite crucible. The absence of nuclei during the cooling is important, as otherwise a mass of small crystals is obtained.

Monsanto Chemical Co. have obtained two patents[149] covering the manufacture of water-soluble basic aluminium sulphate ($Al_2O_3,2SO_3,nH_2O$); the $9H_2O$ compound is made by crystallisation from a solution with an $Al_2O_3 : SO_3$ ratio of 1 : 2 during evaporation at 105°, and the $2H_2O$ product is made by spraying a similar solution on to a bed of crystals in a rotating dryer heated to 270°.

COMPOUNDS OF OTHER METALS.

Beryllium.—The methods used in Germany for the production of beryllia and beryllium at plants of the Deutsche Gold- und Silber-Scheideanstalt have now been published.[150] The ore used contains 10—12% of BeO; it is sintered with lime at 1400° for an hour and then extracted with concentrated sulphuric acid. Calcium, silicon, aluminium, and iron compounds are separated from the solution obtained, and beryllium hydroxide is then precipitated by ammonia and calcined. For making beryllium metal, the hydroxide is converted into the anhydrous chloride by treatment with chlorine in a furnace, and the fused chloride is electrolysed in much the same way as magnesium metal. The more usual way of making beryllia is by the fluoride method described by H. C. Kawecki.[151]

Chromium.—M. J. C. Hutton-Wilson and G. M. Hay[152] have reviewed the German dichromate and chrome compound industry and have given an account of the plants at Bitterfeld, Leverkusen, and Uerdingen. At Bitterfeld, caustic potash is used to dissolve chrome ore, since the former is readily available in the district, and the resulting solution is converted into a frit by introduction into a hydrogen-fired rotary furnace; this frit is treated in an autoclave at 3—5 atm. with water, carbon dioxide, and calcium hydroxide. The mixture is then filter-pressed, concentrated, centrifuged, and again autoclaved with carbon dioxide at 5 atm.; the separated potassium bicarbonate is removed by centrifuge and the dichromate liquor is concentrated and crystallised in circular water-cooled agitated vessels.

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[148] *Combined Intelligence Objectives Sub-Commee.*, 1945, *File* XXII-11. *Item* 22; B., 1946, I, 230.

[149] B.P. 576,557 and U.S.P. 2,323,499; B., 1946, I, 233.

[150] *Brit. Intelligence Objectives Sub-Commee.*, 1946, *Final Rept.* 158, *Item* 21; B., 1946, I, 330.

[151] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 11, 133; B., 1946, I, 231.

[152] *Brit. Intelligence Objectives Sub-Commee.*, 1945–46, *Final Rept.* 265, *Item* 22; B., 1946, I, 327.

Copper.—The process used for making copper sulphate at the Canadian Copper Refiners' plant at Montreal has recently been described.[153] Molten copper from the anodes of an electrolytic cell is run into cold water to make copper shot, which is treated with dilute sulphuric acid in lead- and brick-lined tanks, and air and steam are drawn through; the solution is filtered and concentrated in vacuum evaporators to yield fine crystals, or cooled in the atmosphere to yield large crystals.

Manganese.—The production of electrolytic manganese in the U.S.A. has aroused interest in the native manganese ores. L. W. Dupuy, W. A. Calhoun, and R. T. C. Rasmussen[154] have examined the manganese deposits in the Missouri Valley, in which the manganese occurs either as nodules of carbonates containing 18% of manganese or in a shale containing 1% of manganese, and have decided that the methods necessary for recovery are too expensive for economical production. An examination of ores from Arizona by G. M. Potter, A. O. Ipsen, and R. R. Wells[155] gave more satisfactory results.

W. W. Jukkola (Assr. to Dorr Co., Inc.)[156] described a process for treating siliceous manganese ores with sulphur dioxide and sulphuric acid, to yield aqueous manganese sulphate containing silica in suspension. The sulphur dioxide and ferrous salts are oxidised by aeration or addition of manganese dioxide and the impurities and silica are precipitated by addition of calcium carbonate, after which the manganese salts can be recovered in the known manner.

In the electrolytic manganese winning process described by K. M. Leute (Assr. to Electro Manganese Corp.)[157] in which manganese is deposited from a catholyte comprising manganese sulphate and ammonium sulphate, the liquid anolyte is withdrawn and used to extract fresh manganese ore; the pH of the anolyte is then adjusted by mixing it with catholyte and, after purification by aëration and addition of ammonium sulphide, is returned to the cathode compartment, whereby a flow from cathode to anode is produced.

H. L. Chamberlain (Assr. to Electro Manganese Corp.)[158] states that the build-up of magnesium in a manganese cell must be avoided by circulating the anolyte to cooling towers, where the magnesium is removed as a complex of magnesium, manganese, and ammonia.

S. G. Howden-Simpson[159] has described a method of producing electrolytic potassium permanganate by the electrolysis of 25% caustic potash below 30°, using a nickel gauze cathode surrounded by an asbestos diaphragm, and as anode a deep bed of lump ferromanganese; the

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[153] *Canad. Chem.*, 1946, **30**, 26; B., 1946, I, 264.
[154] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3839; B., 1946, I, 231.
[155] *Ibid.*, 3842; B., 1946, I, 231.
[156] U.S.P. 2,340,188; B., 1946, I, 292.
[157] U.S.P. 2,334,210; B., 1946, I, 97.
[158] U.S.P. 2,339,911; B., 1946, I, 292.
[159] *Manufg. Chem.*, 1946, **17**, 55; B., 1946, I, 165.

anolyte is circulated continuously through the anode bed to remove oxides and is cooled.

Titanium.—Titanium minerals are enriched in titanium value by a process of O. Möklebust and A. J. Ravnestad.[160] Oxide ores containing titanium and impurities such as iron, manganese, etc. are reduced in a known manner with coal, coke, or reducing gases, and then the metallic iron is oxidised at 40—90° by treatment with water, air, or steam; the iron oxide so formed is readily separated by mechanical means. The oxidation step may be accelerated by addition of sodium chloride, magnesium chloride, or carbon dioxide.

L. G. Bousquet and M. J. Brooks (Assrs. to General Chemical Co.)[161] state that titanium dioxide may be recovered from insoluble residues containing titanium dioxide, basic titanium sulphate, etc. by mixing them with 98% sulphuric acid, evaporating to dryness, then heating at 250—300°, crushing, and stirring with water; after reducing ferric iron by the addition of metallic iron, some 88% of the titanium dioxide content may be recovered by hydrolysis of the filtered solution.

Several processes have been suggested for recovering titanium dioxide in special forms. The recovery of titanium dioxide as rutile and of high pigmentary strength from titanium chloride solution is described by British Titan Products Co., Ltd.,[162] who add a solution containing titanium chloride and hydrochloric acid to an equal volume of boiling water; the suspension is maintained at boiling point for an hour and the titanium oxide is then collected, washed, and calcined at 800°. C. M. Olson (Assr. to E. I. Du Pont de Nemours & Co.)[163] obtains a desirable form of titanium dioxide from titanium sulphate solution by adding a small fraction of the solution to a large volume of water to form non-colloidal nuclei, which are allowed to age for a short time; the remainder of the titanium sulphate solution is then added to disperse the nuclei to a uniform colloidal phase and the solution hydrolysed by heating. J. L. Keats and H. M. Stark (Assrs. to E. I. Du Pont de Nemours & Co.)[164] produce a nucleating agent for accelerating the hydrolysis of aqueous titanium sulphate by treating moist titanium filter-cake with sulphuric acid until a translucent syrup is formed. A. T. McCord and H. F. Saunders (Assrs. to Sherwin–Williams Co.)[165] produce a nucleating agent for hydrolysis of titanium sulphate–ferrous sulphate solution from γ-titanic acid, which is made by precipitation with ammonia of an aqueous fluorine compound of titanium. Another nucleating agent comprises anatase titanium dioxide prepared by heating to approximately 60° a suspension of γ-titanic acid in aqueous sulphuric acid; hydrolysis can be carried out in the presence of an extender to give extended pigments.

[160] U.S.P. 2,339,793 and 2,339,808; B., 1946, I, 292.
[161] U.S.P. 2,327,166; B., 1946, I, 233.
[162] B.P. 576,588; B., 1946, I, 233.
[163] U.S.P. 2,331,496; B., 1946, I, 22.
[164] U.S.P. 2,321,490; B., 1945, I, 388.
[165] U.S.P. 2,333,660–3; B., 1946, I, 132.

An electrolytic method of hydrolysing the iron chloride liquors obtained in the chloride process for titanium dioxide manufacture has been patented by British Titan Products Co. Ltd.[166] The ferrous chloride solution is treated with ferrous sulphate or sulphuric acid to precipitate calcium sulphate, neutralised with iron hydroxides from a later stage, reduced with scrap iron, and finally purified by addition of barium sulphide; this conditioned solution is made the catholyte and aqueous calcium chloride the anolyte in a divided cell with carbon anode and iron cathode. The products are iron and chlorine. Spent catholyte is treated with lime or calcium carbonate to precipitate iron hydroxides, which are separated and used in the process and the residual calcium chloride solution is re-used as anolyte after concentration.

Uranium.—A study of the unusual colours that can be produced by uranium in glasses, by W. Colbert and N. J. Kreidl,[167] may have future applications in the production of glasses with unusual transmission spectra. Three types of glass are recognised, (i) faint yellow glasses with a strong green fluorescence, obtained by introducing uranium into ordinary soda-lime-silicate glasses under oxidising conditions, (ii) non-fluorescent yellow glasses obtained under oxidising conditions in high alkali silicates and borates and lead glasses, (iii) non-fluorescent brown and green glasses, obtained under strongly reducing conditions.

Zinc.—H. M. Cyr (Assr. to New Jersey Zinc Co.)[168] has patented a means of making acicular zinc oxide from zinc vapour and air in a furnace; he recommends the presence of an inert diluent such as producer gas and a feed rate not less than one twentyfifth of the volume of the furnace per minute, or preheating the mixture of zinc vapour and air and removing the zinc oxide from the combustion zone as soon as it is formed so as to avoid contact with burning zinc.

Zirconium.—A novel method has been described by J. B. Miller[169] for producing zirconia in a very fine state of subdivision and of low density, suitable for use as an opacifier. A zirconium ore is mixed with carbon and heated in an electric furnace; the compound formed is then spread in a thin layer on a hearth made of insulating firebrick. Combustion is started on the layer of the zirconium compound at several points and spreads rapidly through the mass.

HYDROGEN PEROXIDE.

The technical investigation of German industry which followed the cessation of hostilities in Europe has revealed the large-scale development of the production of concentrated hydrogen peroxide for war purposes, which took place in Germany just prior to and during the 1939–45

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[166] B.P. 572,866; B., 1946, I, 96.
[167] *J. Opt. Soc. Amer.*, 1945, **35**, 731; B., 1946, I, 170.
[168] U.S.P. 2,200,873 and 2,331,599; B., 1946, I, 19.
[169] U.S.P. 2,392,605.

war.[170–172] This development was effectively kept secret as a war potential of paramount importance, but hydrogen peroxide was sold to Japan for military use. The application in Germany of a concentrated solution of hydrogen peroxide (80—85%) as a fuel in connexion with jet propulsion of rockets, driving submarines, propelling torpedoes, and starting aeroplanes dates from the 1914–18 war, but the production of high-test peroxide was impossible at that time owing to inadequate knowledge of methods of stabilisation and to lack of suitable materials for plant construction. Successful research on the subject led to production on an unprecedentedly large scale. It is interesting to note that the development was carried out by industry and chiefly by the Elektrochemische Werke, Muenchen.

Hydrogen peroxide was prepared by four different processes: (*a*) electrolytic preparation of persulphate subsequently decomposed with water, (*b*) reduction and oxidation of 2-ethylanthraquinone, (*c*) direct synthesis by electric discharge, (*d*) reaction of barium peroxide with sulphuric acid. No revolutionary method for producing 35% hydrogen peroxide was developed, but the concentration to 80—85% by vacuum distillation on the large industrial scale employed represents a remarkable engineering accomplishment.[173] The electrolytic process of Pietsch and Adolf for producing the 30—35% solution was favoured and was used on the plant at Bad Lauterberg, which had an output of 1200 tons a month of 80—85% hydrogen peroxide. A similar plant in course of erection at Rhumspringe had a projected capacity of 2100 tons a month, which, with the Bad Lauterberg plant, gave a potential capacity nearly ten times that of the rest of the industry.

Shortage of platinum for electrolytic processes led to the investigation by the I.G. Farbenindustrie of the process involving the reduction of 2-ethylanthraquinone in the presence of Raney nickel catalyst, followed by oxidation of the quinhydrone to yield hydrogen peroxide and the quinone.[171] Two very large plants were being built by the German Government at Heidebreck and Waldenberg to operate this process, but it was considered by the experts in Germany[172] to be an undesirable one; there is an explosion risk due apparently to the organic matter in the aqueous solution of hydrogen peroxide.

The direct synthesis process has been investigated for fourteen years by Dr. Krutzsch of Elektrochemische Werke, Muenchen, but in the opinion of the Germans the process has not reached the stage of competing with the electrolytic process. The consumption of electric power is higher but the labour cost is lower owing to the use of fully automatic controls. It involves the circulation of hydrogen containing 5% of oxygen

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[170] *Combined Intelligence Objectives Sub-Commee.*, 1945, *File* XIX-4, *Item* 22; B., 1946, I, 265.

[171] *Ibid.*, *File* XXIII-18, *Item* 22; B., 1946, I, 166.

[172] *Brit. Intelligence Objectives Sub-Commee.*, 1946, *Final Rept.* 294, *Item* 22.

[173] *Chem. Industries*, 1946, **58**, 957.

and saturated with water vapour between quartz plates coated with aluminium on the outer side; high-voltage, high-frequency electric discharge results in the formation of hydrogen peroxide and water. The gases are passed to a heat exchanger and a scrubbing tower from which the hydrogen peroxide is recovered. Pilot plants up to 10 kw. have been operated and a 200-kw. unit was planned.

The production of 80—85% hydrogen peroxide, in which the greatest advances were made, was carried out in two identical distillation units in series. These were constructed entirely of stoneware with the exception of the retort heating coils, which were of highly polished stainless steel, and the condensers, which were of the purest aluminium (99·5—99·8%); Krupp V14A stainless steel (Cr 18, Ni 8, Mo 5%) was used for the heating coils. A large range of items such as gaskets, stoppers, valves, etc. were made from polyvinyl chloride compositions of differing molecular weight and plasticiser content. In general, the plant equipment created a strong impression of the wide variety and highly developed state of chemical plant units and special materials which were available to the German chemical industry.[172]

Each distillation unit consisted of a steam-heated retort, a Raschig ring separator, a Raschig ring rectifying column, a surface condenser, a barometric condenser with trap, and a vacuum pump. The 30—40% hydrogen peroxide from the Pietsch-Adolf process was treated with ammonia to leave 0·5 g. of free sulphuric acid per litre and then stabilised with 120 mg. of ammonium pyrophosphate per litre; the stabilised solution was fed to the first retort and distilled continuously at 45 mm. absolute pressure and 66°. All the impurities were retained in the retort, which was one of the principal reasons for the stability of the product. The quantity of water used for scrubbing in the rectifying column was arranged to give a product of 65% concentration, which was then fed to the second retort. Distillation was carried out continuously at an absolute pressure of 45 mm. and 75° so that the concentration in the retort was maintained at 80%. The product was cooled and stored in welded aluminium tanks after the addition of 23 mg. of 87% orthophosphoric acid per litre as a stabiliser. The retorts of the first unit were operated until the salt concentration reached about 50 g. per litre, which took about a week, and were then washed out and restarted. The use of two units in series instead of one reduced the steam consumption and avoided the presence of impurities in the more concentrated solutions.

The stability of 80—85% hydrogen peroxide prepared in this way was such that a loss of about 1% per annum occurred, largely during the first month, when stored in pure aluminium tanks outdoors. Only 5—6% loss took place in 25 hours at 96°. Shipment and storage in the tropics were shown to be practical. It was considered by the Germans[171] that this stability was due to the complete absence of heavy metal impurities, particularly iron, copper, and manganese, and to the lowered activity of hydrogen peroxide at high concentrations. The addition of phosphoric acid was thought to improve the stability, especially at high temperatures, by rendering iron, aluminium, etc. insoluble.

The product was safely stored and transported in all-welded tanks of pure aluminium (99·5—99·8%) containing less than 0·5% of silicon and iron, 0·03% of titanium, and 0·05% of copper and zinc. The surface of the aluminium was rendered as smooth and free from scratches as possible and carefully treated to make the metal passive; usually the surface was first washed with a concentrated solution of a commercial cleanser stated to be a mixture of caustic soda, sodium orthophosphate, and sodium metasilicate, followed by rinsing in distilled water (less than 1 mg. of iron per litre), and then treated with 25—30% nitric acid for 6—8 hours. All distilled water used was obtained from aluminium, stainless steel, or stoneware condensers as the smallest trace of copper is very deleterious. An alternative method, employing 7—15% caustic soda solution at elevated temperatures until hydrogen was evolved followed by washing and acid treatment, was also used; this method resulted, however, in greater losses of aluminium.

INDUSTRIAL GASES.

The large-scale manufacture of hydrogen and gases containing hydrogen is considered chiefly in its relation to the synthesis of ammonia and methanol, and in the production of synthetic petrol, both by hydrogenation of coal, oil, and tar, and by the Fischer–Tropsch process. There appear to be few developments in processes used for working up water-gas and synthesis gas into a purified condition, suitable for their ultimate use, and the only fresh details disclosed concern steps, such as the conversion of carbon monoxide into carbon dioxide with steam, removal of carbon dioxide by scrubbing with water under pressure, and removal of unconverted carbon monoxide by scrubbing with a solution of ammoniacal cuprous salts, which are familiar operations.

Reports on the operation of German plants give details of technical advances and wartime expedients. The conversion of carbon monoxide with steam was carried out in several German factories[174] at pressures of 5—30 atm. with the object of conserving steel and reducing compression costs; considerable difficulty, however, was experienced with corrosion, which partly, at least, offset these advantages. Iron oxide catalysts were normally used, often promoted with chromium. The final removal of carbon monoxide was carried out at a pressure of 200—350 atm. but the copper liquor used contained no added formic acid as is usual in this country and in the U.S.A.; the acid radical was only carbonate.[175] In several factories "let-down engines" were used, to recover power, whereby the liquor from the absorption towers was made to help drive the pumps injecting fresh liquor into the towers.

Hydrogen was also made in large quantities in Germany by liquefying

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[174] *Combined Intelligence Objectives Sub-Commee.*, *File* XXX–103, *Item* 30.

[175] *Ibid.*, *File* XXXII–107, *Item* 30.

coke-oven gas,[176,177] which, with methane and by-product refinery hydrocarbon gases, was used to manufacture hydrogen and synthesis gases in other ways. In the Koppers cracking process[178] a cyclic process was operated, in which coke-oven gas and steam were passed over chequer brickwork maintained between 1300° and 1500° by periodic reheating with coke-oven gas burnt with air. At Pölitz and Wesseling[179] the methane–steam process was operated, in which the hydrocarbon gases, mixed with steam, were passed over a nickel catalyst, maintained at 700—800°, in externally heated alloy tubes. At Oppau[174] and Linz[180] preheated coke-oven gas was burnt with preheated, oxygen-enriched air, together with some steam, in a vessel containing a nickel catalyst; no external heating was required, as the process was autothermic; coke filters were used to remove small particles of soot from the gas. By suitable modification this process was used in Germany to manufacture acetylene, and a similar process, operated at 250 lb. per sq. in. and using natural gas instead of coke-oven gas, is becoming very important in the U.S.A. in connexion with the Fischer–Tropsch synthesis of petrol.

Descriptions have now been published of the processes used to make ammonia synthesis gas from natural gas in several war-time factories in the U.S.A. and Canada, *e.g.*, Lake Charles,[181] Ozark,[182] and Calgary.[183] Some of these used the methane–steam process, *i.e.*, reaction of natural gas and steam over a nickel catalyst in externally heated tubes of austenitic steel containing Cr 25% and Ni 20%, followed by the usual conversion of carbon monoxide with steam at atmospheric pressure, removal of carbon dioxide by scrubbing under pressure with water or a solution of monoethanolamine, and final removal of residual carbon monoxide with copper liquor. The necessary nitrogen was introduced as flue gas from separate plant, or as spent gases from nitric acid plants, or by burning air in the converted gases leaving the furnace; the last method had the advantage that the mixed gases were thereby raised to 1000°, so that they could be passed over more nickel catalyst, and so enable any methane still remaining in the gases leaving the externally heated tubes to be converted.

Reports on German industry show that some by-product hydrogen was produced in several processes, including electrolysis, but no advances in the deliberate manufacture by electrolysis or by the steam–iron process are disclosed.

In an ammonia factory to be erected at Travancore[184] the synthesis gas will be made from charcoal producer gas by the steam–iron process.

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[176] *Field Information Agency, Technical, Final Rept.* 566.

[177] *Combined Intelligence Objectives Sub-Commee., File* XXVII–55, *Item* 30; B., 1947, I, 103.

[178] *Ibid., File* XXVIII–36, *Item* 30; B., 1946, I, 159.

[179] *Ibid., File* XXVIII–30, *Item* 30.

[180] *Field Information Agency, Technical, Final Rept.* 481.

[181] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 94.

[182] *Petrol. Refiner*, 1946, **25**, *No.* 6, 97.

[183] *Canad. Chem.*, 1945, **29**, 392.

[184] *Chem. Age*, 1945, **53**, 84.

This is the first time that this process has been chosen for such large-scale operation. Water-gas cannot be made economically from charcoal because of its high reactivity and low density.

V. A. Roiter[185] has made a fresh study of the kinetics of the catalytic conversion of carbon monoxide with steam; he examined the effects of space velocity, total pressure, partial pressure, temperature, and particle size. The results were not sufficiently precise for the establishment of a kinetic equation, and moreover, they could not be fitted to any equation previously put forward.

There have been appreciable expansions during the war in the manufacture of oxygen in Germany and important developments in the U.S.A., and a new Russian journal,[186] devoted entirely to production and uses of oxygen, illustrates the continued interest in this subject in Russia.

The large-scale manufacture of oxygen in Germany has been thoroughly investigated.[187] The Linde–Frankl process for liquefying and separating air was used almost exclusively: by the end of the war no less than 76 units, of capacity varying from 500 to 4000 cu.m. of oxygen per hour, had been built by Gesellschaft fur Linde's Eismaschinen, most of them in Germany. This is in striking contrast to Britain, where only two small Linde–Frankl units are installed, although there are, of course, several Linde plants. In Germany, the process was mostly used in conjunction with gasification of coke, brown coal, brown-coal coke, etc., where its use made possible the utilisation of cheap but low-grade fuels. No major developments were discovered, but it was found that the power consumption in practice was appreciably greater than the 0·45 kw.-hr. per cu.m. claimed by Linde; figures of 0·6 to 0·7 kw.-hr. per cu.m. were more usual. Running costs were of the order of 2·0 to 2·5 pf. per cu.m. and capital costs of the order of 500 RM. per cu.m. per hour.

The last year has seen a lively interest in the U.S.A. in the large-scale manufacture of oxygen, primarily again for gasification processes. A large plant is now being built in Texas by Carthage Hydrocol Inc.[188] for the manufacture of synthetic petrol using the Fischer–Tropsch process. The synthesis gas is made by partial combustion of natural gas with oxygen at a pressure of 250 lb. per sq. in.; the process is autothermic, and gives directly a mixture with a volume ratio of hydrogen to carbon monoxide of 2 : 1 and at the right pressure for synthesis without further compression. The oxygen plant is reported to have the extraordinarily large capacity of 2000 short tons per day from only two units. Although manufacture appears to be based on the Linde–Frankl process, with the air compressed only to 75 lb. per sq. in., considerable cheapening of oxygen is expected from the scale of operations and from the application of modern American engineering; the capital cost is claimed to be as low as

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[185] *J. Appl. Chem. Russ.*, 1945, **18**, 438.

[186] *Kislorod*: quarterly journal, first published in 1944.

[187] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 591.

[188] *Oil and Gas J.*, 1946, **45**, *No.* 6, 102.

\$1750 per short ton per day. Several sources[189] lend authority to an estimated operating cost of about \$4 per short ton of oxygen. Other manufacturers in the U.S.A. are interested in oxygen manufacture for similar purposes but it must be emphasised that as yet no large plant is working and this cost has still to be achieved.

A light-weight, semi-portable small-scale oxygen plant[190] was developed during the war, to produce "chemically pure" oxygen on the spot in isolated places and so save shipping space for cylinders : the maximum air pressure used was only 100 lb. per sq. in., no chemicals were required, and to ensure oil-free oxygen the compressor used no oil lubrication ; a special heat exchanger, using paper-thin copper ribbon, proved very successful in keeping down the size. There are indications that experience with such units will have peace-time applications, and manufacturers in the U.S.A. are active. A chemical process has been described[191] for production of oxygen, using a solid cobaltous chelate as an absorbent regenerated by heat : it works between 20° and 100°, with air at 20 lb. per sq. in. gauge, but at present does not appear to be economic.

Little work has been reported on the manufacture of carbon dioxide. G. T. Reich[192] has described three operating cycles for the production of "dry ice" from typical gases containing carbon dioxide, with an energy consumption of the order of 270 kw.-hr. per ton of "dry ice." A novel method of removing carbon dioxide from a gaseous mixture is claimed by H. Biederbeck and G. Fischer[193]; the gas is passed upwards through a tower, countercurrent to a stream of dried and preheated, artificially shaped, globular particles of lime.

Investigation of German industry has revealed[175] a new use for carbon monoxide, in a reaction which promises to become of increasing industrial importance; this so-called "OXO" synthesis involves the simultaneous addition of hydrogen and carbon monoxide to an olefine, yielding a higher aldehyde : *e.g.*, $C_2H_4 + CO + H_2 = CH_3{\cdot}CH_2{\cdot}CHO$.[194]

During the war acetylene and ethylene were very valuable raw materials[195] in German chemical industry, owing to lack of petroleum reserves and carbohydrate material, and many syntheses started from these two substances. About 238,000 metric tons a year of acetylene were made from calcium carbide, but one large plant at Hüls[195] made 70,000 metric tons annually by the arc process applied to hydrocarbon gases. Another plant at Oppau used a process involving the partial combustion of methane with oxygen. The preheated reactants were fed to a reaction chamber in which they reached a temperature of about

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[189] *Chem. Met. Eng.*, 1946, **53**, *No.* 10, 276.

[190] *Ibid.*, *No.* 3, 125 ; *No.* 12, 106.

[191] *Ibid.*, *No.* 4, 176.

[192] *Ibid.*, *No.* 1, 120 ; B., 1946, I, 165.

[193] U.S.P. 2,332,887 ; B., 1946, I, 199.

[194] Cf. *Combined Intelligence Objectives Sub-Commee.*, 1945, *File* XXVII–18, *Item* 22 ; B., 1946, II, 151.

[195] *Chem. Met. Eng.*, 1946, **53**, *No.* 10, 116.

1500°, but the products were quenched in less than 0·01 second to a temperature below 100°; in this way, a yield of acetylene of over 20% by weight was obtained. After separating the acetylene by scrubbing with water, the remaining gases, rich in hydrogen and carbon monoxide, were used to make synthesis gas for ammonia production after a further partial combustion with oxygen to remove remaining acetylene and unconverted methane.

Several familiar processes were used to manufacture ethylene, such as recovery from coke-oven gas and dehydration of ethyl alcohol, but a considerable amount was made by the controlled hydrogenation of acetylene. At Leuna[175] ethylene was made by the thermal cracking of ethane in admixture with oxygen. The total capacity for ethylene manufacture in Germany was over 70,000 metric tons a year. The main uses of ethylene were in the manufacture of Buna rubber, synthetic lubricating oil, ethylene glycol, and ethylene dichloride, whilst acetylene was chiefly used for Buna rubber,[197] acetaldehyde, acetone, acetic acid, solvents, and plastics.

The production of liquid nitrous oxide was developed in Germany during the war for use in aircraft engines as a means of obtaining greatly enhanced performances for short periods. The production during 1944 in Germany was about 300—400 tons a month; this did not represent the full available plant capacity. R. J. Bender[198] considers that while the use of nitrous oxide for aeroplane engines is of great interest, it was probably a make-shift and considerably more could be accomplished by other means. Another interesting wartime use also developed in Germany was for the quick freezing of foods,[199] which were immersed in liquid nitrous oxide at atmospheric pressure and a temperature of −88·7°; the gas evolved from the frozen food was recovered, recompressed, and condensed and the food was then stored in a cooled chamber. The liquid nitrous oxide is made by thermal decomposition of ammonium nitrate,[198] a 70% by weight solution of which was fed continuously into a heated vessel containing a molten mixture of sodium and potassium nitrates at 255°, the nitrous oxide and water being removed continuously; the salt bath slowly deteriorates and must eventually be discarded. The consumption of sodium and potassium nitrates is about 0·67 kg. per ton of nitrous oxide produced. The gases are cooled and water-condensed. The cooled gas is scrubbed with caustic soda solution to remove nitric oxide and nitrogen dioxide and is filtered through coke; finally the gas is scrubbed with alkaline permanganate to remove residual nitric oxide and dried with sulphuric acid. The dry gas is compressed to 35 atm. and cooled to 75° before being expanded to atmospheric pressure. The cooling on expansion results in partial liquefaction and the gas is recycled to the compressor

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[196] *Combined Intelligence Objectives Sub-Commee.*, *File* XXX–23, *Item* 22; cf. B., 1946, II, 269.

[197] *Ibid.*, *File* XXII–22, *Item* 22.

[198] *Ibid.*, *File* XXXII–44.

[199] *Field Information Agency, Technical* (1945), *Final Rept.* 82.

section. The liquid is stored under atmospheric pressure at −89° in thermally insulated vessels.

OIL CATALYSTS.

A historical account of the catalytic hydrogenation of coal, creosote, and gas oils carried out in this country before and during the war has been given by K. Gordon.[200] Of particular interest, catalytically, are the liquid- and vapour-phase hydrogenations of creosote and gas oils. Tungsten disulphide has been used as a catalyst for liquid-phase hydrogenation but complete removal of asphalt and solids from the feed oil is necessary. Tungsten disulphide is the preferred catalyst for vapour-phase hydrogenation, replacing the earlier known catalyst of zinc, magnesium, and molybdenum oxides. Some splitting of the oil to lower hydrocarbons occurs when tungsten sulphide is used, but the product is largely aromatic and has a low knock rating. A mixed catalyst composed of 10% of tungsten sulphide on activated earth gives a product of improved knock rating. The new catalyst rapidly loses its activity if coal or tar oils are used without pretreatment, and a two-stage hydrogenation splitting process was devised in which tungsten disulphide was used in the first stage and the mixed catalyst in the second. To obtain petrols of higher knock rating, *e.g.*, for aviation fuels, an improved splitting catalyst was developed; in this tungsten is replaced by iron.

Methods of preparation of oil hydrogenation catalysts have been described in the patent literature. F. K. Signaigo (Assr. to E. I. Du Pont de Nemours & Co.)[201] describes an active sulphide catalyst for hydrogenation under mild temperature conditions, made by treating finely-divided metals such as cobalt, nickel, molybdenum, iron, tungsten, etc. with sulphur and/or hydrogen sulphide, carbon disulphide, etc. below 150°. R. Watts (Assr. to Standard Catalytic Co.)[202] makes a sulphided hydrogenation catalyst by dissolving molybdic or tungstic acid in ammonium sulphide and absorbing on clay previously activated by hydrogen fluoride.

A new method of making a synthetic silica–alumina bead catalyst for catalytic cracking processes is described by R. W. Porter[203]; a similar process is patented by Socony–Vacuum Oil Co.[204] The beads are made by co-precipitating silica and alumina in the form of a hydrated gel, which is sprayed immediately into an oil-filled tower, forming beads of about $\frac{1}{8}$ in. diameter; these harden as they fall through the oil and are then transferred as a slurry with water to wash tanks where washing with hot water, aluminium sulphate solution, and finally cold water gives a bead containing less than 1% of sodium. The beads are dried on a continuous stainless steel belt by superheated steam up to 175°; in drying, the beads

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[200] *J. Inst. Fuel*, 1946, **20**, 42.

[201] B.P. 574,514; B., 1946, I, 168.

[202] U.S.P. 2,330,098; B., 1946, I, 131.

[203] *Chem. Met. Eng.*, 1946, **53**, *No.* 4, 94; B., 1946, I, 265.

[204] B.P. 576,058; B., 1946, I, 199.

shrink to about one eleventh of their original volume although they still contain about 10% of water, which is removed in a final heat-treatment.

A large number of variations in the methods of making hydroforming catalysts have been claimed. Among these may be mentioned that of A. E. Smith, O. A. Beeck, and Shell Development Co.[205] in which the carrier for the active body (which may be molybdic acid) is made by treating alumina with a solution of aluminium and zirconium nitrates and an acid; after impregnation with up to 10% alkaline-earth salt, the support is heated to give the alkaline-earth oxide and alumina. Other hydroforming catalysts using molybdena supported on alumina are described by M. W. Tamele, V. C. Irvine, J. F. Maher, and Shell Development Co.[206] and Universal Oil Products Co.[207] A similar catalyst for dehydrogenation is made by J. Turkevitch[208] by reducing an ammonium salt of a phospho- or alumino-molybdate mixture.

LUMINESCENT MATERIALS.

Several new fluorescent materials have been reported consisting of substances with strained ionic lattices, demanding in their preparation controlled heating treatments and a careful selection of "impurities" which can be taken up in the crystal lattice to produce the required strain. It is not always clear from the various publications whether the added materials are activators, fluxes, suppressors, or for other purposes, and it is in the joint sense of all these that they are described as impurities. Special interest is attached to discoveries which apparently represent new aspects. One is a complex silicate luminescent material claimed by S. Isenberg (Assr. to General Luminescent Corporation)[209] to give white light on excitation, which would therefore be suitable for fluorescent lighting with good colour rendering. Another, patented by W. A. Weyl (Assr. to American Optical Co.),[210] is a fluorescent material excited by unusually long wave-lengths (3000 A.) although it is not clear where the purpose lies in having a material which is excitable at the long-wave-length end of the ultra-violet region. The third is a phosphor which radiates in the erythemal ultra-violet when excited by short-wave ultra-violet radiation, and has no visible fluorescence.[211]

The interest in fluorescent materials excited by X-rays or γ-rays is shown by the discovery by H. S. Tasker[212] of new materials of this type; these materials are mixtures of lead compounds such as the sulphate with alkaline-earth metal sulphates, heat-treated at 1000° for an hour. The increased use of the cathode-ray tube in research, industry, and television

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[205] B.P. 571,352; B., 1946, I, 21.
[206] B.P. 573,393; B., 1946, I, 61.
[207] B.P. 571,252 and 577,385; B., 1946, I, 21, 329.
[208] U.S.P. 2,325,015; B., 1946, I, 266.
[209] U.S.P. 2,192,864; B., 1946, I, 20.
[210] U.S.P. 2,322,265; B., 1946, I, 20.
[211] B.P. 577,693–4; B., 1946, I, 320.
[212] B.P. 571,324 and 574,494; B., 1946, I, 19, 168.

has stimulated research in the preparation of fluorescent screens suitable for the exacting demands of such instruments. A means of achieving an even coating of fluorescent powder over the relatively large screen surface, which is essential for these purposes, has been evolved by settling the materials from suspensions[213] The recent demand for cathode-ray tubes giving records which persist for a comparatively long time has been met by the production by A. C. Cossor Ltd., F. M. Walker, and E. E. Shelton[214] of a double phosphor giving both an immediate response and an afterglow differing in colour, by using appropriate light filters, either the immediate response or the afterglow can be observed selectively on the one screen.

During the rapid expansion of the modern uses of fluorescent phenomena and the patenting of large numbers of new luminescent materials, one is apt to overlook the fluorescent properties of certain minerals. It is to be welcomed therefore that J. W. Vanderwilt[215] has recently reviewed the use of these properties in the discovery and development of fluorescent mineral deposits, with special reference to the mineral scheelite ($CaWO_4$). In surveying or working deposits, the minerals are observed *in situ* by their characteristic fluorescence when illuminated by ultra-violet light.

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[213] A. C. Cossor Ltd., B. E. Waye, and A. G. Mitchell, B.P. 571,639; B., 1946, I, 20. W. H. Painter, Assr. to Radio Corp. of America, U.S.P. 2,328,292, B., 1946, I, 20.

[214] B.P. 578,582, B, 1946, I, 329.

[215] *Amer. Inst Min. Met. Eng.*, 1946, *Tech. Publ.* 1967; B., 1946, I, 264

GLASS.

By R. E. BASTICK, B.Sc., Ph.D., A.Inst.P.,

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THERE has again been an increase in the volume of work of importance to the glass industry and it has been necessary to select items rather than to include references to all the published work. A certain number of papers from abroad published in earlier years have become available in this country and those of importance have been included in this review.

During the course of the year, an important new publication, *Bulletin de l'Institut du Verre*, published in Paris, made its appearance and is a valuable addition to the literature on glass technology.

Probably the more important researches published during the year are those relating to the strength of glass.

THE CONSTITUTION OF GLASSES AND VITREOUS SILICATES.

Several papers on the subject of the constitution of glasses have been published during the year. J. M. Stevels[1] has discussed the crystalline and vitreous states on the basis of geometrical and valency considerations and shows that the tetrahedron is the fundamental building unit of the glass structure. He develops the argument to show how the density and electrical conductivity of glasses can be related quantitatively to the present structural theory. J. E. Stanworth[2] has criticised Stevels' treatment, pointing out, for example, that Stevels' theory takes no account of variation in size of the various ions which enter into the interstices in the network. Stanworth discusses the glass-forming properties of various elements in relation to the periodic classification.

The rules for glass formation have been reviewed by K. H. Sun,[3] who has classified glass-forming substances according to their chemical nature; the review includes a comprehensive bibliography of the subject. W. A. Weyl[4] has considered the phenomena of fluorescence and photo-chemistry of glass in relation to the structural theory and shows how the phenomena may be used to extend the theory.

The formation of glasses and silicate compounds and their relation to devitrification phenomena have been discussed by A. Dietzel[5] in terms of the cation field intensities. In a second paper,[6] Dietzel has related the separation of heavy-metal halides as colloidal suspensions in glasses to the polarisability of the anions relative to that of the glass solvent.

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[1] *J. Soc. Glass Tech.*, 1946, **30**, 34T; *Philips Tech. Rev.*, 1946, **8**, 231.

[2] *J. Soc. Glass Tech.*, 1946, **30**, 54T.

[3] *Glass Ind.*, 1946, **27**, 552.

[4] *Ibid.*, 395; A., 1946, I, 336.

[5] *Z. Elektrochem.*, 1942, **48**, 9.

[6] *Naturwiss.*, 1944, **32**, 217; A., 1946, I, 99.

The properties and structure of glasses and clays based on the laws of crystal chemistry have been described by R. M. King.[7]

The new family of materials known as the silicones, which are derived from silicon–oxygen bonded structures in which some of the oxygens have been replaced by hydrocarbon groups, is quickly becoming known in the chemical industry. The formation and properties of liquid silicones, silicone greases, resins, pigment vehicles, varnishes, and rubbers have been described.[8]

Although there appears to be overwhelming evidence in favour of the random network theory of glass structure, the theory for the existence of crystallites and of definite chemical compounds has its adherents. Thus R. C. Ray, P. B. Ganguly, and B. P. Sarkar[9] conclude, from measurements of the potentials at glass-electrolyte boundaries, that soda–lime–silica glass contains a definite complex silicate of the formula $6SiO_2,CaO,Na_2O$.

The unidentified lines found by S. K. Majumdar, B. K. Banerjee, and K. Banerjee[10] in the X-ray diffraction spectra of borates containing dissolved alkali halides have now been attributed to a variety of crystalline B_2O_3 in the boric oxide glass and to anhydrous borax in the case of the borax glass.[11] It was thought that the alkali halide lattice might exist within the non-repeating network of B_2O_3 but this would entail an enlargement of the lattice. Later work suggests that the lattice spacings are unaltered in the glass and this result is confirmed by measurement of the spacings between planes when gold and platinum were dispersed in the glass; such spacings were in agreement with those measured on gold and platinum in the form of wire, and the results suggest that there is no change of spacing on dispersion.

The American Society for Testing Materials has put forward a definition of glass and this has been discussed by S. R. Scholes.[12]

GLASS-MAKING MATERIALS AND STUDIES IN GLASS MELTING.

Materials.

During the course of the year, a series of papers have been published which deal with various aspects of the problem of sands for glass making. F. W. Adams[13] has determined the heavy mineral content of a number of British and foreign glass sands and has established the minimum permissible amounts of iron and chromium oxides in soda–lime–silica glass if satisfactory decolorising is to be effected. Thus for colourless bottles, a completely decolorised glass could be obtained when the glass contained 0·03% of Fe_2O_3 and 0·0009% of Cr_2O_3; a faint yellowish-green was observed

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[7] *Bull. Amer. Ceram. Soc.*, 1946, **25**, 286; C., 1946, 82.

[8] S. L. Bass, J. F. Hyde, and R. R. McGregor, *J. Amer. Ceram. Soc.*, 1946, **29**, 66; B., 1946, II, 211.

[9] *J. Indian Chem. Soc.*, 1942, **19**, 61.

[10] *Nature*, 1945, **156**, 423; cf. A., 1946, I, 383.

[11] *Ibid.*, 1946, **158**, 753.

[12] *Glass Ind.*, 1945, **26**, 417.

[13] *J. Soc. Glass Tech.*, 1945, **29**, 250T; B., 1946, I, 200.

when the glass contained 0·045% of Fe_2O_3 and 0·0004% of Cr_2O_3 and additions of decoloriser sufficient to neutralise the tint reduced the brilliance of the glass. Adams suggests that purification can be carried out successfully by magnetting, by wet screening, and by using separating tables. A rapid method for determining chromium in the sand and in the glass is described.

H. P. Rooksby[14] has identified the heavy minerals present in glass-making sands by the *X*-ray diffraction method. The magnetic minerals consist of an iron-rich spinel type phase which bears chromium and a mineral of distorted rutile type structure which has been termed ferro-rutile. In many Continental sands, a third well-crystallised iron-bearing mineral, iron-rich tourmaline, was the most prominent constituent. W. Davies and W. J. Rees[15] have separated the heavy minerals present in some British glass-making sands and have identified them as magnetite, limonite, ilmenite, leucoxene, tourmaline, kyanite, zircon, garnet, and chromite : the heavy mineral contents varied from 0·03 to 0·3%. In a second paper[16] Davies and Rees have discussed the use of millstone grits from the Yorkshire dales as a source of glass-making sand and consider that they are suitable for this purpose ; chemical and physical analyses of grits from various localities are given. A. Sherlock[17] has reviewed methods of purifying glass sands by application of water washing, sieving, tabling, and magnetting ; he describes a method of chemical purification which reduces the iron oxide content of Lochaline sand from 0·012 to 0·005%.

A description of the actual and potential sources of high-grade silica in Scotland has been given by the Geological Survey of Great Britain[18] ; the report includes 25 analyses. W. Davies and W. J. Rees[19] have discussed the specific surface and grain shape of silica sands for glass making : methods recently evolved for the measurement of specific surface and for comparison of grain shape are surveyed.

Turning to other glass-making materials, W. A. Fraser suggests that alkali metal acid fluorides may be used advantageously as the source of fluorine in optical glass batches. It is claimed that the temperature of decomposition is lower than for the fluoride usually employed and that the fluorine is retained at an early stage of melting. The method is covered by a patent[20] and fluoride opals and enamels are included.

G. Östlund and H. Stübner[21] have discussed the advantages and disadvantages of using sodium sulphate, crude sodium carbonate, Swedish

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[14] *J. Soc. Glass Tech.*, 1945, **29**, 258T ; B., 1946, I, 200.

[15] *Ibid.*, 266T ; B., 1946, I, 167.

[16] *Ibid.*, 273T ; B., 1946, I, 200.

[17] *Ibid.*, 268T ; B., 1946, I, 200.

[18] *Dept. Sci. Ind. Res. Geol. Survey, Gt. Britain, Wartime Pamph. No.* 7 ; J. G. C. Anderson.

[19] *J. Soc. Glass Tech.*, 1945, **29**, 279T ; B., 1946, I, 200 ; C., 1946, 149.

[20] U.S.P. 2,407,874.

[21] *Tekn. Tidskr.*, 1945, **75**, 271.

felspar, and electrically smelted sodium silicate as substitutes for pure sodium carbonate. A general review of the use of sodium sulphate in glass manufacture has been published.[22]

Glass Melting.

Continuing their work on the achievement of homogeneity in glass melting, F. V. Tooley and R. L. Tiede[23] have investigated the effects of batch mixing time and grain size for a glass of composition SiO_2 73, Na_2O 17, and CaO 10%. Materials of grain size +60, 60—80, 80—140, 140—200, and 200— were used and various times and methods of mixing were employed. The homogeneity of the glass was determined by measuring the density spread. It was found that the results were practically independent of batch mixing conditions but the method of melting had an appreciable effect. Thus a melting time of 4 hours in a rotating crucible gave a glass with slightly less density spread than that for a glass melted for 16 hours in a stationary crucible. For any given melting conditions, decreasing grain size lowered the density spread.

The effect of grain size of the raw materials of a soda–lime–silica batch on the rate of decomposition of the silica at different temperatures has been studied by A. Fröhlich.[24] In addition, states of aggregation, and the viscosity and reactivity of the intermediate products, were studied. Primarily the double sodium calcium carbonate is formed at 720° and this reacts with the sand grains. At higher temperatures, the carbonate is decomposed, forming the liquid phase. The effect of grain size was examined for each of the batch materials individually, and while grain sizes of 0·2 mm. diameter were found to be the most favourable for rapid melting, the size of the sand grain was found to be the most important. This conclusion appears to be in agreement with the results of some work carried out in the U.S.S.R. on the melting and plaining of glasses of the hard borosilicate type from which it was concluded that the most favourable grain size for the sand and felspar in the batch is 0·12—0·15 mm. diameter, the batch composition being sand 78·5, soda ash 4·0, nitre 6·05, boric acid 23·4, felspar 5·5, and arsenic oxide 0·5.[25] Several plaining agents including sodium silicofluoride, sodium sulphate, ammonium nitrate, and ammonium chloride were investigated but these had little or even an adverse effect. The best plaining results were obtained with arsenic oxide and sodium chloride.

In an attempt to reduce the amounts of boric oxide in a glass without affecting appreciably the rate of melting, A. Dietzel[26] has found that considerable advantage can be gained by choosing the correct grain size distribution among the raw materials; the optimum ratios have to be determined for each individual case. It was found advantageous to

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[22] J. E. Fein, *Legkaja Prom.*, 1946, *No.* 1, 37; *No.* 2, 39.

[23] *J. Amer. Ceram. Soc.*, 1946, **29**, 197.

[24] *Trans. Chalmers Univ. Technol. Gothenburg*, 1946, *No.* 49, 3.

[25] I. I. Kitaigorodski *et al.*, *Stekol. i Keram. Prom.*, 1944, *No.* 1—2, 9.

[26] *Glastech. Ber.*, 1943, **21**, 198; Anon., *Glass Ind.*, 1946, **27**, 345.

include moisture-retaining materials in the batch as water vapour is a powerful fluxing agent. The inclusion of titanates was also found to be useful on account of their fluxing action. In the experimental work, Dietzel recorded electrically the loss in weight from the batch, using a constant heating rate, and he also measured the thermal conductivities of the batch in the study of the effect of grain size. A second method for the determination of melting rate was to observe the time for a conical pile of the batch to deform a given amount.

The significance of particle size of the reducing agent in the melting of glasses containing sodium sulphate has been investigated; anthracite in three ranges of grain size, 0—0·2 mm., 0—0·5 mm., and 1·5—2·0 mm., was used.[27] A deficiency of reducing agent caused gall while an excess caused discoloration. Coarse anthracite was more reactive than fine and the optimum amount for which no gall formation and no discoloration occurred was reached more rapidly with the coaser-grained anthracite.

The problems associated with melting and fining have been summarised by H. Jebsen-Marwedel,[28] who concludes that gases are expelled by thermal disintegration of sulphate, by replacement of sulphur trioxide by silica, and by chemical reaction of the atmosphere at the surface of the melt particularly in a reducing atmosphere , in such an atmosphere, there is a marked decrease in the ability of sulphate-containing melts to form blisters. Jebsen-Marwedel[29] has also discussed the effect of furnace atmosphere on striæ, composition, surface tension, colour, and on chemical stability, particularly in relation to the formation of sulphate during annealing.

O. Pridal[30] has found that at least 0·5% of As_2O_3 is required in a soda-lime glass for efficient fining and that 0·4% of sodium antimonate is equally efficient. J. W. Wright[31] has patented a method of fining tank glass by passing gas bubbles from the forehearth through the glass.

R. Halle and W. E. S. Turner[32] have made a further contribution to the study of the temperature distribution through molten glass in a tank and have investigated the effect of iron oxide and its state of oxidation on the heat transmission. The experiments were carried out in a small tank divided along its length into two parallel compartments, one containing the parent glass and the other the derived glasses which contained varying proportions of iron oxide up to 3·75%. The ferrous iron content was varied from 7·6 to 68·5% of the total iron. The temperature gradients were determined in the two compartments and the conclusions may be summarised thus: (1) with increasing iron oxide content, the proportion of ferrous iron decreased; (2) the surface temperature of the colourless glass was always less than that of the coloured and the difference increased

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[27] E. Z. Shitomirskaja, *Stekol. i Keram. Prom.*, 1946, *No.* 1—2, 11.

[28] *Sprechsaal*, 1942, **75**, 120.

[29] *Ibid.*, 1943, **76**, 331.

[30] *Sklarske Rozhledy*, 1942, **19**, 70.

[31] U.S.P. 2,387,222.

[32] *J. Soc. Glass Tech.*, 1945, **29**, 170T; B., 1946, I, 132.

with total iron content and with increasing proportion of ferrous iron in the total; (3) the temperature gradient at a depth of 3—4 in. increased with increased total iron content and with increased proportions of ferrous iron; thus the gradient rose from 9° to 111° per inch as the Fe_2O_3 content rose from 0·25 to 3·0% at a constant FeO proportion of 20% and from 35° to 80° per inch as the FeO proportion rose from 19 to 63·5% in glasses with a constant Fe_2O_3 content of 0·5%; (4) no linear relationship existed between either total iron content or the proportion of ferrous iron and the temperature gradient; (5) increase in total iron content or in the ferrous iron proportion reduced the heat losses through the bottom of the tank: (6) as a direct consequence of the increased heat absorption in the surface layers of the coloured glass, the refractory material of the tank suffers greater corrosion with increasing iron content and with increasing proportions of ferrous iron.

One of the problems of the electrical melting of glass by conduction between graphite electrodes is the colouring action of the electrode particles in contact with sulphur-containing materials. B. Long[33] claims that the colouring action can be overcome by adding zinc and cadmium oxides to glass containing arsenic and antimony.

The physical bases of the melting of glass by electrical conduction have been discussed by I. Peychès,[34] who has studied the conductivity of the glass, the electrical resistance of the melting tank, and the energy phenomena accompanying the melting process. A complicated relationship exists between the conductivity and the viscosity and this is discussed in relation to the glass structure.

Devitrification.

The influence of devitrification on the electrical conductivity of sodium silicate glasses has been investigated by M. Foëx.[35] The variation of resistivity with temperature was given by $\rho = Ae^{B/T}$, where ρ = specific resistivity and T = absolute temperature, A and B being constants. The temperature coefficient was smaller for the vitreous as compared with the devitrified materials and the coefficient reached a maximum for the compositions corresponding to the compounds $2SiO_2,Na_2O$ and SiO_2,Na_2O. At these compositions the resistivity had either maximum or minimum values.

The occurrence of cassiterite (stannic oxide) as a stone in glass has been reported[36]; the material was probably present as an impurity in the sand used.

A description, illustrated with photomicrographs, of the methods of examination and the techniques adopted for the petrographic identification of stones commonly encountered in glass making has been given.[37]

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[33] U.S.P. 2,396,585.

[34] *Rev. gén. élect.*, 1946, **55**, 143.

[35] *Compt. rend.*, 1944, **218**, 196.

[36] B. L. Steierman, *J. Amer. Ceram. Soc.*, 1946, **29**, 367.

[37] V. D. Fréchette and W. E. Hauth, *J. Canad. Ceram. Soc.*, 1946, **15**, 77.

Furnaces and Refractories.

From time to time, attempts have been made to trace the flow of glass in tank furnaces and reports of two such investigations have been published during the year. In order to determine the amount, velocity, and direction of surface flow, F. L. Bishop[38] introduced about 0·3% of cerium hydroxide into the glass batch at intervals and measured the resultant fluorescence or the changes in the transmission at chosen wave-lengths in the ultra-violet both on dip samples from the tank and on the finished products ; the data for surface flow were calculated from these measurements. V. W. Lenz[39] studied the flow by introducing cobalt blue glass cullet into the tank ; the glass in the tank was allowed to cool and was then quarried. Photographs of sections of the tank were taken and a general flow diagram was constructed. From a knowledge of the temperatures, specific gravities, and viscosities at various points in a tank, A. A. Sokolov has carried out a mathematical analysis of the currents in a tank[40] ; it is claimed that the method of computation makes possible the calculation of the quantity of heat carried from the melting end to the working end by virtue of the currents. A discussion on the currents in glass tanks has been published.[41]

B. P. Dudding has continued his statistical study of the performance of tank furnaces and in a recent paper deals with a furnace fired by coke-oven gas.[42] The utility of plotting the thermal performance index Q is emphasised, particularly for directing attention to changes in performance which require a technical explanation. The amount of fuel required to produce a ton of glass is estimated and the magnitude of the fuel change which it is necessary to make to accord with changes in throughput can be calculated. Detailed analysis of data obtained daily shows that there are marked differences in the throughput which are not necessarily accompanied by changes in the fuel consumed and this suggests possibilities of fuel economy.

The British Standards Institution has published a code for the evaluation of the performance and efficiency of regenerative glass tank furnaces.[43]

J. R. Green[44] has discussed the advantages of a study of reversal frequency in regenerative furnaces so far as it affects temperature stability, uniformity of temperature distribution, chequer and tank life, refractory and fuel costs, and furnace efficiency.

A method of attaining homogeneity by mechanical stirring in the working end of a tank has been patented[45] and a design of a tank in which it is possible to control the circulation of the glass has been put forward.[46]

[38] *J. Amer. Ceram. Soc.*, 1945, **28**, 308 ; B., 1946, I, 62.

[39] *Ibid.*, 1946, **29**, 8 ; B., 1946, I, 169.

[40] *Stekol. i Keram. Prom.*, 1944, *No.* 4—5, 7 ; *No.* 6, 7.

[41] Anon., *Ceram. Ind.*, 1945, **45**, 68 ; 1946, **46**, 94.

[42] *J. Soc. Glass Tech.*, 1946, **30**, 13T.

[43] B.S.S. 1312, 1946.

[44] *Ceram. Ind.*, 1946, **46**, 56.

[45] U.S.P. 2,394,893.

[46] G. D. Campbell, U.S.P. 2,387,880.

W. A. Moorshead[47] has advocated the use of waste-heat boilers as a means of recovering waste heat from pot and tank furnaces.

A. L. Pasquier[48] has described the results of using a burner specially designed to give a highly luminous flame with a gas of high calorific value; such a flame facilitates melting but the life of the refractories is prolonged and with such a system it was possible to extend the life of a furnace to 100 months without a major repair, the previous life being 15 months. An approximate mathematical method for determining the heat losses through steel supporting members and their effect on refractory temperatures has been worked out[49]; the results are presented in a series of charts relating heat loss and surface temperature with the thickness and thermal conductivity of the refractories.

It has been shown by J. Boow and G. E. Walker[50] that the measurement of the rate of elongation under load gives a useful indication of the durability of refractory materials; their results were based on an examination of four types of sillimanite tank blocks available commercially and the rates of elongation were correlated with texture, apparent porosity, and corrosion-resistance. G. A. Loomis[51] has traced the development of refractories for glass tanks over the past thirty years and describes methods of testing. The development of zircon as a refractory material has been described by N. R. Thielke and H. W. Jamison,[52] whose paper includes a comprehensive bibliography. Two patent specifications concerning zirconia refractories have been published.[53]

During the war, plant was installed at the U.S. Bureau of Standards for the slip casting of pots for the manufacture of optical glasses. A description of the equipment and methods has now been published.[54] The conditions for obtaining a pot free from pores, with high resistance to thermal shock and with maximum resistance to corrosion, were investigated. The experience gained with the melting of various kinds of optical glass in lined and unlined pots at the Bureau of Standards has been described in a second paper.[55] The results of an examination of two hundred pots for depth of glass penetration and the nature of the reaction products at the glass–refractory interface are described and illustrated by numerous photographs.

Analysis and Testing of Glass and Glass-making Materials.

Many analytical procedures have been published during the year and of these it has been possible to choose only a few which are likely to be of interest to glass analysts.

[47] *J. Inst. Fuel*, 1946, **19**, 180; B., 1946, I, 292.

[48] *Ceram. Ind.*, 1945, **44**, 122.

[49] H. T. Smyth, *J. Amer. Ceram. Soc.*, 1946, **29**, 31; B., 1946, I, 169.

[50] *J. Soc. Glass Tech.*, 1946, **30**, 5T;

[51] *Ohio State Univ. Eng. Exp. Sta. News*, 1945, **17**, 22.

[52] *Bull. Amer. Ceram. Soc.*, 1945, **24**, 452; B., 1946, I, 133.

[53] E. Wainer, Can.P. 435,029; cf. B., 1945, I, 225. Titanium Alloy Manufg. Co., B.P. 578,409; B., 1946, I, 333.

[54] R. A. Heindl, G. B. Massengale, and L. G. Cossette, *Glass Ind.*, 1946, **27**, 177.

[55] W. H. Parsons and H. Insley, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 31; B., 1946, I, 330.

Of the general methods available, P. Wenger and Z. Besso[56] have described methods for the micro-analysis of silicates and their procedures deal with SiO_2, Al_2O_3, CaO, MgO, Na_2O, and Fe_2O_3. B. B. Osthaus[57] has described a procedure for the complete elimination of excess of hydrofluoric acid in silicate analysis; in the usual procedure, the hydrofluoric acid which remains after decomposition of the glass is troublesome in preventing complete precipitation of aluminium in the R_2O_3 group. The determination of boron is one of the most difficult in glass analysis and a new method has been developed by M. Hollander and W. Rieman 3rd[58]; it is claimed that the method is more accurate and more rapid than those previously used, errors being of the order of ±0·04% with glasses containing up to 15% of B_2O_3. Two procedures are given, one using an indicator and the other using a pH meter. E. C. Owen[59] has described a microanalytical method for boric acid using its colour reaction with quinalizarin, colour comparison with a standard being made on the absorptiometer.

S. Kallmann[60] has described a method for the determination of sodium and potassium in silicates in which the two alkali metals are precipitated quantitatively by a 20% solution of hydrochloric acid in anhydrous *n*-butyl alcohol from a butyl alcohol solution of the metal perchlorates. An approximate method for the rapid determination of sodium and potassium by measurement of the light emitted when aqueous solutions of the metals are atomised in a gas flame has been published[61]; an accuracy of ± 3% is claimed for a measurement, which is accomplished in a few minutes. A description of the spectrographic determination of sodium, potassium, and lithium in a direct-current carbon arc using silver as an internal standard has been given.[62]

I. Zlotowski and I. M. Kolthoff[63] have given a method for the polarographic determination of calcium, alone and in the presence of other alkaline-earth metals, tetraethylammonium iodide is used as the supporting electrolyte and the polarographic behaviour of calcium in water and in water–ethanol mixture is investigated. R. E. Scott and C. R. Johnson[64] have determined calcium spectrophotometrically by precipitating as oxalate and colorimetric measurement of the permanganate. The oxalate method has been used by E. R. Wright and R. H. Delaune[65] for the separation of calcium from magnesium in samples of high magnesium/calcium ratio; by careful control of the relative concentrations of the

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[56] *Helv. Chim. Acta*, 1944, **27**, 1038; B., 1945, I, 128.

[57] *J. Amer. Ceram. Soc.*, 1946, **29**, 114: C., 1946, 235.

[58] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 788, C., 1947, **56**.

[59] *Analyst*, 1946, **71**, 210.

[60] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 678; C., 1947, **53**.

[61] R. B. Barnes, D. Richardson, J. W. Berry, and R. L. Hood, *ibid.*, 1945, **17**, 605; C., 1946, 127.

[62] A. W. Helz, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 129; C., 1945, 221.

[63] *J. Physical Chem.*, 1945, **49**, 386; C., 1946, 4.

[64] *Chemist-Analyst*, 1945, **34**, 81; *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 504; C., 1946, 3.

[65] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 426; C., 1946, 232.

magnesium and oxalate ions it is possible to achieve separations of calcium by direct precipitation of calcium oxalate in samples with a Mg : Ca ratio of 20 : 1 or greater.

A rapid method for the determination of aluminium has been put forward by I. Baker and G. Martin[66]; the determination is carried out by alkali fusion and subsequent precipitation and titration of the aluminium as the 8-hydroxyquinoline compound. C. H. R. Gentry and L. G. Sherrington[67] have described a rapid routine method for the analysis of lead glasses, in which the lead is precipitated as iodate.

G. F. Smith[68] has investigated the Györy method for the estimation of antimony and arsenic. The usual procedure, which comprises titration of solutions of the tervalent forms of the elements in concentrated hydrochloric acid using potassium bromate with methyl-orange or indigosulphonate as indicators, requires the reaction to be carried out at 80—90°. Smith's study shows that the high temperature can be eliminated and the equivalent point determined potentiometrically.

Several new methods are available for the determination of iron. J. L. Henry and R. W. Gelbach[69] have modified the method of G. H. Walden *et al.*,[70] using potassium dichromate in place of ceric ammonium sulphate to titrate the reduced iron, and diphenylaminesulphonic acid as indicator. The method has the advantage that N-hydrochloric acid is used in place of sulphuric acid of higher concentration. R. H. Greenburg[71] has put forward a colorimetric method for the estimation of iron in the presence of large quantities of copper and nickel; the method is an extension of the use of disodium pyrocatechol-3 : 5-disulphonate. The spectrophotometric determination of iron in ores has been investigated by J. P. Mehlig and M. J. Shepherd[72]; after reduction with hydroxylamine hydrochloride, the light transmittancy at 535 mμ. of the colour produced by thioglycollic acid in ammoniacal solution is determined. W. Pugh[73] has used mercurous perchlorate as a reagent for the volumetric estimation of iron, the function of the perchlorate being to reduce the ferric thiocyanate complex to the ferrous state; the conditions have also been determined for which the reagent can be used without the necessity for reduction. A. F. Colson[74] has applied the silver reductor to the micro-volumetric determination of iron and describes the apparatus and procedure for the estimation of 1·0 mg. of Fe with an accuracy of 1·0—5·0%.

The use of tannin as a selective reagent for zirconium has been extended further by W. R. Schoeller and H. Holness,[75] who have now applied it to

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[66] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 488; C., 1946, 5.

[67] *Analyst*, 1946, **71**, 31; C., 1946, 75.

[68] *J. Amer. Ceram. Soc.*, 1946, **29**, 143; C., 1946, 237.

[69] *Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 14; C., 1944, 65.

[70] *J. Amer. Chem. Soc.*, 1934, **56**, 350.

[71] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 255; C., 1946, 240.

[72] *Chemist-Analyst*, 1946, **35**, 8.

[73] *J.C.S.*, 1946, 588; C., 1945, 224.

[74] *Analyst*, 1945, **70**, 255; C., 1945, 293.

[75] *Ibid.*, 319; C., 1945, 226.

separate titanium from aluminium, iron, and vanadium; in chloride solution, tannin precipitates zirconium at a higher acidity than it does titanium, whilst the reverse occurs in oxalate solution. According to A. Weissler,[76] titanium, vanadium, and molybdenum may be determined simultaneously by determination of the absorption spectra of their hydrogen peroxide complexes in perchloric acid solution.

A rapid and accurate method for the colorimetric determination of cobalt with ammonium thiocyanate has been described by R. S. Young and A. J. Hall[77], the method can be used in the presence of other ions. The determination of manganese based on potentiometric titration of the manganous ion with the permanganate ion in neutral pyrophosphate solution has been given by J. J. Lingane and R. Karplus.[78]

The use of the Geiger counter X-ray spectrometer as an instrument for manufacturing control in the glass and ceramic industries has been described by F. G. Firth[79]; a variety of specific applications is suggested.

Annealing and Tempering.

The behaviour of glass as a function of temperature has been studied by A. Winter,[80] whose work indicates the existence of a temperature region below the softening point where the structure varies with time. For every temperature in this region of transformation there is an exact state which is not attained instantaneously, and Winter determined the rate at which equilibrium was attained at various temperatures. For all temperatures below the lower limit of the transformation region the glass is found in a single identical state of equilibrium. A knowledge of the laws of transformation leads to the establishment of an annealing curve which can be used to achieve a stable refractive index at room temperature in a minimum cooling time.

The relationship between the inelastic deformability and the thermal expansion of glass in the annealing range has been studied by A. Q. Tool[81]; this work again is concerned with the attainment of equilibrium. Glass is a purely viscous liquid in and above the annealing range and it can be easily superheated or undercooled in this region because its viscosity is high. Below its annealing range glass behaves as an elastic solid but there is an intermediate range where it possesses plastico-viscous properties. The condition of both the undercooled and superheated glass usually corresponds to some condition of equilibrium in the annealing range and the degree of undercooling or superheating may therefore be regarded as the difference between the equilibrium and actual temperatures. Changes in the actual or equilibrium temperatures affect the properties of the glass and the rate at which the equilibrium temperature

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[76] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 695; C., 1946, 74.

[77] *Ibid.*, 1946, **18**, 264; *Chem. and Ind.*, 1946, 394; C., 1947, 7.

[78] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 191; C., 1946, 153.

[79] *J. Amer. Ceram. Soc.*, 1945, **28**, 363; B., 1946 I 99.

[80] *Bull. Inst. Verre*, 1946, *No.* 1, 3.

[81] *J. Amer. Ceram. Soc.*, 1946, **29**, 240; B., 1947, I, 25.

changes is proportional to the degree of undercooling or superheating. When glass is heated from an undercooled condition it contracts and an exothermal reaction occurs but when equilibrium is approached from a superheated condition, the reverse occurs. The rates at which the effects develop depend on the rate at which the difference between actual and equilibrium temperatures is decreased and this is controlled by the inelastic deformability. On this basis Tool derives an equation which relates the rates to the inelastic deformability and discusses its applications.

During the past few years, the variation of refractive index with annealing temperature has engaged the attention of a number of workers. V. A. Florinskaja[82] has now examined the changes in the dispersions of optical glasses on annealing; the extent of the change was found to vary with the annealing temperature and for flint glasses was about 20 times that for crown glasses. Details of some work carried out by F. H. Zschacke[83] on the calculation of annealing temperatures from chemical compositions which were published in Germany in 1942 have now become available. The design of an electric kiln for annealing optical glasses has been patented,[84] the main feature being the provision of heating elements on all internal surfaces.

The use of standard strain discs for routine testing of internal strain in commercial glassware has been adopted generally throughout the glass industry. T. D. Green[85] has described the method of preparation of the discs in America, and a similar account has been given by A. J. Holland[86] of the methods used by the Society of Glass Technology in this country.

A detailed discussion of the tempering of safety lenses has been given by C. D. Oughton,[87] who deals with the effect of shape and dimensions of the glass, furnace temperature and time in furnace, air pressure and temperature, nozzle orifice design, and the mass and design of the lens holder.

A method of tempering which causes zones of different tension to be produced in the glass surface, so that some of the glass remains clear on fracture, formed the subject of a patent specification of B. Long.[88] The method has now been modified by providing a means for uniformly chilling the surface before application of the differential chilling and, in this way, surface deformation is prevented.[89] A method of tempering using gaseous streams, the intensity of which is alternately increased and decreased, has been patented.[90]

[82] *J. Tech. Phys. U.S.S.R.*, 1945, **15**, 681.

[83] *Sprechsaal*, 1942, **75**, 476.

[84] Chance Bros. Ltd., W. N. Wheat, and R. Bullock, B.P. 577,952; B., 1946, I, 373; U.S.P. 2,400,056.

[85] *J. Soc. Glass Tech.*, 1945, **29**, 129T; C., 1946, 128.

[86] *Ibid.*, 148T; C., 1946, 128.

[87] *Glass Ind.*, 1946, **27**, 121.

[88] U.S.P. 2,244,715.

[89] U.S.P. 2,365,967.

[90] T. G. White, U.S.P. 2,401,442.

A novel method of producing a glass of high mechanical and thermal strength has been described by I. A. Smirnova[91]; two or more layers of glass having the same thermal expansion coefficients and different rates of solidification are sealed together, thus setting up compressional stresses in the composite sheet.

DURABILITY.

The use of radium to prevent the growth of fungi in optical instruments has been described by R. E. Vicklund.[92] Radium sulphate was applied to metal foil to the extent of 15 μg. per sq. in. and the metal foil was incorporated within the instrument; this had a marked effect in preventing fungoid growth on the glass surfaces and this was attributed to α-particle radiation. The effects are demonstrated by photographs.

The ageing of optical glass surfaces has been studied by A. H. Pfund,[93] who made observations on the refractive index of the surface films and on the reflexion of infra-red radiation between 7 and 12 μ. The refractive indices were generally lower for the aged surfaces than for the fresh surfaces and the aged surfaces invariably revealed reflexion maxima at 9·25 μ. corresponding to the reflexion maximum for fused silica. An accelerated ageing test was developed in which the specimens were exposed in a bottle to the combustion products from a small gas flame: an exposure of 24 hours in this test was found to be equivalent to one year's natural exposure.

D. Hubbard[94] has suggested that the hydrogen electrode function or pH response is a suitable means of determining the serviceability of glasses to weathering. Serviceability is largely dependent on hygroscopicity, which in turn is a primary factor for determining the suitability of a glass for pH measurements. Hubbard has applied such methods to a series of potash–silica glasses, for which the pH response and the hygroscopicity were determined, and all the glasses investigated showed high hygroscopicity with an accompanying pH response. Between pH 2 and 4, glasses of 71·8 and 73·6% SiO_2 gave response values higher than the 59 mv. per pH unit predicted from the Nernst equation and electrodes prepared from all members of the series showed large voltage departures from the linear relationships with increasing alkalinity of the buffer solutions; these voltage departures were found to correlate better with the magnitude of the chemical attack than with the pNa concentration of the solutions.

J. S. Turner, E. I. McLennan, J. S. Rogers, and E. Matthaei[95] have described the use and method of application of sodium ethylmercury salicylate (M.T.S.) as a fungicide for the tropical proofing of optical instruments. The chemistry of M.T.S. has been described elsewhere.[96]

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[91] *Trud. Moskov. Chim-Tech. Inst. Mendeleeva*, 1940, *No.* 6, 93.
[92] *Ind. Eng. Chem.*, 1946, **38**, 774; C., 1946, 298.
[93] *J. Opt. Soc. Amer.*, 1946, **36**, 95; C., 1946, 297.
[94] *J. Res. Nat. Bur. Stand.*, 1946, **37**, 223.
[95] *Nature*, 1946, **158**, 469.
[96] *Ibid.*, 472.

The resistance of plate glass (SiO_2 72, Na_2O 13·7, CaO 11·5, MgO 2·5, Al_2O_3 0·3%) to attack by alkaline solutions has been investigated by M. S. Tarnopol and A. E. Junge,[97] sodium and potassium hydroxides and carbonates and sodium pyrophosphate being used at various concentrations and temperatures, and the attack being measured as penetration in mm. per year. In general, the hydroxides were less corrosive than the alkaline salts and the sodium salts were more corrosive than the potassium salts. Temperature had a marked effect on the corrosion rate, but the attack was not appreciably affected by increases in concentration above 10%. The amount of staining could not be regarded as a reliable guide to the amount of attack.

M. A. Besborodov[98] has examined the chemical resistances of a series of soda–lime–silica glasses under storage conditions in contact with sodium carbonate solution and concludes that the compositions for optimum resistance are SiO_2 75, CaO 10, Na_2O 15%, and SiO_2 75%, CaO 5, Na_2O 20% ; for resistance to both sodium carbonate and water the best composition is SiO_2 75, CaO 10, Na_2O 15%.

A lead–nickel silicate glass has been developed for the purpose of supplying nickel ions to battery electrolytes[99] ; by this means, the end-of-charge voltage is reduced and the capacity of the battery improved.

A glass resistant to hydrofluoric acid and fluoride attack has been patented by A. G. Pincus[100] ; its composition lies within the limits P_2O_5 60—85, Al_2O_3 10—20, and one of the oxides ZnO, BeO, or PbO 0·5—30%, the melting being accomplished in an aluminium silicate container.

The method of applying liquid dimethylsilicones for obtaining water-repellent surfaces on glass insulator bodies has been described by O. K. Johannson and J. J. Torok.[101]

PHYSICAL PROPERTIES.

Density and Thermal Expansion.

In recent years, the use of density measurements as a means of production control for glass tanks has been described by several workers and M. A. Knight[102] has now described an apparatus for obtaining rapidly the necessary data. Several lumps of glass of approximately 2 g. weight and of unknown density together with a sample of known density are placed in a heavy liquids mixture in a tube which is immersed in a water-bath heated at a uniform rate ; as the lumps settle, the temperature at which they pass a reference mark is noted and the density of each sample is expressed simply in terms of the difference between its temperature and that for the standard sample. The reproducibility of results is

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[97] *J. Amer. Ceram. Soc.*, 1946, **29**, 36 ; B., 1946, I, 170.

[98] *Legkaja Prom.*, 1945, *No.* 7/8, 12.

[99] F. J. Williams and J. A. Orsino, *J. Amer. Ceram. Soc.*, 1946, **29**, 313; B., 1947, I, 104.

[100] U.S.P. 2,381,925.

[101] *Proc. Inst. Radio Eng.*, 1946, **34**, 296.

[102] *J. Amer. Ceram. Soc.*, 1945, **28**, 297 ; B., 1946, I, 62 ; C., 1946, 222.

represented by a standard deviation of ±0·0001 g. per c.c. The method of sampling, procedure, and the calculation of the results are described in detail. R. A. Elliott[103] has devised factors for calculating changes in density corresponding to moderate changes in composition.

Most of the work on thermal expansion which has been published has been concerned with glass with expansion coefficients suitable for sealing to metals and metal alloys. Thus a glass suitable for sealing to iron lying within the composition limits SiO_2 40—48, PbO 32—38, Al_2O_3 1—8, Li_2O 1—2·5, Na_2O 2—5, K_2O 12—17% with a total alkali content not greater than 19% has been patented by R. W. Goodwin.[104] A borosilicate glass suitable for sealing tungsten to fused quartz and consisting of SiO_2 83·25, Al_2O_3 4·5, B_2O_3 12, and Li_2O 0·25% has been patented by K. C. Lyon[105]; this amount of lithium oxide is stated to render the glass sufficiently conducting to be melted by passing current through it after preheating. A glass consisting of PbO 69, SiO_2 15, B_2O_3 11, BaO 5% for sealing to non-magnetic nickel–iron alloys has been covered by a Norwegian patent.[106] The composition of a phosphate glass lying within the range P_2O_5 28—38, Al_2O_3 8–16, B_2O_3 13—22, ZnO + MgO + BaO 24—34, and Na_2O 6—10%, for sealing together glasses of different compositions or for sealing glasses to ceramic materials or iron alloys, is due to J. E. Stanworth[107]; the coefficient of linear expansion is approximately 90×10^{-7}.

A series of papers by A. J. Monack discusses the theory and practice of glass-to-metal seals.[108] The physical properties of the available metals and alloys are enumerated and theories of the mechanism of sealing are outlined. The theory of Hull and Burger based on Poritsky's equations is discussed and the divergencies between the stresses calculated and observed are explained with reference to the rate of working, the plastic flow during cooling, and the changes produced by heat-treatment. In the final section, Monack deals with electrolysis in glass–metal combinations. A general discussion on the problem of glass–metal seals has been given by P. J. Gaylor.[109] G. D. Redston and J. E. Stanworth[110] have discussed the stresses in sandwich seals with British-made alloys of the Kovar type and a suitable borosilicate glass.

Owing to the shortage of boric acid and borax on the Continent during the war, it became necessary to devise compositions for low-expansion resistance glasses in which the boric oxide was replaced by combinations of other constituents. O. Pridal[111] has described the physical properties of a series of such glasses with B_2O_3 replaced by Al_2O_3, ZnO, CaO, and MgO

[103] *J. Amer. Ceram. Soc.*, 1945, **28**, 303; B., 1946, I, 62.
[104] U.S.P. 2,389,305.
[105] U.S.P. 2,408,468.
[106] Norw.P. 65,936.
[107] U.S.P. 2,390,191.
[108] *Glass Ind.*, 1946,, **27**, 389 446, 502, 556.
[109] *Ibid.*, 1945, **26**, 509.
[110] *J. Sci. Instr.*, 1946, **23**, 53; cf. B., 1945, I, 389.
[111] *Sklarske Rozhledy*, 1941, **18**, 184.

in combination. A low-expansion glass which was made in Sweden has been described by S. Lindroth.[112]

Thermal Endurance. Thermal Conductivity and Specific Heat.

The theory of fracture under thermal shock has been analysed by O. H. Clark,[113] who points out that the analysis of stresses is complicated by unknown degrees of stress relief and transfer in flexure. There are, however, a group of thermal shock phenomena in which flexure is not a factor, for example, shocks arising from complete immersion, shocks administered to cylindrical tubes, and shocking from one side only. The duration of the stress is also of importance and the theory developed in the paper is regarded as an improvement over that already available since the flexure effect does not exist and the stress duration is considered.

J. E. Descrivières[114] has reviewed the application of the laws of thermal conductivity to simple and multiple glass walls and has investigated the heat balance of inhabited places containing glass walls.

S. Anderson[115] has measured the specific heat of plate glass of composition SiO_2 72, Na_2O 13·7, CaO 11·5, MgO 2·5, and Al_2O_3 0·3% in the temperature range 500—1000°. The mean specific heat between 40° and temperatures at approximately 25° intervals between 500° and 1100 was also determined and was found to be a linear function of temperature. The specific heat at 1000° was 0·301 and for a glass of similar base composition containing added iron oxide for infra-red absorption the value rose to 0·309.

P. H. Keesom[116] has given the thermal conductivity of Thuringian glass at 1·3° K. as 8×10^{-5} g.-cal. $cm.^{-1}$ $sec.^{-1}$ $deg.^{-1}$

The Strength of Glass.

The problem of the mechanical strength of glass continues to occupy the attention of a number of workers and several general reviews which are of value to the worker undertaking investigations in the field have been produced. W. A. Weyl[117] has pointed out that if the tensile strength of glass is to be compared with that of other materials the tests must be carried out under conditions where surface flaws and environment have comparable influences. The discrepancy between the measured strength of solids and the value calculated from the electrical forces is due to local regions of weakness, such as lattice defects, flaws, and surface cracks, and this is particularly true when the material is tested under conditions where chemical reaction between the material and its surroundings can occur. Weyl discusses the basis on which the strength of metals, glasses, and plastics can be compared.

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[112] *Tekn. Tidskr.*, 1945, **75**, 1239.

[113] *J. Amer. Ceram. Soc.*, 1946, **29**, 133; B., 1946, I, 370.

[114] *Bull. Inst. Verre*, 1946, *No.* 3, 11.

[115] *J. Amer. Ceram. Soc.*, 1946, **29**, 368.

[116] *Physica*, 1945, **11**, 339; A., 1946, I, 139.

[117] *Glass Ind.*, 1946, **27**, 17, 74, 126.

The recent work of Murgatroyd and Jones[118] has been reviewed by A. F. Turner,[119] who suggests that there is a relationship between the elastic moduli, the viscosity, the delayed elastic effect, and the strength of glass ; the structure of glass fibres differs from that of massive glass in that it shows an anisotropic character in the nature of a chain structure. C. Gurney[120] has discussed the effect of duration of loading on the strength of glass and attempts to correlate the work of Murgatroyd and Sykes with that of Orowan. The Murgatroyd–Sykes experiments showed that the ultimate breaking strength of glass is not significantly reduced by pre-stressing whilst Orowan concludes that the effect of pre-stressing should be to reduce the ultimate breaking stress. Gurney deduces an expression for the ratio of the vapour pressure of a stressed and an unstressed solid in terms of the stress, specific volume, Young's modulus, and absolute temperature and deduces that the vapour pressure at the ends of cracks where the material is stressed to the breaking load is of the order of 10^{20}—10^{30} times that elsewhere in the material. The rate of crack spreading by evaporation can be estimated, and if the material does not break until the vapour pressure becomes high relative to that at the ends of the crack before it starts to spread then a relationship can be derived between the duration of loading and the averâge stress required to cause fracture.

F. W. Preston and his colleagues have continued their work on various aspects of the strength problem. Together with T. C. Baker[121] he has described an apparatus for testing the strength of glass rods in flexure by means of which the load is applied in 2—3 milliseconds and the duration of stress is 0·01 second. The fatigue of glass and porcelain rods has been measured for times ranging from 10 milliseconds to 24 hours and the test samples had their surfaces wetted. The breaking stress for a load duration of 10 milliseconds was three times that for a load duration of 24 hours and the ratio was approximately the same for all glassy materials. F. W. Preston and J. L. Glathart[122] have obtained an empirical relationship which indicates that the reciprocal of the breaking stress is a linear function of the logarithm of the duration ; the law is valid for stress duration times varying from 10^{-2} to 10^{-5} second. T. C. Baker and F. W. Preston[123] have also investigated the effect of environment on the strength of glass, making measurements in dry air, vacuum, in aqueous solutions containing carbon dioxide, calcium hydroxide, and sodium hydroxide, and in an autoclave at steam pressures of 600—800 lb. per sq. in. In high vacuum, glass which had been baked had a strength which was independent of duration of load up to 10 seconds ; glass exposed to moisture loses its strength rapidly under stress.

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[118] *J. Soc. Glass Tech.*, 1944, **28**, 368T, 388T, 406T, 432T.

[119] *Glass Ind.*, 1946, **27**, 69, 88.

[120] *Nature*, 1946, **157**, 662; B., 1947, I, 129.

[121] *J. Appl. Physics*, 1946, **17**, 162 ; C., 1946, 227.

[122] *Ibid.*, 189 ; B., 1946, I, 293.

[123] *Ibid.*, 179 ; B., 1946, I, 293.

F. S. Jones[124] has demonstrated that if ground and polished surfaces which had been milled to shape by a diamond-charged wheel were etched with acid, the milling pattern would reappear. This effect was interpreted as being due to tiny vertical fractures similar to those which arise when glass is cut with a diamond; the fractures cause a lowering of tensile strength and of resistance to weathering.

A method of measuring the elastic constants of small fragments of isotropic material has been developed by S. Bhagavantam and B. R. Rao[125]; characteristic thickness shear modes can be transmitted through the material and communicated to liquids in the form of longitudinal strains. Values for Young's modulus for glass obtained by this method are given.

Softening Point, Viscosity, and Surface Tension.

J. Boow and W. E. S. Turner[126] have continued their series of researches on the viscosity and working characteristics of glass. Their previous measurements on the rate of cooling during gathering and shaping by hand have been supplemented by a study of the glass temperatures during shaping by gravity for automatic machines. Two glasses were studied, a colourless glass of composition SiO_2 74·1, CaO 9·7, Na_2O 15·2, MgO 0·1, and R_2O_3 0·85% and an amber glass SiO_2 73·75, CaO 9·4, Na_2O 15·6, and R_2O_3 1·25%, and the machines included a Hartford–Fairmont press and blow machine, a Lynch L.A., a Lynch 10, and a mechanical press. The temperature and therefore the viscosity at each stage of the operation were found to depend on the particular machine and on the weight and colour of the glass. The following general results were obtained for the viscosity at the various stages of manipulation; gob formation 2000—11,000 poises, when leaving parison mould $1·8 \times 10^4$—6×10^4, entry into blow mould 9×10^4—$2·3 \times 10^5$, and at discharge from the blow mould the viscosity in a bottle base was 10^6—10^8; values for the viscosities for other mechanical processes are also given. In a second paper Boow and Turner[127] report their temperature measurements made on the glass and on the mould parts during the manipulation by semi-automatic machines of pressed articles varying in weight from 9 to 58 oz. The viscosity of gathering was from 1200 to 2200 poises, for entry into the press mould 2000—5000 poises, at the commencement of pressing 3000—6000 poises, for completion of pressing $10^{4·7}$—$10^{6·0}$ poises, and at removal from the mould $10^{3·9}$—$10^{7·1}$ poises. Two glasses were investigated having compositions SiO_2 73·5, CaO 9·2, Na_2O 15·4, and R_2O_3 1·4% and SiO_2 72·4, CaO 8·8, Na_2O 17·5, and R_2O_3 0·9%.

Several studies of the viscosities of various silicate systems have been published. The system CaO–MgO–Al_2O_3–SiO_2 within the range

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[124] *J. Amer. Ceram. Soc.*, 1946, **29**, 108; B., 1946, I, 293.

[125] *Nature*, 1946, **157**, 624.

[126] *J. Soc. Glass Tech.*, 1945, **29**, 199T; B., 1946, I, 169.

[127] *Ibid.*, 233T; B., 1946, I, 169.

of compositions SiO_2 40, CaO 15—45, MgO 0—30, and Al_2O_3 5—30% has been studied for all compositional increments of 5% and the results were expressed as isokoms for the various temperatures between 1100° and 1500°[128]; a theory of the effect of composition on viscosity is discussed. A number of similar studies published in the U.S.S.R. in 1941 have become available in this country. B. A. Pospelov and K. S. Evstropiev[129] have investigated the viscosity of the system $Na_2Si_2O_5$–$PbSiO_3$ in the temperature range 400—1400° (viscosity 10^{15}—10 poises) and found that the equation proposed by S. C. Waterton can be used to express the results. A. S. Konovalov and K. S. Evstropiev[130] have reported the viscosities of glasses within the system SiO_2–PbO and find that the equation $\log \eta = A + (a/\theta^2)$ expresses the results in the temperature range 600—1400°, a and A being functions of composition; a similar equation may be used to cover the viscosity in the system Na_2SiO_3–SiO_2 in the temperature range 800—1400°.[131] M. V. Ochotin[132] has investigated viscosities in the five-component system SiO_2 69—75, Al_2O_3 1—5, CaO 5—11, Na_2O 12—16, MgO 3%, the results being expressed as relations between viscosity–temperature and viscosity–composition.

The effect of dissolved gases on the viscosity of a commercial glass has been investigated by W. A. Graff and A. E. Badger,[133] who found that the softening point, annealing point, and strain point for the glass melted *in vacuo* were respectively 726°, 549°, and 516°; for the same glass melted in a carbon dioxide atmosphere the values were 730°, 543°, and 510° and in an atmosphere saturated with water vapour 725°, 540°, and 510°. No significant differences were observed at a temperature of 1370°.

A. E. Dale and J. E. Stanworth[134] have studied the viscosity of some borosilicate glasses and some soda–lime–silica glasses in the annealing range (viscosity 10^{11}—10^{13} poises) and find that the soda–lime glasses approach equilibrium much more rapidly than the borosilicates but the absolute values of viscosity are similar after stabilisation; the longer times required by the borosilicate glasses were attributed to changes in the boron co-ordination.

An apparatus for measuring simultaneously the thermal expansion, transformation temperature, and softening temperature has been described by S. Lindroth.[135]

W. A. Weyl[136] has reviewed the surface chemistry of glass on the basis of the modern concept of glass structure; he discusses the replacement of alkali ions under the action of furnace gases and by treatment with

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[128] J. S. Machin and D. L. Hanna, *J. Amer. Ceram. Soc.*, 1945, **28**, 310; B., 1946, I, 62.

[129] *J. Phys. Chem. Russ.*, 1941, **15**, 125.

[130] *Ibid.*, 109.

[131] M. M. Skorniakov, A. J. Kuznetsov, and K. S. Evstropiev, *ibid.*, 116.

[132] *Conf. on Viscosity of Liquids and Colloidal Solutions*, 1941, **3**, 78.

[133] *Physical Rev.*, 1946, [ii], **70**, 220.

[134] *J. Soc. Glass Tech.*, 1945, **29**, 414T.

[135] *Bull. Amer. Ceram. Soc.*, 1945, **24**, 450; C., 1946, 129.

[136] *Bull. Inst. Verre*, 1946, *No.* 3, 1.

calcined kaolin, and also the introduction of organic silicon chlorides to render the surface hydrophobic.

C. R. Amberg[137] has used the dropping-weight method to investigate the effect on surface tension of the addition of certain oxides to silicate melts. The results of additions of MoO_3, V_2O_5, WO_3, Sb_2O_3, Nd_3O_4, Co_3O_4, MnO_2, UO_2, and As_2O_3 to the extent of 1% and 3% are described; the addition of molybdenum oxide was shown to have a marked effect on the reduction of surface tension. A. O. Prater and A. E. Badger[138] have put forward a factor to correct surface tensions measured by the drop-weight method to absolute values.

A comprehensive review of the methods of measurement and the effects of various constituents on the surface tension of glasses has been given by P. Gilard.[139]

Electrical Properties.

With the increased use of glass for electrical purposes, work on the measurement of electrical properties and patents on glasses having specific electrical properties continue to increase.

L. Navias and R. L. Green[140] have determined the dielectric constants and dielectric losses of 104 glasses at frequencies of 3000 and 10,000 megacycles. The power factor data are correlated with compositions and a qualitative explanation of the mechanisms producing energy absorption and dielectric losses in the micro-wave range is proposed. These mechanisms are determined by the nature of the bonds joining the atoms and ions in the random network. The silica and boric oxide networks are relatively transparent to centimetric wave-lengths and the absorption of energy and dielectric losses are therefore low. The addition of network-modifying ions yields glasses of greater energy absorption owing to the oscillation of interstitial ions, particularly for the alkali ions, for which the losses are high. Glasses containing combinations of alkali ions show lower losses than equivalent compositions with only one alkali. Glasses containing large amounts of barium or lead oxides have high power factors.

W. H. Armistead is responsible for three patents on lead and barium glasses with low power factor. The first of these[141] is for glasses within the composition range SiO_2 10—50, B_2O_3 5—65, PbO 20—40, and Al_2O_3 5—15% with a power factor less than 0·07% and a dielectric constant greater than 5. The second patent[142] covers a glass with a power factor less than 0·07% and a dielectric constant greater than 4 lying within the composition range SiO_2 0—55, B_2O_3 22—80, Al_2O_3 5—20, BaO 10—30%. The third patent[143] covers a glass with similar electrical properties to the

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[137] *J. Amer. Ceram. Soc.*, 1946, **29**, 87; B., 1946, I, 294.

[138] *Glass Ind.*, 1946, **27**, 339; C., 1946, 309.

[139] *Bull. Inst. Verre*, 1946, *No.* 2, 1.

[140] *J. Amer. Ceram. Soc.* 1946, **29**, 267; A., 1947, I, 36.

[141] U.S.P. 2,393,448.

[142] U.S.P. 2,393,449.

[143] U.S.P. 2,393,450.

first but lying within the composition range SiO_2 0—50, B_2O_3 10—75, Al_2O_3 5—15, and PbO + BaO 10—40%, the ratio PbO/BaO being at least 3 when PbO + BaO is near 40%. H. P. Hood[144] has been granted a patent covering a glass of low power factor containing 70% of silica.

Lead–alkali–silica glasses containing up to 30% of lead oxide are usually used for sheathing the current-carrying leads for electric lamps, and J. H. Partridge[145] has investigated the possibilities of replacing the lead oxide by other oxides without reducing the electrical resistance or increasing the viscosity of the glass. It has been found that the lead oxide content can be reduced to 15% without affecting adversely the electrical resistance, but such glasses are generally harder than the parent glass. However, satisfactory glasses containing 20% of PbO can be made by substituting strontium, barium, and magnesium oxides for lead oxide ; the electrical properties and thermal expansions of the glasses thus developed are tabulated. A patent on a lead glass composition which combines ease of working with high electrical conductivity and containing strontium oxide in addition to lead oxide has been granted to Partridge.[146]

J. Gallup[147] has studied the cracking he observed along soft glass stems carrying the leads of rectifier bulbs and has found that it is due to electrolysis ; the potential which caused rupture was found to be due to glass bombardment by reverse emission from the rectifier plates. The gas produced in the electrolytic process was analysed on the mass spectrometer and gave composition results agreeing with those expected from the electrolytic decomposition of soft glass.

Some measurements of the electrical resistivity of various commercial glasses in the temperature range 400—1000° have been reported[148] ; the logarithm of the viscosity was found to be inversely proportional to absolute temperature between 500° and 800° c. and the relationship between viscosity and resistivity may be expressed as a power law. R. H. Dalton[149] is responsible for a patent on a glass of high resistivity and durability lying within the composition range SiO_2 67—67·5, B_2O_3 15—16, Al_2O_3 7·5, Na_2O 1—3, K_2O 3—5, BaO 3, and Li_2O 1%. A patent specification covering electrical condensers made by embedding metal foil in glass has been published.[150]

Optical Properties.

The optical properties of glasses can generally be calculated to a fair degree of accuracy from the composition by the use of the factors which have been published from time to time. The agreement between the calculated and measured values usually breaks down for glasses containing

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[144] U.S.P. 2,410,286.
[145] *J. Soc. Glass Tech.*, 1945, **29**, 434T.
[146] U.S.P. 2,388,866 ; B.P. 574,275 ; B., 1946, I, 172.
[147] *J. Amer. Ceram. Soc.*, 1946, **29**, 277 ; B., 1947, I, 65.
[148] Kinving Leung. *Compt. rend.*, 1946, **223**, 236.
[149] U.S.P. 2,392,314.
[150] Jenaer Glaswerk, Swiss P. 227,689.

boric oxide and alkali, and on this account some recent work published by T. H. Wang and W. E. S. Turner[151] on the influence of boric oxide on the refractive index and dispersion of soda–boric oxide–silica glasses is of value. Three series of glasses having the general compositions (*a*) $SiO_2 + B_2O_3$ 80, Na_2O 20%, (*b*) $SiO_2 + B_2O_3$ 85, Na_2O 15%, and (*c*) $SiO_2 + B_2O_3$ 90, Na_2O 10% were prepared by melting in a platinum crucible and the optical constants were determined on 19 glasses. The results are shown in the form of curves relating refractive index with B_2O_3 content for constant soda content, and the curves show that substitution of B_2O_3 for SiO_2 gives a maximum value for refractive index, the maximum being displaced towards higher B_2O_3 content as the Na_2O content is increased. With increasing B_2O_3 content, the reciprocal dispersive power (V value) tends towards a constant value which is the same for all three series

M L Huggins and K H Sun[152] have studied the effect of chemical composition on the relationships between refractive index and V value for binary silicate systems The Na_2O–SiO_2 system is discussed in particular and equations are deduced relating n_D and V value at any composition The initial values of the slope of the curve at the SiO_2 end are tabulated for various SiO_2–M_mO_n systems The method is extended by M. L. Huggins, K. H. Sun, and R. M. Welch[153] to the ternary system SiO_2–Na_2O–CaO. The effect of titanium and lead oxides on refractive index and density when added to a glass of composition $Na_2O,3SiO_2$ has been investigated by W. Colbert[154] the two oxides were added in 5% steps up to a maximum of 35% by weight. On a weight percentage basis, titania has the greater effect on refractive index but on a molecular percentage basis titania and lead oxides have equal effects up to 5%; beyond that, the refractive index increases proportionally to the titania content. For density, the lead oxide glasses increase more rapidly than the titania glasses on both the weight percentage and molecular percentage bases. The molecular refractivities of the two oxides are similar.

An investigation on the yellow colour of heavy lead silicate glasses has been reported by W. M. Hampton[155] and it is concluded that for compositions which give refractive indices up to 1·9 the colour can be ascribed to the effect of impurities; the colouring effects of iron oxide, copper oxide, and chromium oxide are in the ratios 1 : 2 : 40 for equal weight percentages in the glass of refractive index 1·9.

A series of patent specifications have been published covering the compositions of optical glasses containing substantial quantities of lanthanum and thorium oxides and having high refractive indices combined

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[151] *J. Soc. Glass Tech.*, 1945, **29**, 390T.

[152] *Ibid.*, 192T; *J. Amer. Ceram. Soc.*, 1945, **28**, 306; B., 1946, I, 63.

[153] *J. Soc. Glass Tech.*, 1945, **29**, 428T; *J. Amer. Ceram. Soc.*, 1946, **29**, 159; B., 1946, I, 292; C., 1946, 149.

[154] *J. Amer. Ceram. Soc.*, 1946, **29**, 45; B., 1946, I, 171.

[155] *Nature*, 1946, **158**, 582; B., 1947, I, 129.

with high *V* value.[156] H. W. Lee[157] has discussed the properties of recently developed optical glasses containing oxides of the rare earth metals and of hafnium, tantalum, tungsten, and yttrium.

S. K. Majumdar and A. K. Sarma[158] have given the refractive index and density for various compositions in the system B_2O_3–alkali halide.

The theory of four methods of measurement of the light absorption in optical glasses has been discussed by T. Smith,[159] who stresses the importance of accuracy and the necessity to separate the effects of absorption and reflexion; he concludes that the accuracy of the four methods is similar provided that the appropriate conditions are satisfied. A description of a direct-reading refractometer has been given by J. G. Holmes.[160]

Throughout the year under review a number of general reviews on non-reflecting and highly reflecting films have been published. A short descriptive note on both anti-reflexion and high-reflexion films is given by S. Weintroub.[161] S. Bateson and A. J. Bachmeier[162] have outlined the conditions for producing thermally evaporated magnesium fluoride films and P. Selma[163] has discussed the principles of lens coating and describes the methods of coating by vacuum deposition of lithium, calcium, and magnesium fluorides and cryolite. The coating of glass with interference films to give neutral and colour filters of high optical efficiency has been described by K. M. Greenland[164]

COLOURED GLASSES.

W. A. Weyl[165] has continued his monograph on coloured glasses, dealing with the colours produced by metals; the general fundamental principles concerning the relationships between metals and glass, the absorption of light by metals, and the specific effects of gold in gold rubies, silver in silver staining, and copper in copper ruby glasses are discussed. A review of this section of the monograph has been given by N. J. Kreidl.[166] W. Colbert[167] has investigated the colouring effects of iron, copper, uranium, cerium, and manganese in glasses containing titanium and lead oxides as major constituents, and the colour imparted to the glass has been correlated with the position of the colouring ion in the structure; it is concluded that additions of titania and lead oxide cause the colouring ions to enter into the network. Spectrophotometric curves for the various

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[156] Chance Bros. Ltd., R. E. Bastick, and T. H. Wang, B.P. 578,326; B., 1946, I, 333. Chance Bros. Ltd., R. E. Bastick, and W. M. Hampton, B.P. 579,423; B., 1946, I, 373. Chance Bros. Ltd., R. E. Bastick, W. M Hampton, and T. H. Wang, B.P. 579,832; B., 1946, I, 413.

[157] *Sci. Progr.*, 1946, **34**, 533.

[158] *J. Indian Chem. Soc.*, 1942, **19**, 241.

[159] *Proc. Physical Soc.*, 1946, **58**, 472; C., 1947, 39.

[160] *J. Sci. Instr.*, 1945, **22**, 219; C., 1946, 55.

[161] *Nature*, 1946, **158**, 422.

[162] *Ibid.*, 133; B., 1947, I, 65.

[163] *Phot. Rev.*, 1946, **58**, 80.

[164] *J. Sci. Instr.*, 1946, **23**, 48; C., 1946, 212.

[165] *J. Soc. Glass Tech.*, 1945, **29**, 289T; B., 1947, I, 25

[166] *Glass Ind.*, 1946, **27**, 450.

[167] *J. Amer. Ceram. Soc.*, 1946, **29**, 40; B., 1946, I, 170.

glasses are included in the paper. Some unusual colours obtained by introducing uranium into glasses of unusual composition have been reported by W. Colbert and N. J. Kreidl,[168] who give transmission curves (*a*) for the uranyl group in a glass of composition $Na_2O,4SiO_2$, (*b*) the uranate group in a lead glass of low silica content, (*c*) for lead metasilicate glasses containing various amounts of uranium, (*d*) uranium in a barium crown glass, (*e*) for neodymium oxide in a barium crown glass containing uranium, (*f*) for the uranous ion in $Na_2O,4SiO_2$ glass, (*g*) for the uranous ion in a borosilicate glass, (*h*) uranous ion in glasses of composition $Na_2O,RO,4SiO_2$ where R is Ca, Ba, Sr, Mg, or Zn, and (*i*) for the uranous ion in various phosphate glasses.

L. V. Gagin, G. S. Bachman, and A. E. Badger[169] have discussed the colour and solarisation of glasses containing combinations of colouring oxides, pointing out that owing to interaction, the colours produced by combinations of oxides are not necessarily additive. Colour combinations produced by pairs of 13 common oxides in a soda–lime–silica base glass were studied and the effects produced by manganese and chromium in combination with one another and with copper, vanadium, and cerium are discussed in detail. The solarisation experiments showed that more fading occurred in glasses containing combinations of colouring oxides than in glasses containing single oxides. The fading of glass containing cerium–arsenic and copper–arsenic combinations was so marked that the use of such glasses for measuring the intensity of sunlight is suggested. G. S. Bachman, R. B. Fischer, and A. E. Badger[170] have measured the size of gold particles produced by heat-treatment of a soda–lime–silica glass containing gold; the glass was dissolved away from the particles and the observations were made using the electron microscope. In a typical ruby glass, the particles appeared as cubes of 60 mμ. edge and in a blue glass they were about double this size; the sizes are in agreement with other measurements made on colloidal gold particles.

Some work carried out by V. Ctyroky[171] which has recently become known in this country shows that the dichroism of glasses containing pure neodymium or praseodymium oxides can be altered appreciably by the addition of selenium; glasses containing commercial didymium are not affected in the same manner. Transmission curves for 15 glasses are included in the paper.

The production of an amber-coloured glass by the precipitation of colloidal silver particles by ultra-violet irradiation at 400° from a colourless silicate glass containing a small amount of silver has been reported by A. E. Badger and F. A. Hummel.[172] A selenium ruby glass within the composition range SiO_2 69—74, $Na_2O + K_2O$ 13—16, $CaO + MgO$ 7—13, Al_2O_3 1—4%, ZnO less than 1%, and at least 0·03% of selenium and

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[168] *J. Opt. Soc. Amer.*, 1945, **35**, 731; B., 1946, I, 170.

[169] *Glass Ind.*, 1946, **27**, 500.

[170] *Ibid.*, 399; B., 1946, I, 370.

[171] *Glastech. Ber.*, 1942, **20**, 102.

[172] *Physical Rev.*, 1945, [ii], **68**, 231.

cadmium up to 0·78% and sulphur up to 0·22% and melted in a reducing atmosphere has been covered by C. R. Austin and J. D. Sullivan.[173] A number of compositions covering glasses which are transparent to the far ultra-violet have been patented. Thus a colourless glass comprising essentially silica, boric oxide, alumina, and an alkali metal oxide and substantially free from zinc and antimony is claimed by H. P. Hood[174] to have a transmission of at least 1% in 1 mm. thickness at a wave-length of 185 mμ. A coloured glass having a transmission of 50% at 254 mμ. in 1 mm. thickness and consisting of cobalt and nickel oxides on a phosphate base has been claimed by J. G. Hooley.[175]

An ultra-violet-absorbing glass patented by W. H. Armistead[176] consists of a borosilicate glass containing ferric chloride, and it is claimed that the sharpness of the cut-off depends on the amount of halogen present, alumina is added to reduce the volatilisation of the halogen. The glass is claimed to be completely opaque in 1 mm. thickness at 365 mμ.

The increasing use of high-energy light sources for projection and certain types of illumination often necessitates the use of some form of heat-absorbing filter and several patent specifications for such filters have appeared. A patent granted to A. G. Pincus[177] covers a heat-absorbing glass having aluminium metaphosphate as the main constituent and lying within the composition range P_2O_5 45—80, Al_2O_3 8—25, SiO_2 1—30% and containing iron in the ferrous state. The properties of an aluminium phosphate heat-absorbing glass developed in the U.S.S.R. have been described.[178] F. W. Adams[179] has patented a novel method of producing a glass resistant to the transmission of ultra-violet and infra-red radiation; the glass is treated with acid to remove the soluble constituents, and ferrous and ferric sulphates or chlorides can then be introduced into the surface by immersion in an aqueous solution of these salts. The film is hardened by baking.

G. C. Mook and R. W. Ricker[180] claim that a heat-absorbing glass obtained with ferrous iron on a soda–lime–silica base can be improved by introducing a halide such as chlorine or fluorine.

J. G. Holmes[181] has patented a heat-transmitting glass suitable for screening lamps bulbs used in drying by infra-red radiation; the glass contains the oxides of manganese and chromium in the ratio lying between 4 : 1 and 2 : 1.

The production of yellow- and amber-coloured glass by the use of iridium oxide has been disclosed by A. G. Arend.[182]

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[173] U.S.P. 2,382,282.

[174] U.S.P. 2,382,056.

[175] U.S.P. 2,398,530.

[176] U.S.P. 2,409,412.

[177] U.S.P. 2,359,789.

[178] *Glass Ind.*, 1946, **27**, 77.

[179] U.S.P. 2,401,537.

[180] U.S.P. 2,397,195.

[181] B.P. 570,946; B., 1945, I, 360.

[182] *Chem. Age*, 1945, **53**, 313.

The composition of an opal glass consisting substantially of SiO_2 54—66, Al_2O_3 0—6, $Na_2O + K_2O$ 12—17%, CaO up to 12%, BaO up to 4%, PbO up to 5%, F 0—50, B_2O_3 0—1, As_2O_3 2·5—5, P_2O_5 4—9%, in which the sum of the bivalent oxides does not exceed 21% by weight of the composition, has been patented by W. A. Weyl and N. J. Kreidl[183]; sufficient fluorine-containing minerals are added to the mixture to ensure the formation of fluorapatite in the glass.

The effect of iron on the fluorescence of a calcium phosphate glass containing uranium oxide has been investigated by L Thorington, R. Russell, jun . and A Silverman.[184] The spectral absorption curves and the fluorescence spectra indicate that iron absorbs a large proportion of the exciting radiation, thus decreasing the fluorescent emission ; the absorbed radiation is re-emitted in the infra-red. Iron also causes an electrical disturbance around the fluorescing centres and prevents absorption of exciting radiation by these centres. A weakening of the glass structure is also apparent and this has the effect of shifting the fluorescence spectrum towards shorter wave-lengths.

Two patents on fluorescent glass compositions have been granted to J. G. Hooley. The first of these consists of an aluminium phosphate glass containing cerium and an oxide of a metal of the second periodic group having an atomic weight not greater than 38.[185] The second patent covers a glass of composition P_2O_5 60—71, ZnO 20—35, Al_2O_3 more than 4%, activated by the addition of 2—12% of tin and manganese up to 2·5%.[186]

NEW MANUFACTURING METHODS.

There is little to report on new manufacturing methods but probably the most important papers which have been published are those concerning electrical methods of melting as such methods are receiving increasing attention from glass makers. The melting and finishing of glass by high-frequency and dielectric heating has been considered by M. Descarsin[187]; an experimental dielectric loss furnace is described and the difficulties which are encountered are discussed. A review of this paper in English has been published.[188]

A novel method of producing homogeneous glass has been patented by A. J. Deyrup[189]; the molten glass is flowed into a succession of chambers in which the glass mass is alternately split into a number of streams and then recombined. The method is stated to be capable of producing high-grade optical glass. H. J. Nachod[190] has been granted a patent for an apparatus for the continuous production of fused silica glass, by means

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[183] U.S.P. 2,394,502.
[184] *J. Amer. Ceram. Soc.*, 1946, **29**, 151; B., 1946, I, 292.
[185] U.S.P. 2,393,469.
[186] U.S.P. 2,400,147.
[187] *Bull. Inst. Verre*, 1946, *No.* 1, 17.
[188] *Glass Ind.*, 1946, **27**, 184.
[189] U.S.P. 2,411,031.
[190] U.S.P. 2,398,952.

of which the inclusion of air in the mass can be prevented. A patent granted to H. P. Hood[191] covers a method of making glass by heating the batch to between 600° and 800° and passing a current of air, free from carbon dioxide and water vapour, over the batch until the gaseous products have been removed; the batch is then melted in the usual manner. An apparatus for making glass fibres of 0·00012 in. diameter has been patented by J. A. Hoffmann.[192]

MISCELLANEOUS.

Several reports have been published which deal with the subject of glass-to-metal sealing. The practical aspect of the subject has been surveyed by A. G. Long,[193] who discusses the production of seals ranging from those of the pinch type using wire to cylindrical seals of 4 in. diameter. Reference is made to vacuum-tight sealing, and swaged tungsten wire is recommended as drawn wire has hair lines or channels which are liable to cause leakage. The various sealing metals and alloys are described. A specification for glasses used for glass-to-glass and glass-to-metal sealing has been put forward by W. C. Hynd.[194] The use and properties of sintered glass powder for glass-to-metal seals in lamps and electronic devices have been described by E. C. Dorgelo.[195]

W. A. Weyl[196] has given a useful review of the mechanism of adhesion between glass and various materials and E. M. S. Wood[197] has described the process of welding of glass to metal in which finely divided fused aluminium is sprayed on to the preheated glass surface at 300°; the aluminium deposit has a variety of uses, for example, for resistance heaters and as a means of soldering metal objects to the glass.

A novel method of fabricating thin glass in such a way that it may be used as a substitute for mica has been described by J. M. Stevels[198]; thin glass plates 1—5 μ. thick in suspension in a suitable medium orient parallel to one another and settle under gravity, thus building up a composite plate. The plates adhere under van der Waals forces when the medium is removed. Favourable electrolyte concentrations and pH values are given for the suspension medium and the electrical properties are tabulated.

A method of making porous glass plates has been patented by H. B. Law[199]; thin glass sheets 0·001—0·005 in. thick are coated on one side with rubber cement and dusted with 600-mesh silicon carbide and heated at 800° for 5 minutes. Bubbles form under each particle of silicon carbide and hydrofluoric acid is used to remove the carbide and part of the glass

[191] U.S.P. 2,386,685.
[192] U.S.P. 2,405,036.
[193] *J. Soc. Glass Tech.*, 1946, **30**, 67T.
[194] *Ibid.*, 1945, **29**, 47P.
[195] *Glass Ind.*, 1946, **27**, 347; B., 1946, I, 370
[196] *Ibid.*, 1945, **26**, 557.
[197] *Ibid.*, 1946, **27**, 24.
[198] *Ibid.*, 607.
[199] U.S.P. 2,403,224.

surface, leaving the glass covered with minute bubbles; the use of a strong acid leaves a porous plate. According to a further patent,[200] the pores are arranged in a controlled array.

J. J. Hopfield[201] has reported the appearance of spiral cracks when Pyrex capillary tubing heated at one end between 500° and 600° is plunged into cold water. Data have been given on precision bore glass tubing.[202] A. M. Robertson[203] has described the methods of manufacture and processing of glass fibre and its uses in the chemical industry. The technique of the production and application of rare-earth oxide polishing powders for glass have been described by A. W. Wylie and R. W. Urie.[204] Recent developments in glass have been outlined by Atma Ram and Y. P. Varshney[205] and summaries of French patents for the year 1944[206] and for American patents for the years 1940–45 have been given.[207]

W. E. Thrum and H. K. McGrath[208] have made a chemical study of the working surfaces of glass-making moulds, using semi-quantitative methods to establish the gain or loss of constituents on or from the surface as compared with the interior of the mould; particular reference is made to the effect of nitridation, and of silicon, phosphorus, magnesium, and sulphur.

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[200] U.S.P. 2,403,225.

[201] *Nature*, 1946, **158**, 582.

[202] Anon., *Ind. Chem.*, 1945, **21**, 532.

[203] *Chem. and Ind.*, 1946, 138; B., 1946, I, 234.

[204] *Chem. Eng. Min. Rev.*, 1946, **38**, 125.

[205] *J. Sci. Ind. Res., India*, 1946, **4**, 402.

[206] *Bull. Inst. Verre*, 1946, *No.* 3, 30.

[207] *Ibid.*, 21.

[208] *Glass Ind.*, 1946, **27**, 340; B., 1946, I, 370.

CERAMICS, REFRACTORIES, AND CEMENTS.

By S. W. Ratcliffe,
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Development in the pottery industry is restricted by lack of labour and fuel, although the demand for tunnel kilns is high, and construction is proceeding slowly. A kiln for the firing of bone china biscuit is now being built ; this is a new venture, but built on conventional lines. Whether the tunnel kiln of the future will be of smaller cross-section has yet to be proved, but already experiments are proceeding on a practical scale in which the goods travel through the kiln on a metal belt at a very short firing cycle. More work is necessary on the properties of the fired body to prove whether a "skin effect" is produced on the ware due to lack of the necessary soaking at the maximum temperature, and also to obtain data on the economics of firing such a kiln. Mechanisation in the industry is proceeding, and machines for cups, plates, saucers, and cup handling are now installed in some factories. In the present state of development automatic devices are not sufficiently flexible to adjust themselves to changes in clay plasticity, due partly to lack of control of water content in filter-pressing, and it is therefore necessary to operate these machines with experienced makers, who can regulate the supply of water on the machine when faults develop.

In the porcelain industry much research has been reported on the titanate groups of ceramics for high-frequency work, probably because most of this work was done during the war and was not published for security reasons.

In the refractories industry greatest attention has been focussed on the iron and steel industry, in which the production of a satisfactory material to build an all-basic lining still attracts the attention of research workers and users, although there is still much interest shown in the silica materials. Very few papers appear to have been published in this country for the enamelling industry, but research in America follows accepted lines.

Clays and Other Raw Materials.

Clays are the basis of the industry and research work on fundamental properties and constitution[1] still continues. The ball clays have received attention,[2] although some of the information is not new. It is well known that all ball clays do not give fluid slips at the same pint weight ; for example, Dorset clays usually give viscous slips whilst those of South

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[1] R. W. Grimshaw, E. Heaton, and A. L. Roberts, *Trans. Brit. Ceram. Soc.*, 1945, **44**, 69, 76 ; B., 1945, I, 360.

[2] E. Sharratt and M. Francis, *ibid.*, 100 ; B., 1946, I, 25.

Devon, which contain organic matter, give fluid slips, and the effect of the salts of lime and magnesia is to thicken them. It is suggested that the wax material in the organic matter is the main contributor to fluid slips, and on extracting the wax material the clay slips decrease in fluidity, which can be partly increased by replacing the wax. The fluidity of clay slips changes on ageing, and attains a maximum in about four days. These changes may be due to the decomposition of felspar in the clay, because it is of such a grain size as to be decomposed by water, causing a change in hydrogen-ion concentration. Base exchange may also influence the fluidity changes.

The suggestion that variation in composition of clays can be due to the migration of clay minerals is made by W. T. Allen.[3] In clay beds veins of a different clay are often noticed and occlusions of a totally different type are sometimes seen; for example, veins of kaolinite and fine quartz may cut a light-coloured refractory clay or a red clay. This is explained by the cracks and fissures in the original clay being filled by minerals which have migrated. Many examples of this migration are reported and it appears that the amount of water circulating through the clay, and particularly if the water contains a dispersing agent, will influence the migration of one clay into the beds of another.

With the cutting of supplies of French flint pebbles for grinding media other sources have been sought, and G. F. Metz[4] found that the use of zircon balls of sp. gr. 3·7 gave a greater grinding efficiency and mill output than is possible with silica or porcelain balls. The high specific gravity is an advantage but the cost of the zircon balls for grinding media is prohibitive. If the price could be reduced, it is possible that they would have a wider use. The pottery industry is gradually changing to cylinder grinding, with some continuous grinding plant. One difficulty of continuous grinding is the feeder control, which should be automatic and constant, and to overcome this problem an automatic feed control operated by an acoustic relay[5] has been devised which is sensitive to the change in noise from the mill, as it becomes over- or under-fed.

Organic binders of different kinds have been used for some time to improve adhesion and strength. They have been added to short bodies to improve binding power, and now C. C. Treischel and E. W. Emrich[6] have studied the effect of a number of binders on a talc–water mixture. They included flours, starches, gums, alcohols and cellulose derivatives, wood extract, and alginates, but no outstanding material was found. Considered as groups, the best possibilities are among the gums, alginates, and alcohol and cellulose derivatives; these products are fairly expensive but there are certainly many good choices among the more economical

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[3] *J. Amer. Ceram. Soc.*, 1945, **28**, 265; B., 1946, I, 24.

[4] *Bull. Amer. Ceram. Soc.*, 1945, **24**, 357; B., 1946, I, 25; also W. B. Donahue, U.S.P. 2,204,582; B., 1946,I, 100.

[5] *Bull. Amer. Ceram. Soc.*, 1945, **24**, 357: B., 1946, I, 25.

[6] *J. Amer. Ceram. Soc.*, 1946, **29**, 129.

materials such as flours, starches, and wood extract. The use of partly hydrolysed ethyl silicate as a binder is also suggested.[7]

To improve the workability of a short body is always interesting to the ceramist because of its value in reducing loss in industry. Illite can be added to a clay of mediocre plasticity in the proportion of 5—10%, resulting in the duplication of the plastic working properties of ball clays with a contraction less than that of ball clays, and L. Mathyasovsky-Zsolnay[8] believes that this material may reduce making costs and improve the quality of porcelain.

It has been previously reported that stone is only effective as a flux in dust-pressed bodies when fired to a high temperature and this is confirmed by D. A. Holdridge and M. Francis,[9] who found that fine grinding of stone as a means of strengthening a tile body mechanically can be effective only if the body is fired at temperatures higher than those normally employed in firing biscuit tiles.

A process for the bleaching of clays has been described[10] in which zinc hyposulphite or sodium hyposulphite and zinc powder is used.

The extraction of alumina from clays is still receiving attention[11] and R. E. Grim, J. S. Machin, and W. F. Bradley[12] have studied the effect of sintering temperature of various types of clays on the extraction of alumina by the lime and lime-soda methods. The yield of alumina varies with the type of clay and the sintering temperature. The diaspore and bauxitic clays may yield 90% of their alumina by the lime-soda process when they are relatively free from iron and other clay minerals, and the yield is good over a sintering range of 1000—1300°, whereas pure kaolinite clays yield only 75% and this over a sintering range of 1000—1100°. Montmorillonite clays yield none of their alumina on sintering to 1100°, but 90% on sintering to 1300°. Illite clays require sintering above 1200° to obtain the maximum yield.

A process for the manufacture of magnesia products from dolomite and other magnesium minerals has been described, in which a slurry of the material is treated with carbon dioxide and the hydrogen-ion concentration is controlled.[13] The use of finely-divided mineral magnesium silicate mixed with calcined dolomite materials and heated in an atmosphere of steam is also claimed,[14] as well as the extraction of magnesium from olivine by hydrochloric acid attack and thermal dissociation of the resulting chloride salt.[15]

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[7] C. Shaw and C. Marsden, *Ind. Chem.*, 1946, **22**, 61; B., 1947, II, 121.

[8] *J. Amer. Ceram. Soc.*, 1946, **29**, 254; B., 1946, I, 413.

[9] *Trans. Brit. Ceram. Soc.*, 1946, **45**, 111: B., 1946, I, 372.

[10] I. Williams and N. Millman, U.S.P. 2,339,594-5; B., 1946, I, 294.

[11] E. P. Flint, E. S. Newman, L. Shartsis, D. L. Bishop, and L. S. Wells, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 63; B., 1946, I, 328. S. C. Lyons, U.S.P. 2,388,983. J. D. Edwards, *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1833; B., 1946, I, 130.

[12] *Illinois State Geol. Surv.*, 1945, *Bull.* 69.

[13] Basic Refractories, B.P. 573,943; B., 1946, I, 134.

[14] N. R. Thielke and H. W. Jamison, *Bull. Amer. Ceram. Soc.*, 1945, **24**, 452; B., 1946, I, 133.

[15] G. W. Pawel, *J. Amer. Ceram. Soc.*, 1945, **28**, 360; B., 1946, I, 94.

Zircon has been used as an addition to ceramic products to give certain properties, in refractories when high temperatures are required, in electrical insulators, and in glazes and enamels for hardness and opacity. It is suggested[16] that future development is likely in the manufacture of kiln furniture, high-temperature insulating bricks, and grinding media.

The effect of atmosphere on the thermal decomposition of kaolin[17] and the reaction between the heated clay and lime[18] have interested the research workers. The decomposition of kaolin on heating results in the production of metakaolin. When treated with dilute hydrochloric acid some of the alumina dissolves, but the rate of dissolution of the alumina is greater when the heating has been performed in carbon monoxide or carbon dioxide as compared with heating in air. Finely powdered lime reacts with metakaolin, which has been produced by firing kaolin to about 1000°, beginning at about 400° and reaching a maximum at 500°. This reaction with lime at these temperatures occurs only with materials that produce free alumina and silica on heating, and such materials as mullite, muscovite, and orthoclase felspar do not show it.

CERAMIC BODIES AND MAKING PROCESSES.

The two large groups of low-loss ceramics now used in insulator manufacture can be classified into the titania group and the steatite group. In the manufacture of the latter group[19] there has been experienced a large degree of discontinuity in firing shrinkage of extruded steatite bodies in consecutive consignments of talc, even when every attempt has been made to follow uniform procedures. As a result, rigid specifications have been set up for all raw materials but shrinkage control is still a problem and whether this is due to pressure distribution during the extrusion process has not yet been made clear.

Extensive studies have been made in the last four years to explore the best methods for preparing materials of the titanate group, but for security reasons these were withheld.[20] The introduction of alkaline-earth and certain other metallic titanates raises the permittivity to much higher values than has previously been known, and is subject to very large changes with temperature, reaching a maximum value at some temperature which is characteristic of the material itself. The shape of the permittivity–temperature curves can be modified by the addition of other materials than titanates, for example, zirconia with one or more other metallic oxides. The temperature coefficient of capacitance of capacitors containing these dielectrics can be chosen at will for a predetermined

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[16] N. R. Thielke and H. W. Jamison, *Bull. Amer. Ceram. Soc.*, 1945, **24**, 452; B., 1946, I, 133.

[17] J. A. Hedvall and M. Blomkvist, *Arkiv Kemi, Min., Geol.*, 1945, **19**, **A**, *No.* 22; B., 1946, I, 24.

[18] J. A. Hedvall, *Chalmers Tekn. Högsk. Handl.*, 1942, *No.* 2; B., 1945, I, 390.

[19] R. L. Stone, *North Carolina State Coll. Eng. Expt. Sta.*, 1945, *Bull.* 29.

[20] P. R. Coursey and K. G. Brand, *Nature*, 1946, **157**, 297. Dubilier Condenser Co. Ltd., and P. R. Coursey, B.P. 574,577; B., 1946, I, 172.

temperature range to be either positive or negative. The crystal lattices of the titanates of calcium, strontium, and barium are different from those of magnesium and cadmium and the dielectric constant is correlated with the size of the alkaline-earth ion and with the distance between the titanium and oxygen ions.[21] The size relationships in the lattice determine the extent to which each unit can exercise its properties and thus determine whether the permittivity will be high or low.[22]

Binary and ternary combinations of magnesia, lime, barium oxide, beryllia, alumina, thoria, and zirconia in relation to their use as porcelains have been introduced into the field.[23] High temperatures are required to produce vitreous specimens from these series, with the probable exception of some in the lime system The $BeO–Al_2O_3$ system may be of little value for electrical porcelain because of its high electrical conductivity, but a number of compositions in the $MgO–BeO–Al_2O_3$ system, particularly in the high-BeO area, have good dielectric properties and may be of value to ceramics. It is possible that with those mixtures which do not give a vitreous specimen, the addition of a percentage of lime or magnesia will improve vitrification without any loss of properties.

A ceramic material suitable for use in a photo-electric cell has been prepared containing titania and two metallic oxides.[24]

A method to manufacture thin-wall ceramic insulators is suggested[25] in which finely-divided titania is applied as a layer to a support of carbon and the whole is heated firstly in a non-oxidising atmosphere to sinter the insulator and then in an oxidising atmosphere to remove carbon.

The literature on felspar and the effect of variation in potash and soda content on its properties alone and in whiteware bodies is voluminous. C. J. Koenig in 1936 drew attention to the use of nepheline syenite in bodies, but there appears to be little published information relating to the effect on casting of soda felspar bodies as compared with potash felspar bodies. It is interesting to note therefore that G. A. Loomis and A. R. Blackburn[26] compare the casting properties of such felspars in semi-vitreous bodies and sanitary porcelain, and there is no indication that the castability or control of the slip will be affected by the use of the soda felspar.

The influence of the glaze on the modulus of rupture of bodies is well established, the strength depending on whether the glaze is in tension or compression. A similar phenomenon exists in unglazed extruded steatite tubes, the strength of which varies according to the ratio of internal to external diameter ; the less is the wall thickness the less the modulus of

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[21] B. Vul, *J. Physics U.S.S.R.*, 1946, **10**, 95 : A., 1946, I, 300.

[22] E. Wainer, *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 3, 47 ; B., 1946, I, 201.

[23] R. F. Geller, P. J. Yavorsky, B. L. Steierman, and H. S. Creamer, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 277 ; B., 1946, I, 332.

[24] E. Wainer, U.S.P. 2,331,444 ; B., 1946, I, 65.

[25] J. H. de Boer, E. J. W. Verwey, and M. G. van Bruggen, U.S.P. 2,339,003; B., 1946, I, 295.

[26] *J. Amer. Ceram. Soc.*, 1946, **29**, 48 ; B., 1946, I, 171.

rupture.[27] During the firing of the tubes a natural fire coating is received and this coating acts like a glaze under tension, decreasing the strength; by sandblasting the surface of the tube to remove the "glaze," the strength is increased.

Ceramic cutting tools made from alumina and optionally small amounts of tungsten carbide have been patented.[28]

A ceramic material which has a thermal expansion coefficient in the same range as that of Invar has been developed[29]; it has a high resistance to thermal shock and withstands a temperature of 1370°.

With a tendency for bigger outputs and in many cases limitation of floor space, quick methods of drying are attractive, and the use of infra-red[30] and high-frequency heating[31] has been suggested as a means of attaining this result. The limitations of infra-red drying in pottery manufacture are now clearly realised and an efficient convection dryer[32] with good air circulation will be less expensive in fuel, but a combination of infra-red and convection drying may have advantages over either method by itself. Drying by high frequency is still in the experimental stage and it is claimed to be possible to heat uniformly very thick layers of a material that may be a very poor conductor of heat. The centre of a wet poorly conducting body, such as clay, is heated instantly and soon becomes hotter than the outer layers, which are cooled by evaporation. This is entirely different from infra-red drying because it may be accepted that there is no appreciable penetration of a solid by the rays, which means that infra-red radiations set up a high rate of surface evaporation and are therefore most useful for film drying. The cost of apparatus and equipment for high-frequency heating is high and it is doubtful whether it will be possible to compete with other methods of drying in ceramics.

GLAZES AND COLOURS.

At normal glost oven temperatures the ordinary leadless glazes are viscous, and it is difficult to obtain high gloss, whereas the lead glazes have long maturing range, ability to heal scars, durability, brilliancy, and good crazing-resistance, and therefore the lead glazes are far more popular with manufacturers for use at normal earthenware glost temperatures. For high-temperature glazes, leadless are the only ones possible. The low-temperature leadless glazes depend on high alkalis and boric acid for their development. The high alkalis produce a high expansion in the glaze, and although their effect may be counteracted by the correct boric

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[27] J. J. Gingold, *J. Amer. Ceram. Soc.*, 1946, **29**, 228; B., 1946, I, 372.

[28] Hard Metal Tools, Ltd., and B. Westmoreland-White, B.P. 575,753; B., 1946, I, 202.

[29] *Chem. Industries*, 1946, **58**, 86.

[30] S. W. Ratcliffe and H. W. Webb, *Trans. Brit. Ceram. Soc.*, 1945, **44**, 119; B., 1946, I, 25. Anon., *Ceram. Age*, 1945, 108. L. H. Hepner, *Bull. Amer. Ceram. Soc.*, 1945, **24**, 415; B., 1946, I, 63.

[31] D. Harrell, *Brick and Clay Rec.*, 1946, **108**, *No.* 2, 46. L. Hartshorn, *Nature*, 1946, **157**, 607.

[32] J. A. Johnson, B.P. 574,761; B., 1946, I, 201.

acid content, the crazing-resistance is not usually as good as that of lead glazes. The introduction of bismuth, strontium, lithium, and fluorine into glazes in controlled proportions in the place of lead appears to give more encouragement for further work. H. S. Oulowski and J. Marquis[33] under experimental conditions have produced a series of bismuth glazes with the high gloss and mirror finish of the lead glazes, but because of the high cost these have not been prepared under plant conditions. A glaze which is suggested as excellent, having good appearance, can be prepared containing both lithium and strontium with optionally some fluorine. These glazes do not have a long maturing range and it is quite possible that variations can be obtained in the same glost oven. As a result of a comparison of the effect of the above glazes on the tint of under-glaze colours with that of lead glazes, it is suggested that the results are similar.

The effect of surface tension in enamels bears a relation to adherence and beading tendencies, and in glazes to crawling. A surface tension reducer or wetting agent in the ceramic industry may well lead to many important developments, and although there is much in the literature on this subject the work of C. R. Amberg[34] is interesting. The effect of the more unusual elements such as the oxides of molybdenum, vanadium, tungsten, antimony, nickel, cobalt, manganese, uranium, and arsenic has been tried on a glaze, glass, and an enamel. Molybdenum proved outstanding as a surface tension reducer in the three types. Vanadium, tungsten, and arsenic are fairly consistent in lowering surface tension. Antimony, nickel, cobalt, manganese, and uranium raise the surface tension of the glass but lower that of the glaze In the enamel, antimony, nickel, and uranium lower the surface tension, but cobalt and manganese increase it. By the use of 0·05—0·2% of molybdenum improvements have already been found in the production of carbon-bonded crucibles, and in the bonds for grinding and polishing wheels.

An unusual glaze for steatite porcelain firing to cone 10 is suggested,[35] containing lead boro-aluminosilicate frit with additions of plastic clays as suspension media ; it is claimed that the glaze produces practically no increase in power factor compared with an unglazed specimen, while high-alkali glaze increases the power factor by 25%. Glazes containing lead usually show signs of volatilisation at this temperature and it is surprising that such a difficulty was not experienced with the above glaze.

ENAMELS.

W. A. Deringer in 1943 suggested the presence of a hydrogen layer at the steel surface to explain the faults of lack of adherence, reboiling, and fish scaling, but other investigators[36] believe that the faults are due to

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[33] *J. Amer. Ceram. Soc.*, 1945, **28**, 343 ; B., 1946, I, 170.

[34] *Ibid.*, 1946, **29**, 87 ; B., 1946, I, 294.

[35] L. E. Thiess, *ibid.*, 84 ; B., 1946, I, 200.

[36] G. F. Comstock, *ibid.*, 1 ; B., 1946, I, 179. G. F. Comstock and E. Wainer, *Iron Age*, 1945, **155**, *No.* 7, 60, 152 ; B., 1945, I, 360. E. Wainer, *Bull. Amer. Ceram. Soc.*, 1946, **25**, 248 ; B., 1946, I, 370.

iron carbide, which oxidises during the enamelling cycle. The use of titanium steel as a preventive appears to be well established[37] and it has been suggested by G. F. Comstock that the titanium content must be more than 4·5 times the carbon content; the function of the titanium is to produce a titanium carbide which is stable. W. A. Deringer[38] shows a further interest in the hydrogen theory for various metals and suggests that the defects are caused by the hydrogen formed from the water in the enamel, some of it being broken down into elemental hydrogen by catalytic action and then dissolving in the metal. During the cooling some of the hydrogen in solution is liberated due to the lowering of solubility as the temperature drops. The effect of titanium in the steel is to decrease hydrogen formation and render the metal impenetrable to diffusion of atomic hydrogen.

The use of titanium as a mill addition and in frits[39] is being developed and one-coat finishes are becoming increasingly used in America.[40] Interest has been shown in enamels for use on aluminium[41] and for vitreous enamelled ware, particularly tanks, and for architectural purpose.[42]

The thermal shock-resistance of enamels in relation to the thermal expansion of the ground coat and cover coat has been further investigated[43] and the results suggest that for best thermal shock-resistance the ground coat should have an expansion below that of the metal, and the cover coat a still lower expansion so that there is an intermediate layer with an expansion between that of the metal and the cover-coat enamel.

Although the advantages of nickel dip in relation to promotion of enamel adherence have been discussed for some fifteen years, many papers have appeared during the period under review.[44]

Andrews in 1930 studied the relationship between the acid-resistance of an enamel and its chemical composition, and concluded that the acid-resistance did not depend so much on the presence of any particular compound as on a carefully quantitatively balanced composition, and studied the limiting percentage of oxides which could be used to give an acid resistant enamel. Further work on the effect of composition on the acid-resisting properties of enamels[45] and on the fusibility of enamels is

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[37] G. F. Comstock, *J. Amer. Ceram. Soc.*, 1946, **29**, 1; B., 1946, I, 179. F. R. Porter, *Bull. Amer. Ceram. Soc.*, 1946, **25**, 259; B., 1946, I, 370.

[38] *J. Amer. Ceram. Soc.*, 1946, **29**, 332; B., 1947, I, 105.

[39] G. H. McIntyre, *Steel*, 1946, **118**, *No.* 3, 98; *Enamellist*, 1946, **23**, *No.* 2, 16; *Finish*, 1946, **3**, *No.* 1, 17.

[40] G. F. Comstock, *J. Amer. Ceram. Soc.*, 1946, **29**, 1; B., 1946, I, 179.

[41] J. F. Mason, *Iron Age*, 1946, **158**, *No.* 7, 60.

[42] M. von der Kloet, *Finish*, 1946, **3**, *No.* 5, 17. Anon., *ibid.*, *No.* 4, 19.

[43] F. A. Petersen and A. I. Andrews, *J. Amer. Ceram. Soc.*, 1946, **29**, 288; B., 1947, I, 66.

[44] G. H. McIntyre, *Bull. Amer. Ceram. Soc.*, 1946, **25**, 333; B., 1947, I, 37. E. Wainer and W. J. Baldwin, *J. Amer. Ceram. Soc.*, 1945, **28**, 317; B., 1946, I, 63. *Better Enamelling*, 1946, **17**, *No.* 4, 6. G. H. McIntyre, *Enamellist*, 1946, **23**, *No.* 1, 13.

[45] R. L. Cook and A. I. Andrews, *J. Amer. Ceram. Soc.*, 1945, **28**, 229; B., 1945, I, 390. B. K. Nicklewski, *ibid.*, 1946, **29**, 316; B., 1947, I, 105.

published.[46] B. K. Nicklewski suggests that the acid-resistance depends on the bond strength between various ions, and the following series is an arrangement of the bond strength according to increasing values: K, Na, Ba, Pb, Ca, Fe¨, Zn, Mg, Be, Fe‴, Al, Zr, Sn, Ti, and Si. The results of his investigation show that the favourable influence on the acid-resistance increases in accordance with this series. The introduction of 3% of iron oxide improves the acid-resistance as well as lowering the temperature of fusibility; larger additions, however, show unfavourable effects.

In general practice the user of clays for enamel suspension is concerned with cleanliness, degree of suspendibility, "pick up," formation of bubbles, and effect on gloss and surface durability. R. L. Cook[47] reports that clays containing an appreciable amount of organic matter are the cause of bubbles and from the study of clays it is to be expected that the "pick up" and suspendibility vary with the type, and will be influenced by the soluble materials dissolved from the frit. Ageing also has an effect which cannot always be predicted and it appears that for any particular enamel the clay must be carefully chosen.

Results of investigations of common defects produced in manufacture and service are published. W. J. Baldwin[48] discusses the cause of blistering due to the ground coat being either too thin or too thick, and emphasises the importance of cleanliness in the manufacturing process, since otherwise many faults will develop. The crazing of enamels on stoves in service has been investigated by R. L. Fellows[49] and, as expected, the crazing is due to the expansion of the metal causing a reversal in stresses from compression to tensile which occurs during rapid heating. Improvements can be made in crazing-resistance by attention to the materials. The strength of enamels by bending decreases with rise in temperature and an enamel of cubical thermal expansion 325×10^{-7} applied at 60 g. per sq. ft. is about one half the strength at approximately 274° compared with its strength at room temperatures and is likely to craze on a stove in service. By using an enamel of lower expansion (291×10^{-7}) and a thinner coat the crazing-resistance is increased, and this may also be helped by increasing the gauge of metal used, but it is to be expected that heating and cooling over long periods will tend to induce crazing.

The effect of porcelain enamel on iron to produce an increased resistance to bending has been recognised for many years and is important in applications involving flat surfaces to be used at normal temperature. D. S. Wolford and G. E. Selby[50] have now published formulæ by which it is possible to calculate the thickness of enamel necessary to produce a strength equal to that of sheet iron of thicker cross-section. Such formulæ should be useful for practical design problems.

[46] Nicklewski, *loc. cit.*

[47] *Ibid.*, 1945, **28**, 206 ; B., 1945, I, 359.

[48] *Finish*, 1946, **3**, *No.* 6, 21.

[49] *J. Amer. Ceram. Soc.*, 1945, **28**, 275 ; B., 1946, I, 24.

[50] *Ibid.*, 1946, **29**, 162 ; B., 1946, I, 293.

The restriction of tin for use as an opacifier affected both the sanitary ware and the enamel industry, and the development of other opacifiers was a problem. Zirconium silicate as an opacifier has been suggested and used for some time. An addition to the literature on sanitary ware glazes is given by R. R. Danielson.[51] The substitutes for tin oxide are generally recognised to have less opacifying effect, but a material which is claimed to be equal to tin oxide in enamels is reported by C. J. Harbert and J. W. Iliff[52]; this is an antimony–titania opacifier, having an approximate formula $7(CaO,CaF_2),6TiO_2,2Sb_2O_3$ and is produced by the calcination of antimony oxide, titanium oxide, fluorspar, and compounds yielding calcium oxide. Comparing the percentage of opacifier with the percentage of tin oxide, less of the new opacifier is required to give a similar opacity.

Interest in gas opacifiers still continues although patents have appeared since about 1928. The objection to this type of opacifier is the control of the distribution and size of the gas bubbles, because if the bubbles are comparatively large and unevenly distributed the opacity is limited in effect. Another fault is the surface hardness, which is considerably affected. P. A. Huppert suggests that these faults can now be controlled by the use of new gas opacifiers.[53]

REFRACTORIES.

The development of the all-basic open-hearth furnace roofs progresses. but it is not so far advanced at present as is their use in end construction, More results of tests must be accumulated before safe estimates of the relative worth of basic roofs can be made. The combination and condition of chrome ores and magnesite best suited for basic roofs have not yet been definitely ascertained, and the style and support which give best results have not been established, although it is considered[54] that basic roofs should be of the suspended type. The development of a brick such as the chrome–magnesite more resistant to penetration by iron oxide and bursting is necessary and research is proceeding on the production of such a brick. The most reasonable explanation for this bursting is the absorption of magnetite by the chromite crystals. A test to observe the bursting of chrome–magnesite bricks is suggested.[55] Mullite has been found to be resistant to penetration by iron oxide and Rees and Chadeyron in 1942 showed the marked increase in the resistance of sillimanite resulting from the incorporation of 15% of chromic oxide; any increase over this percentage, however, resulted in a lowering of the under-load value and no improvement in slag-resistance was apparent. The reason is given by

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[51] *J. Amer. Ceram. Soc.*, 1946, **29** 282; B., 1947, I, 66.

[52] *Ibid.*, 93; B., 1946, I, 293.

[53] *Ceram. Ind.*, 1946, **46**, *No.* 4, 86.

[54] R. B. Sosman, *Proc. Nat. Open Hearth Comm.*, 1945, **28**, 54. C. R. Fondersmith, *ibid.*, 47.

[55] S. Zerfoss and H. M. Davis, *J. Amer. Ceram. Soc.*, 1946, **29**, 15; B., 1946, I, 171.

W. F. Ford and W. J. Rees,[56] who suggest that mullite can take into solid solution about 8% by weight of chromic oxide, and further additions of chromic oxide result in the dissociation of the mullite. The mullite–chrome brick would eventually consist of an alumina–chromic oxide solid solution and a percentage of glass, which explains the lowering of refractoriness under load.

Basic refractories have as yet been used only in the chequers and superstructure of glass furnaces and it is possible that the use of these materials may in future be extended to the tank itself.[57]

The general aim for research, according to R. E. Birch,[58] is the development of refractories for processes requiring temperatures of 1800°. Although there are many elements yielding compounds which can qualify, many of them are expensive and available in small tonnages only; therefore, at the present time, we are limited to a few promising refractory oxides, viz., magnesia, alumina, zirconia, and titania, and it is suggested that alumina and magnesia, already extensively used as refractories, are destined to become even more important.

The type of refractory best suited to a particular industry is always receiving attention and a study has been made[59] of the type most suitable for lining a shaft furnace for the distillation of magnesium metal. Ordinary magnesite bricks spall readily, dead-burned magnesite and chemical magnesia are too porous, those of fusion-cast alumina develop cracks, and plumbago bricks give fairly satisfactory results, but for the lining of such a furnace a mixture of dead-burned magnesite and flaked graphite is the best. The durability of refractory materials in the carbonising industry has been studied.[60]

Silica bricks are the most common refractory material used in the construction of the roof of the basic open-hearth furnace, and although it can hardly be said that silica refractories have not had their fair share of attention, there is still much to interest the investigators. T. W. Howie[61] reports on spalling and suggests that the amount of spalling which occurs is dependent on the heating rate; the maximum safe rate of heating for hard-fired silica bricks is 5—6° per minute, but with soft-fired bricks a somewhat greater heating rate is permissible. Spalling of silica bricks is largely due to the cristobalite present and the stresses induced by the temperature gradient. This gradient can be reduced by soaking the bricks in creosote with a consequent greater spalling-resistance, due most probably to the creosote distilling when the hot face is in the temperature range 200—300°, and the bricks heat up more slowly for a

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[56] *Trans. Brit. Ceram. Soc.*, 1946, **45**, 125; B., 1946, I, 371.

[57] Anon., *Brick and Clay Rec.*, 1945, **107**, *No.* 5, 61. Anon., *Ceram. Ind.*, 1945, **40**, *No.* 5, 67. R. G. Abbey, *Glass Ind.*, 1945, **26**, 279.

[58] *Brick and Clay Rec.*, 1945, **107**, *No.* 6, 57. *Ceram. Age*, 1946, **47**, 11. *Refract. J.*, 1946, **22**, 56.

[59] L. R. Michels, *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3806, p. 40; B., 1945, I, 396.

[60] E. Heaton, F. H. Clews, and A. T. Green, *Inst. Fuel Bull.*, 1946, *Oct.*, 27; B., 1947, I, 26.

[61] *Trans. Brit. Ceram. Soc.*, 1946, **45**, 45; B., 1946, I, 331.

given heat input. The observations of other workers on the temperature gradient are of interest. G. R. Rigby, R. P. White, H. Booth, and A. T. Green[62] have reported that the temperature of the outside of the majority of specimens could fall from 400° to 170° without the specimen spalling as long as the centre was maintained at a temperature above 300°. The spalling tendency of bricks is due not only to the thermal expansion but also to the elasticity. The modulus of elasticity of silica bricks measured in compression was found by the above authors to vary from 5×10^5 to 26×10^5 lb. per sq. in. A general relationship exists between spalling-resistance, thermal expansion, and the modulus of elasticity. The thermal expansion of silica bricks is dependent on the forms of silica which exist in the brick, but the cristobalite content does not give any indication of the total expansion between 200° and 300°. It is suggested that a certain proportion of the volume expansion consequent on the cristobalite inversion is accommodated within the brick structure, the proportion generally being highest in bricks having a coarse grading. This should be of some practical significance in relation to spalling. The formation of tridymite in bricks does not take place until the bulk of the quartz has been converted. Thus bricks containing more than 10% of quartz contain a higher proportion of cristobalite than tridymite, whereas bricks having a high tridymite content are low in quartz.

If the only crystals normally present in a silica brick are the various forms of silica, the glass must be compounded of the impurities. The amount and the composition of the glass at the final temperature of firing of a silica brick oven cannot be predicted, but it has been assumed to consist of about two thirds by weight of silica. According to S. English and W. E. S. Turner[63] the densities and thermal expansion properties of glass are additive and can be calculated from equations of the type : $100/D = x_1/d_1 + x_2/d_2 + x_3/d_3 + \ldots$, where D is the value for the glass, x_1, x_2, x_3 are the percentages of the various oxides in the glass and d_1, d_2, d_3 are constants for each oxide. By applying the constants the density of the glass is approximately 2·6. The amount of glass in silica bricks is about 13%. The percentage of tridymite and cristobalite varies according to the heat-treatment, but a brick containing all tridymite of specific gravity 2·26, and 13% of glass, would have a specific gravity of 2·30, which would be the lowest specific gravity possible. Actually few silica bricks of specific gravity less than 2·30 have been reported. It would appear therefore that calculations of the amounts of quartz, cristobalite, and tridymite in a brick from the specific gravity are erroneous unless the percentage and specific gravity of the glass are considered.

The contraction of highly aluminous materials is well recognised and the reduction in life of these materials in certain furnaces has been traced to this particular fault. Additions, such as sand, have been made to

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[62] *Trans. Brit. Ceram. Soc.*, 1946, **45**, 69 ; B., 1946, I, 331.

[63] *J. Soc. Glass Tech.*, 1922, **6**, 228.

counteract the shrinkage and it is now suggested[64] that by the addition of soluble sulphur compounds to the unfired mixture a shrinkage can be turned into an after-expansion on reheating. The effect is due to bloating, caused by the sulphur compounds, and it is claimed that the effect has been proved in long-period commercial production, but to rely on bloating to give an expansion appears to be precarious. Highly refractory clays are not subject to overfiring until a high temperature is reached and therefore bloating will not occur because there is not sufficient glassy material present to cause swelling, and the controlled addition of the suggested materials will probably be successful, but in the presence of impurities, more of the glassy material will exist and uncontrolled bloating will occur. This may be particularly true if a reducing atmosphere exists. A further use of sulphur as well as arsenides, antimony oxides, and tellurides is suggested in a patent[65] for increasing the strength of basic refractories in the temperature range 500—1300°.

Vermiculite when heated to 900—950° expands into cellular granules about fifteen times its original size; it is an efficient insulator and is therefore useful for thermal insulation of roofs and walls. Bonded with fireclay, bentonite, colloidal magnesium silicate, or refractory cement it is used as an insulating lining for furnaces and for the construction of furnaces for intermediate temperatures.[66]

The use of dolomite in a basic electric arc furnace is discussed by E. C. Brampton, H. Farnham, and J. White,[67] who found that a life of 57 heats under severe conditions was given by the use of unstabilised dolomite. During the working life of the brick, lime in the form of fusible compounds migrates away from the hot face, and the working surface of the brick tends to acquire increased resistance for fluxing, due to the face becoming richer in spinel and periclase. A similar phenomenon is noticed with silica bricks in the roof of the basic open-hearth furnace, but in this case the face of the brick is cristobalite and various zones of concentrations of lime and iron are noticed as they proceed from the hot end. The fluxes in the dolomite brick penetrate to a distance of 1—2 in., which may be the cause of the "flaking" which is experienced. It is also observed with these bricks that a softening occurs just below the limit of flux penetration, and these workers, by printing on bromide paper, have shown that the sulphur concentration reaches a maximum in the light-coloured zones some distance into the brick and suggest that the sulphur influences the softening.

ANALYTICAL AND PHYSICAL MEASUREMENTS.

Further interest in the important property of grain size is indicated in the literature and the methods for its determination can be summarised

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[64] A. R. Lesar, C. A. Krmbill, jun., W. D. Keller, and R. S. Bradley, *J. Amer. Ceram. Soc.*, 1946, **29**, 70; B., 1946, I, 201.

[65] Basic Refractories, Inc., B.P. 573,939; B., 1946, I, 134.

[66] N. C. Jones, *Chem. and Ind.*, 1946, 195; B., 1946, I, 269. G. T. Haddock, *Met. and Alloys*, 1945, **21**, 395, 714; B., 1945, I, 391.

[67] *J. Iron and Steel Inst.*, 1945, **152**, 341P; B., 1946, I, 25.

as (1) the transmission of light through a suspension,[68] (2) microscope examination,[69] (3) permeability methods.[70] Unfortunately the first method is subject to a number of errors because the mathematical laws of transmission of light through a suspension of particles are only partly obeyed in practice. In the method of particle size determination with the microscope, a difficulty arises in making the measurement because the investigator is often confronted with the problem of deciding what constitutes the ultimate particle, for flocculated particles can be mistaken for a single particle. The aim of the permeability methods is to determine the specific surface of the powder. It is well known in ceramics that the grain size distribution is of great importance and any method which does not show the distribution is misleading. An *X*-ray diffraction method for the determination of particle size is suggested by F. G. Firth,[71] who states that the time required to prepare a specimen, and also the error, are less than with the electron miscroscope.

The use of the electron miscroscope is suggested as a means of investigating the structure of ceramic materials.[72]

The determination of moisture in clays and bodies is usually a lengthy procedure requiring a number of weighings and many precautions against water absorption during the test. An apparatus using high-frequency current is reported.[73] The sample may be granular, need not be finely ground, and is placed either inside a solenoid or between condenser plates and is weighed while heating proceeds ; when the absorption of power drops owing to water having been driven off, an automatic device cuts off the supply.

The sampling and testing of fired samples from a furnace where there is a variation in temperature, and in consequence a variation in properties, is always difficult. How many samples must be taken from a variable batch to ensure that an adequate sample has been selected and what is the error involved in the method of testing ? These questions can be answered only when there are sufficient statistical data on the subject and these points are discussed in the current literature.[74]

FIRING.

Noble-metal travelling thermocouples attached to a car of a 400-ft.

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[68] H. E. Rose and H. B. Lloyd, *J.S.C.I.*, 1946, **65**, 52, 65 ; C., 1946, 210. E. D. Bailey, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 365 : C., 1946, 310.

[69] H. Green, *Ind. Eng. Chem.*, 1946, **38**, 679 ; A., 1946, I, 314. A. M. Cravath, A. E. Smith, J. R. Vinograd, and J. N. Wilson, *J. Appl. Physics*, 1946, **17**, 309 ; C., 1946, 304.

[70] A. Pechukas and F. W. Gage, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 370 ; C., 1946, 310. W. F. Keyes, *ibid.*, 33 ; C., 1946, 136. W. R. Holmes, *Nature*, 1946, **157**, 694.

[71] *J. Amer. Ceram. Soc.*, 1945, **28**, 363 ; B., 1946, I, 99.

[72] I. I. Kitaigorodski, *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **48**, 563 ; B., 1946, I, 235.

[73] Marconi Instruments Ltd., and W. B. Bartley, B.P. 569,889 ; C., 1945, 291.

[74] T. R. Lynam and I. M. D. Halliday, *Trans. Brit. Ceram. Soc.*, 1945, **44**, 167 ; B., 1946, I, 171. J. H. Chesters and I. M. D. Halliday, *ibid.*, 135 ; B., 1946, I, 134. E. H. M. Badger, *ibid.*, 1946, **45**, 33 ; B., 1946, I, 332.

biscuit tile tunnel kiln fired with producer gas have been used[75] to obtain true firing curves, and these temperatures have been compared with those of the fixed works thermocouples. Buller's rings, which are really a measure of the heatwork and not actual temperature, show up the differences in the setting, but only give an indication of the final vitrification of the ware. The thermocouples show the fluctuations of temperature along the length of the kiln, in addition to inequalities between the temperatures in various parts of the setting. On any truck the tops are usually hotter than the centre bottom, and the temperature at the sides fluctuates most. A knowledge of the differences between the temperatures indicated by the thermocouples fixed through the crown of the kiln and those in different parts of the setting is of assistance, when it is desired to make use of the readings of the fixed couples in order to control the firing of the kiln. In the preheating zone the temperatures given by the thermocouples in the crown of the kiln are appreciably higher than those attained by any part of the setting, whereas in the cooling end they are lower than those of the upper part of the setting in the corresponding position.

A circular tunnel kiln in which the hearth supporting the goods or the heat-insulating walls and roof actually rotate has been patented.[76] The advantage claimed for this type is that the heat-insulating parts rotate faster than the rotation of the heat cycle in the goods, so that a hot part of the furnace transfers heat to the goods being heated.

A self-closing damper for kiln flues is suggested.[77] The damper is actually a fireclay slab which when flat entirely closes the aperture, and during the setting of the kiln this slab is propped up by one or more pyrometric cones, the number employed depending on its size ; when the temperature reaches the fusion point of the cone it melts and the slab drops, closing the aperture. Although the method is ingenious it will have a limited use, because in the firing of many kilns it is necessary to regulate the damper according to conditions other than temperature.

Some basic principles of the utilisation of radiant energy for heating purposes are given in a report by A. L. Roberts and R. Long.[78] Much interest is being shown in radiant heating methods and the patents for types of burners are increasing in number.[79] The intermittent oven is still extensively used in the industry and therefore the reduction in fuel consumption in this type of oven is a matter of concern. The effect of insulation on the fuel used and a complete firing schedule are published[80] for the firing of a 30-ft. diameter round downdraught kiln containing silica bricks. Methods of preheating air for use in intermittent and tunnel

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[75] E. R. Rowden, R. J. Waller, and M. Francis, *Trans. Brit. Ceram. Soc.*, 1946, **45**, 1 ; B., 1946, I, 331.

[76] A. J. Campbell, B.P. 570,677 ; B., 1945, I, 360.

[77] Anon., *Brit. Clay Worker*, 1946, **54**, 248.

[78] *Gas Res. Board*, 1945, *Comm.* G.R.B. 15 ; B., 1946, I, 117.

[79] Incandescent Heat Co. Ltd., and J. Fallow, B.P. 575,973 ; B., 1946, I, 310. Radiant Heating Ltd., and H. Docking, B.P. 573,552.

[80] T. R. Lynam, *Trans. Brit. Ceram. Soc.*, 1945, **44**, 207 ; B., 1946, I, 171.

ovens have been published. The injection of air tangentially into the cooling zone of a tunnel, and the injection of warm air tangentially into the firing zone, has been patented,[81] as also has the preheating of air through flues passing around the firebox and thence into the heart of the fire,[82] as well as the introduction of secondary air in the flue near to the well hole of an intermittent kiln.[83]

CEMENT.

The effect of gypsum on the setting of cement has interested many investigators, who suggest that it is due to the formation of a protective coating which interferes with the attainment of equilibria, and is similar to the retardation of the slaking of lime in a magnesium sulphate solution, as a result of the formation of a protective coating of magnesium hydroxide. F. E. Jones[84] suggests that in the system Portland cement–water, the formation of protective coatings is of particular importance, since it is to such coatings that the action of gypsum and other compounds in retarding the set of Portland cement can be ascribed. When crystals of $3CaO,Al_2O_3$ are placed in a solution of calcium sulphate dihydrate they are immediately surrounded by a border of fine crystalline material and it is suggested that these crystals constitute a solid solution involving CaO, Al_2O_3, and SO_3. It may well be that the retardation of the hydration of $3CaO.Al_2O_3$ and therefore of set does depend on the formation of such a solid solution deposit. In the opinion of R. Hedin,[85] when water and cement are mixed, all the minerals dissolve, preserving the stoicheiometric oxide proportions ; the solutions contain ions of lime, silicates, and aluminates, and as a result of hydrolysis free silica and aluminium hydroxide are present. The action of dissolved salts, such as calcium sulphate dihydrate, is to displace the equilibria. If the aluminate ion concentration is high, the free silica and aluminium hydroxide are precipitated and owing to the consequent low concentration of calcium silicates the exothermic dissolution of the cement is initially rapid, but the gel formation around the grain retards the reaction. If the lime concentration is high, due to the composition of the cement itself or to additions, coagulation of the alumina does not occur, but hydrated ions are formed which have a lower solubility than the other ions. The solution is therefore continually supersaturated with hydrated ions which crystallise out and so the reaction proceeds until all the water is exhausted. The composition of the hydrates depends on the concentration conditions and in presence of calcium sulphate complex sulphates are formed. In high lime concentrations the $3CaO,2SiO_2$ may give rise to $2CaO,SiO_2$ and lime may crystallise. The alkali aluminates in cement cause the coagulation of the silicon

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[81] Internat. Furnaces Equipment Co. Ltd., and L. Bailly, B.P. 575,730 ; B., 1946, I, 267.

[82] B.P. 575,557 ; B., 1946, I, 267.

[83] N. Bosson, B.P. 570,510 ; B., 1945, I, 360.

[84] *J. Physical Chem.*, 1945, **49**, 344 ; B., 1946, I, 66.

[85] *Handl. Svenska Forsk. Int. Cement o. Betong, Stockholm*, 1945, *No.* 3 ; B., 1945, I, 392.

hydroxide, even in the presence of calcium hydroxide, but if excess of calcium sulphate is present, coagulation does not occur. The quick setting effect of addition of calcium chloride is due to the formation of the less soluble aluminium hydroxide which binds the cement grains together. The addition of borax, humus, and sugar lowers the calcium ion concentration and coagulates the silicon hydroxide, resulting in rapid setting.

The effect of gypsum in cement depends to some extent on the grinding temperature.[86] The present limit for added gypsum is 2·5% SO_3, but if the grinding temperature is kept below 175 F. (80°) the limit for added gypsum may be safely raised to give 3·5% of SO_3.

The formation of a coating on plaster in presence of borax is suggested as one of the causes of the retarding effect.[87] Up to 2% of borax in aqueous solution reacts with plaster of Paris to form a surface film of CaB_4O_7 or its hydrolysis products $Ca(BO_2)_2$ or $Ca(OH)_2$, which retard the crystal growth. Other suggestions for the suppression of the growth, by the same author, are the reduction in activity of those minute gypsum nuclei which normally favour growth of more calcium sulphate dihydrate and the precipitation as CaB_4O_7 of such calcium ions as pass into solution.

The use of saponified pine wood resin to impart certain properties to cements is patented by Hercules Power Co. and G. F. Hogg[88] ; it is claimed to act as a dispersing agent which decreases the normal tendency of cement to absorb moisture, and this moisture leads to hydration and setting during storage. By the introduction of this resin or metallic salts of ligninsulphonic acid[89] the water content of cement slurry can be reduced some 10—15%. On the other hand, T. C. Powers[90] considers wetting agents and dispersing agents to be unnecessary for use in cements. High-alumina cements produce low strength in warm climates, and where the shade temperature is above 85° F. the strength should not be expected to be greater than 600 lb. per sq. in.[91] The transverse strength of plastic board or set gypsum plaster is reduced by approximately 50% when 5% of water is present in the material. The rate of reduction in strength falls as the percentage is increased above 5. The strength is not affected by wetting and drying up to 10 cycles if the specimens are tested dry, but over 10 cycles or continuous exposure to very damp conditions causes a loss in strength up to 60%.[92]

A relatively pure aluminous cement made in an electric furnace having a composition approximately equivalent to the formula $3CaO,5Al_2O_3$ has a higher refractoriness and less expansion when heated to 1300° than the

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[86] A. C. Whittaker and V. E. Wessels, *Rock Products*, 1945, **48**, *No.* 8, 95 ; B., 1946, I, 102.

[87] A. S. Buchanan and H. K. Worner, *J.S.C.I.*, 1946, **65**, 23 ; B., 1946, I, 174.

[88] B.P. 572,817 ; B., 1946, I, 67.

[89] R. L. Sherman and C. R. Bartels, U.S.P. 2,390,225.

[90] *J. Amer. Concr. Inst.*, 1945, **17**, 117 ; B., 1946, I, 101.

[91] G. C. Haggar, *Concr. Const. Eng.*, 1946, **41**, 210 ; B., 1946, I, 295.

[92] H. Andrews, *J.S.C.I.*, 1946, **65**, 125; B., 1946, I, 295.

commercial high-alumina cement and would therefore make tighter joints in brickwork.[93]

The use of Vinsol resin as an air-entraining agent to control the air voids in concrete is suggested by C. E. Wuerpel[94]; the air voids should be kept rigorously between 3 and 7% and the concrete will then have increased plasticity and durability.

The attack on cement by water, a solution of calcium sulphate, a 20% solution of magnesium sulphate, and artificial sea-water made up of 0·2N-magnesium chloride has been investigated by G. Batta.[95] Normal cement is attacked primarily through its free lime content, whereas in a supersulphated cement the lime combined with silica is largely attacked. A very high rate of attack can be expected with pure water, but under practical conditions a protective carbonate film is formed which prevents attack.

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[93] G. R. Pole and D. G. More, *J. Amer. Ceram. Soc.*, 1946, **29**, 20; B., 1946, I, 173.

[94] *J. Amer. Concr. Inst.*, 1945, **17**, 49; B., 1946, I, 173.

[95] *Bull. Soc. chim. Belg.*, 1944, **53**, 1; B., 1946, I, 66.

IRON AND STEEL.

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Despite the difficulties arising from the coal situation, the iron and steel industries of Great Britain show an excellent record for 1946. The production of pig iron during the year reached 7,761,000 tons compared with 7,107,400 tons in 1945, 8,204,600 tons in 1940 (the most prolific of the war years), and an average of 7,658,500 tons for the three years 1936—1938 inclusive. The amount of steel produced during 1946 was 12,693,000 tons compared with 11,824,400 in 1945, 13,221,300 in 1939, and an average of 11,722,100 for the three years 1936—1938. The production of alloy steel, which fell from 1,595,600 tons in 1943 to 706,500 tons in 1945, was maintained at approximately the same figure (about half a million tons), which was usual in the pre-war years.

The coal situation has given the industry much concern and attention is being paid to alternative fuels, the most important of which is fuel oil. One firm has already equipped four 80-ton open-hearth steel furnaces with installations burning fuel oil.

During 1946 reports became available of the results of the investigations of the various teams chosen to ascertain, examine, and assess German war-time industrial activities. In all, some 10,000 targets were investigated, including 494 which were purely metallurgical.

The new British Iron and Steel Research Association is now well established. Research committees under its control have been initiated, and old ones, previously sponsored by the Iron and Steel Institute, have been reorganised.

Production of Iron.

Problems connected with heat conservation and the economical use of fuels have received considerable attention. N. H. Turner and F. A. Gray[1] discuss blast-furnace gas, its utilisation, the variation in quantity and quality produced, and the importance of cleaning it; the advantages of coke ovens on the spot and the use of coke-oven gas; the value of instruments and regulating equipment; steam-raising, using gas with pulverised-fuel alternative, washery refuse, and waste heat recuperation; and gas-storage, distribution, and control. Diagrammatic comparison of results achieved at the Appleby–Frodingham and Templeborough works, and sundry other data, are given. Subjects discussed by C. Hulse and R. J. Sarjant[2] include a comparison of solid (including pulverised), liquid, and gaseous fuels, and furnace practice and design, *e.g.*, mechanisation,

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[1] *J. Iron and Steel Inst.*, 1946, **153**, 183P; B., 1946, I, 269.

[2] *Ibid.*, 165P; B., 1946, I, 269.

automatic control, waste-heat utilisation, recuperation, gas-permeability of furnaces, and forced circulation of gases. Examples of plant-survey work are given, together with a list of problems requiring solution; the need for more high-temperature thermal data is stressed. J. Durand[3] considers that the main general factors which cause loss of heat are intermittent working, inadequate measurement and regulation of temperature, gas analysis, etc., and poor design of gas producers, furnaces, and regenerators. Starting with the delivered price of coal at a blast-furnace washery, subsequent items, including yields of washed coal, ash in washed coal, operating costs at washery and ovens, quality of coke, and cost of pig iron, are considered by W. M. Bertholf[4] in a study of fuel cost economy.

The effects of charging borings, turnings, and mixer and runner scrap to a battery of blast furnaces are discussed by K. Neustaetter.[5] The weight of scrap and the frequency of additions must be carefully controlled; otherwise, chilling of the hearth and interference with the passage of the blast will cause erratic working of the furnace. Metallic yields, coke consumption, and the production of flue dust are compared. It is concluded that borings and turnings can effectively increase the tonnage only when used in furnaces operating smoothly on somewhat less than full blast.

The rate of reduction of iron ore by blast-furnace gas between 450° and 850°, conditioned by the presence of limestone and lime, is studied by H. L. Saunders and H. J. Tress.[6] At 450—550° very little ore is reduced, limestone behaving as a diluent; if, however, the calcium addition is made as lime, this combines with carbon dioxide and carbon deposition is accelerated. At 700—750° carbon dioxide from the brisk reduction of ore eventually reverses decomposition of limestone, and at 850° limestone finally decomposes and reverses the deoxidation of the ore.

A method of producing low-carbon pig iron is described by A. D. Williams.[7] A design of blast furnace is proposed in which the stock and fuel are directed in front of the tuyères and supported while the molten iron is drained into a "decanter" crucible. Contact between the fuel carbon and the iron is thus reduced, resulting in a pig iron low in carbon, the use of which in the open-hearth furnace would considerably reduce the refining time. An experiment produced a mixture of slag and iron, the carbon content of the latter being less than 2%. It is claimed that the productivity of the circular blast furnace would be increased.

FOUNDRY PRACTICE.

The properties of cores prepared with linseed oil and with plastic binders have been compared by W. C. Morgan.[8] Plastic binders are particularly

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[3] *Rev. Mét.*, 1942, **39**, 289; B., 1946, I, 176.
[4] *Steel*, 1946, **119**, *No.* 3, 122; B., 1946, I, 335.
[5] *Ibid.*, *No.* 1, 122; B., 1946, I, 297.
[6] *J. Iron and Steel Inst.*, 1946, **154**, 67P; B., 1946, I, 336.
[7] *Blast Furnace and Steel Plant*, 1945, **33**, 849; B., 1946, I, 177.
[8] *Trans. Amer. Found. Assoc.*, 1945, **52**, 1317; B., 1945, I, 363.

useful for aluminium and magnesium castings; mixtures have been prepared for iron and steel castings. The time required for baking the cores and for removing them after casting is much reduced. Less gas is evolved from a core bonded with plastic material, and the gas is reducing in nature.

Mould atmosphere control (during casting of metals) is discussed by H. W. Dietert, R. L. Doelman, and R. W. Bennett.[9] A protective gas envelope can be obtained by injection of reducing or inert gases into the moulding sand or core of a mould before or during the pouring of the metal, by mixing reactive liquids or solids with the sand, or by using a special facing material; in this way the surface of castings can be improved, thus reducing cleaning costs.

The influence of pouring speed in the manufacture of thin-walled castings has been investigated by the Foundry Practice Sub-Committee of the Steel Casting Research Committee of the Iron and Steel Institute and the British Iron and Steel Research Association.[10] Data of casting temperature and pouring speeds compiled from seven foundries making similar products show that the least difficulty is encountered when the moulds are quickly filled and the metal is hot. A pouring speed of less than 35 seconds reduced rejections due to formation of hot tears and pulls to about 2%, and a casting temperature of more than 1580° gave much better results than one below 1550°. S. L. Fry[11] describes a method of studying the flow of molten metals during the filling of a sand mould in which a kine film is made of a fluorescent screen excited by a beam of *X*-rays which passes through the mould; the results illustrate such phenomena as the "fountain" or "jet" in the filling of a mould.

I. Jenkins and S. V. Williams[12] state that successful annealing of white-heart malleable cast iron was effected in an atmosphere produced by burning town's gas in twice its volume of air; the process is economic and suitable for use on an industrial scale. Under properly controlled conditions the annealing time is very much less than that necessary with the ore-annealing process, and difficulties associated with handling the ore are avoided.

A patent has been granted to the Ford Motor Co., Ltd., P. W. Waters, and J. Shackleton,[13] for the production of malleable cast iron. The alloys, when cast, consist of iron with C 1—1·5 (1—1·3), Si 1·5—2·0 (1·7—1·9), Cu 1·0—2·0 (1·0—1·5), Mn 0·25—0·75 (0·4—0·6), S not more than 0·08, and P not more than 0·08%. A small quantity of a carbide-stabilising element (*e.g.*, not more than 0·5% of chromium or molybdenum) may also be added. The alloy is heat-treated by soaking at 930—955° for 1½—2 hours, cooling quickly to about 650°, soaking for 2—3 hours at 760—

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[9] *Trans. Amer. Found. Assoc.*, 1945, **52**, 1053; B., 1945, I, 363.

[10] *J. Iron and Steel Inst.*, 1945, **152**, 519P; B., 1946, I, 270.

[11] *Found. Tr. J.*, 1945, **76**, 213, 239; B., 1945, I, 363.

[12] *Ibid.*, 77, 91, 113; B., 1946, I, 177.

[13] B.P. 572,853; B., 1946, I, 74.

800°, cooling to 680° at a rate of not more than 20° per hour, and then cooling normally in air.

In a specification for the heat-treatment of austenitic white cast-iron alloys[14] the alloys are heated for 5—30 hours at 850—1150° (preferably 1000—1100°) so as to convert into graphite all the carbide in the alloy except that remaining in solution in the austenite, and the alloy is then cooled. The alloys contain iron with Mn 9—18, Ni 2—5, C 2—6, Si 1·5—4·5, and P 0—0·15%. All or part of the nickel and/or silicon may be replaced by copper and/or aluminium in a ratio of 2 parts of copper or 1 part of aluminium to 1 part of nickel or silicon. Not more than 5% (not more than 12% in all) of chromium, molybdenum, titanium, tungsten, and vanadium may also be present.

According to W. J. Sparling,[15] a white cast iron containing Mn 0·65—1·1, Cu 0·5—1·5, C 1·9—3, P 0·08—0·16, Si 1·3—0·6, and S 0·05—0·12% is rendered malleable in known manner to decompose massive cementite, then heated at 760—925° to recombine carbon, quenched to 650°, and reheated at 650—705° (688°) for 10—35 hours to spheroidise the cementite: it is finally heated at 720—738° to cause the spheroidised cementite to rearrange at the ferrite grain boundaries and produce an interlocked structure, and is then quenched in air, oil, or water. G. Kritzler and H. Killing[16] state that a marked increase in the surface hardness of ferritic iron was noted after flame-hardening various qualities of cast iron.

The poor hot-tinning quality of grey cast iron is attributed by R. A. Cresswell[17] to the presence of graphite flakes. In a new method the iron is cleaned mechanically, immersed in a fused eutectic mixture of zinc chloride (82·2%) and sodium chloride at 300—350°, and dipped in tin covered with the same salt mixture at 300°. When the tinned iron is bonded to white metal, adhesion values of 2—2·8 tons per sq. in. are obtained. The method can be adapted to tinning by wiping. For maximum adhesion the iron is lightly pickled, immersed for 15 minutes in a fused eutectic mixture of sodium nitrate (48·7%) and potassium nitrate at 300—350°, again lightly pickled in hydrofluoric acid, fluxed, and tinned. The surface graphite flakes are oxidised, and the tin penetrates the cavities which they occupied.

STEEL MAKING.

The reduction of silica by molten steel is discussed by W. Geller.[18]

R. T. C. Rasmussen[19] reports on the use of ladle additions of electrolytic manganese instead of ferromanganese to acid-steel heats (open-hearth

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[14] Birmingham Electric Furnaces Ltd., A. G. E. Robiette, and P. F. Hancock, B.P. 573,521; B., 1946, I, 111.

[15] Assr. to Chain Belt Co., U.S.P. 2,196,084; B., 1946, I, 111.

[16] *Giesserei*, 1942, **29**, 429; B., 1946, I, 205.

[17] *J. Iron and Steel Inst.*, 1945, **152**, 157P; B., 1946, I, 205.

[18] *Arch. Eisenhüttenw.*, 1941–42, **15**, 479; B., 1946, I, 29.

[19] *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3830; B., 1946, 1, 137.

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Practical methods of measuring slag fluidity and a standard fluidity test for acid open-hearth slags are described by G. R. Fitterer, J. W. Linhart, B. B. Rosenbaum, J. B. Kopec, and W. G. Wilson.[20] The significance of the test is discussed. As the slag fluidity decreases during a heat the silica content of the slag increases, the ferrous oxide and density decrease, and the temperature of the metal rises. A simple control procedure based on these relations and the slag-fluidity tests is described. There are two appendices, one on theories of viscosity, and the other on laboratory determinations of slag density.

The conditions of formation and stability of inclusions are examined by G. Ranque[21] in order that a working procedure leading to their elimination may be evolved. Elements which form endogeneous inclusions, originally dissolved in the steel bath, react together when the physico-chemical equilibria are changed by variation of temperature or composition of the steel or slag. These inclusion-forming elements are divided into two classes: generators (*e.g.*, oxygen, sulphur, and nitrogen) and fixers; these latter are subdivided into active fixers (*e.g.*, silicon, manganese, chromium, iron) and passive fixers (*e.g.*, magnesium, calcium, aluminium, titanium). The effects of addition of fixers or diluents (*e.g.*, lime) to the slag or steel bath are discussed. In a slag containing diluent, the active fixers combine with the generators and the primary fraction of the compound is dissolved in the diluent and obeys the Nernst law of partition; a second fraction exists in a free state and its concentration must be kept low to prevent its entry into the steel bath. Fixers added to the bath to remove free constituents should also provoke re-dissolution of pre-existing inclusions; to do this, the fixer should be active, since if it is passive, pre-existing active inclusions are replaced by passive insoluble ones. The influence of pouring and solidification and the reaction $FeO + C \rightleftharpoons Fe + CO$ are discussed. Exogeneous inclusions are derived mainly from the hearth bottom and also from furnace refractories and the ladle by chemical action and mechanical erosion. Ferro-alloys often introduce inclusions and their addition in the ladle is therefore not recommended. The effect of casting refractories is discussed; these should be of high quality and chosen to resist reaction with the steel, not with the slag. Phase equilibrium diagrams between constituents of non-metallic inclusions, particularly the ternary $MnO–Al_2O_3–SiO_2$ system,

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[20] *Acid Open Hearth Res. Assoc., Sept.*, 1945; B., 1946, I, 297.
[21] *Rev. Mét.*, 1942, **39**, 331; B., 1946, I, 178.

800°, cooling to 680° at a rate of not more than 20° per hour, and then cooling normally in air.

In a specification for the heat-treatment of austenitic white cast-iron alloys[14] the alloys are heated for 5—30 hours at 850—1150° (preferably 1000—1100°) so as to convert into graphite all the carbide in the alloy except that remaining in solution in the austenite, and the alloy is then cooled. The alloys contain iron with Mn 9—18, Ni 2—5, C 2—6, Si 1·5—4·5, and P 0—0·15%. All or part of the nickel and/or silicon may be replaced by copper and/or aluminium in a ratio of 2 parts of copper or 1 part of aluminium to 1 part of nickel or silicon. Not more than 5% (not more than 12% in all) of chromium, molybdenum, titanium, tungsten, and vanadium may also be present.

According to W. J. Sparling,[15] a white cast iron containing Mn 0·65—1·1, Cu 0·5—1·5, C 1·9—3, P 0·08—0·16, Si 1·3—0·6, and S 0·05—0·12% is rendered malleable in known manner to decompose massive cementite, then heated at 760—925° to recombine carbon, quenched to 650°, and reheated at 650—705° (688°) for 10—35 hours to spheroidise the cementite: it is finally heated at 720—738° to cause the spheroidised cementite to rearrange at the ferrite grain boundaries and produce an interlocked structure, and is then quenched in air, oil, or water. G. Kritzler and H. Killing[16] state that a marked increase in the surface hardness of ferritic iron was noted after flame-hardening various qualities of cast iron.

The poor hot-tinning quality of grey cast iron is attributed by R. A. Cresswell[17] to the presence of graphite flakes. In a new method the iron is cleaned mechanically, immersed in a fused eutectic mixture of zinc chloride (82·2%) and sodium chloride at 300—350°, and dipped in tin covered with the same salt mixture at 300°. When the tinned iron is bonded to white metal, adhesion values of 2—2·8 tons per sq. in. are obtained. The method can be adapted to tinning by wiping. For maximum adhesion the iron is lightly pickled, immersed for 15 minutes in a fused eutectic mixture of sodium nitrate (48·7%) and potassium nitrate at 300—350°, again lightly pickled in hydrofluoric acid, fluxed, and tinned. The surface graphite flakes are oxidised, and the tin penetrates the cavities which they occupied.

STEEL MAKING.

The reduction of silica by molten steel is discussed by W. Geller.[18]

R. T. C. Rasmussen[19] reports on the use of ladle additions of electrolytic manganese instead of ferromanganese to acid-steel heats (open-hearth

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[15] Assr. to Chain Belt Co., U.S.P. 2,196,084; B., 1946, I, 111.

[16] *Giesserei*, 1942, **29**, 429; B., 1946, I, 205.

[17] *J. Iron and Steel Inst.*, 1945, **152**, 157P; B., 1946, I, 205.

[18] *Arch. Eisenhüttenw.*, 1941–42, **15**, 479; B., 1946, I, 29.

[19] *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3830; B., 1946, I, 137.

and electric furnace). Electrolytic manganese proved to be a satisfactory form of manganese addition in the low- and medium-carbon ranges, and the average manganese recovery is at least as good as when ferromanganese is added. Larger additions of manganese than are considered advisable when using ferromanganese can be made in the ladle, and there is no evidence of manganese segregation. Some improvement in the physical properties of the steels is noted, and there is evidence of increased ductility and quicker response to heat-treatment with carbon steels.

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are examined and the most probable phases occurring in the complex system $CaO-MgO-FeO-MnO-SiO_2-Al_2O_3$ are described by J. R. Rait and H. W. Pinder.[22] Many different types of inclusions in acid open-hearth and basic electric furnace steels are identified by extraction and the use of phase diagrams, chemical analysis, metallographic and X-ray examination. A number of photomicrographs and X-ray photographs are included. A table summarising the most common inclusions and their probable sources is given and practical suggestions are made for reducing the incidence of harmful inclusions. Poor melting and deoxidation procedures will give rise to dirty steels, but many inclusions originate from furnace, ladle, or mould refractories by reaction or erosion.

HEAT-TREATMENT.

In a symposium on the subject, the effects of overheating on the serviceability of steel drop forgings, particularly in their relation to their use in aero-engine construction, are discussed by H. J. Merchant[23]; the methods used to detect overheating are described and an account is given of methods of preventing overheating and of reclaiming overheated steel. F. C. Thompson and L. R. Stanton[24] discuss the effect of oxygen on the isothermal transformation of steel and suggest a test for burning in which test bars burnt locally are examined microscopically after isothermal quenching to various temperatures. It is said to be possible to differentiate clearly between normal and burnt states in some, but not all, cases. The effect is too erratic to offer a universal test for burning. The presence of oxygen, directly or indirectly, makes the steel more reactive, *i.e.*, the inherent S curve is displaced to the left. A. Preece, A. Hartley, S. E. Mayer, and J. Nutting[25] state that overheating occurs from 1250° upwards and is indicated by the appearance of facets in the fracture (preferably after impact) and can also be revealed by special etching reagents (*e.g.*, 10% sulphuric acid + 10% nitric acid or electrolytic ammonium nitrate). No clear relation is found between the temperature of overheating and the normal analysis of the steel or its oxygen and nitrogen contents. Unexpectedly it is found that steels of low inclusion content possess a low overheating temperature. For open-hearth steels generally this temperature is higher than that for electric steels, but the composition of the furnace atmosphere appears to have no influence. Impact strength and tensile properties are not seriously impaired in the initial stages of overheating. The phenomenon is said to result from diffusion processes in the austenite grain which operate during cooling through the overheating range. The rate of cooling has an important influence on the development of an overheated structure, which is suppressed by very slow cooling. Resuscitation by slowly cooling through the overheating range is more effective than are methods now

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[22] *J. Iron and Steel Inst.*, 1946, **154**, 371P; B., 1946, I, 299.
[23] *Ibid.* **153**, 217P.
[24] *Ibid.*, 259P; B., 1946, I, 240.
[25] *Ibid.*, 237P; B., 1946, I, 240.

normally used. J. Woolman and H. W. Kirkby[26] observe that for each steel there is a minimum temperature above which overheating occurs over a range of temperature. The minimum overheating temperature varies with different steels and different melts of apparently the same steel. Overheating is affected by the method of steel-making ; *e.g.*, basic electric-arc steels possess a considerably lower minimum overheating temperature than corresponding open-hearth steels. Addition of aluminium as deoxidant appears to lower this minimum temperature in some cases In addition to oxygen, the sulphur content appears to affect the facet-forming tendencies. The rate of cooling has a critical effect on overheating ; a very quick or very slow rate may suppress facet formation. Remelting in a vacuum tends to lower a very high minimum overheating temperature. Forging above this minimum temperature apparently raises the temperature by 75—100° and reduces facet size. Facet formation, austenitic grain size at overheating temperature, and the network revealed by a special etching solution (sulphuric and nitric acid) are almost certainly interrelated. It is suggested that overheating is a precipitation effect and that the precipitate is already present in the steel as cast and persists as a network at the grain boundaries. This network is reflected in the fracture by interruptions in the path of the crack which gives the typical faceted appearance. W. E. Goodrich[27] examined forged nickel–chromium–molybdenum–vanadium steel for overheating (faceted fracture) after heating at 1250—1400° followed by various cooling treatments and, in some cases, standard oil-hardening and tempering. Comparatively rapid cooling through the upper critical range favours the formation of facets on fracture. After oil-hardening from 850° an original granular fracture produced by overheating up to 1350° does not reappear on tempering below about 400°, but appears to a smaller degree on tempering between 400 and 650°, in this range, rising tempering temperature progressively increases the granular characteristics of fractures. Repetition of normal oil-hardening and -tempering or slow cooling from overheating temperatures can appreciably reduce and sometimes eliminate facet formation. Heating to above 1350° produces metallographic changes (denoted by white zones when etched with nitric acid in alcohol) which apparently take place in the solid state at the grain boundaries and also originate from non-metallic nuclei within the grains. The relation between sensitiveness to superheating and content of aluminium compounds in unalloyed mild steel is investigated by H. Kornfeld and G. Hartleif[28] ; in all three cases examined an increase in the content of aluminium compounds, chiefly alumina, was associated with a marked decrease in the grain-coarsening temperature, but neither the total aluminium content nor the amount of metallic aluminium affected this temperature.

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[26] *J. Iron and Steel Inst.*, 1946, **154**, 265P ; B., 1946, I, 241.
[27] *Ibid.*, 255P ; B., 1946, I, 241.
[28] *Arch. Eisenhüttenw.*, 1942, **16**, 113 ; B., 1946, I, 207.

Structural changes in carbon and molybdenum steels during prolonged heating at 482—593° for periods up to 5000 hours as affected by deoxidation practice have been examined by G. V. Smith, R. F. Miller, and C. O. Tarr.[29] The hardness of most of the carbon steels at first decreased slightly with time and temperature, and then decreased slowly; this behaviour was unaffected by the deoxidation practice used.

J. H. Andrew, H. Lee, A. K. Mallik, and A. G. Quarrell[30] have studied the removal of hydrogen from steel. Specimens of many commercial steels after being soaked in hydrogen at 1100° are quenched in an isothermal bath at 150—750° for 5 hours, and aged for 1 week under paraffin. After cleaning, a determination of the hydrogen is made by vacuum-heating and the result is expressed as number of c.c. per 100 g. In all steels the rate of removal of hydrogen is high in the intermediate range of temperature, and in some steels correlation between removal of hydrogen and transformation in the pearlitic region is indicated by a peak in the removal curve. The retarding effect of small partial pressure of hydrogen surrounding the specimen on the rate of removal of hydrogen at different temperatures is studied. Alloying elements have little effect on the hydrogen-diffusion constant. Embrittlement is found in those steels where the hydrogen content is 1·0—3·0 c.c. per 100 g. Evidence of the formation of hair-line cracks under various conditions is obtained; it is considered that until the problem of low-alloy steels in general is more thoroughly understood, no detailed explanation of hair-line crack formation can be expected.

K. L. Clark and J. H. Richards[31] carried out tests to determine whether the hardenability of forged steel is the same as that of cast steel of the same composition. Tests were made on 14 low-alloy chromium–nickel–molybdenum steels, some of which contained copper and aluminium and two boron. For practical purposes cast steels have the same hardenability as forged steels of the same composition and grain size. Within the range of steels studied, normalising treatments as high as 1090° prior to quenching from 900° did not materially affect the hardenability of cast steel except in so far as they altered the as-quenched grain size. The methods and factors used for calculating the hardenability of wrought steels were applicable to cast steels. Boron can greatly increase the hardenability of cast steel; some of its effect is lost if high pouring temperatures are necessary. When relatively high hardenability is desired in 0·35—0·45% carbon cast steels addition of strong carbide-formers, *e.g.*, chromium and molybdenum, should be limited, whilst more should be added in the case of 0·15—0·25% carbon steels.

J. W. Donaldson[32] reviews war-time developments in industrial heat-treatment of ferrous and non-ferrous alloys. Practical application of

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[29] *Proc. Amer. Soc. Test. Mat.*, 1945, **45**, 486; B., 1946, I, 241.

[30] *J. Iron and Steel Inst.*, 1946, **153**, 67P; B., 1946, I, 270.

[31] *Trans. Amer. Found. Assoc.*, 1945, **52**, 1325; B., 1946, I, 363.

[32] *Metallurgia*, 1946, **34**, 25; B., 1946, I, 272.

iso-thermal transformation curves has been an outstanding development in the heat-treatment of steel, and the processes of austempering and martempering have been extended. In the fields of bright-annealing and age-hardening of non-ferrous metals, changes have been in the production of new heat-treatable alloys, in the methods of processing the older alloys, and in an extended use of salt baths for heating and protective atmosphere for annealing.

According to F. F. Dodson,[33] production of soft spots when nitriding DTD.87A or DTD.306 steels could not be correlated with the presence of oxide or grease coatings on the surface, and the extent and hardness of the case were not affected by prior heat-treatment. The time of nitriding can be considerably reduced by purging the containers for 10 minutes only, charging into a furnace at 520°, and cooling the containers with an air blast after nitriding. Soft spots are attributed to regions of stagnant gas in the container and can be avoided by increasing the rate of flow of ammonia. Attempts to accelerate the nitriding of steel are discussed by E. Kunze.[34] The application of certain granular materials, particularly calcium chloride, increases the rate of absorption of nitrogen but not the concentration at the surface. Phosphatising before nitriding is the only method of increasing both the depth and the concentration at the surface. H. Bennek and O. Rüdiger[35] state that if a glow discharge is created in an atmosphere containing nitrogen, nitrogen ions with a positive charge are attracted to the cathode at high velocity. This principle has been applied to the nitriding of steel. Several tests were run under various conditions of time, temperature, suction, and current. The depth of the nitrided layer and the Vickers hardness were determined and compared with the results obtained in the normal nitriding process. For equal times of treatment, up to 7 or 8 hours, greater hardness and a slightly deeper case were obtained by the glow-discharge method; with increasing time the effects of the treatments became more and more similar.

TESTING.

Changes in the elastic modulus and damping capacity of metallic materials under fatigue stresses are examined by A. Karius.[36] Both plain and notched alternating bend-test specimens were tested in a Schenck machine, and after various numbers of cycles the damping and change in elastic modulus were determined in a Förster apparatus. It is concluded that, in all polycrystalline materials, the changes due to fatigue are of the same nature and follow the same course with increase in cycles of stress. Damping capacity rises and the elastic modulus falls, at first, as the number of cycles is increased, due apparently to cold-working. With further time of testing at moderate stresses these effects practically disappear, but

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[33] *Metallurgia*, 1945, **32**, 149; B., 1946, I, 106.

[34] *Arch. Eisenhüttenw.*, 1944, **18**, 57; B., 1946, I, 243.

[35] *Ibid.*, 61; B., 1946, I, 243.

[36] *Metallwirts.*, 1944, **23**, 419; B., 1946, I, 108.

they recur shortly before fracture, due to macroscopic cracks. The initial changes in properties depend on the volume of stressed material in the test-piece; the effects extend throughout this volume, and are not confined to the points where failure occurs later. The changes in properties just before fracture are independent of the volume. Specimens with sharp notches did not confirm this effect of volume, but this was traced to cracks at the notch. Preliminary static or dynamic stressing of the specimen reduces the extent to which the damping and modulus are changed by fatigue, but if the preliminary dynamic stressing is high the reverse can occur, due to formation of submicroscopic cracks. The effects occurring in the early stages of fatigue testing are partly removed by resting at room temperature, and completely at 150°, so they must be due to slight displacement in the lattice, and not to normal plastic deformation. The benefit of rest or low-temperature treatment is due to the reduction of internal stresses which later lead to macroscopic cracks. Submicroscopic cracks in individual crystals can be prevented only by annealing above the recrystallisation temperature. F. Bollenrath and H. Cornelius[37] carried out a series of tensile fatigue tests on specimens of a number of metals and alloys representing a wide variety of lattice structures and mechanical properties, and the effects of periods of rest on the ability of the material to resist a limited number of reversals at above the fatigue strength, *i.e.*, the time-resistance, were studied; the data showed that rest periods had no effect on the Wohler curves.

Steels treated to produce common microstructures were subjected to tensile and torsional stresses and the data therefrom compared by M. C. Fetzer.[38] Tensile determination of the yield point is preferable when solid specimens are used, but as a measure of true strength the torsional method is considered superior to the tensile, as the data obtained by the latter method are complicated by notch effect when necking of the test-piece begins. Angle of twist is a truer test of ductility than elongation and reduction of area, and torsional data are preferred in estimating work-hardenability.

To determine the effect of combined stresses on mechanical properties of steels between room temperature and −188°, D. J. McAdam, jun., G. W. Geil, and R. W. Mebs[39] carried out tension tests on a number of notched and unnotched specimens of steels and non-ferrous metals and alloys at various temperatures from room temperature to that of liquid air (−188°) and the tensile values obtained are correlated with stress ratio (axial to radial), notch angle, length ratio, and temperature. The carbon steels show a rapid increase of yield stress to abnormally high values (about three times the value at room temperature) at −188°, together with a reduction of ductility to nearly zero.

Yielding and fracture of medium-carbon steel under combined stress

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[37] *Z. Ver. deut. Ing.*, 1940, **84**, 295; B., 1946, I, 306.
[38] *Steel*, 1946, **118**, *No.* 25, 92; B., 1946, I, 301.
[39] *Proc. Amer. Soc. Test. Mat.*, 1945, **45**, 448; B., 1946, I, 105.

are studied by E. A. Davis,[40] particular attention being paid to the magnitude and distribution of the stresses and strains at the instant preceding fracture. M. J. Manjoine[41] discusses the influence of rate of strain and temperature on yield stresses of mild steel. Tensile tests are reported for room temperature, 200°, 400°, and 600° at rates of strain from 10^{-6} to 10^3 per second. At room temperature the ultimate strength decreases slightly at very low rates of strain, and then increases with strain rate, showing a 40% increase at the highest rate. The lower yield point increases throughout the range of rates, with an average overall increase of 170%. The total elongation for the higher rates is practically constant at 40%. At the higher temperature the yield stresses are greatly affected by strain-ageing. In general, as the strain rate is increased a higher temperature and strain are necessary to accelerate strain-ageing. At 600° the influence of strain-ageing is reduced or completely eliminated by annealing and recrystallisation, and the yield stresses increase with strain rate over the entire range.

The significance of the flow stress and fracture stress curves for steel is discussed by C. Zener[42]; the point of fracture is indicated by their intersection. The effects of different conditions of loading or testing on the mode of failure are explained with reference to changes in the form of these curves.

X-Ray stress determinations carried out by F. Bollenrath and E. Osswald[43] showed that a state of internal stress existed in steel specimens subjected to compressive stresses exceeding the yield point, irrespective of the stress distribution in the elastic state. The internal stresses were concentrated at the core of the specimen. R. Glocker and H. Hasenmaier,[44] using cobalt and chromium radiation, which have different penetrations, found that flow began in a 0·01-mm. surface layer at a stress which was only 50—66% of the elastic limit; this applied both in tensile and torsional tests.

Brittleness and toughness of metals at high temperature are investigated by W. Siegfried.[45] In continuation of earlier work, two extensive series of creep tests are described. Tin–cadmium alloys were used in the first series because they behave at room temperature in the same way that steel does at high temperature; cold-drawn as well as heat-treated specimens, notched and unnotched, were tested to examine the effect of the microstructure. In the second series, notched steel specimens were prepared with 12 different notch contours so as to study the effect of the notch angle and the radius at the bottom of the notch. The results proved that the embrittlement followed physical laws which embrace

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[40] *J. Appl. Mechanics*, 1945, **12**, A13; B., 1946, I, 180.
[41] *Ibid.*, 1944, **11**, A211; B., 1946, I, 180.
[42] *Rev. Mod. Physics*, 1945, **17**, 20; B., 1946, I, 68.
[43] *Z. Ver deut. Ing.*, 1940, **84**, 539; B., 1946, I, 300.
[44] *Ibid.*, 825; B., 1946, I, 300.
[45] *Schweiz. Archiv*, 1945, **11**, 1, 43; B., 1946, I, 306.

not only low-alloy steels at 500° but also tin alloys. Additional tests at 650° on 30–15 and 12–15 austenitic chromium–nickel steels proved that the results with the softer materials were applicable to austenitic steels. A method of determining the behaviours of steels at high temperature which does not involve creep tests lasting several thousand hours is described. Creep tests are made on unnotched specimens; the total elongation at fracture and the reduction in area are measured, and these values are used to calculate the uniform elongation and the local elongation by Kuntze's formula. Necking elongation divided by uniform elongation is a measure of the cohesion of the steel.

The influence of treatment and microstructure on scatter of result of creep tests on austenitic heat-resisting steels has been investigated by E. Morlet.[46] The materials investigated comprised several steels (rolled and forged) containing (approximately) C 0·2—0·35, Cr 18, Ni 8, W 3·5%, and one (cast and forged) containing (approximately) C 0·35, Cr 25, and Ni 13%. To minimise the scatter of creep-test results, heat-treatments, particularly the quench from 1150°, must be closely controlled, since appreciable grain growth may take place at this temperature. The maximum resistance to creep is obtained by annealing at 900° for 6 hours after quenching from the high temperature. Steels with a large grain size have greater resistance to creep than those with small grains. The scatter is greater when the duration of the test is increased. Prolonged heating of the 25–12 alloy causes disappearance of ferrite from the structure and precipitation of additional carbide, without appreciable change in grain size. As a result apparently of this structural change, there is a progressive increase in the creep rate in prolonged tests.

PROPERTIES.

A number of investigations have been directed to the development of permanent-magnet alloys. According to A. Torry[47] factors responsible for high coercivity in the nickel–iron–aluminium alloys are associated with weak intergranular structure. Excessive brittleness is attributed to differences in rates of contraction or expansion of the phases already present or being precipitated. The Alni, Alnico, and Alcomax series of alloys were studied with regard to the influence of aluminium, copper, and titanium in affecting uniform expansion or contraction (as-cast and heat-treated). By suitable control of the proportions of the elements present, in the light of knowledge of their separate effects on magnetic characteristics, heat-treatment, and dilatation behaviour, economic production has been improved without loss of magnetic performance. Darwins Ltd., A. Linley, and A. Torry[48] claim that anisotropic properties are produced in magnets of the iron–aluminium–cobalt–nickel type by casting the alloy in contact with polar faces of bodies embedded in

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[46] *Rev. Mét.*, 1944, **41**, 161, 284, 346; B., 1946, I, 207.

[47] *Metallurgia*, 1946, **34**, 147; B., 1946, I, 303.

[48] B.P. 573,238; B., 1946, I, 112.

moulding sand and connected in a magnetic circuit so that the bodies acts as chills to promote a rapid initial cooling rate (3—10° per second), which, owing to the heat supply of the runner and feeder, is slowed to about 3° per second, while the temperature is still above the Curie point, so that the casting takes about 1½ hours to cool to 600° and about 4 hours to cool to 500°. Hot-workable iron alloys claimed by International Nickel Co., Inc.,[49] contain Al 4—9·5 (6—8) (8—9·5), Ti 1—3, Ni 15—30 (24—27), and Co 2—15 (5—10)%, the Ni + Co content being not more than 34 (not more than 30)%. D. A. Oliver and W. Jessop & Sons, Ltd.,[50] claim that anisotropic characteristics are produced in an alloy consisting of iron with Co 13—30, Ni 8—20, Al 5—10, Cu 0—6, and/or Ti 0—4%, by rotating the alloy in a magnetic field while cooling it from a temperature above to one below the Curie point. According to J. L. Snoek,[51] the magnetic properties of iron–nickel–aluminium alloys containing, *e.g.*, Fe 61·2, Ni 26·5, and Al 12·3% are improved by cooling from above 1000° (1200°) down to 700° while maintaining a temperature gradient in the alloy, in the direction corresponding with that in which it is to be magnetised, by alowly immersing the alloy in a cooling fluid (water). Vicalloy—a workably alloy for permanent magnets—is discussed by E. A. Nesbitt.[52] The Vicalloy alloys are machinable in the cast condition and with care can be rolled to thin sheet or drawn to fine wire. Vicalloy I contains Fe 38·5, Co 52, and V 9·5% and is cast or lightly hot-worked to the desired form. A magnetic energy product of $1·0 \times 10^6$ is obtained by quenching or slow cooling from 1100—1200°, followed by precipitation treatment at 600°. Vicalloy II contains Fe 35, Co 52, and V 13%, and after hot-swaging is severely cold-worked and aged at 600°. High magnetic properties (energy product $2—3·5 \times 10^6$) are obtained in the direction of working, but the properties at right-angles are inferior. After heat-treatment both alloys are very hard. The differences between Vicalloy and other precipitation-hardening alloys are explained by reference to existing phase diagrams. Methods of melting and fabrication are described. British Thomson-Houston Co. Ltd.[53] describe a composite body comprising an alloy having high magnetic retentivity and an easily machinable portion formed by assembling in a die the powder ingredients, *e.g.*, Al 6—15, Ni 12—35, Co up to 18%, and balance iron, for the magnetic portion, and soft iron powder for the machinable portion, then pressing and sintering to form the composite body. G. H. Howe[54] describes a stable, brittle master alloy containing Fe 50 and Al 50%, made by heating iron at 1000° with aluminium, used in the manufacture by powder metallurgy of (i) iron–nickel–aluminium alloys, (ii) alloys containing iron and Al 8—12%, or Cr 35, Al 8, and Fe 57%, or Fe 55—67,

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[49] B.P. 575,102; B., 1946, I, 211.

[50] B.P. 572,409; B., 1946, I, 39.

[51] U.S.P. 2,323,944; B., 1946, I, 39.

[52] *Amer. Inst. Min. Met. Eng.*, 1946, *Tech. Publ.* 1973; B., 1946, I, 339.

[53] With F. Widnall, B.P. 576,754; B., 1946, I, 273.

[54] Assr. to General Electric Co., U.S.P. 2,192,741-4; B., 1946, I, 39.

Al 8—12, and Cr 37—24%, (iii) iron alloys containing Ni and/or Co 10—45 and Al 5—20 (6—15)%, (iv) machinable iron alloys containing Ni 14—25 (17), Al 8—13 (10), Co 2—18 (12·5), and Cu 2—16 (6)%.

According to R. P. Cross, jun., and A. N. Ogden,[55] a magnetic alloy which is to be converted into powder cores is manufactured by first melting the materials (nickel, iron, molybdenum) to form a massive alloy, which is broken up into comparatively large pieces by working; these are thoroughly oxidised by heat (650°) and oxygen, and the oxide powder is further pulverised to finer than 5 μ. and then reduced by heat (537°) and a reducing agent (hydrogen). The general effects of stress on magnetisation are reviewed by R. M. Bozorth and H. J. Williams.[56] Measurements have been made with small cyclic stresses on the stress-sensitivity (Λ) of nickel–iron alloys and on permalloy 45. The form of the Λ/B curve, where B is the induction, has been established, showing cyclical change of induction with stress to be dependent on polarising induction. The value of Λ depends on the more fundamental constituents of saturation magnetostriction, saturation magnetisation, and crystalline anisotropy; this dependence is derived from domain theory and is applicable to the materials studied. In the nickel–iron alloys Λ_{max} shows a minimum at 90% and a maximum at 60% Ni.

An examination of recent literature by G. D. Boyer[57] shows that sulphur is no longer regarded as always harmful to steel. The most harmful effects are encountered in hot-working if the sulphur exists as ferrous sulphide, but in presence of sufficient manganese this does not occur and up to 0·1% of sulphur can be tolerated. Sulphite-treated alloys such as 8640 have an average sulphur content of 0·045% and very seldom above 0·06%. Since the manganese ranges of these steels vary from 0·60—0·90 to 0·75—1·0%, any inclusions exist as manganous sulphide as shown by micrographs.

The effect of copper on properties of cast carbon–molybdenum steel was studied by N. A. Ziegler and W. L. Meinhart.[58] Increasing the addition of copper up to 1·5% may increase the tensile strength by about 100%; the increase in hardness and the decrease in ductility are not great enough to be objectionable. Addition of 1% of copper to 0·1% carbon–0·5% molybdenum steel develops properties in the heat-treated steel equivalent to those of a cast molybdenum steel containing about 0·25% of carbon. Addition of copper reduces the maximum hardness of the heat-affected zone of welded carbon–molybdenum steel. G. K. Manning and P. C. Rosenthal[59] also survey the use of copper as an alloying element in iron and steel. Plain carbon steel sheets containing 0·15—0·20% of copper offer an increased resistance to atmospheric corrosion.

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[55] Assrs. to Western Electric *Co.*, U.S.P. 2,200,491; B., 1946, I, 39.

[56] *Rev. Mod. Physics*, 1945, **17**, 72; B., 1946, I, 69.

[57] *Steel*, 1946, **119**, *No.* 2, 96; B., 1946, I, 337.

[58] *Trans. Amer. Found. Assoc.*, 1945, **52**, 1151; B., 1945, I, 362.

[59] *Min. and Met.*, 1946, **26**, 601; B., 1946, I, 136.

Structural steels are improved by addition of copper, which confers on them high yield strength. Added to 18–8 stainless steels, copper further increases their resistance to highly corrosive media. When 0·5% or more of copper is added to steel, a precipitation-hardening can be obtained after suitable heat-treatment; this property is valuable in the production of steel castings, which latter can be hardened at comparatively low temperature after being machined, without distortion or the excessive formation of scale. The properties of grey, chilled, and malleable irons also benefit from additions of copper.

G. P. Contractor and J. S. Vatchaghandy[60] state that the addition of 0·10—0·20% of vanadium to low- or medium-carbon steels of intermediate manganese content improves their structure and physical properties when the steels are cooled rapidly in air. The grain refinement obtained reacts favourably on the critical cooling rate, and the usual manganese-rich segregate having a martensitic structure is avoided. High impact values, which are more than those of highly-alloyed steels, are obtained, and the general mechanical properties compare favourably with those of low-nickel chrome steels. Cast test-blocks from a series of experimental heats were used for the investigation, and illustrations of microstructures are shown.

The effects of titanium on the properties of 12% chromium, 17% manganese austenitic steel were studied by G. F. Comstock.[61] 0·14% of titanium increased the yield strength in the quenched and tempered state by 15—20%. With 0·75% Ti a greater increase in the yield strength was obtained with little loss of ductility and resistance to impact. With 1·6—3% Ti hardness values of Rockwell C40 and C60, respectively, were obtained by temper-hardening, but the steels were either unforgeable or had a very low impact-rresistance. The same investigator[62] found that a steel in which the carbon is combined with not less than 4·5 times its amount of titanium takes a white cover-coat enamel (without a ground-coat) satisfactorily and does not blister or "black-speck." Precautions are necessary to prevent the oxidation of the titanium and its contact with the slag. The best method of treating basic-hearth steel is to deoxidise it with aluminium in the ladle as it flows from the furnace, and to add the titanium in a second ladle. A powder, *e.g.*, lime, is used as heat insulation on the top of the metal. The steel is excellent for deep-drawing, has no definite yield point, even when normalised, so that stretcher strains cannot occur, and is not subject to strain-ageing even when strained to 17% and aged at 230°; it is also resistant to caustic embrittlement and hydrogen attack and is more sag-resisting than ordinary steels at enamelling temperature. The yield strength is low, but stronger steels (26·8 tons per sq. in. yield strength) with the same good enamelling

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[60] *J. Sci. Ind. Res., India,* 1945, **4**, 171; B., 1946, I, 69.

[61] *Iron Age,* 1945, **156**, *No.* 6, 62; B., 1946, I, 179.

[62] *J. Amer. Ceram. Soc.,* 1946, **29**, 1; B., 1946, I, 179.

qualities have been made experimentally; a good specification is: C not more than 0·08, Ti not less than 5 times the carbon content, Mn 1·3—1·6, and Si, Cu, Ni, and Mo (optional) 0·4—0·6% each. This steel has excellent ductility and toughness, fair weldability, good resistance to strain-ageing and embrittlement, and better resistance to grain growth than has the simpler titanium steel. The effect of titanium on creep strength of steel has been examined by P. Bardenheuer and W. A. Fischer.[63] A Ti : C ratio of 6—9 in steels (0·2% C) which had been water-quenched and tempered at 600° produced the optimum creep strength at 500°. The value of the optimum creep strength depended on the carbon content and was highest when carbon was more than 0·08%. The range of the above ratio giving the optimum creep strength was widened by chromium additions. E. Houdremont and G. Bandel[64] studied the effect of titanium, of the heat-treatment, and of the contents of carbon, manganese, silicon, chromium, molybdenum, and vanadium on the creep strength of steel. The creep strength in the 400—600° range of annealed steels increased steadily with increasing titanium content; this is only partly due to the titanium dissolved in the α-solid solution. An important factor is the precipitation, which is very sluggish during the annealing without deformation; this becomes effective only on applying the load in the creep test. This is shown in the time–extension curves by a high inital and permanent elongation and a low creep rate. E. Houdremont, F. K. Naumann, and H. Schrader[65] state that two carbides occur in the iron-titanium–carbon system, the easily soluble Fe_3C and the difficultly soluble TiC. Fe_3C disappears when the Ti : C ratio is more than 4. The solubility of TiC appears to change with different titanium and carbon contents in the steel. With high titanium contents there are two forms of carbide, a primary coarse precipitate and a finely-divided form precipitated out of the γ-iron. The results of numerous tests on steels containing up to 3·7% of titanium are presented and discussed.

Analyses of steels used in the plastics industry are given by J. Burke.[66] For dies, oil-hardening steel (C 0·90, Mn 1·15, Cr 0·50, W 0·50%) is used; it is lapped to a mirror finish and hardened to Rockwell C hardness of about 54—56. For excessive pressures, the steel contains C 0·30, Mn 0·75, Si 0·50, Cr 0·80, and Mo 0·30%. For making hobs, either a "dead-soft" (C not more than 0·05, Mn 0·10%) or a low-carbon alloy steel (C not more than 0·10, Mn 0·50, Cr 0·50, Ni 1·25%) is preferable.

A compilation of information from the literature on the σ phase—a hard, brittle, non-magnetic constituent formed in certain high-chromium steels—is presented by F. B. Foley.[67] If present in appreciable amounts the steel loses ductility. σ appears to be the intermetallic compound FeCr

[63] *Arch. Eisenhuttenw.*, 1942, **16**, 31; B., 1946, I, 206.
[64] *Ibid.*, 85; B., 1946, I, 206.
[65] *Ibid.*, 57; B., 1946, I, 206.
[66] *Canad. Plastics*, 1945, **3**, *No.* 6, 31; B., 1945, I, 362.
[67] *Metallurgia*, 1946, **34**, 139; B., 1946, I, 301.

in which the chromium in iron–chromium alloys richer in iron than 50 at.-% may be replaced by iron atoms. The range of pure σ covers chromium 44—50 at.-%. In the binary Fe–Cr system, σ persists as a phase in equilibrium with α in the chromium-rich alloys containing up to 71 at.-%, and in the iron-rich alloys with down to 26 at.-% Cr. σ recrystallises in the simple body-centred cubic lattice structure of α in iron–chromium alloys above about 820°. The reverse transformation from α to σ is sluggish. With addition of nickel to the Fe–Cr system the σ phase persists up to 920° and its limits are extended. Whilst the occurrence of this phase is commercially most important with the iron–chromium and iron-chromium–nickel alloys, it may be present in other ferrous alloy systems including molybdenum, silicon, vanadium, manganese, and aluminium. σ may be detected by X-ray crystal diffraction, magnetic analysis, or, if present in considerable quantity, by microscopical examination. Double etching (equal parts of hydrochloric acid and water followed by hot 10% alkaline potassium ferricyanide, or a reagent prepared by mixing 30 g. each of potassium hydroxide and potassium ferricyanide with 60 ml. of water made fresh and used at the boiling point) may be used to reveal the phase.

The heat-resistance of El–69 steel (an austenitic steel containing Cr 13, Ni 13, W 2%, and sometimes Si about 2 and Mo about 0·5%) is reported by Z. L. Minz and G. V. Akimov[68] to be very appreciably raised by heating at 1200—1250° instead of the usual 1050—1100°. This is accompanied by a considerable increase in size of the austenite polyhedra in the steel, and a decrease in plasticity. The relation between the growth of grains and the temperature and duration of heating has been examined. As the temperature rises more of the carbides dissolve. Grain growth begins to accelerate pronouncedly between 1200° and 1250°, corresponding to a practically complete dissolution of the carbides in the steel. For all temperatures above 900° increasing the duration of heating results in a decrease in the number of visible carbide grains.

The oxidation of alloys at temperatures between 900° and 1100° was studied by H. Cornelius,[69] using an apparatus which simulated the conditions in an internal-combustion engine. Alloys having a composition range of C 1·0—2·2, Si 0·84—2·41, Mn 0·18—0·45, Co 0 to about 60, Cr about 22—29, and W 0—7·6% were used. The cobalt content in the range 30—60% had little influence on the rate of oxidation, but a cobalt-free steel oxidised much more rapidly.

Tubes for use in oxidising or reducing conditions, with intermittent heating and cooling, which are heat-resistant and free from hardening under such conditions, are claimed by A. L. Feild.[70] They are formed from steel containing Cr 20—22, Mn 0·25—2, Si 0·25—2, and C 0·05—2%, with or without Mo 0·25—2 and/or Cu 0·25—2%.

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[68] *Compt. rend Acad. Sci. U.R.S.S.*, 1945, **48**, 185; B., 1946, I, 270.

[69] *Stahl u. Eisen* 1944, **64**, 529; B., 1946, I, 270.

[70] Assr. to Rustless Iron & Steel Corporation, U.S.P. 2,200,545; B., 1946, I, 37.

A heat-erosion-resistant alloy which can be readily machined and forged is claimed by G. Charlton,[71] containing C 0·25—1, Mn 5—20, Cr 15—30, Si 0·25—1·5, Co 5—30, Ni 0·5—3·5, W 0·5—2·5, and Mo 0·5—2·5%.

W. H. Hatfield and H. Green[72] are the inventors of steels of abnormally high creep-resistance, for heavy duty up to 800°, which contain iron with C not more than 1·5, Ni 15—25, Cr 12—20, Mo 2—6, Cu 2—6, and Ti 0·25—2% ; Si up to 2, Mn up to 2, and V up to 1% may also be present. A steel containing C 0·08, Si 0·28, Mn 0·24, Ni 16·93, Cr 13·87, Mo 4·31, Cu 4·47, Ti 0·51%, with remainder iron, is specifically claimed.

Steels resistant to reducing-type corrosives are claimed by R. Franks.[73] They contain (i) Cr 4—30, Sb 0·1—2, Mn 0·1—1, Si 0·1—1, C not more than 0·5, and N not more than 0·3% ; (ii) Cr 12—30, Ni 5—16, Sb 0·1—1·5, Mn not more than 5, Si not more than 1, C + N not more than 0·15, and Ni + Mn not more than 16%, with or without ferrite-promoting elements (Nb and/or Mo) 0·1—6·5%.

Processes for bonding a bronze lining to a steel bearing shell are described by E. Knipp.[74] The steel shell may first be coated by dipping in molten bronze, and then placed in a sand mould and the bronze cast in. Alternatively, the lining may be applied by dipping the shell fitted with a lining jig into a bath of bronze, or the lining may be cast on to the shell in a centrifugal machine. The influence of casting temperature on bond strength is determined, using a tensile test ; bonding at 1000—1150° gives the best results. Ordinary tin- or lead-bronze may be applied and may subsequently be coated with bearing metal. The bonding of heavy metals to steel is discussed together with economic considerations. A. G. E. Robiette[75] discusses the manufacture of composite or clad metals. Steel faced on one side or on both sides with nickel, copper, nickel–copper alloys, or stainless steel is produced by heating the two components by high-frequency heating in a non-oxidising atmosphere and then bonding them by pressure, *e.g.*, rolling, while still in the non-oxidising atmosphere. A layer of iron powder may be introduced between the two components, or one component may be slightly decarburised to assist bonding.

CORROSION.

Practical problems connected with metallic corrosion are discussed by U. R. Evans.[76] If steel can be thoroughly cleaned, preferably by shot-blasting, excellent protection against corrosion is secured by first spraying with aluminium from a wire pistol and then painting. For uncleaned steel, promising results have been obtained by the use of inorganic cementiferous paints (composition not yet revealed) or organic paints

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[71] Assr. to Eaton Manufacturing Co., U.S.P. 2,202,648 ; B., 1946, I, 37.

[72] B.P. 577,892 ; B., 1946, I, 341.

[73] Assr. to Electro Metallurgical Co., U.S.P. 2,334,869–70 ; B., 1946, I, 144.

[74] *Metallwirts.*, 1940, **19**, 421 ; B., 1946, I, 37.

[75] B.P. 571,937 ; B., 1946, I, 39.

[76] *J. Birmingham Met. Soc.*, 1945, **24**, 228 ; B., 1946, I, 68.

with a polystyrene or chlororubber base richly pigmented with sufficient zinc dust to be electrically conducting. For cooling systems, where anodic inhibitors are known to be dangerous (they may accelerate attack if present in insufficient amounts), the use of cathodic and anodic inhibitors for alternate periods may be safe and efficient. Tests on corrosion-fatigue indicate that exposure to this condition for only a short period may have a most damaging effect on the resistance of steel when subsequently exposed to simple fatigue stressing, even though all corrosive influences are then excluded. The effect of different methods of cleaning on the subsequent indoor atmospheric corrosion of mild steel has been investigated by C. W. Smith.[77] Solvent, alkaline, and electrolytic cleaning methods left the surface readily corrodible. Different emulsions of a mixture of moderately volatile petroleum solvents cleaned the steel, and left a surface which could be stored or further processed without rusting.

G. Seelmeyer[78] reports on the corrosion of steel plates with copper inserts by distilled water and 1% sodium chloride solution. The rate of attack by the latter is roughly twice that by water. Generally, as the ratio of copper area to iron area is increased, the rusting and loss in weight are diminished. After 60 days' immersion, weight loss was greatest with iron alone. Only after 10- and 24-day tests is the weight loss of iron alone less than that when small areas of copper (up to 10%) are present.

The corrosion of austenitic stainless steels at artificial crevices produced by contact with bakelite washers has been studied in sea-water, and the effect of different protective compounds investigated by E. H. Wyche, L. R. Voigt, and F. L. La Que.[79] The latter comprised lead soaps in polymerised oxygenated hydrocarbons (*e.g.*, Alox 707A, with and without shellac), a paste of copper powder in petrolatum, petrolatum alone, and other proprietary greases and soaps. The copper paste was less effective than petrolatum alone, but more effective than the other compounds. The use of copper instead of bakelite washers had no beneficial effect. Practical recommendations for the avoidance of crevice-corrosion are given. E. M. Mahla and N. A. Nielsen[80] have treated austenitic and ferritic stainless steels in nitric acid, nitric acid with potassium dichromate, and other acid or basic oxidising solutions, and by heating and electrolytic oxidation. Breakthrough-potential and immersion-corrosion tests showed that no lasting protection is obtained in media which normally corrode the untreated metal. Reflexion electron diffraction studies provided no definite evidence of passive films, but bulk oxides produced on 18–8 steel by chemical or atmospheric oxidation consisted mainly of chromic oxide. The bulk oxides produced on iron–chromium alloys by atmospheric oxidation consisted of ferrous, ferrosoferric, and ferric oxides. The different mechanism of oxidation of the two types of steel remains unexplained.

[77] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 25, 289; B., 1946, I, 300.

[78] *Korros. u. Metallschutz*, 1943, **19**, 38; B., 1946, I, 69.

[79] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 23, 265; B., 1946, I, 300.

[80] *Ibid.*, *Preprint* 27, 319; B., 1946, I, 300.

NON-FERROUS METALS.

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Ores and Extraction.

Details of plant and a process are described[1] for the selective concentration by flotation of complex Peruvian lead–zinc ores containing copper (0·75—2·75%) mainly as pyrite, zinc (7—20%) as sphalerite, lead (trace—7·5%) as galena, and silver (4·3—13 oz. per ton) as argentiferous tetrahedrite-tennantite. The ores are mixed, ground to 60% passing 200-mesh, and fed into the flotation mill. Lead and copper are separated first by usual flotation methods; zinc sulphate and cyanides are used to depress the sphalerite. About 90% of the silver, 85% of the copper, and 80% of the lead are recovered in the bulk concentrate. For zinc flotation a fairly high alkalinity is maintained to depress pyrite and about 80% of the zinc is recovered.

Molybdenite in Colorado ores is concentrated by grinding in steel ball mills in closed circuit with Atkins high-weir classifiers, and the classifier overthrow is transferred to the flotation sections, consisting of 39 Weinig sub-aëration cells in series[2]; copper and iron are eliminated by flotation, using pine oil with the addition of white oil and a wetting agent. R. E. Cuthbertson[3] describes an investigation of the dressing of molybdenite in an experimental plant. Grinding with steel balls is shown to contaminate the molybdenum sulphide with iron, and a higher recovery (99·8%) is obtained with a porcelain mill. Increased recovery is made possible by the use of improved flotation reagents. Copper can be eliminated by leaching with sodium cyanide solution.

F. C. Mannox and H. J. Miller[4] have reported on copper smelting and refining at Nord-Deutsche Affinerie, Hamburg. The concentrates were roasted, smelted in reverberatory furnaces, and blown in converters to blister copper, which was refined in reverberatory furnaces and cast into anodes or wire bars; the anodes were refined electrolytically. A description of concentrating and smelting operations of the Magma Copper Co., Arizona, has been given by E. J. Caldwell[5]; copper–zinc concentrates are recovered by flotation and the copper concentrates are roasted in Herreshoff roasters, smelted in a natural gas-fired reverberatory furnace, and blown to blister copper in magnesite-lined converters.

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[1] T. R. Wright, *Min. and Met.*, 1945, **26**, 534; B., 1946, I, 70.

[2] E. J. Duggan, *ibid.*, 1946, **27**, 323; B., 1946, I, 339.

[3] *Ibid.*, 346; B., 1946, I, 339.

[4] *Brit. Intelligence Objectives Sub-Commee.*, 1946, *Final Rept.* 26, *Item* 21; B., 1946 I, 303.

[5] *U.S. Bur. Mines*, 1944, *Inf. Circ.* 7300; B., 1946, I, 337.

An investigation of the German tin smelting and allied industries has been carried out and reported on by P. G. J. Gueterbock, E. S. Hedges, E. H. Jones, C. Waite, and W. J. Wilcoxson.[6] The greater part of this report is concerned with three firms engaged in treating low-grade ores and residues for the recovery of tin and other metallic constituents in saleable form. At the works of Berzelius Metallhütten, G.m.b.H., Duisburg, the final products were tin, solder, and tin- and lead-base bearing alloys. The raw material, consisting of ores, slags, oxides, ashes, residues, etc., was smelted in a reducing blast furnace of conventional design. The products of this stage were unrefined tin, slags containing 3—7% of tin, matte, and flue dust. Thç flue dust was collected in an electrostatic plant and returned to the blast furnace; the matte was blown in a converter; slags containing more than 4% of tin were returned to the reducing blast furnace, but those containing less tin went to the volatilisation blast furnace. The unrefined tin was liquated, the drosses being returned to the blast furnace, while the liquated tin was refined in kettles for removal of copper, iron, arsenic, and zinc. The refined tin was cast into ingots or into anodes for electrolytic refining, or made into solder or bearing metal. A large tubular rotary furnace, with electrostatic fume collector, was used for separating zinc from materials containing zinc, tin, lead, etc. Two processes were carried out in the tubular furnace: (*a*) the Waelz process, in which the metals are volatilised and recovered as tin–lead–zinc oxides, and (*b*) the Berzelius process, in which the charge is mixed with coal and washing soda, the zinc being volatilised and recovered as zinc oxide, while tin and lead are reduced to a fluid alloy. At the works of Nord-Deutsche Affinerie, Hamburg, tin–lead–zinc fume from the converting of bronzes was mixed with coal and soda and smelted in a reverberatory furnace, the zinc being volatilised. After removal of copper and arsenic, an alloy containing about 60% of tin, 2% of antimony, and the remainder lead was marketed. Any tin metal recovered was on orthodox lines from the refining of lead by the Harris process. At the Zinnwerke Wilhelmsburg, G.m.b.H., Hamburg, tin–lead alloy was recovered from converter and blast-furnace fumes. By careful segregation of raw materials into brass and bronze scrap, respectively, the fume was made either high enough in zinc for sale to zinc smelters or to be used as pigment, or, on the other hand, was made low in zinc and rich in tin. Tin and lead were separated from zinc by reduction in a reverberatory furnace with re-oxidation of zinc after volatilisation. The impure tin alloy was refined by conventional methods. The report also covers a visit to Goldschmidt's works at Essen, where tin was recovered from tinplate scrap by the well-known chlorine process and also by a non-electrolytic alkaline process. In the latter process the baled scrap was torn apart by machinery of special design and stripped with concentrated alkali and sodium nitrate. Sodium stannate, obtained by

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[6] *Brit. Intelligence Objectives Sub-Commee.*, 1946, *Final Rept.* 372, *Item* 21.

crystallisation, was recrystallised and smelted to 99·9% tin in a reverberatory furnace. A lower grade, containing 99·5% of tin, was made when the stannate was not recrystallised, the impurity being lead. The de-tinning plants were entirely wrecked by bombing.

J. M. Avery and R. F. Evans[7] have described the production of magnesium from dolomitic lime used in the ammonia stills of the ammonia-soda process; magnesium chloride is recovered from the blow-off liquor. The solution is thickened and, after filtering off calcium carbonate, is evaporated to produce the feed for Dow electrolytic cells. E. C. Houston[8] reports that partly hydrated magnesium chloride, suitable for treatment by the Dow process, has been produced from olivine on a pilot-plant scale. The finely ground olivine is extracted with 20% hydrochloric acid, neutralised with magnesia, and the siliceous residue separated by decantation. The solution, after purification by adding magnesia and filtering off precipitated hydroxides, is evaporated to produce feed for the Dow cells. The production of electrolytic magnesium starting with magnesia in a pilot plant is described by R. R. Lloyd, C. K. Stoddard, K. L. Mattingley, E. T. Leidigh, and R. G. Knickerbocker[9]; the final stage consists in electrolysis at 800—815° of a melt containing magnesium, sodium, and calcium chlorides. W. J. Kroll[10] has compiled an annotated review of methods of producing beryllium and its alloys.

A process for the electrolytic production of 99·94% manganese from Chamberlain (S. Dakota) nodules has been worked out on a pilot-plant scale by J. H. Jacobs and J. W. Hunter[11]; after successive stages for the removal of iron, nickel, copper, sulphur, arsenic, molybdenum, and magnesium, the final electrolysis is carried out in lead-lined wood cells with anodes of 99% lead, 1% silver and cathodes of stainless steel; recovery is 82—86%. G. L. Allen, J. H. Jacobs, and J. W. Hunter[12] discuss plants for the utilisation of an unmined reserve of about 3 million tons of manganese ore in Nevada. J. H. Jacobs, F. K. Shelton, and R. G. Knickerbocker[13] have examined the cobalt contents of a large number of manganese ores and devised means of separating and electrodepositing manganese and cobalt from the electrolytes. F. K. Shelton[14] has investigated the analysis of cobalt ores, their concentration by flotation, leaching of cobalt concentrates, the purification of leached solutions, and electrolysis to obtain cobalt.

The production of metallic calcium by reduction of lime with aluminium in a vacuum at 1200° is described by C. C. Loomis.[15] The calcium distils over and is condensed in a water-cooled receiver; it may be extruded into

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[7] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1829; B., 1946, I, 140.

[8] *Ibid.*, 1828; B., 1946, I, 141.

[9] *Ibid.*, 1848; B., 1946, I, 140.

[10] *U.S. Bur. Mines*, 1945, *Inf. Circ.* 7326; B., 1946, I, 247.

[11] *Ibid.*, 1946, *Rept. Invest.* 3862; B., 1946, I, 271.

[12] *Ibid.*, 1945, *Rept. Invest.* 3815; B., 1946, I, 338.

[13] *Ibid.*, 1946, *Rept. Invest.* 3866; B., 1946, I, 304.

[14] *Ibid.*, 3836; B., 1946, I, 208.

[15] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 9, 119; B., 1946, I, 208.

rods and subsequently rolled. W. J. Kroll[16] has discussed the chemistry of the Guntz process for making barium by reduction of the oxide with aluminium or silicon. Ductile zirconium has been made from zircon sand.[17] Mixed zirconium and silicon carbides, made by heating the sand with carbon, are chlorinated and the zirconium tetrachloride is purified by sublimation in hydrogen and reduced by magnesium; excess of magnesium and magnesium chloride is removed by vacuum distillation and the zirconium residue melted in a vacuum arc furnace.

PROPERTIES.

In an investigation of the damping capacity and change in elastic modulus of a number of metals and alloys, A. Karius[18] concludes that in all polycrystalline materials the changes due to fatigue are of the same nature and follow the same course with increased cycles of stress. As the number of cycles is increased damping capacity rises and elastic modulus falls, apparently owing to cold-working. Although these effects practically disappear with further time of testing at moderate stresses, they recur shortly before fracture, owing to the formation of macroscopic cracks. The volume of stressed material in the test piece determines the initial changes in properties and the effects extend throughout that volume and are not confined to points where failure occurs later. The changes in properties just before fracture are independent of the volume, except in specimens with sharp notches, where deviations can be traced to cracks at the notch. The effects occurring in the early stages of fatigue testing can be eliminated in part by storing at room temperature or by low-temperature heat-treatment, owing to the reduction of internal stress which would lead later to the formation of macroscopic cracks.

P. W. Bridgman[19] has reviewed some of the effects of high hydrostatic pressure on the plastic properties of metals. Under these conditions most metals show greatly increased ductility and a small increase in tensile strength. As the surrounding pressure is increased, tensile test pieces break with progressively greater reduction of area. Tensile tests carried out at atmospheric pressure after subjecting the material to high pressure show that anisotropy has been developed.

D. J. McAdam, jun., G. W. Geil, and R. W. Mebs[20] have carried out tension tests of notched rods of monel, nickel, plain and leaded phosphor-bronzes, and commercial and high-purity aluminium from room temperature down to that of liquid air and obtained correlations between the stress system and the resistance to plastic deformation, resistance to fracture, and ductility, respectively; the effect of plastic deformation on cohesive strength was found to be much greater than is usually claimed.

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[16] *U.S. Bur. Mines*, 1945, *Inf. Circ.* 7327; B., 1946, I, 32.

[17] W. J. Kroll, A. W. Schlechten, and L. A. Yerkes, *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 29, 365; B., 1946, I, 304.

[18] *Metallwirts.*, 1944, **23**, 419; B., 1946, I, 108.

[19] *Rev. Mod. Physics*, 1945, **17**, 3; B., 1946, I, 73.

[20] *Amer. Soc. Metals*, 1945, *Preprint* 18; B., 1946, I, 167.

The influence of small amounts (up to 0·05%) of phosphorus, arsenic, sulphur, and selenium on the electrical conductivity of copper has been determined by J. S. Smart, jun., and A. A. Smith, jun.[21]; softening temperatures of the cold-worked alloys were also determined and from the results the solubilities of the added elements in solid copper under the annealing treatments employed were estimated.

W. T. Pell-Walpole[22] has determined the density, mechanical properties, and rolling and annealing characteristics of binary tin bronzes containing from 2 to 14% of tin, prepared by methods devised to give maximum soundness and freedom from porosity. The density curve is shown to have a shallow minimum at 6% of tin. The tensile strength of cast alloys increases rapidly with increasing tin content to 25 tons per sq. in. at 10% of tin and then slowly to 26·5 tons per sq. in. at 14% of tin. When the δ phase is eliminated by annealing, the density falls slightly in all alloys and a slight decrease in tensile strength occurs in alloys with tin contents below 10%, but at higher tin contents the tensile strength increases to a maximum of 29 tons per sq. in. with 14% of tin. The work-hardening capacity of these bronzes in the wrought condition increases regularly with tin content up to 8% and then remains constant up to 14% of tin. The softening range for rolled strip is 300—350° for all the compositions, but with further increase of annealing temperature up to 650° a gradual decrease in hardness and strength and an increase in elongation occur, probably owing to grain growth. Using the same methods of ensuring sound ingots, K. Winterton[23] has measured the density, hardness, and tensile properties of chill-cast bronzes containing 10—20% of tin with 0—0·7% of phosphorus and 5—10% of tin with 0—2·5% of phosphorus, respectively. W. T. Pell-Walpole, V. Kondic, and P. G. Forrester[24] have determined the solidus and α solubility limits for aluminium–tin bronzes containing 5—18% of tin and 0—8% of aluminium and investigated the working properties of these alloys; difficulties in rolling are shown to be associated with interdendritic porosity which may result from gas absorption, or from shrinkage effects, or from the entrapping of oxide films during pouring, but by suitable melting and casting procedure the porosity may be reduced sufficiently to permit hot and cold rolling of alloys in the α range. The work-hardening and annealing characteristics of the alloys are, in general, similar to those of binary tin bronzes; the mechanical properties vary regularly with both tin and aluminium contents, 1% of aluminium being approximately equivalent to 2% of tin in this respect. All the alloys recrystallise completely after one hour at 350—400°. Low-temperature heat-treatment (50—250°) of the hard-rolled alloys causes slight temper-hardening, accompanied by intercrystalline precipitation.

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[21] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1807.

[22] *J. Inst. Metals*, 1946, **72**, 19; B., 1946, I, 138.

[23] *Ibid.*, 1945, **71**, 581; B., 1946, I, 138.

[24] *Ibid.*, 1946, **72**, 293; B., 1946, I, 425.

The mechanical properties of a series of copper–manganese–zinc alloys containing 60% of copper and from 5 to 25% of manganese have been investigated in the annealed and cold-worked states by R. S. Dean, J. R. Long, T. R. Graham, and R. G. Feustel.[25] The maximum strength occurs in the 5% manganese alloy, which when annealed has a tensile strength of 67,000 lb. per sq. in., Rockwell hardness B61, and elongation 39%. The effects of annealing treatments on the properties and structure of the alloys were examined.

T. E. Leontis and J. P. Murphy[26] have examined the properties of magnesium–cerium alloys containing up to 10% of cerium at temperatures up to 370°. These alloys retain much of their strength at about 200° and show high creep-resistance over a wide range of temperatures. These properties are further improved by addition of manganese, and if the manganese exceeds 1·1% corrosion-resistance in sodium chloride solution is also greatly increased. Additions of aluminium increase the ductility and electrical conductivity, but at the expense of loss of strength at high temperatures.

The heat content of manganese between 298·16° K. and 1440° K. has been measured by B. F. Naylor,[27] and three transitions at 1000 ± 2°, 1374 ± 5°, and 1440 ± 5° K. were observed. C. H. Shomate[28] has determined the specific heats of α- and γ-manganese over the range 52—298° K. B. F. Naylor[29] has also determined the heat contents of manganese–copper alloys containing from 25 to 90% of manganese in the range 450—850°. O. Kubaschewski[30] has measured the mean specific heats between room temperature and temperatures in the region of the melting points for alloys of gold and silver with zinc and cadmium and for the intermetallic compounds AuSn and $AuPb_2$.

F. Trombe and M. Foex[31] deduce from magnetic measurements on cerium that three allotropic forms of the metal exist. γ-Cerium, which is formed when the fused metal is cooled quickly, is stable at room temperature; this form is transformed into β when cooled slowly from 200° to room temperature, but the transformation is complete only after several cycles of slow heating and cooling between room temperature and −195°; α-Cerium is formed when γ is cooled rapidly to about −195°; the reverse transformation occurs at about −100° on warming. The preparation of ductile titanium by reduction of titanium tetrachloride by molten magnesium, followed by compacting and sintering at 1000° of the powdered metal, has been described by R. S. Dean, J. R. Long, F. S. Wartman, and E. L. Anderson.[32] A further paper by R. S. Dean, J. R.

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[25] *Amer. Inst. Min. Met. Eng.*, 1946, *Tech. Publ.* 1956; B., 1947, I, 36.

[26] *Ibid.*, *Tech. Publ.* 1995; B.,1946, I, 382.

[27] *J. Chem. Physics*, 1945, **13**, 329; A., 1945, I, 299.

[28] *Ibid.*, 326; A., 1945, I, 299.

[29] *U.S. Bur. Mines*, 1946, *Rept. Invest.* 3835; A., 1946, I, 180.

[30] *Z. physikal. Chem.*, 1943, **192**, 292; A., 1946, I, 87.

[31] *Ann. Chim.*, 1944, [xi], **19**, 417; A., 1945, I, 332.

[32] *Amer. Inst. Min. Met. Eng.*, 1946, *Tech. Publ.* 1961; B., 1946, I, 339.

Long, F. S. Wartman, and E. T. Hayes[33] describes the physical properties and fabrication of this product. The sintered material, after reduction by about 25% by cold forging, has a tensile strength of 115,000 lb. per sq. in. with 6% elongation. The forged and annealed material may be cold-rolled to about 50% reduction, giving a tensile strength of 123,000 lb. per sq. in. On rolling at 500° a tensile strength of 101,700 lb. per sq. in. with 10% elongation is attained with 80% reduction. Rods of the material have been drawn into wire with intermediate annealing in air at 600°.

A paper on the adhesion of tin-base bearing alloys to steel has been published by P. G. Forrester and L. T. Greenfield.[34] The value of the adhesion depends on the composition of the whitemetal; in particular, alloys of high copper content have low bond strengths, owing to a tendency for the brittle Cu_6Sn_5 phase to form on the bond, but by very rapid cooling the segregation of Cu_6Sn_5 may be wholly or partly overcome. Whilst the existence of this layer greatly reduces the resistance of the bond to tearing or to impact, its effect is not shown up by a pure shear test. The bond is weakened in a similar manner by a thick layer of $FeSn_2$ formed by prolonged pre-tinning treatment or by tinning at high temperatures. It is shown that when up to 3% of cadmium is added to tin–antimony–copper alloys good bond strengths may be obtained by slow cooling.

The frictional properties of bearing alloys have continued to receive study. F. P. Bowden and A. J. W. Moore[35] have demonstrated that when a clean, curved, copper slider is passed under load over a steel surface, welding of the two metals takes place extensively; with lubricated surfaces welding occurs to a smaller extent. D. Tabor[36] has made comparisons in both tin-base and lead-base bearing alloy systems of alloys containing particles of a hard disperse phase with alloys of the composition of the matrix. Sliding-friction measurements on a steel surface with and without lubrication showed that the hard particles are without appreciable influence on the frictional properties. The friction coefficient–temperature curves of the bearing alloy and of the matrix alloy agreed, but differed strongly from those of the pure metals tin or lead. New apparatus and technique for the measurement of kinetic friction in or near the region of boundary lubrication have been described by B. Chalmers, P. G. Forrester, and E. F. Phelps.[37] With the aid of this apparatus, P. G. Forrester[38] has investigated the causes underlying change of friction with sliding velocity. Several combinations of materials, including bearing alloys, were examined (*a*) in the clean, dry state, (*b*) with excess of various lubricants, and (*c*) with thin films of lubricants. It is concluded that the following factors are involved in defining the frictional properties of a combination of materials: (1) the friction–velocity curve without

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[33] *Amer. Inst. Min. Met. Eng.*, 1946, *Tech. Publ.*, 1965; B., 1946, I, 339.
[34] *J. Inst. Metals*, 1946, **73**, 91.
[35] *Nature*, 1945, **145**, 451; B., 1946, I, 70.
[36] *J. Appl. Physics*, 1945, **16**, 325; B., 1945, I, 365.
[37] *Proc. Roy. Soc.*, 1946, **A**, **187**, 430.
[38] *Ibid.*, **439**.

lubrication ; (2) the resistance to breakdown of the boundary film ; (3) the low-speed value of friction coefficient, representing an approximation to the true boundary coefficient; (4) the effect of running-in on the low-speed value of friction; (5) the tendency to fluid film formation and the effect of running-in on this tendency; (6) the influence of surface finish on the low-speed value of friction and on the transition from boundary to fluid film formation.

CONSTITUTION AND STRUCTURE.

In the ternary system magnesium–aluminium–silver, V. G. Kuznetzov and L. N. Guseva[39] have distinguished by thermal analysis and micrographic methods the existence of three intermetallic compound phases, Mg_3Ag, Mg_4Al_3, and MgAg. V. G. Kuznetzov[40] has also determined the lattice parameters of the ternary solid solution of aluminium and silver in magnesium at various temperatures, using the X-ray powder method. The common solubility of silver and aluminium in magnesium increases with temperature, as in a binary system. The solubility of magnesium at 300° and 200° increases markedly with addition of aluminium. At 300° the solubility of aluminium is not changed by the addition of silver; at higher temperatures it first increases and then decreases. The existence of the compound $Mg_4Na_4Pb_3$ has been shown by thermal investigation of the magnesium–sodium–lead system[41]; the compound is corroded by moist air and reacts vigorously with water or acid.

W. A. Anderson and R. F. Mehl[42] have measured the rate of recrystallisation of cold-worked high-purity aluminium. In sheets so thin that the recrystallised grain size is greater than the sheet thickness, the rate of nucleation increases with time at any temperature, but the rate of growth remains invariant. Both rates increase with increase in deformation, but nucleation increases more rapidly, thus producing a fine grain size after severe deformation. Thick sheet recrystallises less rapidly, probably owing to the effect of preferred orientation. Microscopical examination and chemical evidence indicate that AlAs is the only definite compound formed in the aluminium–arsenic system[43]; this compound, which may be obtained by the action of arsenic on aluminium at 400°, is decomposed by water or moist air, liberating arsine. Solidus determinations in this system cannot be made, as arsenic is lost by evaporation before fusion. The constitution of the aluminium-rich ternary and quaternary alloys of aluminium–magnesium–silicon and iron has been investigated both as slowly cooled and in the equilibrium condition by H. W. L. Phillips.[44] In addition to the constituents Mg_2Si,

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[39] *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 297; A., 1946, I, 80.
[40] *Ibid.*, 420; A., 1946, I, 245.
[41] G. Calingaert, H. Shapiro, and I. T. Krohn, *J. Amer. Chem. Soc.*, 1946, **68**, 520; A., 1946, I, 261.
[42] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1805; B., 1946, I, 182.
[43] E. Montignie, *Bull. Soc. chim.*, 1942, [v], **9**, 739; A., 1945, I, 315.
[44] *J. Inst. Metals*, 1946, **72**, 151; A., 1947, I, 46.

Mg_2Al_3, $FeAl_3$, α, β, and silicon, all of which occur in the various binary and ternary systems, the quaternary alloys contain a phase of variable composition designated π; this is the product of a peritectic reaction between β and liquid, but may crystallise independently. These alloys may be modified by addition of sodium, which causes selective under-cooling of the silicon, thus bringing about corresponding shifts in the phase boundaries. A thermodynamical treatment of the quaternary system has also been published by H. W. L. Phillips.[45]

Using new experimental technique, N. B. Bever and C. F. Floe[46] fix the solubility of carbon in molten copper at about 0·0001% at 1100° and 0·003% at 1700°; it is suggested that these amounts, although small, may be a contributory cause of gas porosity in copper and copper-base alloys. L. Northcott[47] has studied the dendritic structure of columnar crystals in specially prepared ingots of an α-copper–aluminium alloy. Wide columnar crystals are composed of a series of cruciform columns oriented n the direction of growth with very little side branching and do not consist of rods having rod-shaped secondary and tertiary branches. The columnar nature of the dendritic structure is governed by the ratio of the temperature gradient normal to the cooling face to that parallel to the cooling face. A welcome addition to the scanty literature on the structure of electrolytically deposited alloys has been published by E. Raub and D. Krause.[48] *X*-Ray examination of copper–zinc alloys deposited under different conditions of electrolysis shows that, apart from the super-structure of β-brass, the same phases occur as in corresponding alloys prepared by melting and casting, and the phase limits agree closely. There is, however, considerable lattice distortion, particularly with the α phase, but this is without influence on the specific resistance of the alloys. Electrodeposited α-brass is harder than the cast form, but there is no corresponding difference in the hardness of the β, γ, and ϵ phases.

The crystallisation of tin has been studied by J. J. Arlman and R. Kronig.[49] Peculiarities in the Laue photographs are interpreted by supposing that in the tin crystals there are regions of larger extent in which the location of the atoms conforms with the ideal lattice and in which the Laue spots originate. Between them are transition regions in which the correlation of the interatomic distances is lost by a displacement of entire rows of tin atoms along their own direction parallel to one of the a-axes, and such rows will then scatter as one-dimensional lattices. C. G. Fink, E. R. Jette, S. Catz, and F. J. Schettler[50] have presented a phase diagram for the tin–indium system based on lattice constant, density, thermal, and conductivity measurements. The phases β and γ, both of which are soft and ductile, are formed by peritectic reactions at

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[45] *J. Inst. Metals*, 1946, **72**, 229; A., 1947, I, 46.

[46] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1802.

[47] *J. Inst. Metals*, 1946, **72**, 283; A., 1947, I, 45.

[48] *Z. Elektrochem.*, 1944, **50**, 91; B., 1946, I, 70.

[49] *Physica*, 1943, **10**, 795; A., 1946, I, 307.

[50] *Trans. Electrochem. Soc.*, 1945, **88**, *Preprint* 15, 161; A., 1946, I, 44.

126·5° and 124·0° respectively, but no arrest points were detected for the peritectic reaction on the indium-rich side of γ; the eutectic point is at 116·3° and 48·5 at.-% of tin. R. O. Frantik and H. J. McDonald[51] have reported thermodynamical studies of the tin–antimony and tin–silver systems. Thermodynamical studies of molten binary alloys of tin with gold, antimony, and silver have also been made.[52] Deviations of the activities of the solvent increasing with the concentration of the solute are negative for alloys containing gold or antimony and positive for those containing silver. The crystal structure of Ni_5Sn_4 has been determined by H. Nowotny and K. Schubert[53]; the unit cell has a 12·20, b 4·055, c 5·215 A., β 105° 2′, and contains two molecules. As the temperature is raised the narrow range of existence of the compound is extended to higher concentrations of nickel (29%). The cell undergoes gradual change to a 12·29, b 4·055, c 5·171 A., β 103° 57′, with increase of nickel concentration. New determinations of the solid solubilities of tin and lead have been carried out by G. Borelius, F. Larris, and E. Ohlsson[54]; the solubility of tin in lead is placed at 18 wt.-% at 182·5° and that of lead in tin at 2·5 wt.-% at 183°. These data were obtained in the course of an investigation of the kinetics of precipitation in this alloy system. The system tin–lead–silver has been investigated by L. G. Earle[55]; the composition of the ternary eutectic is determined as Sn 62·5, Pb 36·15, Ag 1·35%, and its melting point 178°. The data obtained are discussed from the viewpoint of application of the tin–lead–silver alloys to soft soldering. Equilibrium in the ternary system bismuth–lead–zinc has been studied by S. D. Muzaffer and R. Chand[56]; a ternary eutectic occurs at Bi 55, Pb 43, Zn 2%, solidifying at 124°.

The lattice spacing of lithium at 20°, as determined by K. Lonsdale and W. Hume-Rothery,[57] is $a = 3{\cdot}503$ A.; the corresponding value at −183° is 3·4762 A. W. Hume-Rothery and K. Lonsdale[58] report the lattice spacing of rubidium at −183° as 5·624 A. and at 18·5° 5·698 or 5·699 A. F. Endter and W. Klemm[59] report that the interatomic distances in Mn_2Gd are Mn—Gd 3·21 A., Gd—Gd 3·22 A. The solubility of silver in mercury has been determined by D. R. Hudson[60] over the temperature range 16—961°. Between 330° and 450° the solubility can be represented by $\log N = 2{\cdot}9065 - 2481{\cdot}8T^{-1}$, where N is the molecular fraction of silver in mercury; below and above this temperature range $\log N = 0{\cdot}67035 - 1134{\cdot}7T^{-1}$ and $0{\cdot}7441 - 918{\cdot}2T^{-1}$, respectively.

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[51] *Trans. Electrochem. Soc.*, 1945, **88**, *Preprint* 21, 219; *Preprint* 22, 229; A., 1946, I, 77.

[52] J. A. Yanko, A. E. Drake, and A. Hovorka, *ibid.*, 1946, **89**, *Preprint* 31, 151; A., 1946, I, 247.

[53] *Naturwiss.*, 1944, **32**, 76; A., 1946, I, 147.

[54] *Arkiv Mat., Astron., Fys.*, 1944, **31**, A.

[55] *J. Inst. Metals*, 1946, **72**, 403; B.. 1946, I, 425.

[56] *J. Amer. Chem. Soc.*, 1944, **66**, 1374; A., 1945, I, 22.

[57] *Phil. Mag.*, 1945, [vii], **36**, 799.

[58] *Ibid.*, 842.

[59] *Z. anorg. Chem.*, 1944, **252**, 377; A., 1946, I, 76.

[60] *J. Physical Chem.*, 1945, **49**, 483; A., 1946, I, 114.

An interesting investigation of the structure of electrolytically polished metal surfaces, using electron interference as a method of examination, has been published by W. Kranert, K. H. Leise, and H. Raether.[61] A better polish can be obtained on a single-crystal surface than on a polycrystalline surface. The interference diagram of a polycrystalline electrolytically polished surface shows points in place of the usual ring, the points being elongated towards angles less than the corresponding Bragg angle. The upper ends of the tailed spots lie on the normal powder ring. Interference patterns show that electrolytic polishing is effected by removal of projections on the surface, in contrast to mechanical polishing where the projections are pushed into hollows. The roughening of a surface by electrolytic etching of previously electrolytically polished surfaces can also be followed by the appearance of the spots on the interference diagram, which become rounder as the surface becomes rougher. With orthophosphoric acid as electrolyte a layer about 1000 A. thick can be removed before the roughening of the surface is detectable.

HEAT-TREATMENT AND PRECIPITATION-HARDENING.

M. L. V. Gayler[62] has studied the changes in microstructure occurring on ageing at room temperature and at 130° of a high-purity aluminium alloy containing 4% of copper, cooled at different rates from the solution heat-treatment temperature, and has correlated the results with changes in Brinell hardness. Decrease in the rate of quenching has a pronounced effect on subsequent ageing at room temperature, but ageing curves at 130° differ only in the early stages. The evidence is stated to prove that the age-hardening of these alloys is due to the precipitation of copper or copper-rich particles and to the simultaneous formation of crystallites of the aluminium solid solution stable at the temperature of ageing and not to the precipitation of either α- or β-$CuAl_2$. The precipitation of the copper-rich aggregates is a discontinuous process, whilst the precipitation of α-$CuAl_2$ in alloys aged above room temperature is a continuous process. Further work by the same author[63] is concerned with the effect of cold-work on the same alloy in relation to its age-hardening properties. It is shown that cold-work accelerates the rate of ageing by an amount determined by the degree of cold-work given. The effect of cold-work on a quenched specimen is to bring it into the fully aged state normally produced by ageing at room temperature. Lattice strain caused by cold-work is relieved by the formation of sub-microscopic or microscopic crystallites and, simultaneously, sub-microscopic precipitates of copper-rich particles. The mechanism of the relief of strain caused by cold-work is similar to that which occurs in the relief of strains set up during age-hardening. G. Borelius and L. Ström[64] have measured the heat evolution

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[61] *Z. Physik*, 1944, **122**, 248; A., 1946, I, 70.

[62] *J. Inst. Metals*, 1946, **72**, 243; B., 1946, I, 428.

[63] *Ibid.*, 543.

[64] *Arkiv Mat., Astron., Fys.*, 1945, **32**, **A**.

corresponding to precipitation at 225° as a function of time for alloys containing from 2·0 to 4·5% of copper. The dominating process is said to be the precipitation of fine, flat grains of the metastable θ' phase having the composition $CuAl_2$. The heat evolution–time curves are initially linear, pass through a maximum, and then decrease approximately exponentially with time.

The mechanical properties and corrosion-resistance of age-hardened aluminium–zinc–magnesium–copper alloys have been investigated by K. L. Dreyer and H. J. Seeman[65]; the best alloy contains Zn 4·5, Mg 1·5, Cu 1·5, and Mn 0·7%. P. Lacombe[66] has conducted thermal, electrode-potential, metallographic, and X-ray investigations on aluminium–magnesium, aluminium–zinc, aluminium–magnesium–zinc, and aluminium–copper alloys after different heat-treatments. In the aluminium–magnesium alloys X-ray examination during the process of ageing showed an increase of the lattice parameter before precipitation and a decrease after precipitation had begun. The stages in the decomposition of the solution are considered to be: disordered solution, ordered solution, formation of unstable intermediate phase oriented with respect to the solid solution, and formation of a stable coalesced phase of random orientation. A slight addition of zinc to aluminium–magnesium alloys makes them susceptible to age-hardening at room temperature.

The mechanism of age-hardening of copper containing 2·3% of beryllium has been studied by A. Guinier and P. Jacquet[67] by the microscopical and X-ray examination of electropolished specimens. The first stage in the decomposition of the homogeneous α solid solution on heating consists in the formation of small, flat nuclei dispersed parallel to the cubic faces of the crystals, the composition being different from that of the solution. Other beryllium atoms migrate to the nuclei and the γ phase is progressively formed. H. Thomas[68] has measured the volume and electrical resistance changes occurring in a series of quenched and age-hardened alloys of copper containing from 0·9 to 3·6% of beryllium. At 170° there was noticed a contraction in volume and an increase in resistance due to low-temperature temper-hardening; at 280° some reversion phenomena occurred; at 300—375° volume and resistance decreased quickly as a result of precipitation-hardening; and at 400—600° reversion phenomena again occurred, accompanied by a slow increase in volume and resistance. Anomalous changes occurring in alloys containing more than 3·6% of beryllium are ascribed to the eutectoid transformation $\alpha + \gamma = \beta$, which takes place between 601° and 618°, causing an increase in volume and resistance.

The casting, work-hardening, annealing, and heat-treatment characteristics and physical properties of copper rich alloys containing up to 30%

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[65] *Aluminium*, 1944, **26**, 76.

[66] *Rev. Mét.*, 1944, **41**, 180, 217, 259; B., 1946, I, 209.

[67] *Ibid.*, 1; B., 1946, I, 208.

[68] *Z. Metallk.*, 1944, **36**, 136.

each of nickel and manganese have been investigated by M. Cook and W. O. Alexander.[69] Alloys containing more than 7% each of nickel and manganese can be temper-hardened, the extent of the hardening increasing with the nickel and manganese contents. For a given amount of alloying additions the maximum hardening effect is obtained in alloys containing equal proportions of nickel and manganese. The optimum solution heat-treatment is two hours at 800°. At the optimum temper-hardening temperature of 450°, the re-heating period to produce maximum hardness increment is from two to seven days for alloys containing respectively 20% and 7% each of nickel and manganese.

CORROSION AND PROTECTION.

A novel method of investigating the atmospheric oxidation of aluminium has been described by P. Morize and P. Lacombe.[70] An oxide-free surface of aluminium was prepared by electrolytic polishing in perchloric acid–acetic anhydride, avoiding any access of water or air. The absence of oxide film was demonstrated by e.m.f. measurements, which method is claimed to be more sensitive than that of electron diffraction. When the electrolytically polished specimen was exposed to the air an initially rapid fall in p.d. occurred, afterwards slowly reaching a limiting value characteristic of mechanically polished surfaces. Oxidation was slower in dry than in moist air.

The oxide coating formed on magnesium and some of its alloys becomes looser and less protective as the temperature in air is raised from 412° to 575°, and combustion may occur at the highest temperature[71]; in general, alloying increases the rate of oxidation if the alloying element depresses the melting point appreciably. L. Horn[72] has determined the rate of scaling of some binary nickel alloys in air at temperatures up to 1200°. Alloys containing up to 1·7% of cerium or up to 3·4% of thorium form only one type of oxide film and follow the well-known parabolic law of oxidation. Deviations from this law occur with alloys containing up to 2·25% of beryllium or up to 29·2% of chromium, where more than one type of oxide film is formed. The scale was mainly NiO in alloys containing up to 8% of chromium, a mixture of NiO and Cr_2O_3 in alloys with 8—19% of chromium, and mainly Cr_2O_3 with 29·2% of chromium.

The resistance of copper to scaling in dry air at 400° is shown by A. P. C. Hallowes and E. Voce[73] to be increased by small additions of cadmium, chromium, manganese, phosphorus, nickel, tin, or zinc and especially by silicon or aluminium. Addition of water vapour to the atmosphere has little influence on scaling, but attack on all the alloys is

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[69] *J. Inst. Metals*, 1946, **72**, 381; B., 1946, I, 425.

[70] *Compt. rend.*, 1946, **222**, 658; A., 1946, I, 259.

[71] T. E. Leontis and F. N. Rhines, *Amer. Inst. Min. Met. Eng.*, 1946, *Tech. Publ.* 2003; B., 1946, I, 427.

[72] *Z. Metallk.*, 1944, **36**, 142.

[73] *Metallurgia*, 1946, **34**, 95; B., 1946, I, 303.

markedly increased by addition of sulphur dioxide or moist hydrogen chloride. The same authors[74] report that aluminium bronzes, although unattacked by pure steam, are attacked by steam contaminated with a small amount of sulphur dioxide.

In tests on the corrosion of magnesium alloys containing aluminium immersed in 3% sodium chloride solution, F. A. Fox and C. J. Bushrod[75] find that the method of preparing the surface of the specimens has a profound influence on their corrosion behaviour; the relatively high rate of corrosion of specimens prepared with IF emery paper is traced to the pick up of ferric oxide from the abrasive. F. A. Fox[76] has shown that the addition of 0·4—0·5% of zinc to magnesium alloys of normal purity containing 8 and 9·5% of aluminium improves corrosion-resistance on immersion in 3% sodium chloride solution, but with alloys of high purity the addition of zinc has an adverse effect on corrosion-resistance. A detailed survey of methods of protection of magnesium and its alloys has been compiled by J. M. Bleiweis and A. J. Fusco.[77]

Corrosion-time curves for very pure aluminium in N-potassium chloride have been determined by F. A. Champion,[78] using a technique in which both hydrogen evolution and oxygen absorption are measured. Over a large part of the curves the proportion of corrosion associated with hydrogen evolution bears a linear relation to the total corrosion; the corrosion rate is not controlled by the rate at which oxygen is supplied. G. V. Akimov and A. I. Gluchova[79] have shown by means of e.m.f. measurements that the rate of corrosion of aluminium in presence of chloride, sulphate, and nitrate ions varies with pH in such a way that curves roughly symmetrical about the neutral region are obtained; at a given pH the rate of corrosion in the presence of chloride is about 1000 times that in the presence of sulphate, although in strongly alkaline solutions the anion has little influence. Service failures in aluminium alloy rivets containing 7% and 5% of magnesium are attributed by G. J. Metcalfe[80] to intercrystalline corrosion, probably accentuated by stress; when such rivets are subjected to tropical temperatures for long periods precipitation of the β phase occurs, which renders them susceptible to intercrystalline attack. H. G. Petri, G. Siebel, and H. Vosskühler[81] have shown that the susceptibility of aluminium–magnesium–zinc alloys to stress corrosion increases with the sum of magnesium and zinc contents. In tests on an alloy containing 3·5% of magnesium and 4·5% of zinc subjected to alternating stresses in artificial sea-water it was found that corrosion-resistance could be varied considerably by the addition of

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[74] *Metallurgia*, 1946, **34**, 119; B., 1946, I, 383.
[75] *J. Inst. Metals*, 1946, **72**, 51; B., 1946, I, 141.
[76] *Ibid.*, **73**, 229.
[77] *Met. and Alloys*, 1945, **21**, 417; B., 1945, I, 397.
[78] *Trans. Faraday Soc.*, 1945, **41**, 593; A., 1946, I, 53.
[79] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **49**, 194; A., 1946, I, 322.
[80] *J. Inst. Metals*, 1946, **72**, 487; B., 1946, I, 428.
[81] *Aluminium*, 1944, **26**, 2.

fractions of a per cent. of other metals. The best corrosion-resistance is obtained by additions of chromium + copper + manganese, to which vanadium or titanium may be further added. Existing information on inhibitors of corrosion of aluminium has been reviewed by G. G. Eldredge and R. B. Mears.[82]

J. W. Cuthbertson[83] has studied the corrosion-resisting properties of certain α-tin and α-tin–aluminium bronzes, especially from the viewpoint of their suitability for use as condenser tubes. The investigation comprised the evaluation of resistance of the alloys to impingement attack, to deposit attack, and to simple corrosion by immersion in sea-water; cupro-nickel and aluminium brass were also examined as comparison materials. Solid-solution binary bronzes containing not less than 10% of tin were found to be extremely resistant to impingement attack, exceeding the behaviour of cupro-nickel or aluminium brass. The addition of aluminium did not significantly affect their resistance to impingement corrosion. although their resistance to other forms of corrosion was improved, but in bronzes containing as little as 8% of tin the addition of aluminium was essential to enable them to withstand impingement attack. In aërated sea-water the rate of deposit attack and of general attack of all the bronzes was increased but not to the same extent as with cupro-nickel or aluminium brass. The resistance of the bronzes to impingement and general corrosion can be improved by a pre-filming process. The resistance of tinned steel to rusting is greatly improved by immersion in a hot alkaline solution containing trisodium phosphate, sodium chromate, and a wetting agent.[84] The treatment produces a protective film on the tin which renders it immune to sulphur attack, and also passivates small areas of steel exposed at pores in the tin coating. As the protective film withstands forming operations, the treatment can be applied to tinplate sheets before fabrication into containers or other shapes. In its application to the canning industry, this treatment gives the advantages of (*a*) retarded rusting on the outside of the can, (*b*) freedom from sulphur staining inside the can, and (*c*) reduced absorption of tin by the food during storage.

A. H. Du Rose[85] has carried out measurements of the protective value of electrodeposited lead and lead–tin alloy deposits on steel; a good degree of protection by lead deposits was noted under outdoor conditions, while the incorporation of 5·5% of tin in the deposit was found to improve the protective value. Considerable interest has been aroused in the protective effect of electrodeposited tin–zinc alloys[86] from an electrolyte containing sodium stannate and sodium zinc cyanide. Whilst a wide range of alloy compositions can be deposited, two compositions (namely 80% Sn, 20%

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[82] *Ind. Eng. Chem.*, 1945, **37**, 736; B., 1945, I, 366.

[83] *J. Inst. Metals*, 1946, **13**, 317; B., 1946, I, 425.

[84] R. Kerr, *J.S.C.I.*, 1946, **65**, 101; B., 1946, I, 271.

[85] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 7, 101; B., 1946, I, 208.

[86] R. M. Angles, *J. Electrodep. Tech. Soc.*, 1946, **21**, 45; B., 1946, I, 138.

Zn and 50% Sn, 50% Zn) have been selected as having specially favourable corrosion-resistant properties; the 50/50 alloy shares some of the sacrificial properties of zinc and is especially useful under conditions of exposure to sea-water where damage to the coating may occur. R. M. Angles and R. Kerr[87] made a comparison of the corrosion-resisting properties of electrodeposited tin–zinc alloys with those of electrodeposited tin, cadmium, and zinc, and hot-dipped zinc coatings. These tests demonstrated the excellent corrosion-resistance of the tin–zinc alloys in the salt spray test, in the K.110 humidity chamber test, and in hot water. The corrosion-resistance of the alloy coatings can be further increased by subjecting them to a chemical filming or passivating treatment. E. S. Hedges[88] has reviewed recent developments on improving the corrosion-resistance of tin and tin alloy coatings.

Some attention has been given to the corrosion of bearing alloys by lubricating oils. To this end C. F. Prutton, D. Turnbull, and D. R. Frey[89] have studied the corrosion of pure lead by fatty acids and organic peroxides in hydrocarbon media. The important effect of peroxide concentration is emphasised, but the presence of other oxidising agents also causes corrosion. The more thermally stable oxidising agents are the most damaging at high temperatures.

H. H. Zuidema[90] states that corrosion by oil is most evident in bearings of copper–lead, alkali metal–lead, and cadmium alloys; indium-plated cadmium alloy is less corrodible, and tin-base Babbitt practically free from corrosion. For corrosion to occur it is essential for an oxidising agent to be present, but corrosion is also influenced by temperature, oxidation-stability of the oil, acid products formed in the oil, the presence of water, and other factors. The presence of sulphur can cause the formation of passive films on the bearing surfaces, which may reduce corrosion.

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[87] *Engineering*, 1946, **161**, 289.

[88] *Chem. and Ind.*, 1945, 370; B., 1946, I, 31.

[89] *Ind. Eng. Chem.*, 1945, **37**, 917; B., 1946, I, 107.

[90] *Oil and Gas J.*, 1946, **44**, *No.* 41, 100; *No.* 42, 151; *No.* 43, 66; B., 1946, I, 340.

ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES.

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Under wartime conditions it was impossible to obtain and inadmissible to publish full information on the year to year development of these industries. Restrictions on publication have now been largely removed and during the past twelve months the results of some interesting work carried out during the latter years of the war and hitherto kept secret have been released to the technical press. Moreover, information on the status of these industries in erstwhile enemy countries is now becoming available, and as Germany was one of the foremost manufacturers of electrochemical and electrometallurgical products, the reports of the British and Combined Intelligence Objectives Sub-Committees on this section of her industrial economy are particularly welcome. Reference may be made, for instance, to a report on the production of sulphuric acid, nitric acid, tungsten, molybdenum, ferro-tungsten, ferro-molybdenum, aluminium, and magnesium at the Bitterfeld works of I.-G. Farbenindustrie by R. M. Hunter,[1] and to another on the production and fabrication of magnesium at this company's works at Bitterfeld and Aken by T. W. Vigers, C. J. P. Ball, and J. L. Haughton.[2]

The expansion of these industries during the war years is readily visualised from the remarks of T. R. Rhea and B. R. Connell,[3] who, speaking of rectification and power supply for the production of aluminium, magnesium, chlorine, and for the refining of copper and zinc in Canada and the United States, state that the increase in demand from 1939 to 1945 culminated in an annual consumption of electrical energy of approximately 31×10^9 kw.-hr., representing a greater consumption than for any other single industry. This expansion has necessitated an increase in the capacity of a.c.–d.c. conversion equipment from $1{\cdot}5 \times 10^6$ kw.-hr. to approximately $4{\cdot}5 \times 10^6$ kw.-hr.

During the period under review developments have been recorded in most branches of electrometallurgy. In the electrodeposition field perhaps the greatest interest has been in the production and utilisation of electrolytic manganese. Amongst new alloy plating processes mention may be made of the electrodeposition of tin–zinc alloy for the protection of iron and steel, and of research on the deposition and protective properties

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[1] *Combined Intelligence Objectives Sub-Commee.*, 1945, *File* XXIV–22, *Item* 22; summary in *Metal Ind.*, 1946, **69**, 73; B., 1947, I, 78.

[2] *Ibid.*, *File* XXIX–3, *Item* 21; summary in *Metal Ind.*, 1946, **69**, 91.

[3] *Trans. Electrochem. Soc.*, 1946, **90**, *Preprint* 5.

of tin–lead alloys. A. W. Hothersall,[4] recording his impressions of the electroplating industry in the United States, gives some interesting information on present-day practice; referring to cyanide baths for the deposition of copper and brass, he states that the substitution of potassium salts for the usual sodium salts is claimed to enable the metal concentration of the electrolyte to be reduced by 50% without affecting the rate of deposition.

ELECTROLYTIC PROCESSES.

EXTRACTION, REFINING, PLATING, SURFACE TREATMENT, AND ELECTRODE REACTIONS OF METALS.

Aluminium.—Research on all aspects of the anodic oxidation of aluminium alloys continues to attract considerable attention. New experimental data advanced by G. V. Akimov, N. L. Tomaschov, and M. N. Tiukina[5] confirm that the growth of the film on aluminium anodically treated in sulphuric acid is the resultant of the simultaneous formation of an oxide layer and chemical attack of the oxide by the electrolyte. With sulphuric acid electrolytes resistance tends to decrease with time of treatment, and the diminishing rate of film formation is attributed to an increasing expenditure of the applied current on a secondary anodic process. Consequently it is wasteful of power to extend the anodising time much beyond 20 minutes. The decrease in resistance as the film grows is explained by its increasing porosity and greater permeability to ions; an increase in the applied voltage causes the resistance of the film to decrease. According to J. Hérenguel and R. Segond,[6] when anodising aluminium–magnesium alloys in 10% sulphuric acid the current density and film thickness increase directly with magnesium content, and consequently with alloys high in magnesium it may be necessary to reduce the applied voltage in order to limit the current density to a safe value. With duralumin the presence of the copper decreases the rate of formation of alumina to approximately half that for aluminium but there is no evidence of any increase in the porosity of the film due to the copper. From a microscopical examination of aluminium and its alloys after anodic treatment in sulphuric acid these authors[7] conclude that the films produced may be homogeneous but under unfavourable conditions, notably when the temperature and concentration of acid are high, may consist of two layers possessing different structures. The duplex structure is attributed to chemical attack by the acid which penetrates into the film, making it porous and impairing its wear-resisting and paint-holding properties. J. Hérenguel[8] considers that the occurrence of defects in anodised coatings on cast aluminium alloys may be associated

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[4] *J. Electrodep. Tech. Soc.*, 1946, **21**, 171.

[5] *J. Gen. Chem. Russ.*, 1942, **12**, 433; B., 1946, I, 182.

[6] *Rev. Mét.*, 1945, **42**, 72; B., 1946, I, 384.

[7] *Ibid.*, 258; B., 1946, I, 272.

[8] *Ibid.*, 1943, **40**, 284; B., 1946, I, 36.

with an excessively high copper content, and to casting defects which trap electrolyte and lead to staining through seepage.

H. Fischer and L. Koch[9] find that anodic treatment in sulphuric acid increases the resistance to stress corrosion of aluminium–magnesium and aluminium–magnesium–zinc alloys, the best results being obtained when the treatment is imparted following both plastic and elastic deformation of the material; considerable improvement results, however, when anodisation follows plastic deformation but precedes elastic deformation. W. Muller[10] finds that, in general, the bending fatigue strength of aluminium alloys is increased by anodic oxidation to an extent depending on the nature of the alloy, its surface condition, and the type of anodising procedure employed.

The use of glycerin in the anodic treatment of aluminium is discussed by G. Leffingwell and M. A. Lesser.[11] Addition of glycerin to sulphuric acid is said to decrease chemical attack on the aluminium and to favour the formation of a more plastic film. Baths of this type are claimed to produce finer-grained, whiter, and smoother films than are obtained from straight sulphuric acid solutions. The addition of sulphuric acid to chromic acid anodising baths was introduced as a wartime economy, according to C. J. Slunder and H. A. Pray.[12] As these solutions are corrosive they recommend the use of carbon cathodes and protection of the tank by painting. A disadvantage of the modified bath is that, when working at the normal voltage of 40, different alloys cannot be treated simultaneously owing to their varying current density requirements. Tests carried out by the Consolidated Vultee Aircraft Corporation[13] indicate, however, that by adding sulphuric acid to a chromic acid anodising bath the corrosion-resisting properties of the resulting anodic coating are markedly increased. The main objection to this type of solution is considered to be its corrosive effect on steel tank linings.

The use of anodic oxidation for the preparation of aluminium alloys for electrodeposition is discussed by H. Bengston.[14] From the viewpoint of bonding the results obtained by preliminary anodising are stated to be quite as good as those given by the zinc immersion method of preparation but the anodic procedure is rather more critical and is more costly in time and equipment. As the anodic layer persists under the electroplate this procedure is not recommended where good electrical continuity is demanded.

An aluminium coulometer is described by M. Tosterud and R. B. Mason[15] and is stated to be useful for measuring relatively large currents; moderate changes in current density and in temperature have little effect

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[9] *Korros. u. Metallschutz*, 1942, **18**, 62; B., 1946, I, 35.
[10] *Ibid.*, 56; B., 1946, I, 35.
[11] *Products Finish.*, 1946, **10**, *No.* 10, 50.
[12] *Ind. Eng. Chem.*, 1946, **38**, 592; B., 1946, I, 305.
[13] *Metal Ind.*, 1946, **68**, 477.
[14] *Trans. Electrochem. Soc.*, 1945, **88**, *Preprint* 25; B., 1946, I, 182.
[15] *Ibid.*, 1946, **90**, *Preprint* 16.

on the efficiency, given as about 100% for aluminium of not less than 99·95% purity, but the new coulometer requires a higher potential than other types.

Beryllium.—J. M. Tien[16] has succeeded in obtaining beryllium powder of over 90% purity by the electrolysis at 220—245° of a molten beryllium chloride–sodium chloride electrolyte protected by hydrogen in a closed cell; a feature of the process is the relatively low temperature at which it is conducted, but despite this advantage Tien is of the opinion that the sodium-vapour chemical reduction process is preferable.

Chromium.—A process for the electro-winning of chromium from tervalent salt solutions has been developed by R. R. Lloyd, W. T. Rawles, and R. G. Feeney[17] of the United States Bureau of Mines for the purpose of utilising low-grade domestic ores. Low-grade chromites from Montana and ores high in iron from the Benbow and Mouat mines have been successfully treated in a pilot plant having an output of 50 lb. per day, the chromium being recovered from a sulphate type of solution at a cathode efficiency of at least 45%. The effects of variations in the composition, concentration, and pH of the electrolyte, in temperature, and in current density have been fully investigated.

The use of electrodeposited chromium for the repair of worn machine parts and for the protection of parts subjected to wear and abrasion is discussed by A. L. Peach,[18] who advocates the use of two plating baths in succession, giving a composite deposit consisting of a soft, adherent, impact-resisting undercoat, and a hard, wear-resisting overcoat of approximately twice the thickness; on certain classes of work the duplex process allows thicker coatings than are normally permissible to be employed. J. M. Hosdowich[19] attributes the usefulness of hard chromium plate not only to its hardness but also to a unique combination of that property with good resistance to chemical attack and low coefficient of friction; he refers to the use of hard chromium for the protection of gauges, cutting tools, rolls and drums for the textile and printing industries, and dies. With regard to the hard chromium facing of press dies, E. A. Ollard and E. B. Smith[20] mention that plating effects substantial economy, both by increasing the life of the die itself and by reducing the cost of finishing the pressings made therefrom. Referring to the porous chromium plating of piston rings, T. C. Jarrett and R. C. Guerke[21] affirm that plating increases the life of the rings by approximately five-fold and reduces cylinder wear by 50% to 80%.

Detailed instructions for the production plating of zinc-base die-castings with chromium over undercoats of nickel and bright copper are given by

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[16] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 19; B., 1946, I, 305.

[17] *Ibid.*, *Preprint* 20; B., 1946, I, 304.

[18] *Metal Ind.*, 1946, **69**, 14; B., 1946, I, 338.

[19] *Mat. & Methods*, 1946, **23**, 896.

[20] *Sheet Metal Ind.*, 1946, **23**, 1129.

[21] *Mat. & Methods*, 1946, **23**, 1293.

H. Chase.[22] In an effort to determine the most suitable treatment to impart to a metallic surface intended to be chromium plated, from the viewpoint of providing the widest bright plating range, W. M. Tucker and R. L. Flint[23] have adapted the Hull cell to a study of anodic and other methods of pretreating copper, nickel, and steel. They find that, in general, neither copper nor steel is acutely sensitive to the method of surface preparation, but steel can be conveniently treated anodically in chromic acid, sulphuric acid, or in a mixture of the two. Nickel is more sensitive and can be advantageously prepared by immersion either in 5·8N-hydrochloric acid or in 5·8N-sulphuric acid. With nickel and steel the chief considerations for obtaining a wide range of bright chromium plating are, firstly, the complete removal of oxide and other interfering films from the cathodic surface and secondly, immersion immediately thereafter in the chromium bath.

K. Sachtleben[24] finds that 70% of the hydrogen retained in chromium-plated articles can be removed by intermittent anodic oxidation of the work in a non-corrosive electrolyte; removal of the hydrogen improves the mechanical properties of the plate and is effected by a process of diffusion of the gas during the idle periods and subsequent oxidation during the active periods.

E. S. Spencer-Timms[25] has made a critical examination of the hydrochloric acid drop test for the determination of the thicknes of thin chromium deposits; he observes that the end-point varies somewhat with different specimens while the temperature coefficient is appreciable, but considers the test to be useful for determining the approximate thickness of commercial deposits up to 0·00006 in. thick on nickel.

Copper.—Economic factors influencing the choice of current and current density in the electrolytic refining of copper are discussed by R. Hoffmann-Schiffner.[26] Theoretically the current density should be adjusted to give the best quality of cathode copper in the shortest time but in practice the cost of electrical energy and of the complete installation have to be taken into consideration. An increase in current density leads to an increase in the rate of production but owing to the higher voltage required the yield per kw.-hr. is reduced while installation costs are also increased. Aluminium is favoured as an alternative to copper for bus bars as it is cheaper and does not involve appreciably higher current losses. Practice in the electrolytic refining of copper at Nord-deutsche Affinerie, Hamburg, is described in a report by F. C. Mannox and H. J. Miller[27] on the extraction of copper from Cyprus and subsequently from Finnish concentrates.

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[22] *Iron Age*, 1946, **157**, *No.* 22, 34.

[23] *Trans. Electrochem. Soc.*, 1945, **88**, *Preprint* 28; B., 1946, I, 181.

[24] *Korros. u. Metallschutz*, 1943, **19**, 104; B., 1946, I, 110.

[25] *J. Electrodep. Tech. Soc.*, 1946, **21**, 79; C., 1946, 152.

[26] *Metall u. Erz*, 1943, **40**, 319; B., 1945, I, 395.

[27] *Brit. Intelligence Objectives Sub-Commee.*, 1946, *Final Rept.* 26, *Item* 21; B., 1946, I, 303.

In the refining process patented by K. A. Lindner and H. M. Shepard[28] foul electrolyte containing arsenic and antimony is withdrawn from the cells and electrolysed with insoluble anodes to yield a deposit containing copper, arsenic, and antimony. The deposit is then roasted at 260° to volatilise some of the arsenic and antimony, and after cooling is leached with caustic soda solution to extract the residual impurities. The residue is smelted to provide anodes for the copper-refining cells.

Solutions of the fluoborate type have been used for the electrodeposition of lead for many years but their application to the plating of other heavy metals is a comparatively recent development. C. Struyk and A. E. Carlson[29] have investigated the deposition of copper from solutions containing copper fluoborate and have succeeded in obtaining excellent deposits at current densities said to be higher than are possible with any other copper-plating bath. The anode and cathode efficiencies are stated to be approximately 100% and the bath is claimed to be simple to prepare and easy to control. Being of an acid nature, the solution deposits copper by immersion on ferrous materials, and preliminary flash plating from the cyanide bath is therefore necessary with this class of work. Developments in the electrodeposition of copper are reviewed by H. Bandes,[30] who refers to solutions of the acid sulphate, cyanide, amine, pyrophosphate, and sulphamate type. L. Greenspan[31] claims that bright, lustrous deposits of copper more than 0·001 in. thick can be deposited from a copper sulphate electrolyte containing diethylenetriamine and ammonium sulphate; pitting is reduced by small additions of a secondary higher alcohol sulphate.

The use of urea in acid copper-plating solutions is discussed by W. Brenner and C. B. F. Young,[32] who affirm that this addition produces smooth, fine-grained deposits of superior colour when used in concentrations of 0·05—1·2 g. per litre. Compared with the effect of thiourea, the characteristic brightening and brittleness are absent, and the ductility of the deposit is maintained even when the amount of urea is increased to 30 g. per litre.

Gold.—Referring to the treatment of antimonial gold ores, R. J. T. Caney[33] mentions the part played by electrolytic refining in the flow sheet of a typical refinery and states that the most suitable procedure is reduction of the stibnite concentrates with iron in a reverberatory furnace or with copper in a blast furnace followed by electrolysis. During electrolysis the precious metal, lead, bismuth, and copper remain in the anode slimes. The cathodes are melted and the arsenic which they still contain is selectively oxidised with an alkaline flux. Alternatively, when large

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[28] U.S.P. 2,329,775; B., 1946, I, 144.

[29] *Metal Ind.*, 1946, **69**, 348; B., 1947, I, 36.

[30] *Trans. Electrochem. Soc.*, 1945, **88**, *Preprint* 26; B., 1946, I, 181.

[31] U.S.P. 2,195,454; B., 1946, I, 112.

[32] *Products Finish.*, 1946, **10**, *No.* 5, 64.

[33] *Proc. Austral. Inst. Min. Met.*, 1944, *No.* 135, 33; B., 1946, I, 245.

amounts of copper, lead, and bismuth are present the concentrates may be leached in a hot solution of either caustic soda or sodium sulphide and electrolysed.

Indium.—According to E. E. Halls,[34] electrodeposited indium has useful lubricative properties and is particularly serviceable as a coating on dies for the drawing of aluminium alloys ; in general, the life of dies can be increased by about 50% by this means. Vandervell Products, Ltd., D. F. Green, and J. E. Salmon[35] favour a solution prepared by adding indium chloride to an alkali cyanide containing glucose or an equivalent saccharide, subsequently stabilised by alkali hydroxide, for the deposition of indium.

Lead.—From a study of the influence of plating conditions on the protective value of lead and lead–tin coatings deposited on steel from the fluoborate bath, A. H. Du Rose[36] concludes that an increase in the concentration of the glue used as an addition agent in the lead fluoborate bath improves covering and throwing power. Lead deposits from this type of bath are said to give good corrosion protection to steel ; the glue is an important factor in ensuring maximum protection as estimated by the salt-spray test.

R. G. Bates, M. Edelstein, and S. F. Acree[37] find that the potential of the lead electrode is markedly influenced by the surface condition of the metal ; the difference between individual samples of lead decreases as the electrodes are progressively etched in an acid solution. Cast lead sticks give the best reproducibility ; the e.m.f. of the lead stick–8% lead amalgam cell measured over the range 0—60° is given by the expression E (International v.) $= 0{\cdot}005347 + 0{\cdot}0000201\theta$, where θ is the temperature.

Magnesium.—Results obtained from a pilot plant producing electrolytic magnesium from magnesia are discussed by R. R. Lloyd, C. K. Stoddard, K. L. Mattingley, E. T. Leidigh, and R. G. Knickerbocker,[38] who have developed a process consisting essentially in feeding a molten chloride electrolyte with magnesium oxide ; continuous operation at a reasonable current efficiency is possible, but the formation of sludge still causes difficulty and is attributed mainly to the formation of colloidal magnesium oxide at the cathode, a reaction favoured by the presence of water, boron trioxide, iron, and sulphate in the cell feed. C. M. Shigley[39] gives a general description of the Dow Magnesium Corporation's plant at Velasco, Texas, which extracts 72,000,000 lb. of magnesium annually from sea-water, whilst J. M. Avery and R. F. Evans[40] outline practice at Painesville, Ohio, where magnesium chloride is prepared from dolomite limestone and is electrolysed in Dow cells. The production and fabrication of

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[34] *Metallurgia,* 1946, **33**, 243 ; B., 1946, I, 210.
[35] B.P. 573,848 ; B., 1946, I, 113.
[36] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 7 ; B., 1946, I, 208.
[37] *J. Res. Nat. Bur. Stand.*, 1946, **36**, 159 ; A., 1946, I, 259.
[38] *Amer. Inst. Min. Met. Eng.*, 1945, *Tech. Publ.* 1848 ; B., 1946, I, 140.
[39] *Ibid.*, 1845 ; B., 1946, I, 140.
[40] *Ibid.*, 1829 ; B., 1946, I, 140.

magnesium at the Bitterfeld and Aken works of I.-G. Farbenindustrie are discussed by T. W. Vigers, C. J. P. Ball, and J. L. Haughton.[41]

Suggestions relating to the most economical and efficient methods of electric metering of magnesium electrolytic cell lines are advanced by E. L. Kirk.[42]

Manganese.—Further work by the United States Bureau of Mines on the electrolytic production of manganese is described in a number of recent reports. G. L. Allen, J. H. Jacobs, and J. W. Hunter[43] present plans for the production of electrolytic manganese from ore from the Three Kids Mine, Nevada, and from unmined reserves containing 19% and 10·5% of manganese anticipate an output of 40 and 10 tons of manganese per day, respectively, whilst J. H. Jacobs and J. W. Hunter[44] have worked out a process for the production of electrolytic manganese from Chamberlain (South Dakota) nodules. The nodules are given a reducing roast and the calcine is then leached and the solution purified to provide the manganese sulphate–ammonium sulphate electrolyte for the cells. Using lead silver alloy anodes and stainless steel cathodes, the recovery is 82—86%, of manganese of 99·94% purity. D. Schlain, J. D. Prater, and B. L. Lukens[45] find that lead containing 1% of silver and 1% of arsenic is the most suitable anode material for the electrolysis of manganese solutions, the new alloy corrodes only 12% as rapidly and oxidises manganese only 45% as rapidly as the binary lead–silver alloy used formerly and is at least as suitable from the viewpoint of cell voltage, current efficiency, and physical properties. These investigators[46] have also studied the influence of impurities in the electrolyte on the electrodeposition of manganese and find that although very small amounts of cobalt and nickel tend to decrease the current efficiency, arsenic in concentrations up to 25 mg. per litre has little effect on efficiency; the impurities normally found in these electrolytes do not adversely affect the ease of stripping of the manganese from the cathodes.

The chief outlet for electrolytic manganese is in the production of steel and its use for this purpose is increasing. From full-scale trials in open-hearth and in electric furnaces R. T. C. Rasmussen and F. Sillers, jun.,[47] conclude that the substitution of electrolytic manganese for ferromanganese has no deleterious influence on the properties of the steel produced, and report elsewhere[43] that 24 American steel plants are finding the new material acceptable for the manufacture of all types of steel and even preferable for the production of stainless and low-carbon steels. R. T. C. Rasmussen[48] states that in the production of acid open-

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[41] *Combined Intelligence Objectives Sub-Commee.*, 1945, *File* XXIX-3, *Item* 21.
[42] *Trans. Electrochem. Soc.*, 1946, **90**, *Preprint* 8; B., 1947, I, 4.
[43] *U.S. Bur. Mines*, 1945, *Rept. Invest.* 3815; B., 1946, I, 338.
[44] *Ibid.*, 1946, *Rept. Invest.* 3862; B., 1946, I, 271.
[45] *Ibid.*, 3863; B., 1946, I, 382.
[46] *Ibid.*, 3872; B., 1946, I, 381.
[47] *Steel*, 1945, **117**, *No.* 21, 138, 188; B., 1946, I, 182.
[48] *U.S. Bur. Mines*, 1945. *Rept. Invest.* 3830; B., 1946, I, 137.

hearth and electric-furnace steels larger additions of electrolytic manganese than are considered advisable when using ferro-manganese can be made in the ladle and there is no evidence of manganese segregation in the ingot. With plain-carbon steels the use of electrolytic manganese is said to lead to increased ductility and to a quicker response to heat-treatment. Rasmussen[49] claims that in the manufacture of stainless steels the substitution of electrolytic manganese for low-carbon ferro-manganese allows a greater weight of alloy scrap to be remelted with the charge, thus conserving strategic metals.

Commercial cathode manganese obtained from sulphate solutions containing sulphite is generally believed to consist mainly of brittle α-manganese superimposed on a thin initial layer of γ-manganese; this duplex structure is desirable as it is associated with a high cathode efficiency and good stripping qualities. According to J. Koster[50] the deposition of manganese from pure solutions free from sulphate cannot be continued for more than about 4 hours as only γ-metal is obtained and this variety is redissolved by the electrolyte. Solutions purified with hydrogen sulphide, however, under proper conditions give satisfactory deposits at a fairly high current efficiency over long periods of time; by adding a hypophosphite or hypoborite to the solution current efficiency and stability are somewhat increased.

B. Cartwright and S. F. Ravitz[51] have succeeded in electrolysing manganese into a molten tin cathode at 700° from a manganous chloride melt and from a suspension of manganous oxide and carbon in fused manganous chloride. The possibilities of using this process for the production of pure manganese are discussed. As an alternative to tin it is considered that zinc may prove to be a more suitable cathode metal.

Nickel.—From a study of the voltage distribution in the electrolytic refining of nickel from alloy anodes containing 3% of copper, M. Loschkarev and G. Lapp[52] find that an increase in current density from 135 amp. per sq. m. to 200—250 amp. per sq. m. demands an increase by a factor of 1·6—2·1 in the conductivity of the electrolyte in order to maintain the same current efficiency. The increase in conductivity is conveniently attained by the addition of 60—80 g. per litre of sodium sulphate to the electrolyte.

A new process, the details of which are not specified, enabling deposits of nickel 0·005—0·01 in. thick to be plated uniformly on the interior surface of tubes 20 ft. long and 2—17 in. in diameter is mentioned by S. G. Bart,[53] who claims that the adhesion obtained is sufficient to permit severe deformation and to allow welding to be carried out after plating. E. A. Ollard and E. B. Smith[54] describe in detail present-day technique

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[49] *U.S. Bur. Mines*, 1945, *Rept. Invest* 3829; B., 1946, I, 106.
[50] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 26; B., 1946, I, 304.
[51] *Ibid.*, *Preprint* 4; B., 1946, I, 209.
[52] *J. Appl. Chem. Russ.*, 1945, **18**, 405.
[53] *Chem. Industries*, 1946, **58**, 51: B., 1946, I, 181.
[54] *Metal Ind.*, 1946, **68**, 246, 286, 325, 366.

in the plating of zinc-base die-castings with nickel preparatory to plating with chromium; information is appended on the deposition of nickel from baths of the Watts type and from bright nickel–cobalt solutions, and particular attention is given to methods of maintenance, control, and purification.

Using the gravimetric method, C. J. B. Zitek and H. J. McDonald[55] have determined the transference number of nickel in 0·1N-nickel sulphate solution and for a temperature of 40° ± 0·1° give the value 0·366.

Silver.—Useful information on the adhesion of silver directly deposited on steel is given by J. S. Hart and C. E. Heussner[56] in a publication on silver plating applied to aircraft engine bearings. Consistent adhesion values of 50,000 lb. per sq. in. have been obtained by a sequence of anodic cleaning and etching treatments followed by a dip in dilute hydrochloric acid, striking in a nickel bath, striking twice in a silver bath, and plating with silver. The tensile strength of electrodeposited silver decreases with an increase in annealing temperature for both air and hydrogen atmospheres. Up to 660° no difference is detected between annealing in air and in hydrogen but at higher temperatures the tensile stress decreased progressively for annealing in air whereas it is almost unchanged for annealing in hydrogen. Fatigue tests on annealed silver-plated bearings show a decrease in fatigue strength with increase in annealing temperature.

Tin.—Discussing the manufacture of electrolytic tinplate, T. G. Timby[57] emphasises that every step in the process influences the quality of the final product and efficient control at each stage is therefore essential; in particular the steel base should be of a suitable quality, should be quite clean before annealing, and should be adequately degreased before it enters the plating tank. With a view to increasing effective anode area in the potassium stannate bath he has compared current distribution on flat, corrugated, and keystone section anodes; for each shape of anode, current density down the front face increases with depth in the solution. A detailed description of a modern continuous plant for the electro-tinning of steel strip, using a solution of the acid type is given by C. Frenkel,[58] whilst P. F. Grove[59] gives data on the electrical equipment required for continuous electro-tinning lines. Grove describes the methods adopted for handling the strip, for supplying the current for electrodeposition, and for flow-melting the deposit in order to obtain a bright finish, and mentions also auxiliary devices for the detection of pin-holes, control of looping, variation of line speed, etc. Recent developments in the use of electrolytic tinplate and of phosphated black-plate are reviewed by W. G. Cass.[60]

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[55] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 24; A., 1946, I, 283.

[56] *Month. Rev. Amer. Electroplaters' Soc.*, 1946, **33**, 142.

[57] *Iron & Steel Eng.*, 1945, **22**, *No.* 8, 40; B., 1946, I, 181.

[58] *J. Electrodep. Tech. Soc.*, 1946, **21**, 129.

[59] *Ibid.*, 139.

[60] *Sheet Metal Ind.*, 1946, **23**, 1917.

E. S. Hedges,[61] speaking of developments in tin and tin alloy coatings, refers to recent research on the porosity of electrodeposited tin coatings and the use of protective oxide films on tinplate; a thin electrodeposit of tin on steel is said to be an extremely suitable basis for paint, ensuring excellent adhesion coupled with protection against corrosion.

Zinc.—A description of the Tainton process for the electro-galvanising of steel wire is given by H. Roebuck and A. Brierley.[62] In this process the sulphate electrolyte is prepared directly from roasted zinc blende ore by leaching followed by a complex refining procedure. Before plating, the wire is annealed in molten lead and is then cleaned by anodic treatment in acid. Electrolysis is carried out at a very high current density and the plated wire after washing and drying is finally polished by rotating blades tipped with tungsten carbide revolving around it at a speed of 2000 r.p.m.

The porosity of zinc coatings electrodeposited from sulphate solution has been studied by H. Fischer and H. Baermann,[63] who find that the critical thickness at which porosity practically disappears decreases with increase in current density, in zinc sulphate concentration, in pH, and also when aluminium sulphate, ammonium chloride, and an aromatic sulphonic acid are added to the electrolyte; the latter additions reduce the critical thickness at low and medium current densities and increase it at higher current densities.

W. Eckardt[64] finds that 1 g. of lead added as sulphate to a zincate bath containing 260 g. of zinc oxide and 1100 g. of sodium hydroxide gives deposits of zinc on iron which at a current density of 1·8 amp. per sq. dm. remain bright for the first 10 minutes and thereafter become spongy; in presence of 3 g. of boric acid operation at a current density of 1 amp. per sq. dm. gives non-spongy deposits for the first 20 minutes whilst no sponginess occurs for several hours when 2 g. of vanillin are added to the electrolyte.

Alloys.—A method of co-depositing tin and zinc devised by R. M. Angles[65] produces alloy coatings having excellent corrosion-resisting properties. The solution contains sodium stannate, sodium hydroxide, zinc cyanide, and sodium cyanide, and is operated with alloy anodes of the same composition as the alloy to be deposited. To ensure dissolution of the tin as Sn^{IV} the anodes are operated in the filmed condition just as in the deposition of tin from the stannate bath. The process mentioned in the preceding Report[66] for the deposition of the copper–tin alloy speculum has been modified by the Pyrene Co. Ltd., W. L. Baker, and E. H. T. Day,[67] who substitute insoluble carbon anodes for the individual tin and

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[61] *Chem. and Ind.*, 1945, 370; B., 1946, I, 31.
[62] *J. Electrodep. Tech. Soc.*, 1946, **21**, 91; B., 1946, I, 302.
[63] *Korros. u. Metallschutz*, 1943, **19**, 97; B., 1946, I, 107.
[64] *Ibid.*, 1942, **18**, 243; B., 1945, I, 395.
[65] *J. Electrodep. Tech. Soc.*, 1946, **21**, 45; B., 1946, I, 138.
[66] See *Ann. Repts.*, 1945, **30**, 265.
[67] B.P. 571,641; B., 1945, I, 401.

copper anodes and adjust the working conditions so that the pH of the solution is maintained within the range 10·5—11·5; the copper and tin cathodically removed from the solution are replenished periodically by the addition of copper cyanide and sodium stannate.

Data on the deposition from the fluoborate bath of lead–tin alloys containing 5—60% of tin are appended by A. E. Carlson and J. M. Kane.[68] Normally alloy anodes are used but if desired the solution may be replenished by using separate lead and tin anodes; the proportions of tin and lead in the deposit correspond approximately to their concentrations in the electrolyte. Electrodeposited lead–tin alloys are claimed to possess good bearing properties and, according to A. H. Du Rose,[69] when containing 5—6% of tin are more resistant to corrosion than is pure lead or than are alloys of higher tin content.

J. L. Andrieux and G. Weiss[70] have succeeded in preparing ferro-tungsten alloys by the electrolysis of fused melts containing borax, sodium fluoride, ferric oxide, and tungsten trioxide. According to the operating conditions the compounds Fe_3W_2 or Fe_2W are obtained; the two compounds are stated to resemble one another in chemical properties. A new aqueous bath for the electrodeposition of tungsten–nickel alloys containing sodium tungstate, nickel sulphate, citric acid, and ammonia is described by L. E. Vaaler and M. L. Holt[71] and is claimed to produce bright, lustrous deposits containing about 35% of tungsten at a cathode efficiency of 40—45%. Bright, adherent deposits of an alloy of nickel, cobalt, and tungsten have been obtained by P. F. Hoglund and M. L. Holt[72] by electrolysing a bath containing nickel sulphate, nickel chloride, cobalt sulphate, sodium tungstate, and boric acid.

C. B. F. Young and C. Struyk[73] have succeeded in depositing nickel–cobalt alloys from a mixed chloride bath containing boric acid and have studied the effect of temperature, solution concentration, pH, current density, and other factors on the composition and nature of the deposit. As the solution contains no organic brighteners it is claimed to be easy to control and to maintain in balance. The deposits obtained are smooth, ductile, fine-grained, and easily buffed.

Electrolytic Polishing.—The present-day status of electro-polishing is reviewed by C. L. Faust.[74] He considers that the process has good future prospects but its advancement depends on the user recognising its limitations as well as its advantages and designing his work accordingly. Stainless steel wire shelves, pressed brass ornaments, aluminium refrigerator ice trays, and small steel parts are instanced as suitable for electro-polishing, and the economics of handling these articles in bulk are

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[68] *Month. Rev. Amer. Electroplaters' Soc.*, 1946, **33**, 255; B., 1947, I, 142.
[69] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 7; B., 1946, I, 208.
[70] *Compt. rend.*, 1946, **222**, 646; A., 1946, I, 261.
[71] *Trans. Electrochem. Soc.*, 1946, **90**, *Preprint* 9; B., 1947, I, 38.
[72] *Ibid.*, 1945, **88**, *Preprint* 24; B., 1946, I, 181.
[73] *Ibid.*, 1946, **89**, *Preprint* 1.
[74] *J. Electrodep. Tech. Soc.*, 1946, **21**, 181; cf. also *Product Eng.*, 1946, **17**, 449.

discussed. According to W. A. Sparks,[75] electrolytic polishing as compared with hand finishing increases the adhesion of electrodeposited nickel and chromium to carbon-manganese steel.

For the electrolytic polishing of cadmium J. Liger[76] favours a solution containing potassium cyanide and potassium cadmium cyanide; electrolysis is carried out at room temperature without agitation, using an iron cathode and a current density of 12—25 amp. per sq. dm. and voltage of 4—5. Referring to the electro-polishing of leaded bronze, zinc, and magnesium, P. A. Jaquet[77] states that with zinc and magnesium in particular, the electrolytic method gives a polish superior to that obtainable by older methods. For the electrolytic polishing of copper and copper alloy micro-specimens, U. J. Hochschild[78] mounts them in a plastic after first embedding in copper powder to establish electrical contact; as the powder is not exposed to the polishing electrolyte it does not interfere with the control of the process.

Miscellaneous.—Methods of overcoming the troubles most commonly encountered in brass, chromium, copper, lead, nickel, silver, tin, and zinc plating solutions are given by P. Berger.[79] E. Engel[80] supplies information on the corrosion-resistance and frictional properties of electroplated finishes and gives some useful comparative data on methods of degreasing, descaling, and electrolytic polishing. A. Weisselberg and his collaborators[81] have established mathematical relationships for the distribution of current along a cylindrical anode situated inside a concentric cathode; their results agree closely with those obtained in practice and in the chromium plating of gun barrels it is shown that for a round anode $\frac{3}{16}$ in. in diameter, owing to heating considerations, no advantage in reduced plating time is gained by employing a current exceeding 70 amp.

ELECTROCHEMICAL PROCESSES.

Chlorine Cells.—R. M. Hunter[82] reporting on six German plants having an output of 10^6 lb. of chlorine per day states that since 1936 all new installations in Germany have been of the mercury cell type. The cells are usually about 25 in. wide and 25 ft. long and are operated at 15,000 amp. Anodes are of unimpregnated graphite and initially are spaced about $\frac{1}{4}$ in. above the surface of the mercury, covering that surface as completely as possible; the life of American anodes is about 300 days and of German anodes about 225 days. Information on the working characteristics of plants of this type and data on the economics of the German chlorine industry are given. W. C. Gardiner[83] states that the main

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[75] *J. Electrodep. Tech. Soc.*, 1946, **21**, 245; B., 1947, I, 136.
[76] *Bull. Soc. chim.*, 1944, [v], **11**, 568; B., 1945, I, 365.
[77] *Rev. Gén. Élect.*, 1945, **54**, 239.
[78] *Met. & Alloys*, 1945, **21**, 409; C., 1945, 285.
[79] *J. Electrodep. Tech. Soc.*, 1946, **21**, 195; B., 1947, I, 115.
[80] *Iron Age*, 1945, **156**, *No.* 10, 70; *No.* 11, 64; *No.* 12, 74; *No.* 13, 65; B., 1946, I, 181.
[81] *Trans. Electrochem. Soc.*, 1946, **90**, *Preprint* 1; B., 1946, I, 381.
[82] *Chem. Met. Eng.*, 1945, **52**, *No.* 10, 104.
[83] *Ibid.*, *No.* 7, 110; B., 1945, I, 356.

difficulty with the two-compartment cell is in obtaining a correct balance between the decomposition (brine) compartment and the denuding (caustic soda) compartment. Economic factors in the operation of cylindrical chlorine cells are discussed by L. P. Wenzell, P. J. Stuber, and S. Cottrell,[84] who find that cells of this type show a straight-line relationship between current efficiency and concentration of caustic soda in the electrolyte, and give the greatest anode life when working at a high current efficiency; they conclude that the cheapest cost of product is obtained with cells operating with one diaphragm renewal, that is with two diaphragms, per anode life.

Electrochemical Oxidation and Reduction.—S. G. Howden-Simpson[85] has investigated the production of potassium permanganate in a diaphragm cell having a nickel gauze cathode and a deep bed of ferro-manganese as an anode, using an electrolyte consisting of a 25% solution of potassium hydroxide, and finds that the current efficiency is 30—40% and decreases with increase in temperature and with decrease in the manganese content of the anode. Permanganate can also be produced by electrolysing a suspension of manganese dioxide in potassium hydroxide at a temperature exceeding 210°. In the electrolysis of stearic acid dissolved in an ethyl alcohol–water mixture using bright platinum anodes and copper foil cathodes, T. Timell[86] finds that a higher current yield of hydrocarbons than has hitherto been reported is obtainable by employing a high current density, high temperature, and a concentrated electrolyte. B. B. Dey, T. R. Govindachari, S. C. Rajagopalan[87] have investigated various methods of producing benzidine by the electrolytic reduction of nitrobenzene and conclude that the most promising from the industrial viewpoint are reduction of nitrobenzene in an alkaline solution, in a solution of either sodium or potassium xylenesulphonate, and in an alkaline emulsion using a diaphragm cell; under favourable circumstances a 90% yield of benzidine is possible. They have modified the Gattermann procedure for the electrolytic reduction of nitrobenzene to *p*-aminophenol and by using less concentrated sulphuric acid have obtained a yield of 90 g. per kw.-hr., which is nearly double that obtainable by the Gattermann method.

Miscellaneous.—L. Streicher[88] has devised a two-compartment cell for softening water electrolytically. The passage of the current separates the water into an anolyte reject and a basic catholyte, and the latter on keeping deposits calcium carbonate and magnesium hydroxide, giving a considerably softer water. Power consumption is stated to be 7 kw.-hr. per 1000 gallons of water treated and a reduction in hardness of approximately 75% is claimed. Discussing the production of hydrofluoric acid

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[84] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 16; B., 1942, I, 23.

[85] *Manufg. Chem.*, 1946, **17**, 55; B., 1946, I, 165.

[86] *Svensk Kem. Tidskr.*, 1946, **58**, 67; A., 1946, I, 260.

[87] *J. Sci. Ind. Res., India*, 1946, **4**, 559, 569, 574, 637; B., 1946, II, 230.

[88] *Civil Eng.*, 1946, **16**, 312; B., 1946, I, 309.

and fluorine in Germany, W. Archer, W. J. V. Ward, and O. S. Whitston[89] describe a process in which fluorine is made by electrolysing potassium hydrogen fluoride at 240—245° in cells having magnesium–manganese cathodes and graphite anodes; the current efficiency is stated to be higher than that obtainable using nickel electrodes. By subjecting acetylene to the silent electrical discharge using a cylindrical ozoniser of special construction, G. Glockler and A. E. Walz[90] have succeeded in preparing the solid acetylene polymer, cuprene. Cuprene absorbs oxygen, and the authors find that it also reacts with hydrogen chloride and with hydrogen bromide; no absorption was detected, however, with hydrogen iodide, chlorine, or nitrogen.

ELECTRONIC DEVICES.

Chemical and physical problems arising in the manufacture of selenium rectifiers are discussed by C. A. Escoffery.[91] He ascribes the inhibition of attack sometimes noticed in the etching of steel base plates in nitric acid to assist adhesion of the selenium layer to the presence of nitrous acid, and states that the trouble can be overcome by adding a trace of sulphuric acid to the etching bath. A hypothesis, based on cathodic reduction of selenium and migration of electronegative selenium ions to the counterelectrode, is advanced to explain the improvement in the asymmetry of these rectifiers which follows the electroforming treatment imparted to the barrier layer during manufacture. A means of determining the characteristics of selenium and copper oxide rectifiers under conditions equivalent to those which they will experience in service has been developed by W. Artus.[92]

Disadvantages of the selenium photocell such as departure from linearity, sensitivity to change in temperature, and fatigue are discussed by G. M. Tomlin and C. Wontner[93] in a dissertation on the manufacture and properties of these devices. The construction of a general-purpose photoelectric photometer for use in the testing of textiles is described by N. H. Chamberlain.[94] The photoelectric properties of thallous sulphide and theory of the thallous sulphide photoelectric cell are discussed by A. von Hippell, F. G. Chesley, H. S. Denmark, P. B. Ulin, and E. S. Rittner, and by A. von Hippell and E. S. Rittner,[95] respectively. For cells of this type the dark current and the current under illumination are proportional to the applied voltage; the former decreases exponentially with increasing temperature, while the latter is proportional to the incident light intensity only at low intensities and decreases rapidly with

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[89] *Brit. Intelligence Objectives Sub-Commee.*, 1945–46, *Final Rept.* 261, *Item* 22; B., 1946, I, 327.

[90] *Trans. Electrochem. Soc.*, 1945, **88**, *Preprint* 14; B., 1946, II, 29.

[91] *Ibid.*, 1946, **90**, *Preprint* 6; B., 1947, I, 4.

[92] *Z. tech. Physik*, 1943, **24**, 296; C., 1946, 132.

[93] *Sci. Forum, Dec.*, 1944, 17; C., 1945, 290.

[94] *J. Soc. Dyers and Col.*, 1945, **61**, 161; C., 1945, 290.

[95] *J. Chem. Physics*, 1946, **14**, 355, 370; A., 1946, I, 283.

temperature. The photoelectric current reaches a maximum value in 5×10^{-5} second when the cell is illuminated by flashes of short duration and decays exponentially, except at the commencement of the decay curve. Pure thallous sulphide exhibits the phenomenon of excess conductivity; as oxidation increases conductivity decreases, photosensitivity increases, and the thermo-electric e.m.f. diminishes to zero and changes sign.

INSULATION MATERIALS.

A number of interesting publications on dielectric materials has recently appeared in the *Transactions of the Electrochemical Society*. Reference may be made to the work of E. Wainer[96] on the properties of high-titania dielectrics, of E. B. Yelton[97] on the properties of polytetrafluoroethylene, of L. M. Debing[98] on the dielectric constant and power factor of phenol–formaldehyde plastics, of T. Hazen[99] on the effect of temperature on the dielectric constant of thermosetting materials, and of S. L. Bass, M. J. Hunter, and T. A. Kauppi[100] on the insulating properties of silicones. Wainer considers that the electrical properties of titanium oxide and compounds derived therefrom are such as to make them suitable not only as substitutes for condenser-grade mica but also for other electrical applications where it is neither possible nor convenient to use alternative dielectrics; he offers an explanation of the dielectric properties of these materials based on their crystallographic structure. Bass, Hunter, and Kauppi express the view that the recently introduced silicone elastomers, owing to their rubber-like properties and high thermal stability, should prove to be particularly attractive dielectric materials, especially for applications where organic polymers are unsuitable.

The dielectric properties of steatite porcelain are discussed by G. N. Howatt,[101] who has collected a considerable amount of data on power factor, dielectric constant, and loss factor of these insulation materials. The dielectric constant and power factor of Indian mica have been investigated by S. Parthasarthy, A. Pande, and M. Pancholy,[102] who consider that many of the qualities of mica available are suitable for use in high-grade electrical condensers, while some of the spotted and stained varieties are of a higher quality than has hitherto been acknowledged. P. C. Mahanti, M. K. Mukherjee, and P. B. Roy[103] have examined the electrical properties of clear, stained, and slightly spotted Bengal ruby mica and Madras green mica, and conclude that the stained and spotted qualities have the highest values for power factor and power loss.

The conductance and capacitance of many solid porous materials

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[96] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 3; B., 1946, I, 201.
[97] *Ibid.*, **90**, *Preprint* 15; B., 1947, II, 85.
[98] *Ibid.*, *Preprint* 3; B., 1946, II, 425.
[99] *Ibid.*, *Preprint* 13.
[100] *Ibid.*, *Preprint* 19; B., 1947, II, 120.
[101] *J. Amer. Ceram. Soc.*, 1946, **29**, 117; B., 1946, I, 372.
[102] *J. Sci. Ind. Res., India*, 1945, **4**, 158; B., 1946, I, 47.
[103] *Indian J. Physics*, 1945, **19**, 83; B., 1946, I, 254.

depend largely on their moisture content. An instrument enabling the moisture content of wheat, grass, straw, etc. to be measured within an accuracy of ±0·5% is described by L. Hartshorn and W. Wilson.[104] The moisture meter described by C. F. Brockelsby[105] depends for its operation on the change in the dielectric constant of the material under investigation. This instrument has been designed specificially for measuring the moisture content of wheat and covers a moisture range of 8—28% ; the accuracy is ±0·4%.

PRIMARY AND SECONDARY CELLS.

The influence of the quality of the starch used in the manufacture of dry cells on their performance in service has been investigated by D. Venkateswarlu[106]; on substituting purified starch containing only 0·5% of impurity for the ordinary variety an improvement of 50% is effected in the number of continuous burning hours, that is, in the time taken for the voltage to fall from the initial value of 1·55 to a final value of 0·6, while the available current is increased by about 20%. The reactions occurring in the Leclanché dry cell are discussed by L. C. Copeland and F. S. Griffith,[107] who provide evidence in support of the theory that the chief reaction during discharge is $Zn + 2MnO_2 \rightarrow ZnO,Mn_2O_3$. The predominating factor at present limiting the capacity of the high-grade heavy-duty type of industrial cell is insufficient depolariser, and improvement in performance would follow from the development of a form of active manganese dioxide–carbon black depolarising mixture which could be packed to a higher density without any sacrifice in conductivity.

Two types of dry cell suitable for use at a temperature of −30° or even lower have been developed by E. Otto, C. K. Morehouse, and G. W. Vinal.[108] One type employs an electrolyte containing methylamine hydrochloride, zinc chloride, and ammonium chloride, while the other uses an electrolyte consisting of a solution of calcium chloride, zinc chloride, and ammonium chloride; the concentrations of the component salts, particularly in the latter case, are critical. In the cell patented by Siemens Bros. & Co., Ltd., C. F. Edwin, and R. J. Wills[109] and claimed to be resistant to the adverse effects of tropical climatic conditions, the carbon and the zinc electrodes, electrolyte, and depolariser are packed in a polythene container which can be hermetically sealed after the unit has been assembled.

The construction of a secondary cell having lead dioxide for the positive paste and lead for the negative plates, capable of being stored in the

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[104] *J. Inst. Elect. Eng.*, 1945, **92**, *Part* II, 403 ; C., 1946, 56.
[105] *J. Sci. Instr.*, 1945, **22**, 243 ; C., 1946, 56.
[106] *Current Sci.*, 1946, **15**, 46 ; B., 1946, I, 217.
[107] *Trans. Electrochem. Soc.*, 1946, **89**, *Preprint* 22 ; B., 1946, I, 279.
[108] *Ibid.*, **90**, *Preprint* 17.
[109] B.P. 573,582 ; B., 1946, I, 156.

unactivated state indefinitely without deterioration, is described by J. P. Schrodt, W. J. Otting, J. O. Schoegler, and D. N. Craig.[110] It is claimed that by activating the cell with an electrolyte in which the lead products formed during the discharge cycle are freely soluble, the effective utilisation of the active lead dioxide is improved, while the necessity for using finely divided and porous lead dioxide is eliminated. Suitable electrolytes, possessing the further essential properties of being available in concentrated solution and of having a low freezing point, include solutions of perchloric, fluoboric, fluosilicic, and some sulphonic acids. L. V. Peakes, jun., R. A. Lloyd, V. S. Barnes, J. H. Berry, and G. J. Ritter[111] have examined five different woods to determine their suitability as substitutes for Port Orford white cedar for storage battery separators. After subjection to the same extraction treatment as that employed for Port Orford cedar, Douglas fir, noble fir, and Alaskan yellow cedar all produced satisfactory separators, having adequate electrical resistance and good mechanical strength; redwood and bald cypress produced separators having good electrical properties but inferior in strength to those made from the other three woods.

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[110] *Trans. Electrochem. Soc.*, 1946, **90**, *Preprint* 21.
[111] *Ind. Eng. Chem.*, 1946, **38**, 780; B., 1946, I, 353.

FATS, FATTY OILS, AND DETERGENTS.

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The many communications which have appeared during the year have dealt for the most part with extensions of research topics which have been developed recently, and have not opened up any definitely fresh fields. Consequently a wide variety of subjects merit notice, but the treatment given must appear more disjointed and less systematic than could be wished. Nevertheless an attempt will be made to bring the diverse information into a more or less homogeneous sequence, on the same general lines as in recent issues of these Reports, and to include as many as possible of the publications which seem to possess sufficient general interest.

Detergents.

Constitution of Soaps and Soap Solutions.—The papers selected for notice merely serve to indicate some lines on which studies in this field have moved during the past year. W. D. Harkins, R. W. Mattoon, and M. L. Corrin[1] have worked on the *X*-ray diffraction exhibited by soap solutions of moderate concentration, in which the results indicate that the soap molecules are arranged in double layers with aqueous layers between them, the alkyl chains being oriented towards each other, and the polar salt-forming groups towards the water layers. When the alkyl chain in a soap ceases to be entirely separate and surrounded by water, and becomes more or less surrounded by other alkyl chains, there is a large decrease in free energy due, it is suggested, to the aggregation of single molecules into soap micelles. When a hydrocarbon dissolves in an aqueous soap solution the distance between the layers of oriented soap molecules increases, and it appears that the hydrocarbon molecules form layers between the oriented alkyl groups of the double layers of soap molecules. A somewhat similar phenomenon studied by S. R. Palit and J. W. McBain[2] was the influence of soaps on the mutual solubility of difficultly miscible liquids—benzene and propylene glycol being the pair selected for investigation. A minimum concentration of soap, which varies according to the temperature, is necessary for complete miscibility, and soaps of greater chain length are in general more effective than those of shorter chain length. The completely miscible solutions are optically clear, non-foaming, and pass through an ultra-filter. The effect is explained on the hypothesis that the soap breaks down the H-bonded structure of the glycol, so enabling benzene molecules to gain access to

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[1] *J. Amer. Chem. Soc.*, 1946, **68**, 220; *J. Colloid Sci.*, 1946, **1**, 105; *J. Chem. Physics*, 1945, **13**, 534; A., 1946, I, 212, 213, 85.

[2] *Ind. Eng. Chem.*, 1946, **38**, 741; A., 1946, I, 309.

the alkyl groups in the glycol. Hexanolamine oleate has been studied by the McBain school, its *X*-ray diffraction patterns being the subject of work by S. Rose and J. W. McBain,[3] and its phase diagrams, osmotic and other physical data for its aqueous solutions having been plotted by E. Gonick and J. W. McBain,[4] who established the existence of isotropic and anisotropic liquid phases of the hexanolamine soap. From *X*-ray diffraction analyses of calcium and sodium palmitates, and sodium *n*-decoate, myristate, stearate, and oleate, K. W. Gardiner, M. J. Buerger, and L. B. Smith[5] followed the changes involved during progressive dehydration of the individual crystalline hydrated soaps; although the molar proportions of water in the products are fractional ($\frac{1}{4}$, $\frac{3}{8}$, or $\frac{1}{2}$ mol. of water per mol. of soap), the results of their work lead the authors to believe that all neutral sodium soap phases represent definite hydrates of the soap molecules.

M. J. Buerger, L. B. Smith, F. V. Ryer, and J. E. Spike[6] have contributed a paper on the crystalline phases of soap, in which several new points of interest are discussed. In the first place, contrary to the view of Ferguson and co-workers,[7] and more in accordance with McBain's findings, they present evidence that more than four—probably at least seven—distinct phases exist. Further, they have attempted to follow the changes which take place when a phase system is altered by change of temperature (as in the cooling of commercial "finished" soaps) in the following manner: the phases which are produced from an original one by change in its environment are termed "descendent phases" and these, when substituted at all points for the phases of the usual "phase diagram," form what is termed a "phase map." The latter is thus a diagram which, for instance, shows the room temperature equivalent of the phases on the phase diagram of a soap system produced at a much higher temperature. Commercial soaps have complex phase maps which naturally differ considerably from one soap to another.

Commercial Soaps etc.—E. J. Better and A. Davidsohn[8] have demonstrated that peroxide values can be directly determined by the Lea method on soaps or on emulsions of fat and water (as in ointments and cosmetics) and can thus be employed, as in the case of ordinary fats, to assess oxidative rancidity or the effect of added antioxidants or other materials. They[9] have also studied the retarding influence on soap rancidity of a number of aromatic compounds usable as soap perfumes, and find that substances of the eugenol or vanillin group, and some amino-compounds, have powerful antioxidant effects, but that their activity is accompanied *pari passu* by darkening effects on the soap.

[3] *J. Amer. Chem. Soc.*, 1946, **68**, 547; A., 1946, I, 304.
[4] *Ibid.*, 683; *J. Colloid Sci.*, 1946, **1**, 127; A., 1946, I, 314, 213.
[5] *J. Physical Chem.*, 1945, **49**, 417; *Amer. Min.*, 1945, **30**, 551; A., 1946, I, 85, 379.
[6] *Proc. Nat. Acad. Sci.*, 1945, **31**, 226; A., 1945, I, 335.
[7] *Ann. Repts.*, 1944, **29**, 237.
[8] *Oil and Soap*, 1945, **22**, 325; B., 1946, II, 253; C., 1946, 171.
[9] *Ibid.*, 1946, **23**, 245; B., 1947, II, 20.

M. W. McKinney and L. D. Edwards[10] have contributed further[11] studies on the irritant action of some of the lower fatty acid soaps on human skin, using a number of binary mixtures, including sodium octoate and laurate, or either of these with sodium myristate, oleate, linoleate, or ricinoleate. Whilst ricinoleate with laurate or octoate shows increased irritant action, linoleate, oleate, or myristate appears to reduce the effect of the laurate or octoate. The authors suggest that the higher degree of dissociation of salts of the two lower acids reduces that of the soaps of higher molecular weight, thereby increasing the proportion of undissociated soaps present, the skin effect being ascribed to the greater wetting power and therefore penetrability of the latter.

The uses of "modified" or processed rosin of different kinds in soap have been discussed by B. S. van Zile and J. N. Borglin.[12] These may be produced by hydrogenation, dehydrogenation, or polymerisation of the natural rosin acids. Polymerised rosin gives a firmer but somewhat darker product than natural rosin when added to the soap charge, and either form compares favourably with ordinary rosin in increasing the quantity and stability of the lather and the rate of solution of the soap as a whole. The hydrogenated rosins, in addition, are very pale and do not darken, increase the wetting power of the soap, and may possess germicidal activity.

Synthetic Detergents.—Salts of alkyl- or alkylaryl-sulphonic acids can be determined, according to T. U. Marron and J. Schifferli,[13] by direct volumetric analysis. Such salts give with *p*-toluidine hydrochloride a *p*-toluidine salt which can be removed quantitatively from aqueous solution by an organic solvent and then determined titrimetrically.

The production of synthetic fatty acids (and fats) in Germany during the war years, mainly by the oxidation of Fischer–Tropsch waxes, has been examined exhaustively by British and United States Commissions in the occupied zones, and several comprehensive reports have been published.[14] Very full descriptions of the processes and plant involved have been given, and not the least interesting information is the estimated potential supply—about 83,000 tons per annum—of synthetic fatty acids from all the plants in action or being erected at the end of the war; the actual production, however, was not more than about 10% of this quantity. The 1938 costs of production of the synthetic fatty acids were estimated to be about 700 Reichsmarks per ton, and it is said that, normally, synthetic acids for soapmaking would cost twice as much as natural soapmaking oils in Germany and on the world market perhaps three times as much.

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[10] *Oil and Soap*, 1946, **23**, 198; B., 1946, II, 386.

[11] *Ann. Repts.*, 1940, **25**, 294.

[12] *Oil and Soap*, 1945, **22**, 331; *Soap*, 1946, **22**, *No.* 6, 43; B., 1946, II, 253, 385.

[13] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 49; C., 1946, 83.

[14] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 182; *Brit. Intelligence Objectives Sub-Commee.*, "Oils and Fats Industry," 1945, *Final Rept.*, 86, *Items* 22, 31, pp. 24, 50; B., 1946, II, 461; III, 257.

The production of Igepons, Igepals, alkylarylsulphonates, detergent and emulsifying products from Fischer–Tropsch oils, and some other types of sulphonated or sulphated materials during the war at I.G. Farbenindustrie, Höchst, is the subject of a similar report[15] by a joint British and United States Commission, which gives a very complete account of many processes and products developed at Höchst. The Commission found that during the war period no improvement involving new structural changes in the detergent molecule had emerged, the chief alterations being those necessary to incorporate such fresh raw materials as necessities of war-time economy dictated. The impression given by this report is that the synthetic detergents, whether from fatty alcohols or from petroleum sources, which are either already being produced or planned to be produced in Great Britain should prove as efficient and serviceable as any of the German products, whilst in a few respects some of the war-time discoveries in the German factories embody new principles which merit the consideration of similar industries in this country. Naturally, the abundance of detailed information in both this and the preceding[14] reports can only be adequately employed after study of the respective monographs.

EXTRACTION AND PROCESSING OF FATS.

General.—A most useful review and survey of the present position in regard to world supplies and demands for fatty oils and oilseeds has been contributed by F. E. Fehr[16]; statistics of the imports to Great Britain for the years 1937—1945 are given with regard to butter, lard, and fats and fatty oils derived from oilseeds, the factors which at present influence and in some degree control the restricted production or import of some fatty oils or their sources are individually analysed, and the prospects of restoring the flow of fats and oilseeds to or beyond the pre-war condition, with suggestions in regard to measures calculated to stimulate this recovery, are discussed.

The condition of the oil extraction and refining industries in Germany during and at the end of the war has been fully described and assessed in the report[14] of the British Intelligence Objectives Sub-Committee quoted earlier, and also by W. H. Goss.[17] Fat extraction, refining, and margarine making were carried out mainly on conventional lines. Expression of fats is largely by double, or sometimes treble, expelling (low-pressure type) or sometimes by closed cage presses; solvent extraction is more frequently continuous rather than a batch process. High-vacuum steam-distillation is used in some factories to remove some of the free fatty acid from crude oils which contain more than 5%. For fat-splitting, autoclaving at 12—40 atm. has almost replaced the Twitchell process, but no continuous fat-splitting plant appeared to be installed. For

[15] *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXVI–2; B., 1946, II, 150, 447, 461.

[16] *Bull Imp. Inst.*, 1946, **44**, 183.

[17] *Oil and Soap*, 1946, **23**, 241; B., 1947, II, 19.

fat hydrogenation the catalyst in general use was nickel formate. Lecithin is separated from all edible oils and finds use as an emulsifying agent in margarine and elsewhere.

Extraction and Refining of Individual Fats.—Amongst a number of communications on various aspects of the extraction of fats from oilseeds the following may be mentioned: solvent extraction of cottonseed oil (H. L. E. Vix, E. F. Pollard, J. J. Spadaro, and E. A. Gastrock[18]), variations in solvent-extracted tung oils (R. S. McKinney and R. E. Oglesbee[19]), expression of tobacco-seed oil (E. Briquet[20]), and yields and characteristics of Chinese vegetable tallow and seed oils grown in Texas (W. M. Potts and D. S. Bolley[21]).

F. E. Deatherage[22] has described tests on a semi-large scale of a new process for rendering lards and tallows in which the fatty tissue is first digested with dilute (1—2%) caustic soda solution at 90° for an hour in presence of 2—5% of dissolved sodium chloride. This effects solubilisation of the cell tissue-proteins, when the fat readily separates and is apparently of generally higher quality than that obtained by the more usual direct rendering with steam. Separation of the alkali-rendered fat from water and any residual tissue is effected by centrifuging. The principle of the method is not new but it has not previously been applied to lards and tallows; it has been applied earlier in the extraction of medicinal cod-liver oil,[23] and has been recommended more recently by W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg[24] for the laboratory isolation of fats from fish livers.

Solid sodium chlorite ($NaClO_2$) is now manufactured in the United States, where it has found use in the bleaching of cotton and textile fibres; J. B. Tuttle and E. R. Woodward[25] have found that tallows can be satisfactorily bleached by chlorine liberated *in situ* by addition of sodium chlorite to the fat agitated in an aqueous solution (pH not above 4).

Technical Separation of Fatty Acids by Crystallisation.—A few years ago[26] suggestions were made for the technical separation of fatty oils into fractions of higher or lower unsaturation by crystallisation from suitable solvents at low temperatures, but the mixed nature of the natural constituent glycerides usually militates against the achievement of any very clear-cut separation. On the other hand, similar separation of the mixed fatty acids from a fatty oil is much more complete and practicable,

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[18] *Ind. Eng. Chem.*, 1946, **38**, 635; B., 1946, II, 336.

[19] *Proc. Amer. Tung Oil Assoc.*, 1945, 43.

[20] *Mitt. Lebensm. Hyg.*, 1945, **36**, 206; B., 1946, II, 169.

[21] *Oil and Soap*, 1946, **23**, 316.

[22] *Ibid.*, 327; B., 1947, II, 84.

[23] Cf. B.P. 293,277; K. Kawai, B.P. 381,342, 465,547; B., 1932, 1090; 1937, 1369; H. N. Brocklesby and K. Green, *Biol. Bd. Canada, Prog. Repts.*, 1934, **22**, 18; 1937, **33**, 7; B., 1938, 80.

[24] *J.S.C.I.*, 1943, **62**, 221; C., 1944, 30.

[25] *Chem. Met. Eng.*, 1946, **53**, *No.* 5, 114; B., 1946, II, 290.

[26] Cf. *Ann. Repts.*, 1943, **28**, 237.

and in this form the low-temperature crystallisation procedure appears to be developing rapidly in technical practice. Thus D. Swern, H. B. Knight, J. T. Scanlan, and W. C. Ault[27] have shown that better quality "stearine" can be produced from tallow fatty acids by crystallising them from 15% solution in acetone at 0° to −20° than by the ordinary pressing process; the crystallised acids have an iodine value of 4—12, whilst the soluble acids (corresponding to "oleine") contain about 85% of oleic, 5% of polyethenoid, and 10% of saturated acids, and can be esterified with glycerin to give an inedible olive oil substitute. Alternatively, further crystallisation of the "oleine" from acetone at −60° removes all but 1% or less of polyethenoid acids from the deposited (about 90% oleic and 10% saturated) acids. In a further paper, D. Swern, J. T. Scanlan, and E. T. Roe[28] have applied the method to similar separation of the acids from partly hydrogenated fats. R. E. Kistler, V. J. Muckerheide, and L. D. Myers[29] have described the "Emersol" continuous process for preparation of "stearines" and "oleines" by crystallising the mixed fatty acids of tallows or other fats from 90% methanol; the relatively sharp separation into solid and liquid acids in one operation is effected, it is stated, at a cost about 65% less than that of the older pressing method.

Application of similar procedure to other fatty acid mixtures has also been under investigation. Thus W. S. Singleton, M. Lambou, and A. E. Bailey[30] have examined the separation of the saturated and unsaturated fatty acids from raw and from hydrogenated cottonseed oils from acetone, methyl acetate, or light petroleum, and it has been suggested elsewhere[31] that tall oil can be resolved into its fatty and resin acid constituents by esterifying it (when only the fatty acids are esterified) and crystallising from acetone or methyl ethyl ketone at a low temperature, when the fatty esters separate and leave the resin acids in solution.

Selective Hydrogenation of Linoleic and Linolenic Glycerides.—Knowledge of the mechanism underlying the "selective" hydrogenation of polyethenoid glyceride groups has been considerably advanced owing to the work of A. E. Bailey and G. S. Fisher,[32] who made further studies of the course of hydrogenation in cottonseed, soya-bean, and linseed oils, and, especially, the esters of linolenic acid. Following Lemon's observation[33] that the octadecadienoic glycerides produced during hydrogenation of the linolenic glycerides of linseed oil do not wholly undergo alkali-isomerisation to a conjugated form and are apparently mainly glycerides of octadeca-9 : 15-dienoic acid, K. F. Mattil[34] and B. F. Daubert and

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[27] *Oil and Soap*, 1945, **22**, 302; B., 1946, II, 207.
[28] *Ibid.*, 1946, **23**, 128; B., 1946, II, 382.
[29] *Ibid.*, 146; B., 1946, II, 382.
[30] *Ibid.*, 1945, **22**, 168; 1946, **23**, 201; B., 1945, II, 345; C., 1946, 257.
[31] *Amer. Perf.*, 1946, 75.
[32] *Oil and Soap*, 1946, **23**, 14; B., 1946, II, 291.
[33] *Ann. Repts.*, 1945, **30**, 277.
[34] *Oil and Soap*, 1945, **22**, 213; B., 1946, II, 51.

L. J. Filer[35] had reported similar anomalies in the spectrophotometric and thiocyanometric analyses of, respectively, hydrogenated soya-bean oil and hydrogenated pure methyl linolenate, thus confirming Lemon's view that an *iso*linoleic derivative incapable of conversion by alkali into a conjugated form had been produced. Bailey and Fisher's work[32] showed that, in the first stages of hydrogenation of a linolenic group, isomeric octadecadienoic groups are produced in the approximate proportions of 50% of the 9 : 15-diene and 50% of the 9 : 12- and 12 : 15-dienes together, whilst a certain proportion of linolenate passes in one stage into the monoethenoid condition; moreover, they found that, taking the "relative reactivity" to hydrogenation of oleate as unity, that of linoleate was 20, and that of linolenate 40 (octadeca-9 : 15-dienoate being 3, and *iso*oleate 1). T. P. Hilditch[36] has pointed out that all the facts now known in regard to "selective" hydrogenation are consistent with the hypothesis that the selectivity is a function of the grouping $-CH:CH{\cdot}CH_2{\cdot}CH:CH-$ and not of polyethenoid systems in general; on this view the "reactive" central methylene group of the system must be supposed to be concerned integrally in the association between metal catalyst and unsaturated system. Restriction of the conception of selective hydrogenation to this specific system is not only in harmony with the relative reactivities observed by Bailey and Fisher and with the intermediate products these workers noted during the hydrogenation of the linolenate group, but also accounts for a number of apparently partial exceptions to selectivity, notably the tetra-, penta-, and hexaenoic glycerides in marine-animal oils. Here, even although the above specific grouping is originally present (often several times in the same molecule), progressive hydrogenation causes rapid separation of the remaining double bonds by more than one $-CH_2-$ group, and consequently the further stages of hydrogenation are non-"selective."

G. V. Pigulevski and P. A. Artamonov[37] have hydrogenated (at room temperature with platinum-black) binary mixtures of octadecenoic acids with double bonds respectively in the 2, 3, 6, and 9 positions, and have observed that the speed of hydrogenation steadily increased with increasing distance between the ethenoid bond and the carboxyl group.

EDIBLE FATS : RANCIDITY.

Milk Fats.

Another study of the component acids of human milk fat, by J. B. Brown and B. M. Orians,[38] confirms in most respects the findings of previous investigators.[39] Only traces of acids lower than *n*-decoic were observed, and total saturated acids formed 45% of the whole; oleic

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[35] *Oil and Soap*, 1945, **22**, 299; B., 1946, II, 209.

[36] *Nature*, 1946, **157**, 586; A., 1947, II, 102.

[37] *J. Gen. Chem. Russ.*, 1942, **12**, 510; A., 1946, II, 247.

[38] *Arch. Biochem.*, 1946, **9**, 201; A., 1946, III, 642.

[39] Cf. *Ann. Repts.*, 1944, **29**, 249.

was the main component of the unsaturated acids, whilst the octadecadienoic acids appeared to be made up in about equal parts of linoleic and of isomeric acids.

The component acids of cow colostrum fat, as observed by C. P. Anantakrishnan, V. R. B. Rao, and T. M. Paul,[40] showed some differences from the previous findings of A. R. Baldwin and H. E. Longenecker,[41] who stated that they were little different from those for typical cow milk fats. The present authors found that the fatty acids of the first day's cow colostrum fat were intermediate in composition between those of the body fat and of the mature milk fat, and also resembled those of human milk fat in their low content of lower saturated acids and their high content of oleic acid; during the first fifteen days of lactation, however, the iodine value of the acids steadily declined and the content of lower saturated acids correspondingly increased.

The glycerides of a typical cow milk fat were separated by E. L. Jack, J. L. Henderson, and E. B. Hinshaw[42] into five fractions by crystallisation from light petroleum at temperatures ranging from −7° to −53°; the component fatty acids and the amount of fully-saturated glycerides were determined in each fraction. The authors found that their results accorded with the general views of Hilditch on the glyceride structure of milk fats. K. T. Achaya and B. N. Banerjee[43] have studied the component fatty acids and proportions of fully-saturated glycerides in Indian buffalo and cow milk and depot fats, and have observed that the palmitic acid contents of both depot and milk fats from Indian animals are about 4 units per cent. higher than in the corresponding European fats; moreover, their fully-saturated glyceride contents fall on a smooth curve (when plotted against the total proportion of saturated acids) which intersects the horizontal axis at a point corresponding with about 35% of saturated acids, whereas the curve for corresponding European fats meets the axis at about 30% of saturated acids. This characteristic difference between Eastern and Western fats may well be connected with the generally higher degree of saturation of the former.

Lards and Tallows.

In pigs fattened entirely on buttermilk W. Tuck, P. B. D. de la Mare, F. B. Shorland, and R. N. Seelye[44] found that the inner back fat was less susceptible to oxidative rancidity than the outer back fat or perinephric fats. J. R. Chipault, W. O. Lundberg, and G. O. Burr[45] found that the

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[40] *Biochem. J.*, 1946, **40**, 292; A., 1946, III, 568.

[41] *Ann. Repts.*, 1945, **30**, 273.

[42] *J. Dairy Sci.*, 1945, **29**, 65; *J. Biol. Chem.*, 1946, **162**, 119; C., 1946, 41; A., 1946, III, 370.

[43] *Current Sci.*, 1946, **15**, 23; *Biochem. J.*, 1946, **40**, 664; B., 1946, II, 252; A., 1946, III, 1031.

[44] *New Zealand J. Sci. Tech.*, 1945, **27**, **A**, 212; B., 1946, II, 125.

[45] *Arch. Biochem.*, 1945, **8**, 321; *Oil and Soap*, 1946, **23**, 382; A., 1946, III, 287; C., 1946, 109.

keeping qualities of edible pig fats are influenced by two factors, namely, their contents of linoleic glycerides and of tocopherols; tocopherols, probably derived from the diet, are the only natural antioxidants present in normal pig fats, and their concentrations in different depot fats from any one animal are similar, but may vary widely in different pigs. These workers also found that tocopherol fed to vitamin-*E*-free rats greatly increased the stability of the body fat, but that quinol or wheat-germ oil had the opposite effect. B. M. Watts, T. J. Cunha, and R. Major[46] fed pigs alternatively on various natural diets and on purified rations with and without added tocopherol; the fat from the latter oxidised less rapidly than that from animals on the natural diets, irrespectively of the presence of added tocopherol, which in the experience of these workers did not afford appreciable additional protective action.

The work of R. W. Riemenschneider, F. E. Luddy, M. L. Swain, and W. C. Ault, briefly referred to in last year's Report,[47] on the glyceride composition of lards and tallows determined by their resolution into seven fractions by low-temperature crystallisation from acetone has been published in full,[48] and it would appear that the conclusions of the authors are not entirely justified. The detailed data given for the component glycerides, in the writer's opinion, agree more closely with the modified type of even distribution found in "stearic-rich" fats than with the "random distribution" which the authors consider to be the "general pattern" of the glycerides of both fats, whilst their finding that the "amount of triunsaturated glycerides in lard is significantly greater than the meagre information in the literature would indicate" is the natural consequence of the unusually high octadecadienoic acid content (12·5%) of the pig fat which they studied. The 18% of triunsaturated glycerides observed by the authors is what is to be expected in a pig fat the acids of which include 50% of oleic and 12·5% of octadecadienoic acids.

Comparative Nutritive Values of Butter and Other Fats.

The "butter–margarine" controversy, referred to in several preceding Reports, has been discussed in detail by H. J. Deuel[49] in an article which summarises all the recent evidence from many different workers indicating that there is no appreciable difference, so far as the fats are concerned, in the growth-promoting values of butter and of edible fats made from blends of vegetable fatty oils. Deuel has also contributed[50] a very useful general article on the rôle of fat in human nutrition, with special reference to U.S. war-time conditions, and with C. Hendrick, E. Movitt, M. E. Crockett, I. M. Smyth, and R. J. Winzler[51] has published further experimental

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[46] *Oil and Soap*, 1946, **23**, 254; B., 1947, II, 18.

[47] *Ann. Repts.*, 1945, **30**, 277.

[48] *Oil and Soap*, 1946, **23**, 276; B., 1947, II, 55; C., 1947, 15.

[49] *Science*, 1946, **101**, 183.

[50] *Oil and Soap*, 1946, **23**, 209.

[51] *J. Nutrition*, 1946, **31**, 737, 747; A., 1946, III, 835.

findings on this subject. H. von Euler and I. Säberg,[52] confirming and extending their earlier work on the subject, have reiterated that no support can be found for the hypothesis that butter fatty acids have more growth-promoting action that those of margarine, nor for the presence of any unique fatty acid factor in butter. E. L. Jack, J. L. Henderson, D. F. Reid, and S. Lepkovsky[53] describe similar experiences, including the observation (also made by S. K. Kon *et al.*[54]) that the most unsaturated mixed glycerides obtained by fractional crystallisation of butter fat promoted growth in rats better than any of the more saturated fractions.

A new suggestion has now been made by J. Boer, B. C. P. Jansen, and A. Kentie,[55] namely, that summer butters have a specific growth-promoting factor present in their fatty acids, which these authors identify with the solid isomer of oleic acid, vaccenic acid, present as a fractional percentage of the fatty acids of butter and of some animal depot fats. Until, however, the specific action of vaccenic acid in this manner has received further confirmation, the matter may well, in view of other suggestions which have subsequently been disproved, and of the extreme difficulty of isolating vaccenic acid in the individual condition, be considered for the time being with some reserve.

In another direction—the assimilation of stearo-glycerides—K. F. Mattil, who last year[56] found that stearic acid was poorly utilised by rats (although somewhat better in mixed glycerides, viz., oleodistearin, than as mixtures of tristearin with triolein), has now[57] made a wide statistical survey of the digestibility by human beings and by rats of fats containing stearic glycerides in differing proportions. Fairly close correlation was established between the values for human adults and for albino rats, whilst the series also indicated that the proportion of stearic or higher saturated acids is the chief limiting factor in digestibility.

Studies on Fat Metabolism.

Whilst it is felt that fundamental work on fat metabolism must be of direct interest to those concerned with edible fats, pressure of other topics for report makes it necessary here merely to cite without adequate discussion a few of the more important recent communications. A. C. Frazer[58] has published further work on the direct absorption of glyceride fat from the intestine, including work on the function of phosphatides in this process, and the effect of choline on fat-absorption. The interaction of fatty acids or soaps with phosphatides in thin layers spread on water has been studied by D. Dervichian and J. Pillet.[59] F. Bullet and

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[52] *Arkiv Kemi, Min. Geol.*, 1944, **17**, **A**, *No.* 10, 15.
[53] *J. Nutrition*, 1945, **30**, 169, 175; A., 1945, III, 869.
[54] *Ann. Repts.*, 1944, **29**, 238.
[55] *Nature*, 1946, **158**, 201;
[56] *Ann. Repts.*, 1945, **30**, 275.
[57] *Oil and Soap*, 1946, **23**, 344.
[58] *J. Physiol.*, 1944, **102**, 24P; *Physiol. Rev.*, 1946, 103; *Nature*, 1946, **157**, 414; A., 1944, III, 595; 1946, III, 824.
[59] *Bull. Soc. Chim. biol.*, 1944, **26**, 454; A., 1946, III, 218.

K. Bernhard[60] fed rats on a fat-free diet with "heavy" water in their drinking water; in the resulting body fats, the deuterium content of oleic acid was less than half that of palmitic and stearic acids, whilst it was absent from linoleic and linolenic acids. Feeding deuterobehenic ester resulted in the appearance of deutero-stearic, -palmitic, and -oleic acids in rat body fats (K. Bernhard and E. Vischer).

Several interesting reports of the specific action of unsaturated acids on development of living organisms have appeared. Linolenic, linoleic, and oleic acids, in decreasing order of activity, have been found by S. Bergström and H. Theorell[61] to suppress or decrease the oxygen uptake of *Mycobact. tubercul.* Hum., and by E. Kodicek and A. N. Worden[62] to inhibit the growth of *Lactobacillus helveticus.* Conversely, G. Fraenkel and M. Blewett[63] have shown that linoleic or linolenic derivatives are indispensable for the development of the adult moth from the pupa of *Ephestia kuehniella* Lep.

Rancidity.

Flavour Reversion in Soya-Bean and Linseed Oils.—This difficult question is receiving much attention in the United States and Canada, in the former country more especially in relation to soya-bean oil, which according to O. H. Alderks[64] is now nearly as important as cottonseed oil, the U.S. 1944 production of soya-bean oil being 600,000 tons. It was mentioned in last year's Report[65] that W. D. McFarlane, following H. W. Lemon, attributed "reversion" in hydrogenated linseed oils to some intermediate product of hydrogenation, possibly octadeca-9 : 15-dienoic glycerides; this view receives some support from further work by C. S. Privett, R. B. Pringle, and W. D. McFarlane,[66] who found that hydrogenation of the acetone-soluble fraction of a heat-polymerised linseed oil gave a fat with no tendency to "revert" as regards flavour. A. E. Bailey,[67] discussing the problem in general, appears to accept the same view in so far as hydrogenated oils are concerned, but he points out that the unhydrogenated oils also share the trouble and this, moreover, after less oxidation than is required for the development of ordinary oxidative rancidity. While suggesting that the reversion may be partly associated with the presence of triethenoid glycerides, Bailey also notes that in some cases reversion seems to be associated with non-fatty, possibly nitrogenous compounds which may accompany the oils. Again, C. Golumbic, C. J. Martin, and B. F. Daubert[68] refer to a number of different specific

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[60] *Helv. Physiol. Pharm. Acta,* 1943, **1**, c, 39; *Helv. Chim. Acta,* 1946, **29**, 929; A., 1944, III, 81; 1946, III, 941.

[61] *Nature,* 1946, **157**, 306.

[62] *Ibid.,* 587; A., 1947, III, 266.

[63] *Biochem. J.,* 1946, **40**, *Proc.,* xxii; A., 1946, III, 663.

[64] *Oil and Soap,* 1945, **22**, 232; B., 1946, II, 51.

[65] *Ann. Repts.,* 1945, **30**, 277.

[66] *Oil and Soap,* 1945, **22**, 287; B., 1946, II, 208.

[67] *Ibid.,* 1946, **23**, 55; B., 1946, II, 382.

[68] *Ibid.,* 187, 360, 380; B., 1946, II, 384.

"reversion" flavours in soya-bean oil, and show that their development can be accelerated by heat or by light without appreciable oxidation, and also that at extremely low pressures of oxygen (0·5%) reversion flavour develops as rapidly as when atmospheric oxygen is present. Spectroscopic examination of the oils showed a certain amount of specific absorption, but it was not possible to correlate this with the off-flavours or with peroxide values. The flavour is removable by re-deodorisation, but the oil has an unaltered tendency to "revert" again on keeping. Sitosterol, stigmasterol, or fractions separated chromatographically from deodorisation condensates did not cause development of the flavour in other edible oils. A "simulated" soya-bean oil synthesised from glycerol and appropriate proportions of the pure fatty acids present in soya-bean oil was intermediate in flavour reversion between cottonseed and soya-bean oils, but grassy and other flavours typical of "reverted" soya-bean oil did not appear in the "simulated" oil.

The problem, it will be seen, is far from solved; whilst polyethenoid glycerides or their semi-hydrogenated products may well be one essential factor, the consensus of results so far seems to suggest that, in soya-bean oil at least, a non-fatty impurity with the oil may be specifically concerned. Indeed, Alderks[64] suggests that improvements in harvesting, storing, and processing the soya beans may largely mitigate the trouble; possibly, also, an intensive "de-sliming" treatment (removal of dispersed mucilage) might be advantageously employed with soya-bean and some other vegetable oils.

Tests for Oxidative Rancidity.—Here, again, space considerations cause only brief mention to be given to recent work. The Kreis rancidity tset has received fresh attention from M. F. Pool and A. N. Prater[69] (who have presented it in a more sensitive form adapted to photocolorimetric measurement) and from B. M. Watts and R. Major[70] (correlation of Kreis and peroxide values). C. H. Lea[71] has given procedures for iodometric determination of peroxide values at room temperature and at the boiling point of the solvent employed.

Tests involving the direct measurement of absorbed oxygen have been further discussed by B. W. Beadle[72] (points for and against the use of "accelerated" tests), M. H. Menaker, M. L. Shaner, and H. O. Triebold,[73] E. W. Eckey,[74] R. Gilmont, H. S. Levenson, and L. W. Elder[75] (all of whom describe different forms of continuous or automatic apparatus for measuring oxygen absorption by fats under controlled conditions), and L. D. Chirgwin[76] (determination of end-point in the Swift stability test

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[69] *Oil and Soap*, 1945, **22**, 215; C., 1946, 23.
[70] *Ibid.*, 1946, **23**, 222; C., 1947, 71.
[71] *J.S.C.I.*, 1946, **65**, 286.
[72] *Oil and Soap*, 1946, **23**, 33; B., 1946, II, 290.
[73] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 518; C., 1946, 64.
[74] *Oil and Soap*, 1946, **23**, 38; C., 1946, 170.
[75] *Ibid.*, 248; C., 1947, 13.
[76] *Ibid.*, 1945, **22**, 254; C., 1946, 91.

by changes in the refractive index–time curve). Further spectrophotometric studies[77] of fats and individual unsaturated esters during autoxidation have been made by R. T. Holman, W. O. Lundberg, and G. O. Burr.[78] L. J. Filer, K. F. Mattil, and H. E. Longenecker[79] have attempted to define some of the chemical changes which go on during autoxidation of unsaturated fats; their results, whilst confirming general characteristics observed by other workers (decrease of total diethenoid concentration, development of conjugated diethenoid unsaturation, etc.), add little fresh data except in showing that no essential alteration takes place until the concentration of peroxides suddenly commences to increase rapidly, that in the early stages linoleic glycerides may be oxidised preferentially before oleic glycerides, and that a fat may become quite rancid organoleptically before 10% of its octadecadienoic glycerides have been attacked by oxygen.

Antioxidants.—C. Golumbic[80] has tested a hypothesis to explain the action of synergists with phenolic antioxidants, namely, that there is an oxidation–reduction action between synergist and an oxidised form of the phenolic compound; this would invoke a difference in oxidation potential between synergist and antioxidants. Golumbic found that the most effective fat antioxidants were those in the potential region 484—848 mv., and that in binary combinations with synergistic activity the component of higher oxidation potential always fell within this range. Application of the hypothesis led to the discovery of several new effective combinations, whilst various combinations incapable of oxidation–reduction action were found to be without synergistic activity.

J. A. Lovern[81] has contributed a review of work on antioxidant effects carried out in Great Britain during the war, and discussed the bearing of the results on the theories of mechanism of antioxidant action, in the course of which he concludes that accelerated tests may not necessarily give a true picture of the efficiency of a given antioxidant at the normal temperature of storage. On the other hand, E. Bickoff and K. T. Williams[82] have obtained results which show that accelerated tests at 75° accord with those at 25°, and that the protection given by, for instance, nordihydroguaiaretic acid or tocopherol at 25° was as good as, or better than, that indicated by tests at 75°. A. Fonyo[83] has described the occurrence and distribution (in Southern U.S. arid regions) of the "creosote bush," the leaves and twigs of which are the source of nordihydroguaiaretic acid; improved methods for the extraction of the compound are suggested, and it is stated that the quantity available and facilities for production

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[77] Cf. *Ann. Repts.*, 1945, **30**, 281.

[78] *J. Amer. Chem. Soc.*, 1945, **67**, 1669; 1946, **68**, 652; *Arch. Biochem.*, 1946, **10**, 519; *Oil and Soap*, 1946, **23**, 10; B., 1946, II, 51; A., 1946, I, 318; A., 1946, III, 960; B., 1946, II, 290.

[79] *Oil and Soap*, 1945, **22**, 196; B., 1945, II, 344.

[80] *Ibid.*, 1946, **23**, 184; A., 1946, I, 318.

[81] *Ibid.*, 40; B., 1946, II, 382.

[82] *Ibid.*, 65; B., 1946, II, 383.

[83] *Ibid.*, 75; B., 1946, II, 386.

are ample. H. T. Spannuth, T. H. McGuine, and G. A. Crapple[84] have described procedures for treating edible fats with 0·1% of tannins as antioxidants.

DRYING OILS: AUTOXIDATION.

Autoxidation.—Important additions to knowledge of the mechanism of addition of oxygen to the characteristic drying oil system $-CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH-$ continued to be made during the past year. Kinetic and thermal studies of the oxidation of linoleic and oleic esters by J. L. Bolland and G. Gee[85] have indicated the possible mechanism of the chain reaction whereby autoxidation may be propagated from one unsaturated molecule to another. Oxidation chains are initiated by thermal decomposition of linoleate or oleate hydroperoxide and the chain propagation reactions were identified as $R- + O_2 \rightarrow RO_2-$ and $RO_2 + RH$ (unsaturated ester) $\rightarrow R{\cdot}OOH + R-$. Whilst the propagation of autoxidation in unsaturated fats (the factor mainly involved in oxidative rancidity) has thus received more logical explanation than formerly, there is less positive evidence as to the primary point of the unsaturated system at which combination with oxygen is effected. It will be recalled that E. H. Farmer[86] suggested that this does not take place at a double bond, but at a methylene group adjacent to a double bond (and especially at one situated between two double bonds), the methylene group initially suffering dissociation of a hydrogen atom or proton, and peroxide oxygen being introduced at this point. More recently this view has been modified by Farmer and his colleagues. Thus Bolland and Gee (*loc. cit.*) have said that, of the two possible points of oxidative attack—double bond or active methylene group—the argument that the latter must be the site is invalid unless the chain length of the oxidation is extremely short, whilst Farmer[87] has pointed out that there is perhaps good justification for postulating universal initiation of autoxidative attack in all the various kinds of olefinic systems by addition occurring at double bond centres.

Meanwhile, although E. H. Farmer and D. A. Sutton[88] had been unable to separate and identify the hydroxystearic acids obtained by reduction of oleate hydroperoxide, S. Bergström[89] identified the corresponding products from linoleate hydroperoxide, produced either by atmospheric or by enzymic (lipoxidase) oxidation, as mixtures of 9- and 13-hydroxystearic acids from which the 11-hydroxy-acid was absent, and suggested that an 11-hydroperoxide initially formed at the reactive 11-methylene group underwent rapid rearrangement. F. D. Gunstone and T. P.

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[84] *Oil and Soap*, 1946, **23**, 110; B., 1946, III, 220.

[85] *Trans. Faraday Soc.*, 1946, **42**, 236, 244; cf. Bolland, *Proc. Roy. Soc.*, 1946, A, **186**, 218.

[86] *Ann. Repts.*, 1942, **27**, 268; 1943, **28**, 235.

[87] *Trans. Faraday Soc.*, 1946, **42**, 228.

[88] *Ann. Repts.*, 1943, **28**, 234.

[89] *Nature*, 1945, **156**, 717; *Arkiv Kemi, Min., Geol.*, 1946, **21**, A, *Nos.* 14, 15; A., 1946, II, 417.

Hilditch,[90] however, have suggested that the first stage in the attack of oxygen is the production of an unstable complex between oxygen and double bond, the consequent reorientation of interatomic forces causing a hydrogen atom attached to a methylene group contiguous to the double bond to be loosened and finally to become combined in the form of a hydroperoxide group at one of the carbon atoms originally concerned in the ethylenic bond : $-{}^*CH{:}CH{\cdot}CH_2- \rightarrow -{}^*CH(OOH){\cdot}CH{:}CH-$. This view implies that a double bond shift is bound to accompany autoxidation. That this is so in linoleates and linolenates is established by the production of conjugated dienes as autoxidation proceeds : with isolated double bonds (oleates) the experimental evidence is not yet clear, since the products of oxidative scission of oleate hydroperoxides would be the same on either hypothesis, and since the reduction products—hydroxystearic acids—from oleate hydroperoxides have yet to be identified. Nevertheless, observations reported in 1945 by D. Swern, H. B. Knight, J. T. Scanlan, and W. C. Ault[91] provide evidence that autoxidation of methyl oleate at 65° in presence of cobalt oleate gives products, including 30—40% of high-boiling polymerised material and also hydroxylated esters, in which double bond shift has taken place. The circumstance that, on the above view, autoxidation of linoleo- or linoleno-glycerides automatically involves conversion of these systems into conjugated forms analogous to those of elæostearic glycerides (tung oil) appears to have an essential bearing on the mechanism whereby linseed and similar drying oils are transformed into polymerised products when exposed as films to the action of atmospheric oxygen.

The autoxidation of methyl oleate has also been re-examined by C. E. Swift, F. G. Dollear, and R. T. O'Connor,[92] who have confirmed the experimental findings of Farmer and Sutton[88] that (unidentified) hydroxystearic acids are obtained by hydrogenation of the hydroperoxides, and of D. Atherton and T. P. Hilditch[93] as regards the oxidative scission products of the latter. They found that the hydroperoxide *per se* is odourless and unlikely to be directly responsible for rancidity flavour, and also that it could be separated more conveniently from unchanged oleate by taking advantage of its much greater solubility in acetone at very low temperatures than by chromatographic adsorption or molecular distillation.

Spectrophotometric Analysis of Drying Oils.

In determining conjugated and non-conjugated di-, tri-, and tetra-ethenoid fatty acids spectrophotometrically before and after isomerisation with alkali, the use of glycerol in place of ethylene glycol as solvent for the alkali is preferred by B. A. Brice and M. L. Swain,[94] who have also

[90] *J.C.S.*, 1946, 1022; A., 1947, II, 106.

[91] *J. Amer. Chem. Soc.*, 1945, **67**, 1132; A., 1945, II, 386.

[92] *Oil and Soap*, 1946, **23**, 355; A., 1947, II, 106.

[93] *Ann. Repts.*, 1944, **29**, 243.

[94] *J. Opt. Soc. Amer.*, 1945, **35**, 532; cf. C., 1946, 22.

advised correction of the spectral data for irrelevant absorption due to traces of non-fatty compounds which may be present. Full reviews of the procedures described to date, with useful tables and graphs of absorption maxima, $E^{1\%}_{1\,\text{cm.}}$ reference values, and other data, and formulæ for calculating the amounts of the various unsaturated acids have been presented by I. I. Rusoff, R. T. Holman, and G. O. Burr,[95] and by B. W. Beadle.[96] The use of the method as a criterion of purity of linoleic and linolenic acids prepared by debromination, and as a control of precautions in the preparations essential to ensure freedom from oxidation and from presence of conjugated impurities, has been stressed by R. T. O'Connor, D. C. Heinzelman, M. Caravella, and S. T. Bauer.[97] Direct alkali-isomerisation of cholesteryl linoleate has been found by J. S. Front and B. F. Daubert[98] to proceed with difficulty; they conclude, doubtless correctly, that this result is due to insolubility of the ester in the glycol or glycerol used as alkali solvent. The same difficulty arises with certain glycerides or methyl esters, and T. P. Hilditch, R. A. Morton, and J. P. Riley recommended earlier[99] that the alkali-isomerisation should always be carried out on mixed acids previously prepared by separate hydrolysis.

From several papers published recently it might be concluded that many fats of which linolenic acid has not hitherto been supposed to be a constituent contain small traces of this acid, since on alkali-isomerisation they exhibit absorption at 268 mμ. to a slight extent ($E^{1\%}_{1\,\text{cm.}}$ of a few units, not exceeding 10); thus B. A. Brice, M. L. Swain, B. B. Schaeffer, and W. C. Ault,[100] after making corrections for irrelevant absorption, have detected small amounts of polyethenoid constituents in lards and tallows, and also in some other fatty oils usually believed to contain only linoleic and oleic acids. It may be questionable, however, whether very small spectral absorption of this order should be attributed to linolenic acid unless its positive identification, *e.g.*, in the form of hexabromostearic acid, can also be effected. A modification of the spectrophotometric method which assists the determination of small proportions of linolenic acids has been given by R. T. O'Connor, D. C. Heinzelman, and F. G. Dollear[101]; this was primarily designed to determine soya-bean oil when mixed with cottonseed or groundnut oils, and a "correction factor" of 0·33%, representing the "apparent linolenic acid content" of the latter oils, is deducted before crediting the observed linolenic acid percentage in terms of soya-bean oil. It was found that the proportion of admixed soya-bean oil could thus be determined to within about 2 units %.

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[95] *Oil and Soap*, 1945, **22**, 290; B., 1946, II, 207.
[96] *Ibid.*, 1946, **23**, 140; C., 1946, 257.
[97] *Ibid.*, 5; A., 1946, II, 418; C., 1946, 161.
[98] *J. Amer. Chem. Soc.*, 1945, **67**, 1509; A., 1946, II, 90; C., 1946, 20.
[99] *Ann. Repts.*, 1945, **30**, 282.
[100] *Oil and Soap*, 1945, **22**, 219; C., 1946, 22.
[101] *Ibid.*, 257; C., 1946, 92.

Polymerisation of Drying Oils.

Conversion of Linoleo- or Linoleno-Glycerides into Conjugated Isomers.—As indicated earlier, polymerisation of linseed or similar oil films in presence of air is almost certainly dependent on rearrangement of the di- and tri-ethenoid acyl groups to conjugated forms as a consequence of the autoxidation reaction. On the other hand, transformation by chemical or physical processes of non-conjugated di- or tri-ene glycerides into conjugated isomers—in other words the conversion of a linseed oil type into a tung oil analogue—remains an attractive technical proposition. Up to the present (apart from dehydration of castor oil) the most direct method has seemed to be alteration of the unsaturation by the action of alkali at high temperatures,[102] a procedure which of course involved hydrolysis of the glycerides and production of fatty acids which then require re-esterification. In connexion with this process, D. E. Terry and D. H. Wheeler[103] have shown that by careful fractionation of the re-esterified methyl esters it should be technically possible to obtain a rich concentrate (75%) of conjugated diene ester; they state that the alkali-isomerisation yields 75% of conjugated and 25% of non-conjugated octadecadienoic acids, the conjugated portion being mainly the 10 : 12-diene acid with smaller proportions of the 9 : 11-diene acid, and the pure conjugated diene acids having $E^{1\%}_{1\,\text{cm.}}$ 1150 at 234 mμ. Clearly, an isomerising agent which could be employed without splitting the glycerides of a natural fatty oil would represent a most important advance in technical procedure, and from this point of view two papers by J. C. Cowan, H. M. Teeter, and co-workers[104] are of the greatest interest; they have found that when linoleo- or linoleno-compounds (fatty oils or methyl esters) are heated at 170—190° with reduced nickel supported on active charcoal ("Nuchar," prepared from residues of sulphite waste liquors), 30—40% of conjugated di- or tri-ene glycerides, and over 60% of conjugated methyl octadecadienoates, are produced, the degree of isomerisation being less with esters of polyhydric than of monohydric alcohols. The rate of heat-polymerisation of drying oils isomerised in this way is increased from two- to five-fold. The specific nature of the charcoal supporting the nickel appears to be critical for the success of the isomeric change. H. I. Waterman *et al.*[105] had indeed observed some years ago that the refractive index of linoleic esters was increased on heating with catalytic nickel or platinum in an inert atmosphere at 200°, and had suggested that the "activated" esters so produced were more readily polymerised by heat than before treatment. From the theoretical viewpoint these observations reinforce the view (quoted earlier[36] in this Report when discussing selective hydrogenation) that metal catalysts interact with the system $-CH:CH\cdot CH_2\cdot CH:CH-$ in such a way that a hydrogen atom

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[102] Cf. *Ann. Repts.*, 1942, **27**, 270.
[103] *Oil and Soap*, 1946, **23**, 88; B., 1946, II, 383.
[104] *Ind. Eng. Chem.*, 1946, **38**, 997, 1002; B., 1947, II, 20.
[105] *Ann. Repts.*, 1937, **22**, 454.

attached to the central methylene group becomes detached, so that, in the absence of a hydrogen atmosphere, isomeric rearrangement to a conjugated diene form may result.

Of more fundamental work on thermal polymerisation the following may be noted. G. Champetier and J. Petit[106] have obtained experimental support for the view that the reaction proceeds by a Diels–Alder condensation, following rearrangement of isolated double bonds to conjugated forms; the condensation involves conjugated groups in two or more different acyl groups and, in the authors' view, it is linear for esters of monohydric alcohols, two-dimensional for glycol esters, and three-dimensional for those of polyhydric alcohols. In this connexion it is interesting to find that J. Ross, A. I. Gebhart, and J. F. Gerecht[107] obtained by heat-treatment of methyl undec-10-enoate, amongst other dimers and polymers, a linear dimer of the structure $CO_2Me\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_{11}\cdot CO_2Me$. E. Sunderland[108] obtained 70% of high polymers, 20% of dimeric forms, and 10% of an octadecadienoic (8 : 11- or 8 : 12-diene) acid by heat-polymerisation of β-elæostearic acid at 270—280° in a vacuum, and, although the nature of the high polymers was not elucidated, some signs that a tetraene acid is transitionally formed during the heat-treatment were detected. The mechanisms indicated by these observations appear to contradict many earlier theoretical speculations on thermal polymerisation, and Sunderland critically reviews much of the literature published on the subject since 1930. H. S. Taylor[109] has contributed a general discussion on the rôle of free radicals in the production of vinyl and diene polymers, and states that such compounds may yield multimolecular radicals by interaction with oxygen ($RH + O_2 \rightarrow R\text{–} + \text{–}O_2H$)' or with another free radical (R–) and that this type of polymer formation is frequently initiated by small proportions of peroxides produced by the action of oxygen on the original compounds.

Vegetable Drying Oils.

Linseed oil produced in New Zealand from flax grown primarily for its fibre is stated by W. J. Newman[110] to reach the standard specification, but imported linseed oils are preferred by the trade. Reports on the oil and meal produced from Canadian sunflower seed have been published by H. R. Sallans.[111]

General schemes for determination of the component acids of drying oils by the spectrophotometric and ester-fractionation techniques after preliminary separation of the mixed fatty acids into several groups by crystallisation from acetone or ether at low temperatures have been outlined for fats containing linolenic, linoleic, and oleic acids by F. D.

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[106] *Bull. Soc. chim.*, 1945, [v], **12**, 680, 689; B., 1946, II, 208.

[107] *J. Amer. Chem. Soc.*, 1945, **67**, 1275; A., 1946, II, 3.

[108] *J. Oil Col. Chem. Assoc.*, 1945, **28**, 137; B., 1946, II, 16.

[109] *J. Amer. Chem. Soc.*, 1945, **67**, 2063; B., 1946, II, 189.

[110] *Paint Manuf.*, 1945, **15**, 316; B., 1946, II, 90.

[111] *Canad. J. Res.*, 1945, **23**, **F**, 91.

Gunstone and T. P. Hilditch,[112] and for fats containing elæostearic acid by T. P. Hilditch and J. P. Riley.[113] In general, concentration of as much linolenic acid as possible in the most soluble fractions, or of elæostearic acid in the sparingly soluble fractions, is to be desired, and it is not necessary to employ ester-fractionation other than in the least soluble portion of the acids (in order here to ascertain the proportions of the homologous saturated acids present). When, as in most drying oils, the amount of saturated acids does not exceed about 10% of the whole, it has been found convenient and expeditious to analyse each crystallised group of acids spectrophotometrically, and to determine palmitic and any lower saturated acids by fractionation of the esters of the total fatty acids after complete hydrogenation; stearic acid is then obtained by difference from the summation of the components of the individual groups as determined by spectrographic analysis. Arachidic acid, when present, must be determined from ester-fractionation of the least soluble group of acids. Typical results obtained for several fatty oils by use of these methods are quoted in the table below. In this table are also given recent data by R. T. Milner, J. E. Hubbard, and M. B. Wiele[114] for American-grown sunflower- and safflower-seed oils, by C. R. Pye[115] for niger-seed and stillingia oils, and by N. I. Ivanoff[116] for neou oil (from *Parinarium macrophyllum*); these analyses were made, so far as is known, on the mixed acids of the oils by iodine and thiocyanometric methods (employing the revised thiocyanogen values for linoleic and linolenic acids).

Oil.	Palmitic.	Stearic.	Oleic.	Linoleic.	Linolenic.	Elæostearic.
Linseed[112]	7	8*	13	17	54	—
Rubber-seed, Ceylon[112]	11	12*	17	35	24	—
,, ,, Nigeria[112]	9	10*	20	39	21	—
Wheat-germ[112]	16	6	12	57	9	—
Safflower, American[114]	←— 10—12 —→		21—39	51—68	—	—
Sunflower seed, Amer.[114]	←— 5—7 —→		15—17	77—79	—	-
Niger-seed[115]	←— 9·5 —→		16	72·5	2	—
Stillingia[115]	←— 7 —→		4·5	67	21·5	—
Tung, Chinese[113]	4	—	9	10	—	77
,, American[113]	4·5†	—	4	8·5	—	82
Essang[113]	9·5	1	9·5	26	—	54
Krobanko[113]	15	9	27	29	—	20
Neou[113]	12	2	40	15	—	31
,, [116]	←— 11 —→		20	35	—	28

* Also 1% of arachidic acid. † Also 1% of myristic acid.

Marine Animal Oils.

The component fatty acids of menhaden oil have been studied in detail by F. A. Smith and J. B. Brown[117]; individual fractions containing esters

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[112] *J.S.C.I.*, 1946, **65**, 8; C., 1946, 91.

[113] *Ibid.*, 74.

[114] *Oil and Soap*, 1946, **22**, 304; B., 1946, II, 208.

[115] *Paint Tech.*, 1945, **10**, 113; B., 1945, II, 378.

[116] *Bull. Soc. chim.*, 1944, [v], **11**, 404; B., 1945, II, 378.

[117] *Oil and Soap*, 1945, **22**, 277, 321; 1946, **23**, 9; B., 1946, II, 209, 253, 291.

of C_{14}—C_{18} acids obtained by distillation of the methyl esters of the mixed fatty acids were further resolved by low-temperature crystallisation from acetone or ether, whilst another portion of the mixed esters was totally hydrogenated and then fractionally distilled. The latter analysis gave the percentages of each homologous acid group as C_{14} 6·9, C_{16} 30·4, C_{18} 26·8, C_{20} 17·5, C_{22} 10·8, C_{24} 4·0, C_{26} 1·2, and above C_{26} 2·4% (wt.). The results of the first-mentioned analysis gave the following data :

Acids	Saturated.	Mono-ene.	Di-ene.	Tri-ene.	Tetra-ene.
C_{12}	Trace	Trace	—	—	—
C_{14}	6·8	0·1	—	—	—
C_{16}	15·5	14·1	—	0·8	—
C_{18}	3·1	15·7	3·6	1·9	2·5

The continued work of W. S. Rapson and his colleagues at the University of Capetown on South African fish products has led to four interesting communications since last year's Report. M. M. Black, W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg[118] have studied the products of the South African seal fishery from the point of view of seal oil and vitamin-*A* production. The blubber oil, although at present of poor quality, could be produced in excellent yield and quality by the use of the alkali digestion method,[24] whilst the seal livers give up to 11% of oil often fairly rich (up to 1·75%) in vitamin-*A* ; the vitamin-*D* content varied from 100 to 900 i.u. per g. of the liver oils. The same authors[119] have furnished detailed component acid data for liver and body fats of the Cape John Dory (*Zeus capensis*) from emaciated and fat fish ; there is less difference than in many fish between the fats from the two sites, probably because in the John Dory the liver, as well as the flesh, is a fat store, but the liver fats contain less highly unsaturated C_{20} and C_{22} acids, and more of the unsaturated C_{18} acids :

	Liver.		Body.	
	Fat.	Thin.	Fat.	Thin.
Fat, % in organ ..	29·1	16·2	6·2	3·9
,, iodine value..	148·9	149·9	167·4	161·6
,, unsaponifiable %	3·4	5·8	2·3	4·4
Acids (% wt.).				
Lauric	—	—	—	0·5
Myristic ..	3·4	3·9	3·1	5·6
Palmitic ..	15·2	15·2	15·7	19·6
Stearic .. .	3·7	3·9	4·0	2·0
Arachidic ..	1·7	0·2	1·8	1·8
Behenic ..	1·1	—	0·5	0·6
Unsaturated C_{12}	—	—	—	0·1 (−2·0H)
,, C_{14}	0·9 (−2·0H)	1·0 (−2·0H)	0·9 (−2·0H)	2·1 (−2·0H)
,, C_{16}	8·5 (−2·0H)	9·5 (−2·0H)	9·4 (−2·0H)	7·4 (−2·0H)
,, C_{18}	32·8 (−2·6H)	34·9 (−2·8H)	23·4 (−2·5H)	23·2 (−3·6H)
,, C_{20}	20·2 (−5·7H)	15·0 (−6·9H)	19·0 (−7·0H)	20·5 (−7·3H)
,, C_{22}	12·5(−10·0H)	12·8(-10·5H)	21·9(−10·5H)	14·7 (−9·8H)
,, C_{24}	—	3·6(−10·0H)	0·3(−10·0H)	1·9(−10·0H)

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[118] *J.S.C.I.*, 1945, **64**, 326 ; B., 1946, III, 51.
[119] *Ibid.*, 1946, **65**, 13 ; B., 1946, III, 76.

Determination of α-glyceryl ethers (batyl, chimyl, selachyl alcohols) in the unsaponifiable matter of fish and other oils can conveniently be effected by measurement of the formaldehyde liberated when these αβ-glycols are oxidised with periodic acid, a method described by M. L. Karnovsky and W. S. Rapson,[120] who point out, however, that in some cases other substances which react with periodic acid may also be present; the authors have applied their method to a very large number and variety of marine animal fats and also to some land animal seed fats. Seasonal and other factors which cause changes in the yield of oil (and of its vitamin content) from the liver of the Cape hake (*Merluccius capensis*) have been followed in some detail by E. R. Roux and C. J. Molteno.[121]

The possibility of making up vitamin-*A* deficiency in the diet of the inhabitants of India from shark-liver oils obtainable from Indian waters has been discussed by I. M. Gajjar and M. Sreenivasaya,[122] who have concluded that, with adequate utilisation of other products (flesh, hides, glue, etc.), the industry could be made economically profitable, although an annual catch of over half a million sharks would be required for a complete solution of the vitamin-*A* deficiency. L. A. Swain[123] has given further accounts of chromatographic separation of the unsaponifiable matter of a number of Pacific marine animal oils, good concentrations of vitamin-*A*, cholesterol, fatty alcohols and glyceryl ethers, squalene, and an unidentified substance or substances being effected; special attention was directed to the unsaponifiable matter (largely glyceryl ethers with squalene) of dogfish liver oils, and those of lingcod, sperm whale, and several species of shark have also been studied. The unsaponifiable content of the liver oil of *Centrina centrina* was found by M. Carrière and J. M. Bonnemaison[124] to be more than 34% (iodine value 52·8) and to consist mainly of glyceryl ethers with some cholesterol; in the form of fatty acid esters these glyceryl ethers would thus account for about 85% of the whole liver oil.

COMPONENT ACIDS AND GLYCERIDES OF FATS: GENERAL.

Individual Fatty Acids etc.

Branched-Chain Saturated Acids.—From *d*(−)-2-methylbutanol ($[\alpha]_D$ −4·66°) S. F. Velick and J. English[125] have, by a series of Grignard actions, synthesised *d*-14-methylpalmitic acid ($[\alpha]_D$ +5·23°) and shown that it is identical with one of the "*anteiso*"-acids isolated by A. W. Weitkamp[126] from wool fat (see p. 348). Six methyl-*n*-decoic acids have

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[120] *J.S.C.I.*, 1946, **65**, 138, 425; C., 1946, 258.
[121] *Ibid.*, 281.
[122] *Current Sci.*, 1945, **14**, 220; B., 1946, II, 209.
[123] *Progr. Rept. Fish. Res. Bd. Canada, Pacific Sta.*, 1945, *No.* 63, 32; *No.* 65, 67; B., 1945, II, 379; 1946, II, 169.
[124] *Bull Soc. chim.*, 1945, [v], **12**, 936; B., 1946, II, 385.
[125] *J. Biol. Chem.*, 1945, **160**, 473; A., 1946, II, 120.
[126] *J. Amer. Chem. Soc.*, 1945, **67**, 447; A., 1945, II, 219.

been synthesised by C. V. Wilson,[127] and S. Ställberg-Stenhagen[128] has synthesised 15-methylheptadecoic acid; the interest of most of these synthetic studies resides in the possible relationship of the products to the natural acids in bacilli waxes. Buu-Hoï and P. Cagniant[129] have indicated methods on the lines of the malonic ester synthesis for obtaining acids such as 2-methylstearic or 2-*cyclo*pent-2-enylstearic acid.

Syntheses etc. in the Chaulmoogric Acid Series.—Reference may be made here to an interesting series of communications during the past few years by Buu-Hoï and co-workers on synthetical and degradative work in the *cyclo*pentenyl-fatty acid seres. A synthesis of dihydrochaulmoogric acid by a new sequence of reactions was described by Buu-Hoï and P. Cagniant,[130] commencing from tridec-12-enoic acid (from undec-10-enyl chloride and malonic ester), which was transformed into ethyl 13-bromotridecoate, the latter being condensed with the potassium derivative of ethyl *cyclo*pentanone-2-carboxylate to yield, after decarboxylation, 2-ketohydrochaulmoogric acid, which by Clemmensen reduction gives dihydrochaulmoogric acid. The same authors, with J. Janicaud and R. Royer,[131] have prepared various 2-alkyl (methyl, allyl, benzyl, etc.) derivatives of chaulmoogric acids by condensing hydnocarpyl bromide or iodide with alkylmalonic esters, in order to study further the therapeutic properties of derivatives of the chaulmoogric group. Formal degradation of chaulmoogric acid by the method of Barbier has led to the progressive shortening of the alkyl chain and production of the lower homologues down to alepric (9-*cyclo*pent-2-enyl-*n*-nonoic) acid.[132] Starting from *cyclo*pentadiene, Buu-Hoï and P. Cagniant[133] have synthesised *cyclo*pent-2-ene-1-carboxylic (aleprolic) acid by Barbier degradation of ethyl *cyclo*pent-2-enylacetate, and *cyclo*pent-1-ene-1-carboxylic (*iso*aleprolic) acid by alcoholic alkaline hydrolysis of 1-cyano*cyclo*pent-2-ene.

Fatty Acid Chlorides.—S. T. Bauer,[134] after examining various methods for preparing the chlorides of fatty acids, has found phosphorus tri- or penta-chloride the most useful agent for the higher saturated acids, and has confirmed that oxalyl chloride is the only satisfactory reagent with oleic or other unsaturated fatty acids; he recommends as a rapid method for analysis of crude fatty acid chlorides their conversion into anilides by interaction in ether with excess of aniline, removing the excess of base as hydrochloride by washing with hot water, and titrating the free fatty acid left in the residual anilide.

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[127] *J. Amer. Chem. Soc.*, 1945, **67**, 2161; A., 1946, II, 303.

[128] *Arkiv Kemi, Min., Geol.*, 1945, **19**, **A**, *No.* 28; A., 1946, II, 64.

[129] *Bull Soc. chim.*, 1945, [v], **10**, 477; *Rec. trav. chim.*, 1946, **65**, 246; A., 1945, II, 183; 1946, II, 473; 1946, III, 765.

[130] *Bull. Soc. chim.*, 1942, [v], **9**, 107; A., 1946, II, 25.

[131] *Compt. rend.*, 1941, **212**, 1105; *Bull. Soc. chim.*, 1942, [v], **9**, 99; *Compt. rend* 1946, **222**, 224; A., 1946, II, 319, 25, 664.

[132] *Ann Chim.*, 1944, [xi], **19**, 446; A., 1946, II, 24.

[133] *Bull. Soc. chim.*, 1945, [v], **12**, 978; A., 1946, II, 536; 1946, III, 765.

[134] *Oil and Soap*, 1946, **23**, 1; A., 1946, II, 416; C., 1946, 161.

Oleic, Linoleic, and Linolenic Acids.—Profound differences in crystal structure of the two dimorphs of oleic acid (m.p. 13° and 16°) are indicated by *X*-ray diffraction diagrams of the two forms examined by E. S. Lutton.[135]

Conversion of oleic or other monoethenoid acids or esters into saturated dihydroxy-acid derivatives by performic acid produced by dissolving 25% hydrogen peroxide in anhydrous formic acid has been effected by D. Swern, G. N. Billen, T. W. Findley, and J. T. Scanlan[136]; the initial addition products are hydroxy-formoxy-derivatives which are quantitatively hydrolysed by 3N-caustic alkali at 100°.

Somewhat contrary to the experience of most workers, H. B. Knight, E. F. Jordan, and D. Swern[137] obtained good yields of tetra- and hexabromostearic acids (identical with those from linoleic and linolenic acids from vegetable sources) from the octadeca-di- and -tri-enoic acids present in small proportions in beef tallow.

Component Acids of Individual Fats.

Hydnocarpus (*Chaulmoogra*) *Oils.*—The composition of several (somewhat oxidised) oils of this group from the Belgian Congo have been recorded by L. Adriaens[138] as follows:

	Hydnocarpus		*Caloncoba*		*Lindackeria*
	Wightiana.	*Anthelmintica.*	*Welwitschii.*	*Glauca.*	*dentata.*
Oil, % in seed ..	43	17—21	45—47	24—32	23 26
,, iodine value ..	95	86—87	89 92	96—100	70—83
Component acids:					
Palmitic	3	13	16	6—7	11
Oleic	14	16	15	14—20	13
Hydnocarpic ..	43	37	18	5—7	11
Chaulmoogric ..	12	7	31	31—45	51
Gorlic	6	Trace	5	7—9	—
Oxidised etc. ..	19	27	14	17—20	13

R. Child and W. R. N. Nathanael[139] have surveyed the *Hydnocarpus* oils of Ceylon and have pointed out that the high content of (maratti) oil in *H. wightiana* renders it the most suitable species for cultivation, whilst *H. anthelmintica* fruit contains too high a percentage (68%) of shell to make it an economic source of the fatty (lukrabo) oil.

Seed Fats (*General*).—Reports of the component acids of a number of these (notably drying oils) have been quoted in earlier pages of this Report; there remain in addition those given in the annexed table (in the forms recorded by the several authors).

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[135] *Oil and Soap*, 1946, **23**, 265; A., 1947, I, 11.

[136] *J. Amer. Chem. Soc.*, 1945, **67**, 1786; A., 1946, II, 120.

[137] *J. Biol. Chem.*, 1946, **164**, 477; A., 1946, III, 828.

[138] *Bull. Soc. chim. Belg.*, 1945, **54**, 101; B., 1946, II, 461.

[139] *Trop. Agric.*, 1944, **99**, 140; B., 1945, III, 259.

	Palmitic.	Stearic.	Oleic.	Linoleic.	Linolenic.
Amaranthus gangeticus[140]	20·8	2·2	43·7	27·3	—
Bacury kernel (*Platonia insignis*)[141] ..	28	28	39	4	—
Beechnut[142]	←—10·1—→		49·6	36·5	—
Buttonweed (*Abutilon theophrasti*)[143]	12·2	0·9	14·1	58·0	Trace
Cassia arereh[144]	←—31·1—→		28·7	40·2	— (*a*)
C. fistula[144]	←—29·1—→		31·9	39·0	— (*a*)
Colza (French)[145]	1·5	—	29	16	1 (*b*)
Cryptostegia grandiflora[146]	8·7	9·5	38·5	27·6	— (*c*)
Erythrina christagalli[147]	10·8	3·7	48·0	17·8	— (*d*)
Erythrophleon guineense[144]	←—29·6—→		26·8	43·6	— (*a*)
Hare's ear mustard seed[148]	2	—	20–30	15–20	— (*e*)
Kahu (Indian lettuce)[149]	1·9	1·3	37·6	56·9	— (*f*)
Maize[150]	8·1	2·5	30·1	56·3	— (*g*)
Mappia foetida[151]	7·1	17·7	38·4	—	36·8
Melon (*Cucumis melo*)[152]	7·3	0·2	43·1	45·1	— (*h*)
,, Sarda (*C. melo.* var.)[152] ..	3·2	5·4	32·7	55·2	— (*i*)
,, water (*Citrullus vulgaris*)[152] ..	7·6	6·1	35·3	48·7	— (*j*)
Milkweed pod[153]	←—6·5—→		55·3	35·4	2·8
,, seed[153]	←—4·4—→		51·8	43·8	—
Mimosa pudica[154]	8·5	8·7	30·3	49·6	0·4
Molinillo seed (*Leonotis* sp.)[155] ..	12·0	8·4	64·6	11·9	— (*k*)
Parkinsonia aculeata[144]	←—23·4—→		20·6	56·0	— (*a*)
Saffron thistle (Australia)[156]	7·5	6·6	12·4	70·4	—
Sideroxylon tomentosum[157]	11·0	17·9	57·8	13·3	—
Solanum nigrum[158]	1·8	1·9	49·7	46·6	—
Sorghum grain[159]	8·3	5·8	36·2	49·4	— (*l*)
Tamarindus indica[144]	←—30·8—→		27·3	41·9	— (*a*)
Terminalia belerica[160]	20·5	20·8	26·7	32·0	-
,, *belerica*[161]	12·1	15·2	43·3	29·4	—
Typha (cat tail)[162]	←—12·0—→		14·2	69·5	0·1
Vicia faba[163]	←—7·2—→		55·2	33·5	—

(*a*) Including respectively 4·4, 4·8, 1·6, 1·0, and 11·8% of saturated C_{20-24} acids.
(*b*) Also 1·5% of lignoceric and 51% of erucic acids.
(*c*) Also 3·7% of arachidic acid.
(*d*) Also 0·4% of decoic, 0·3% of lauric, 1·8% of myristic, 3·0% of arachidic, and 8·4% of eicosenoic acids.
(*e*) Also 2% of higher saturated, 35–45% of erucic, and about 10% of eicosenoic acids.
(*f*) Also 2·2% of hexoic and 0·1% of arachidic acids.
(*g*) Also 0·1% of myristic, 1·2% of hexadecenoic, and 1·7% of higher saturated acids.
(*h*) Also 1·0% of hexoic, 2·0% of octoic, and 1·1% of myristic acids.
(*i*) Also 2·0% of myristic and 0·9% of arachidic acids.
(*j*) Also 0·2% of octoic, 1·1% of decoic, 0·8% of lauric, and 0·2% of myristic acids.
(*k*) Also 1·3% of myristic acid.
(*l*) Also 0·2% of myristic and 0·1% of hexadecenoic acids.

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[140] N. Chidambaram and R. R. Iyer, *J. Indian Chem. Soc.*, 1945, **22**, 117; B., 1946, II, 126.

[141] E. Pechnik and J. M. Chaves, *Rev. Quim. Ind.*, 1945, **14**, *No.* 163.

[142] J. Pritzker and R. Jungkunz, *Mitt. Lebensm. Hyg.*, 1943, **34**, 107; B., 1946, II, 126.

[143] D. R. Carmody, W. De Jong, and T. R. Smith, *Oil and Soap*, 1945, **22**, 263; B., 1946, II, 126.

[144] D. N. Grindley, *J.S.C.I.*, 1946, **65**, 118; B., 1946, II, 291.

[145] M. Rollet and C. Paquot, *Bull Soc. chim.*, 1945, [v], **12**, 1048; B., 1946, II, 385.

[146] R. H. Siddiqui and S. A. Warsi, *Indian J. Pharm.*, 1945, **7**, 75, 88; B., 1946, II, 139.

[147] P. Cattaneo, *Anal. Asoc. Quim. Argentina*, 1945, **33**, 5; B., 1946, II, 91.

[148] C. Y. Hopkins, *Canad. J. Res.*, 1946, **24**, **B**, 211.

Wool Fat.—An important contribution to our knowledge of the component acids of wool grease by A. W. Weitkamp[126] appears to have been omitted by oversight from last year's Report. Weitkamp effected a preliminary separation of the mixed methyl esters of wool fat acids by adsorption on a column of adsorbent clay, followed by elaborate fractional distillation of each group of esters obtained. He reported the following four series of acids and recorded the approximate proportion of the individual acids (from C_9 to C_{31}) in each series : *n*-acids, $CH_3\cdot[CH_2]_n\cdot CO_2H$; *iso*-acids, $CHMe_2\cdot[CH_2]_n\cdot CO_2H$; "*anteiso*"-(*d*-)acids, $CHMeEt\cdot[CH_2]_n\cdot CO_2H$; and optically active acids (2-hydroxy-*n*-tetra- and -*n*-hexa-decoic acids). The "*anteiso*"- and *iso*-acids formed the greater part of the total acids, but no individual acid exceeded 7% of the whole ; seven "*anteiso*"-acids (C_{15} to C_{27}) and seven *iso*-acids (C_{14} to C_{26}) were the chief components, each amounting to from 3% to 7% of the total acids.

C. W. Picard and D. E. Seymour[164] have found that cholesterol can be separated conveniently from the other alcohols of wool fat by formation with anhydrous oxalic acid in ethyl acetate or benzene of a sparingly soluble complex which can be readily separated and from which pure cholesterol or its acetate can readily be regenerated.

Cotton Wax.—The chief constituents of cotton fibre wax have been given by W. H. Tonn, jun., and E. P. Schoch[165] as alcohols 52, sterols 10, hydrocarbons 7%, with 6% of inert matter and 25% of (almost wholly saturated, C_{26}—C_{30}) fatty acids partly free and partly combined as esters with the alcohols present.

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[149] D. R. Dhingra and K. Pershad, *J. Indian Chem. Soc.*, 1945, **22**, 127 ; B., 1946, II, 126.

[150] F. J. Baur and J. B. Brown, *J. Amer. Chem. Soc.*, 1945, **67**, 1899 ; A., 1946, III, 332.

[151] M. D. Nadkarni, J. W. Airan, and S. V. Shah, *J. Univ. Bombay*, 1946, **14**, 26.

[152] S. A. Ahmad, A. K. Biswas, D. R. Dhingra and P. Narain, *J. Indian Chem. Soc.*, 1945, **22**, 119, 123, 337 ; B., 1946, II, 126, 252.

[153] R. W. Watson and N. Levitin, *Canad. J. Res.*, 1946, **24**, **F**, 95 ; B., 1946, II, 302.

[154] J. S. Aggarwal and Karimullah, *J. Sci. Ind. Res., India*, 1945, **4**, 80 ; A., 1946, III, 144.

[155] C. F. Asenjo, J. A. Goyco, and E. Martínez-Pico, *J. Amer. Chem. Soc.*, 1945, **67**, 1936 ; B., 1946, II, 169.

[156] H. H. Hatt and W. J. Troyhan, *J. Counc. Sci. Ind. Res., Australia*, 1946, **19**, 86 ; B., 1946, II, 421.

[157] M. D. Nadkarni, J. W. Airan, and S. V. Shah, *J. Univ. Bombay*, 1946, **14**, 23.

[158] B. K. Singh and A. Kumar, *Proc. Indian Acad. Sci.*, 1945, **22**, **A**, 310 ; B., 1946, II, 209.

[159] F. A. Kummerow, *Oil and Soap*, 1946, **23**, 167, 273 ; B., 1946, II, 385.

[160] A. R. S. Kartha, T. A. Venkitasubramanian and K. N. Menon, *Proc. Indian Acad. Sci.*, 1946, **23**, **A**, 283 ; B., 1946, II, 421.

[161] B. K. Singh and A. Kumar, *ibid.*, 379 ; A., 1946, III, 983 ; B., 1946, II, 422.

[162] J. R. Clopton and R. W. von Korff, *Oil and Soap*, 1945, **22**, 330 ; B., 1946, II, 252.

[163] J. Labarre and S. Pfeffer, *Canad. Chem.*, 1945, **29**, 724 ; B., 1946, II, 90.

[164] *J.S.C.I.*, 1945, **64**, 304 ; B., 1946, II, 29.

[165] *Ind. Eng. Chem.*, 1946, **38**, 413 ; B., 1946, II, 292.

Natural and Synthetic Mixed Glycerides.

Determination of Fully-Saturated Glycerides etc.—F. E. Luddy and R. W. Riemenschneider[166] have reported that good agreement obtains between values for the fully-saturated glyceride contents of raw or hydrogenated lards and tallows determined either by the permanganate–acetone oxidation method or by a simple crystallisation procedure. This consists in crystallising the fat (25—50 g.) from acetone (40 c.c. per g. of fat) at 15° ± 0·3° for 30 hours. The iodine value of the precipitate is assumed to represent mono-oleo-disaturated glycerides, and an appropriate correction is applied for these and for the solubility (0·005 g. per 100 c.c.) of fully-saturated glycerides in acetone at 15°. The method, from the data given, is efficient and is adapted to rapid routine analysis—which certainly is not the case with the tedious oxidation process; the only uncertainty left in the minds of those familiar with the habits of fully-saturated glycerides, and, especially, with "mutual solubility" effects of mixed glycerides soluble in the acetone on the solubility coefficient of the fully-saturated components, may be whether the correction factor for the latter in pure acetone can be accepted as operative in every case which may be encountered. The method, now proposed for routine work, has of course been utilised in part in several recent studies of glyceride structure in which solid fats have been partly resolved by fractional crystallisation prior to more detailed investigation.

A. R. S. Kartha and K. N. Menon[167] have advocated the estimation of the saturated acids remaining as azelao-glycerides after permanganate–acetone oxidation as an aid in determining the mixed glycerides of fats, but in practice the difficulty of quantitative recovery of these azelao-derivatives would appear to restrict the procedure to a few special instances.

Mono- and Di-glycerides.—Interest is probably stimulated in this field by the increasing attention given to monoglycerides as convenient emulsifying agents for different types of edible fats. J. Ross, A. C. Bell, C. J. Arrowsmith, and A. I. Gebhart[168] have stated that monoglycerides (prepared from glycerol and fatty esters by heating in presence of caustic alkali as interesterification catalyst) are oxidised to formaldehyde by periodic acid and therefore are α-monoglycerides, and that (when free from traces of alkali) they can be distilled in a vacuum without decomposition or intramolar rearrangement. N. Ivanoff[169] has also dealt with determination by the periodic acid method of α-monoglycerides in industrial mixtures of mono-, di-, and tri-glycerides. R. O. Feuge and A. E. Bailey[170] have made a detailed study of the proportion of mono-, di-, and tri-glycerides which result when hydrogenated cottonseed oil and

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[166] *Oil and Soap,* 1946, **23**, 385; C., 1947, 71.

[167] *Proc. Indian Acad. Sci.*, 1945, **21**, **A**, 222; *Current Sci.*, 1946, **15**, 43; B., 1946, II, 251.

[168] *Oil and Soap*, 1946, **23**, 257.

[169] *Bull. Mat. Grasses*, 1945, **37**, 45.

[170] *Oil and Soap*, 1946, **23**, 259; B., 1947, II, 19.

glycerol interact at different temperatures and for different periods in presence of an alkaline catalyst; below 200° the glyceryl hydroxyl groups appear to be acylated on a pattern of random distribution, but above 200° there is increasing tendency for diglycerides to preponderate over both mono- and tri-glycerides, and auto-condensation products of glycerol or of mono- and di-glycerides may also commence to appear.

Component Glycerides of some Vegetable Fats.—The work of J. M. Chaves and E. Pechnik[171] suggests that bacury kernel fat possesses somewhat unusual glyceride constitution reflected in its physical properties. With 28% each of palmitic and stearic acids, 39% of oleic and 4% of linoleic in its component acids,[141] it frequently has the remarkably high melting point of 54—56°, whilst its component glycerides, determined by preliminary crystallisation from ether (when a fully-saturated portion—m.p. 67°, 20% of the whole fat—was obtained as the least soluble fraction) and by isolation of fully-saturated glycerides by oxidation, were found to be fully-saturated 24, mono-oleo- 25·5, and di-oleo-glycerides 50·5%. The composition of the mixed glycerides thus appears to differ considerably from what might have been expected from the proportions of its component fatty acids.

The seed fat of *Terminalia belerica* appears to vary somewhat widely from one specimen to another in its component acids, B. K. Singh and A. Kumar[161] stating that oleic and linoleic, the major component acids, may together form from 56% to 84% of the mixed acids. The latter workers examined a specimen the component acids of which were saturated 27, oleic 43, and linoleic 30%, and gave the component glycerides as di-unsaturated 82% (palmito- and stearo-dioleins 3, palmito- and stearo-oleolinoleins 79) and tri-unsaturated 18% (linoleo-diolein and tri-olein each about 9%). On the other hand, a specimen of the same seed fat, with component acids : saturated 41, oleic 27, and linoleic 32%, was similarly investigated by A. R. S. Kartha, T. A. Venkitasubramanian, and K. N. Menon,[160] who gave its components as mono-unsaturated–disaturated 28, di-unsaturated–monosaturated 71, and tri-unsaturated glycerides less than 1%.

Kurchi (*Holarrhena antidysenterica*) seed fat, the component acids of which were saturated 14, oleic 21, linoleic 55, and linolenic 10%, was found by R. J. Irani[172] to yield nearly 10% of its weight of a crystalline bromo-adduct containing 58·2% Br (calculated for bromo-adduct of dilinoleolinolenin 56·1, of linoleodilinolenin 59·4%). The fat may thus have contained nearly 3% of linoleodilinolenin in spite of the minor proportion (10%) of linolenic acid in its total fatty acids.

Synthetic Glycerides.—The phase transformations of the simple glycerides trilaurin, tripalmitin, tristearin, and trilinolein have been re-investigated by G. Ravitsch and G. Zurinov[173] by thermal analysis, who give the

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[171] *Rev. Quim. Ind.*, 1945, **15**, *No.* 165.

[172] *Current Sci.*, 1946, **15**, 161, 191 : B., 1946, II, 421.

[173] *Acta Physicochim. U.R.S.S.*, 1946, **21**, 321; *Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **51**, 369; A., 1946, I, 339, 380.

melting points which they observed in each case for each of the three modifications, which, concurring with Clarkson and Malkin's original view and contrary to the later suggestion of Weygand, they consider to be the only polymorphic crystal forms.

Thermal and *X*-ray diffraction examinations of synthetic triglycerides containing three different saturated acyl groups (C_{10}, C_{12}, C_{14}, or C_{16}) in the molecule have been recorded by C. Chen and B. F. Daubert,[174] with L. J. Filer and S. S. Sidhu, and the three latter authors with H. E. Longenecker[175] have given thermal and *X*-ray data for a group of β-oleo-$\alpha\alpha'$-disaturated glycerides and for tristearin and trielaidin. Comparing the thermal and *X*-ray data for synthetic β-oleodistearin and the natural oleodistearin isolated from the seed fat of *Garcinia indica* (kokum butter), they were able to show that the latter had all the physical properties of β-oleodistearin; details of the *X*-ray diffraction data and melting points for the polymorphic forms of β-oleodistearin from *Garcinia* fat were given separately later by E. S. Lutton.[176]

The synthesis and physical constants of pure, optically active *l*-α-monoglycerides of fourteen homologous acids (acetic to dodecoic inclusive, together with myristic, palmitic, and stearic) from *l*-*iso*propylideneglycerol have been recorded by E. Baer and H. O. L. Fischer[177]; $[\alpha]_D$ ranged from $-10{\cdot}5°$ for α-monoacetin to $-3{\cdot}6°$ for α-monostearin, the molecular rotatory powers tending towards constancy (about 14°). P. E. Verkade, W. D. Cohen, and A. K. Vroege[178] have described the synthesis of mixed $\alpha\beta$-diglycerides by successive esterification of glycerol α-triphenylmethyl ether with two different acyl chlorides, and subsequent removal of the triphenylmethyl radical by hydrogenation in a neutral medium. Both Verkade *et al.* and Baer and Fischer point out that migration of acyl groups from the β- to the α-glyceryl positions occurs much more readily with acyl radicals of aliphatic acids (*e.g.*, stearyl) than with those of aromatic acids (*e.g.*, benzoyl). P. Desnuelle and M. Naudet[179] have stated that during esterification of glycerol with oleic acid from 130° upwards, especially with *p*-toluenesulphonic acid as catalyst, 8% or more of the acid is converted into *iso*oleic (elaidic) acid; this has not previously been remarked, and appears a somewhat surprising and unexpected result.

METHODS OF TESTING AND ANALYSIS.

The topics to which reference is made below are additional to other analytical aspects of fat chemistry which have already received attention in preceding pages of this Report.

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[174] *J. Amer. Chem. Soc.*, 1945, **67**, 1256, 2085; A., 1946, II, 3; I, 145.
[175] *Ibid.*, 1946, **68**, 167; A., 1946, I, 178.
[176] *Ibid.*, 676; A., 1946, II, 473.
[177] *Ibid.*, 1945, **67**, 2031; A., 1946, II, 175.
[178] *Rec. trav. chim.*, 1946, **59**, 1123; A., 1946, II, 416.
[179] *Bull. Soc. chim.*, 1945, [v], **12**, 998; A., 1946, II, 473.

In the course of a general symposium on separation by chromatographic adsorption, K. A. Williams[180] has given a review of the applications of this procedure to the separation of vitamin-*A*, carotene, hydrocarbons, etc., and of free fatty acids from natural fats, and of attempts to separate the constituents of the fats themselves by the same process.

Micro-Analytical Methods.—Micro-methods for determining lipins (after hydrolysis) by titration, and for determination of iodine values (using the Kaufmann reagent), were given by K. Schmidt-Nielsen[181] and by N. Kretchmer, R. T. Holman, and G. O. Burr.[182] More recently K. Marcali and W. Rieman[183] have suggested micro- and semi-micro-methods for the saponification values of fats, modified methods being recommended according to whether specimens of about 5 mg., 5 cg., or 5 dg. are available; a modification of the methods, suitable particularly for fats or waxes soluble only with difficulty in absolute alcohol, has been suggested by D. Ketchum.[184] Apparatus and procedure for micro-determination of refractive index, surface tension, and viscosity have been described by C. L. Wilson.[185]

The influence of the personal factor on the accuracy of ordinary (macro-)estimations of saponification and acid values was tested by N. Strafford,[186] who compared the results obtained for the same fat by forty analysts; accordance was better with saponification than with acid values, the main factor in the latter probably being lack of precision in defining the end-point (persistence of slight pink colour for two minutes) at the end of the titration.

Glycerol.—W. D. Pohle and V. C. Mehlenbacher[187] have compared the older acetin method with the pyridine–acetic anhydride method and the periodic acid method for determination of glycerol in crude, dynamite, and chemically pure glycerins, and have suggested an improved procedure. L. K. Whyte[188] has proposed a new spectrophotometric method for glycerol analysis, based on the intensity of the blue colour of the sodium cupri-glycerol complex produced when a dilute aqueous alkaline solution of glycerol interacts with alcoholic cupric chloride solution under specified conditions; the results obtained on crude or refined glycerins accorded well with those by the acetin or dichromate methods whilst, in conjunction with the latter, they serve to give the proportions of trimethylene glycol and glycerol when the glycol is also present.

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[180] *Analyst*, 1946, **71**, 259, C., 1946, 220.

[181] *Compt. rend. Trav. Lab. Carlsberg, Sér. Chim.*, 1942, **24**, 233; 1944, **25**, 87; C., 1946, 109.

[182] *Arch. Biochem.*, 1946, **10**, 101; C., 1946, 287.

[183] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 144; C., 1946, 91.

[184] *Ibid.*, 1946, **18**, 273; C., 1946, 257.

[185] *Analyst*, 1946, **71**, 117; C., 1946, 221.

[186] *J. Oil Col. Chem. Assoc.*, 1945, **28**, 97; C., 1945, 242.

[187] *Oil and Soap*, 1946, **23**, 48; C., 1946, 248.

[188] *Ibid.*, 323; C., 1947, 65.

Melting Points and Dilatometry of Fats.—The need for comparable rates and times of cooling in the preparation of specimens of commercial fats for melting point determinations is stressed by D. M. Copley,[189] with special reference to cacao butter, for which cooling at between 18° and 22° with constant stirring until the fat has set, followed by keeping for two hours at this temperature, is recommended. Continuing their dilatometric studies, W. S. Singleton and A. E. Bailey[190] have plotted graphs covering the complete melting ranges of specimens of steam lard, oleo oil, and some hydrogenated cooking fats; dilatometric data give more reliable figures for the proportion of solid constituents at a given temperature than thermal data, but different fats containing the same proportion of solid components may exhibit different penetrabilities, the latter (and thus the texture) evidently depending on the constitution of the solid particles as well as on the total solid : liquid ratio. Small variations in this ratio, as previously shown by the authors, also have marked effect on the texture or consistency, and plasticity in particular is confined to fats in which the solid content is restricted to a comparatively limited range.

Unsaturation.—*cis*- and *trans*-Forms of monoethenoid fatty acids react with methyl-alcoholic mercuric acetate solution at widely different rates to form methoxy-mercurial complexes, an observation by T. Connor and G. F. Wright[191] which they have embodied in a method whereby, in a mixture of oleic and elaidic esters or acids, the proportion of the isomers can be estimated with an accuracy of about 4%. P. S. Skell and S. B. Radlove[192] have pointed out that, when accelerated by mercuric acetate solution, the Wijs or Hanus technique should be avoided when ricinoleic derivatives are known to be present. In the course of their studies of thiocyanometric technique, M. C. Lambou and F. G. Dollear[193] have discussed the preparation of lead thiocyanate suitable for preparation of standard thiocyanogen solutions, and have given precise directions for procedure which furnishes reliable and reproducible solutions, subject of course to the exclusion of moisture and to other precautions already known to be essential.

Reports of Analytical Committees etc.—J. Fitelson,[194] on behalf of the U.S. Association of Official Agricultural Chemists, has presented recommendations with reference to the temperature coefficient for the specific gravity of oils, revised "theoretical" values for use in calculating thiocyanogen values, and for the determination of groundnut oil when present to the extent of 10% or above in mixtures with other oils (Evers' test) of squalene in olive, maize, or soya-bean oil, and for the presence of

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[189] *J. Amer. Pharm. Assoc.*, 1946, **35**, 78, 84; C., 1946, 170.
[190] *Oil and Soap*, 1945, **22**, 295; C., 1946, 90.
[191] *J. Amer. Chem. Soc.*, 1946, **68**, 256; C., 1946, 161.
[192] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 67; C., 1946, 84.
[193] *Oil and Soap*, 1946, **23**, 97; A., 1946, I, 323.
[194] *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 282; C., 1945, 243.

sesame oil in olive oil (the Villavecchia test is preferred here to the Baudouin reagent). Work of various Committees of the American Oil Chemists' Society, including those on oil characteristics and on bleaching tests, has been presented,[195] together with further reports[196] on the determination of unsaponifiable matter, and on spectrophotometric determination of small proportions of polyethenoid acids in tallows.

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[195] *Oil and Soap*, 1945, **22**, 224; C., 1946, 23.
[196] *Ibid.*, 1946, **23**, 20; B., 1946, II, 292; C., 1946, 170.

PLASTICS.

BY MEMBERS OF THE PLASTICS GROUP.

THERMOPLASTIC SYNTHETIC RESINS.

By Mervyn G. Church, Ph.D., B.Sc., A.R.I.C.,
Ministry of Supply.

THE relaxation of security restrictions has caused a considerable increase in the volume of published information on thermoplastics. Prominent among the literature is a wealth of information in reports compiled by Allied investigators who have visited the German industry since the occupation. The contents of these reports are far too great to permit them to be summarised satisfactorily in this review and it must suffice to indicate by a few examples the scope of development which has occurred in Germany during the war years. For instance, the German industry has developed tough high-melting polymers from hexolactam suitable for the preparation of fibres and sheets, a magnetic iron oxide used as a filler in a polyvinyl chloride tape to give a new system of recording, polyamides suitable for cast and stretched films and moulding powder, an unplasticized polyvinyl chloride film, a polymer of vinylpyrrolidone for use in blood transfusion, and a polyvinyl alcohol as a filler for body cavities. There seems no doubt from these reports that the Germans were ahead of the Allies in their development and use of certain thermoplastics, but it may be expected that, as a result of the findings of these investigators, rapid strides will be made along the lines of development indicated by these reports. Indeed, some of the literature which has appeared during the year under review suggests that steps have already been made in this direction. On the other hand, the German industry was undoubtedly behind in some respects; to instance two important examples, the Germans appear to have been ignorant of the formation and possibilities of the silicone resins and they do not seem to have developed cross-linked contact laminating resins. Regarding literature from other sources, it is interesting to note the considerable volume of information published on vinyl derivatives. Allyl derivatives also have received considerable attention. In contrast there is little fresh information on acrylates, whilst most of the literature on styrene deals with nuclear-substituted derivatives.

Among matters of general interest is a paper by W. S. Penn[1] giving details of the production of coloured resins obtained by copolymerising an unsaturated compound such as styrene with another which contains a chromophore, for example, vinyl azobenzene ether; the resulting coloured copolymers were very stable.

[1] *India-Rubber J.*, 1946, **110**, 501, 533; B., 1946, II, 254.

The mechanism and kinetics of polymerisation reactions have also been the subject of a considerable amount of literature during the year. The inhibition of reactions has been studied by R. L. Frank and C. E. Adams,[2] who have compared the efficiency of a number of inhibitors; from the effects of twelve inhibitors on the polymerisations of styrene, 3 : 4-dichlorostyrene, and 5-ethyl-2-vinylpyridine, the authors have concluded that the relative effects of the different inhibitors are independent of the type of monomer and that a good inhibitor for one monomer is probably good for another.

The mechanism of reduction activation, that is the activation in a system containing a reducing agent in addition to the monomer and catalyst, has been reported on by R. G. R. Bacon,[3] who has described its effect on the polymerisation of acrylonitrile, styrene, and vinyl chloride; the catalysts were ammonium and potassium persulphates and the reducing agents included sodium sulphite and bisulphite. The results show that the presence of oxygen retards polymerisation catalysed normally or by reduction activation; in the absence of oxygen reduction activation decreases the induction period. Monomers differ in their response to reduction activation catalysts but the order of effectiveness of a range of these catalysts appears unaffected by changes in the monomer. The initiation of polymerisation in systems containing hydrogen peroxide and ferrous ions has been investigated by J. H. Baxendale, M. G. Evans, and G. S. Park[4]; these authors have shown that in the reaction there is competition for the hydroxyl ions, formed by interaction of the hydrogen peroxide and ferrous ions, between the monomer and other ferrous ions, and that by increasing the monomer concentration the reaction with the ferrous ions can be progressively retarded.

The relative polymerisation reactivity of a number of unsaturated monomers has been calculated by T. Alfrey and E. Merz[5] by comparing the rates of addition of the monomers to styrene during copolymerisation.

The rôle of the catalyst, benzoyl peroxide and *p*-chlorobenzoyl peroxide, in the polymerisation of allyl acetate has been studied by P. D. Bartlett and R. Altschul.[6] The catalysts were detected in the end products by determination of chlorine and by carbon dioxide evolution from the unsubstituted peroxide. It was demonstrated by these means that when *p*-chlorobenzoic acid is used as a catalyst, a high proportion of polymer molecules have chlorine-containing end groups mostly in the form of *p*-chlorobenzoate groups. An appreciable proportion of the catalyst is rendered ineffective, apparently as a result of interacting with hydrogen.

W. P. Hohenstein and H. Mark[7] have made a study of the suspension

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[2] *J. Amer. Chem. Soc.*, 1946, **68**, 908; B., 1946, II, 462.
[3] *Trans. Faraday Soc.*, 1946, **42**, 140.
[4] *Ibid.*, 155.
[5] *Polymer Bull.*, 1945, **1**, 86.
[6] *J. Amer. Chem. Soc.*, 1945, **67**, 812; A., 1945, II, 307.
[7] *J. Polymer Sci.*, 1946, **1**, 127.

polymerisation of olefines and diolefines in which they have demonstrated that the pearl size distribution of the polymer formed is usually sharp. Opacity in the pearl is due to water dissolved in the monomer forming a colloidal suspension on polymerisation and can be avoided by the addition to the monomer of a small proportion of plasticiser. The use of suspension stabilisers to prevent agglomeration of the particles during polymerisation and the mechanism of their action are described by the authors.

C. C. Price and C. E. Adams[8] have investigated the kinetics of emulsion polymerisation and have studied the effect of variations in the soap, persulphate concentration, and styrene purity on the induction period, reaction velocity, and molecular weight. Generally the presence of impurities in the styrene increases the induction period but has little effect on the reaction velocity or molecular weight. The addition of a small amount of dodecylthiol causes a marked drop in the average molecular weight, due probably to chain transfer.

A method for calculating absolute values of velocity coefficient in vinyl polymerisation when transfer is appreciable has been presented by C. H. Bamford and M. J. S. Dewar[9] by studying the rate of change of viscosity of the liquid monomer before and after irradiation. The data obtained provide two addition rate equations which permit the calculation of the four velocity coefficients. The method is illustrated by applying it to the polymerisation of styrene using a light of 3000—4000 A. wavelength at 25°.

The kinetics of the polymerisation of allyl acetate, catalysed by peroxide, have been studied by P. D. Bartlett and R. Altschul.[10] The results indicate that the decomposition of the peroxide is almost unimolecular, little change occurring in the rate over a wide range of concentration. A linear relation was observed between the amount of catalyst decomposed and the amount of allyl acetate polymerised throughout the reaction. The authors have concluded that chain termination arises from the collision of a growing free radical with a monomer molecule.

In further studies on the mechanism of polymerisation of vinyl derivatives C. C. Price and D. H. Read[11] have considered the action of chain-transfer agents, such as dichlorobenzoquinone and dichloroquinol, and retarders, such as mono- and di-nitrobenzene and nitrothiophen, on the polymerisation of styrene. The examination of the polymers produced indicated that the quinone and the quinol act only as transfer agents and not as retarders, whilst the residual groups found in polymers produced in the presence of the nitro-derivatives using bromobenzoyl peroxide as catalyst showed that these derivatives have only weak transfer characteristics. Transfer reactions have also been the subject of a paper by R. B. Carlin and N. E. Shakespeare,[12] who have concluded, from a study

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[8] *J. Amer. Chem. Soc.*, 1945, **67**, 1674; A., 1946, II, 90.
[9] *Nature*, 1946, **157**, 845; A., 1946, I, 390.
[10] *J. Amer. Chem. Soc.*, 1945, **67**, 816; A., 1945, I, 279.
[11] *J. Polymer Res.*, 1946, **1**, 44; A., 1946, I, 255.
[12] *J. Amer. Chem. Soc.*, 1946, **68**, 876; B., 1946, II, 462.

of the polymerisation of *p*-chlorostyrene in the presence of polymethyl methacrylate, that growing polymer chains can undergo transfer reactions with polymer molecules containing different monomer units.

H. S. Taylor and A. V. Tobolsky[13] have presented a theory based on free radical mechanisms to account for the reactions occurring during vinyl and diene polymerisation and on ageing, that is, after the apparent completion of polymerisation. These reactions occur with measurable velocities under ordinary conditions and modify the properties of the polymers produced. Multimolecular radicals may be formed by the interaction of the polymer with oxygen or another free radical and the radicals produced may lose successive monomer units to form products of lower molecular weight. The authors consider that the rôle of oxygen is to produce a supply of free radicals from the subsequent reactions of which the modifications to properties are produced. Cross-linking reactions, occurring between long-chain free radicals, may be suppressed by forming dilute solutions. Under these conditions the rate of scission can be measured by observing the change in viscosity of the solution.

Copolymerisation reactions have been studied by T. Alfrey, E. Merz, and H. Mark,[14] who have determined the critical constants in the copolymer composition equation for the systems styrene–2 : 5-dichlorostyrene, styrene–methyl acrylate, styrene–diethyl maleate, and styrene–diethyl chloromaleate. A series of copolymerisation reactions involving vinyl derivatives have been examined by C. C. Price,[15] who has determined the ratios of the rate constants in these reactions and discussed the relation of these ratios to the polarity of the double bonds and to the steric hindrance of the substituent groups. The author concludes that pairs of monomers which polymerise most readily are those in which one monomer contains an electron-rich double bond, that is a monomer in which the substituent groups are electron-repelling, and the other monomer contains an electron-poor double bond in which the substituent groups are electron-attracting. The effect of substituent groups on the polymerisation of styrene has been studied by C. S. Marvel, C. G. Overberger, R. E. Allen, and J. H. Saunders.[16] In this work *m*-trifluoromethylstyrene, *m*-methylstyrene, *m*-nitrostyrene, and *p*-dimethylaminostyrene were prepared and attempts were made to polymerise them under various conditions; polymers were obtained from all but the nitrostyrene.

The copolymerisation occurring in a system containing three monomers has been treated mathematically by T. Alfrey and G. Goldfinger[17] and expressions have been derived for the initial copolymer composition under certain conditions.

R. F. Boyer[18] has described the preparation of probability graph papers

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[13] *J. Amer. Chem. Soc.*, 1945, **67**, 2063 ; B., 1946, II, 46.

[14] *J. Polymer Res.*, 1946, **1**, 37 ; A., 1946, I, 255.

[15] *Ibid.*, 83.

[16] *J. Amer. Chem. Soc.*, 1946, **68**, 736 ; A., 1946, II, 578.

[17] *J. Chem. Physics*, 1946, **14**, 115 ; A., 1946, I, 182.

[18] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 342.

based on the equation of Schulz[19] designed to convert molecular weight distribution data into straight lines; in the application of these graph papers to experimental data a reasonable fit could be found but in no case was complete agreement achieved.

The use of the electron microscope to investigate molecular weight distribution has been reported on by R. F. Boyer and R. D. Heidenreich.[20] A polymer of *p*-chlorostyrene was dissolved in benzene and precipitated successively by the addition of a non-solvent, *n*-propyl alcohol. The authors assume that in mixed medium the polymer molecules coil into compact, spherical, symmetrical configuration which can be studied under the electron microscope. The results support this assumption and suggest that the addition of the precipitant causes the formation of agglomerates consisting of weak gels from which single molecules precipitate at the interface on ageing. Distribution curves have been constructed from the data obtained and the authors have discussed the interpretation of these curves in the light of recent theories.

The interpretation of molecular weight averages obtained by combining data from diffusion and sedimentation has been discussed by S. Singer[21] in a theoretical paper in which the various average molecular weights which may be obtained in this way are compared on the basis of a Lansing and Kraemer distribution curve.

The scattering of light by polymer solutions has been discussed by P. Doty and H. S. Kaufman.[22] According to theory, light scattered by small, spherical isotropic particles should be completely polarised, and the authors have considered the relation between the extent of depolarisation of the transversely scattered light and the particle size and anisotropy. Their experimental results indicate that the cellulose acetate molecule is relatively stiff and anisotropic when the molecular weight is below 100,000; above this figure coiling of the molecule appears to take place to give isotropic configuration. The results for polyvinyl chloride suggest that the molecules are coiled, but not randomly. Polystyrene molecules are indicated as being more anisotropic when the molecular weight is low but in dilute solution the molecules become swollen and more isotropic. The expression derived by Doty, Zimm, and Mark[23] for the determination of molecular weight distribution from measurements of light scattering by polymer solutions has been discussed by J. Waser, R. M. Badger, and V. Schomaker,[24] who have indicated that in some cases this expression may not hold, even in dilute solutions.

J. Rehner[25] has shown that the initial elastic deformation of a cylinder of poly*iso*butylene in a Williams parallel-plate plastometer is proportional

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[19] *Z. physikal. Chem.*, 1939, **B**, **43**, 25.
[20] *J. Appl. Physics*, 1945, **16**, 621; A., 1946, I, 107.
[21] *Polymer Bull.*, 1945, **1**, 79.
[22] *J. Physical Chem.*, 1945, **49**, 583; A., 1946, I, 117.
[23] *J. Chem. Physics*, 1945, **13**, 159; C., 1945, 200.
[24] *Ibid.*, 1946, **14**, 43; A., 1946, I, 154.
[25] *J. Polymer Sci.*, 1946, **1**, 225; C., 1946, 259.

to the molecular weight determined from intrinsic viscosities in di*iso*butylene. A new apparatus for measuring the temperature-dependence of water-permeability has been described by P. M. Doty, W. H. Aiken, and H. Mark,[26] who have measured and reported the permeability of a number of polymeric materials at various temperatures; they have concluded that there is a relation between permeability and crystallinity of the polymeric film and that there is an exponential dependence of the permeation constant on absolute temperature, the exponential term containing the energy of activation for permeation.

P. Doty[27] has studied the relation between the energy of activation for permeation and plasticiser content, and has found that the energy of activation is the same for pure specimens of polyvinyl chloride and polyvinyl chloride acetate but that it is considerably increased on plasticisation of either polymer. He concludes that the increase is due to the change in the heat of dissolution of water in the polymer arising from solvation of the carbon–chlorine dipole by the plasticiser.

The thermodynamics of polymer solutions have been advanced by papers by A. Schuchovitzki,[28] who, from statistical considerations, has derived expressions for the entropy of mixing of polymeric molecules in solution for which good agreement with experimental results is claimed, and by P. J. Flory,[29] who has extended his earlier work on this subject and has derived expressions for osmotic pressure which are in better accord with experimental results. In the same field, B. H. Zimm[30] has derived expressions for solutions of large molecules by extensions of equations for the thermodynamic potentials of the solvent in solutions of simple organic moecules, using continuous molecular distribution functions.

The use of swelling measurements for the determination of polymer–liquid interaction has been described by P. Doty and H. S. Zable,[31] who have measured the swelling of polyvinyl chloride by a number of liquids at two temperatures and have tabulated the liquids in order of solvent ability. A review of the methods used in the determination of size and shape of molecules has been made by P. M. Doty and H. Mark,[32] who have concluded that relatively consistent results for molecular weight may be obtained for some polymers from the absolute methods of osmotic pressure, turbidity, and a combination of diffusion and sedimentation data. Information on solute–solvent interaction may be obtained in good agreement by osmometry or light-scattering measurements. Used in conjunction with data from other methods, streaming birefringence can be used to provide further data on the shape of the dissolved molecule.

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[26] *Ind. Eng. Chem.*, 1946, **38**, 788; C., 1946, 300.

[27] *J. Chem. Physics*, 1946, **14**, 244; A., 1946, I, 251.

[28] *Acta Physicochim. U.R.S.S.*, 1945, **20**, 887; A., 1946, I, 214.

[29] *J. Chem. Physics*, 1945, **13**, 453; A., 1946, I, 84.

[30] *Ibid.*, 1946, **14**, 164; A., 1946, I, 214.

[31] *J. Polymer Sci.*, 1946, **1**, 90.

[32] *Ind. Eng. Chem.*, 1946, **38**, 682; A., 1946, I, 313.

A modified Ostwald-type apparatus for viscometric analysis for dilute solutions, in which the measurements are recorded photographically, has been described by J. L. Riley and G. W. Seymour,[33] whilst R. H. Zimm and I. Myerson[34] have described an osmometer suitable for accurate measurements on very small volumes of solution. P. P. Debye[35] has described a photo-electric instrument for light-scattering measurements and a differential refractometer, and has presented results for the application of the instruments to the determination of the molecular weights of a range of polymers of styrene and vinyl *n*-butyl ether; the results for the polyvinyl ethers indicate that agglomeration of the particles occurs at increased concentration.

In two papers, D. J. Crisp has reported on the formation and structure of surface films of polymers. She has defined four groups of polymers, basing her differentiation on the conditions under which spreading occurs and the gelating pressure of the film. The first paper[36] deals with the group which comprises amorphous polymers which include polyacrylates, polyvinyl acetate, and aldehyde derivatives of polyvinyl alcohol; films of these polymers collapse at relatively high surface pressures. The second paper[37] deals with amorphous polymers, such as the polymethacrylates, which give coherent films collapsing at much lower surface pressures, and semicrystalline polymers with strongly hydrophilic groups such as polyvinyl alcohol, polyacrylic and polymethacrylic acids on acid substrates which readily give fluid films which collapse at low surface pressures.

In a paper describing the theory and application of the parallel-plate plastometer, G. J. Dienes and H. F. Klemm[38] have reported measurements made with this apparatus on polyethylene and polyvinyl chloride–acetate. The results indicate the presence of delayed elastic effects in the polymers which partially mask the viscous flow in the initial stages; the region of these effects was more pronounced in the case of the copolymer. A linear relation was found between viscosity and the square root of the molecular weight, and the viscosity of the copolymer showed a comparatively large variation with temperature.

R. F. Boyer and R. S. Spencer[39] have presented a further treatment of the transition point and mechanism of thermal expansion in high polymers. They consider that in an oriented polymer the expansion normal to the direction of orientation should obey the simple laws of thermal expansion since the cohesive forces holding the chains together are similar to those in compounds of low molecular weight; thus the width–temperature curve should be a straight line. The expansion along the direction of

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[33] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 387; C., 1946, 310.
[34] *J. Amer. Chem. Soc.*, 1946, **68**, 911; C., 1946, 311.
[35] *J. Appl. Physics*, 1946, **17**, 392; C., 1946, 297.
[36] *J. Colloid Sci.*, 1946, **1**, 49; A., 1946, I, 210.
[37] *Ibid.*, 161; A., 1946, I, 210.
[38] *J. Appl. Physics*, 1946, **17**, 458; A., 1946, I, 373.
[39] *Ibid.*, 1945, **16**, 594; A., 1946, I, 109.

orientation involves movement of the chains, that is, viscous flow. At temperatures much below the transition point this flow is small and too slow to keep up with the temperature change and, therefore, the curve is linear. As the transition point is approached the chain movement becomes noticeable and the curve deviates from a straight line, this deviation increasing until the chain displacement can keep pace with temperature change, when a linear relation is again observed. From this statement it follows that oriented polymers should be isotropic and unoriented polymers anisotropic in respect of coefficient of volume expansion, and the authors produce supporting evidence from measurements on polystyrene and Saran. The effect of variables on the transition temperature is also considered and expressions are derived with supporting experimental evidence that this temperature varies linearly with load and is lowered by decreasing the molecular weight and by adding plasticiser.

In a later paper these authors[40] have studied the time effects on the thermal expansion of polymers. It follows from their theory for oriented polymers that, at temperatures below the transition point, the expansion along the direction of orientation is slow but should be observable if sufficient time is allowed for equilibrium to be reached. Evidence in support of this theory was obtained by studying the volume–temperature curve for polystyrene obtained by determining the volume change, over a long period, when the temperature of a sample of polystyrene was raised in a dilatometer.

Evidence from thermal measurements of crystallinity in high-polymers has been presented by W. O. Baker and C. S. Fuller,[41] who have obtained cooling curves for polyethylene, polyesters, and polyamides which showed definite first-order transition points. Softening points of resins have also been considered by V. E. Grostlisch and H. N. Burnstein,[42] who have described a modified ball-and-ring method for determining softening points.

The resistance of a number of plastics to abrasion by high-velocity particles has been measured by M. E. Marks and P. Conrad[43] in an apparatus in which a stream of fine emery dust is blown against the specimen and the abrasion measured by the light scattered by the haze produced; the results indicate that cross-linked polymers have much better abrasion-resistance than normal polymers.

The effect of the presence of electrolytes in plastics on the electrical properties has been studied by D. J. Mead and R. M. Fuoss[44] for the system polyvinyl chloride-diphenylmethane in which tetrabutylammonium chloride was the electrolyte added. They have found that the losses of these dielectrics were greater than the sum of the losses due to the polymer and to normal ionic currents and that the dielectric constant

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[40] *J. Appl. Physics*, 1946, **17**, 398; A., 1946, I, 208.
[41] *Ind. Eng. Chem.*, 1946, **38**, 272; B., 1947, II, 120.
[42] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 476; C., 1945, 244.
[43] *Mod. Plastics*, 1946, **23**, *No.* 7, 165; B., 1946, II, 293.
[44] *J. Amer. Chem. Soc.*, 1945, **67**, 1566; B., 1946, II, 18.

was higher than that of the polymer without added electrolyte. The increment in loss factor equalled that in dielectric constant at a given electrolyte concentration, frequency, and temperature.

ACRYLATES.

A new synthesis of acrylic acid has been described by Reppe[45] involving the direct reaction between carbon monoxide, water, and acetylene with nickel carbonyl as a catalyst; the water may be replaced by alcohols, amines, and other simple compounds to give esters, amides, and corresponding derivatives. Disubstituted acetylenes may be used to give disubstituted acrylic derivatives.

The inhibition of the polymerisation of methacrylates during production or handling by the passage of a stream of gas containing oxygen has been described by E. I. Du Pont de Nemours & Co.[46]; quinol or pyrogallol may also be present. The same company[47] has claimed a method for the purification of alkyl methacrylates, obtained by the thermal depolymerisation of the polymer, involving the treatment with chlorine, which reacts preferentially with the impurities, and subsequent steam-distillation.

L. K. J. Tong and W. O. Kenyon[48] have reported the measurement, in an isothermal calorimeter, of the heats of polymerisation of a number of methacrylic esters; for the esters examined, no substantial difference in the heats measured was found and the authors have attributed this to the ester groups being too far from the reacting double bond to affect the reaction. The thermal polymerisation of methyl methacrylate in the absence of catalyst has been studied by C. Walling and E. R. Briggs,[49] who took precautions in the design of their apparatus and method of procedure to eliminate oxygen and all other contaminants likely to affect the polymerisation. The results are interpreted as indicating a true thermally initiated polymerisation between 100° and 150° with an over-all activation energy of 16 kg.-cal. Assuming the initiation, growth, and termination to be bimolecular, the authors have calculated the activation energy of the thermal initiation reaction to be 22 kg.-cal. with a frequency factor less than unity.

Methods for preparing improved injection moulding compositions have been claimed by E. I. Du Pont de Nemours & Co.[50] involving the polymerisation of esters of methacrylic acid modified, in dispersion, with an unsymmetrical olefine such as trichloroethylene or[51] with a small percentage of α-terpineol. The same company[52] has also described moulding compositions obtained by mixing a copolymer of alkyl methacrylates and styrene or vinyl acetate with polyvinyl acetal or polyvinyl butyral.

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[45] *Mod. Plastics*, 1945, **23**, *No.* 3, 162; B., 1946, II, 109.
[46] B.P. 573,175; B., 1946, II, 75.
[47] B.P. 577,632; B., 1946, II, 317.
[48] *J. Amer. Chem. Soc.*, 1946, **68**, 1355; A., 1947, I, 19.
[49] *Ibid.*, 1141; A., 1947, I, 54.
[50] B.P. 576,071; B., 1946, II, 258.
[51] U.S.P. 2,201,395; B., 1946, II, 334.
[52] U.S.P. 2,326,523; B., 1946, II, 216.

The preparation and polymerisation of carbomethoxymethyl acrylate and methacrylate to compounds resembling the unsubstituted methyl esters have been described by E. M. Filachione, J. H. Lengel, and C. H. Fisher,[53] whilst E. R. Blout and B. E. Ostberg[54] have reported the preparation of a soluble polymer of allyl methacrylate by using ultra-violet irradiation in the presence of benzoyl peroxide. Other reports on new acrylic acid derivatives include a paper describing the preparation of polymeric materials from a range of carbohydrate derivatives of acrylic and methacrylic acid by W. N. Haworth, H. Gregory, and L. F. Wiggins[55] and a claim by Röhm & Haas Co.[56] for the production of a vinyl alcohol–methacrylic ester copolymer by preparing the copolymer with a vinyl ester and then hydrolysing under conditions which do not affect the methacrylic ester.

The effect on mechanical properties of stretching and pressing heated polymethyl methacrylate sheet has been studied by Z. Rogowsky,[57] who has found that the impact strength is considerably increased by strains resulting from hot pressing, above the strength of unstrained material. The strength perpendicular to the direction of the strain did not appear to be affected to the same extent. An increase in bending strength was also found although the notch-sensitivity appeared unaffected. P. Glanzer[58] has differentiated between three stresses present in formed methacrylate sheet and has described methods of detection and removal.

The use of acrylic resins for making dentures has been reviewed by J. Osborne,[59] who has concluded that, as a result of experience extending over five years, acrylic resins have proved to be suitable. The effects of plasticiser content and rate of polymerisation on the fracture-resistance of acrylic resin denture compositions have been studied by S. A. Leader[60]; his results indicate that an improvement is obtained as the plasticiser content is increased to 5% and that rapid polymerisation lowers the resistance to fracture. He reports that plaster moulds may bleach the resin but that this may be obviated by lining the moulds with tin foil. A tooth reconstruction composition comprising a mixture of polymeric and monomeric methyl methacrylate containing a small percentage of allyl methacrylate has been described by E. I. Du Pont de Nemours & Co.[61]

The use of acrylates for the production of optical components has been described by G. A. Boutry and J. Doucerain,[62] P. Pollack,[63] and others.[64,65]

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[53] *J. Amer. Chem. Soc.*, 1946, **68**, 330; A., 1946, II, 363.

[54] *J. Polymer Sci.*, 1946, **1**, 230; B., 1946, II, 389.

[55] *J.C.S.*, 1946, 488; A., 1946, II, 525.

[56] U.S.P. 2,328,922; B., 1946, II, 175.

[57] *Brit. Plastics*, 1946, **18**, 348; B., 1946, II, 425.

[58] *Canad. Plastics*, 1945, **3**, *No.* 9, 40; B., 1946, II, 255.

[59] *Brit. Dent. J.*, 1945, **78**, 324; B., 1946, II, 130.

[60] *Ibid.*, **79**, 183; B., 1946, II, 130.

[61] U.S.P. 2,335,133; B., 1946, II, 299.

[62] *Compt. rend.*, 1940, **211**, 557; B., 1946, II, 212.

[63] *Plastics*, 1946, **4**, *No.* 5, 27.

[64] *Brit. Plastics*, 1946, **18**, 204.

[65] *Chem. Met. Eng.*, 1945, **52**, *No.* 11, 113.

Polymethyl and poly*cyclo*hexyl methacrylates have been found the most suitable acrylates and resemble crown glass in optical properties; they may be used with polystyrene to minimise achromatic aberration. The chief disadvantages of the plastic components were their low surface hardness and their poor retention of polish. A cement to give joints, between polymethyl methacrylate surfaces, of high optical clarity has been described by Imperial Chemical Industries Ltd.[66]

POLYSTYRENE.

The use of bauxite as the dehydrogenation catalyst in the production of styrene from ethylbenzene has been investigated by W. H. Wood and R. G. Cappell[67]; bauxites from various sources were examined and it was concluded that the best results were obtained by using Alabama bauxite. The use of bauxite or magnesia modified with vanadium pentoxide for the catalytic dehydrogenation of ethylbenzene has been described by the Distillers Co. Ltd.[68]

The effect of high-frequency currents on the polymerisation of styrene has been examined by N. V. Schorigina and E. I. Petrova.[69] In an atmosphere of air the application of a high-frequency field, about 30 megacycles per second, resulted in a polymer of lower molecular weight than that of a polymer produced without the high-frequency field; in carbon dioxide the reverse occurred and a polymer of higher molecular weight was obtained. Considerably higher yields of polymer were obtained than in the controls, and higher molecular weights were obtained with pure styrene than with commercial monomer. With higher frequencies, of the order of 300 megacycles per second, the effect appeared to be purely thermal.

R. Mesrobian and A. Tobolsky[70] have described a sealed viscometer which may be used for studying the simultaneous polymerisation and degradation of a polymer in solution, and the results for several samples of polystyrene obtained from different sources show that, when in toluene solution with the same concentration of polymer and benzoyl peroxide, all polymers tend to the same molecular weight as indicated by viscosity changes.

The mechanism of peroxide-initiated polymerisation of styrene has been investigated by H. F. Pfann, V. Z. Williams, and H. Mark,[71] who have shown from infra-red absorption examination the presence of benzoyloxy-groups in the polymer, which suggests that the bromobenzoyloxy-radical from the dissociation of the peroxide initiates chain growth. The carbonyl contents obtained do not agree with bromine determinations and

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[66] B.P. 576,164; B., 1946, II, 261.

[67] *Ind. Eng. Chem.*, 1945, **37**, 1148; B., 1946, II, 152.

[68] B.P. 572,410; B., 1946, II, 35.

[69] *J. Gen. Chem. Russ.*, 1945, **15**, 173; B., 1946, II, 293.

[70] *J. Amer. Chem. Soc.*, 1945, **67**, 785; C., 1945, 298.

[71] *J. Polymer Res.*, 1946, **1**, 14; A., 1946, I, 255.

the authors suggest that this disagreement is due to the decarboxylation of the carboxyl radicals.

The polymerisation of α-methylstyrene has been effected by A. B. Hersberger, J. C. Reid, and R. G. Heiligmann[72] at temperatures as low as −130° in the presence of a Friedel–Crafts catalyst; the product was of high molecular weight and had a higher softening point but lower mechanical strength than polystyrene. Copolymers were obtained with *iso*butylene, butadiene, and maleic anhydride. The polymerisation of other alkyl derivatives of styrene has been investigated by C. S. Marvel, R. E. Allen, and C. G. Overberger,[73] who sought to study the effect of large alkyl groups on the polymerisation reaction; hard polymers were prepared from *m-tert.*-butylstyrene, *m-sec.*-butylstyrene, and *p-cyclo*hexylstyrene in ultra-violet light and all were soluble in benzene and methanol. The molecular weights were low compared with polystyrene but the softening points were high. The polymerisation of the four isomeric dimethylstyrenes has been studied by C. S. Marvel, J. H. Saunders, and C. G. Overberger[74]; the polymers obtained by irradiating with ultra-violet light were all soluble in benzene and were hard resins having high softening points. The molecular weights of the four polymers were similar except for the 2 : 4-derivative, which was considerably lower. A range of alkyloxy- and aryloxy-styrenes has been prepared by R. L. Frank, C. E. Adams, R. E. Allen, R. Gander, and P. V. Smith,[75] and their polymers have been obtained and described.

Polymers of other derivatives of styrene which have been described included cyanostyrenes which have been reported by C. S. Marvel and C. G. Overberger[76] and by the Wingfoot Corporation,[77] and acylstyrenes, such as stearyl-, linolenyl-, and *n*-dodecoyl-styrene, by Armour & Co.[78]; the acylstyrenes can be used as plasticisers for styrene, with which they may also be copolymerised.

Cross-linked copolymers of styrene have been studied by I. Valyi, A. G. Janssen, and H. Mark,[79] who used di*iso*propenyldiphenyl as the cross-linking agent, and the effect of the amount of the cross-linking agent on the properties was examined; it was found that with increasing cross-linking agent the weight average degree of polymerisation increased, although the maximum degree of polymerisation moved to lower values. T. Alfrey and J. G. Harrison, jun.,[80] have studied the copolymerisation of styrene and allyl chloride; their results indicate that the allyl chloride monomer is much less active than styrene in adding to either type of

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[72] *Ind. Eng. Chem.*, 1945, **37**, 1073; B., 1946, II, 92.
[73] *J. Amer. Chem. Soc.*, 1946, **68**, 1088; A., 1946, II, 648.
[74] *Ibid.*, 1085; A., 1946, II, 648.
[75] *Ibid.*, 1365; A., 1946, II, 658.
[76] *Ibid.*, 1945, **67**, 2250; A., 1946, II, 321.
[77] B.P. 571,829; B., 1946, II, 56.
[78] U.S.P. 2,197,709; B., 1946, II, 38.
[79] *J. Physical Chem.*, 1945, **49**, 461.
[80] *J. Amer. Chem. Soc.*, 1946, **68**, 299; A., 1946, I, 254.

radical at the end of a growing chain. Copolymers of styrene and β-chloroallyl ethers have been described by the Dow Chemical Co.[81]

POLYVINYL AND VINYLIDENE CHLORIDES.

Several new and modified processes for producing vinyl chloride have been described. These include a process described by the Distillers Co.[82] for the production of vinyl chloride and similar unsaturated chlorinated hydrocarbons from ethylene dichloride and corresponding compounds by heating at an elevated temperature in the presence of a small percentage of oxygen but in the absence of added halogens or compounds producing halogen. E. I. Du Pont de Nemours & Co.[83] have described the use of mercurous chloride as a catalyst for the interaction of acetylene with hydrogen chloride, whilst the General Electric Co.[84] (of America) have obtained a high yield of vinyl chloride by passing purified generator gas, obtained from the action of an electric arc on hydrocarbon oil, over mercury absorbed on activated carbon after mixing with hydrogen chloride.

The influence of various solvents and catalysts on the polymerisation of vinyl chloride has been investigated by H. E. Fierz-David and H. Zollinger[85] and these authors have also obtained[86] confirmatory evidence of the head-to-tail structure of polyvinyl chloride. The Distillers Co.[87] have described polymers of higher softening point and greater heat-stability obtained by polymerising at a comparatively low temperature n the presence of hexamethylene triperoxide diamine or by polymerising[88] n the absence of water, with a peroxide catalyst, in presence of an organic oxide.

An oven designed for the measurement of the volatility of plasticisers in polyvinyl chloride and copolymers has been described by D. K. Rider and J. K. Sumner.[89] The use of butyl acetylricinoleate as a plasticiser for polyvinyl chloride has been studied by C. Soyka and H. F. Wilson,[90] who have concluded that the incompatibility sometimes observed with this ester is due to the presence in it of high-boiling residues and incompatible esters; the authors have given a formula to which the composition of the plasticiser must conform if it is to be compatible with polyvinyl chloride.

Methods for stabilising polyvinyl chloride have included the addition of potassium antimony tartrate[91] or aminoguanidine,[92] or heating in

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[81] U.S.P. 2,205,390; B., 1946, II, 216.
[82] B.P. 573,559; B., 1946, II, 72.
[83] B.P. 573,670; B., 1946, II, 73.
[84] U.S.P. 2,328,430; B., 1945, II, 360.
[85] *Helv. Chim. Acta*, 1945, **28**, 1197; B., 1946, II, 128.
[86] *Ibid.*, 455; B., 1946, II, 211.
[87] B.P. 570,564; B., 1945, II, 349.
[88] B.P. 572,767; B., 1946, II, 54.
[89] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 730; C., 1946, 142.
[90] *Brit. Plastics*, 1945, **17**, 433.
[91] B.P. 575,649; B., 1946, II, 218.
[92] B.P. 576,293; B., 1946, II, 275.

presence of formamide[93] which have been described by the Wingfoot Corporation. The B. F. Goodrich Co.[94] have claimed the use of alkali, alkaline-earth, or *tert.*-alkyl hypochlorites as stabiliers. The modification of polyvinyl chloride compositions by the addition of chlorinated paraffin wax has been described by Imperial Chemical Industries Ltd.,[95] who claim that this treatment extends the plastic temperature range and renders the composition particularly suitable for extrusion.

No new applications for polyvinyl chloride compositions appear to have been described this year but considerable publicity has been given to the use of unsupported film and fabric coated with polyvinyl chloride compositions for upholstery. Lacquers based on polyvinyl chloride have been described by A. J. Drinberg[96] whilst the English Electric Co.[97] have described an ink suitable for use on dark polyvinyl chloride compositions.

Polyvinylidene chloride compositions have been studied by G. W. Stanton and W. A. Henson,[98] who have reported on water dispersions of these polymers which are used as coating materials.

Polymers of vinylidene chlorofluoride have been described by the American Viscose Corporation,[99] who have reported that the polymers may be used for producing films, filaments, coatings, and moulded masses.

POLYVINYL ACETATE AND ITS DERIVATIVES.

In the preparation of vinyl esters from the corresponding ethylidene diester and acid anhydride, H. F. Oxley, E. B. Thomas, and W. G. B. Mills[100] have reported that the use of aromatic sulphonic acids as catalysts reduces side reactions and results in an increased yield of the ester. The Monsanto Chemical Co.[101] have used a mercury compound promoted by metaboric acid as catalyst for the reaction between acetylene and aliphatic acids.

The structure of polyvinyl alcohol has been investigated by A. D. MacLaren and R. J. Davis[102]; from a study of the oxidation of polyvinyl alcohol with periodic acid these authors have concluded that a very small number of the vinyl residues are linked in the 1 : 2-glycol configuration. The adsorption of polyvinyl alcohol on silver bromide has been reported on by S. E. Sheppard, A. S. O'Brien, and G. L. Beyer,[103] who have concluded that the reaction proceeds to an irreversible saturated single layer, probably with the polymer molecule lying parallel to the surface.

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[93] B.P. 571,597; B., 1945, II, 385.
[94] U.S.P. 2,333,280; B., 1946, II, 296.
[95] B.P. 573,840; B., 1946, II, 134.
[96] *J. Appl. Chem. Russ.*, 1945, **18**, 278.
[97] B.P. 570,915; B., 1945, II, 385.
[98] *Ind. Eng. Chem.*, 1946, **38**, 468; B., 1946, II, 293.
[99] B.P. 570,941; B., 1945, II, 386.
[100] B.P. 576,397; B., 1946, II, 275.
[101] U.S.P. 2,329,644; B., 1945, II, 362.
[102] *J. Amer. Chem. Soc.*, 1946, **68**, 1134; A., 1946, II, 631.
[103] *J. Colloid Sci.*, 1946, **1**, 213; A., 1946, I, 345.

J. I. Jones[104] has described a method in which polyvinyl alcohol is modified with a small percentage of a phenolic resin to give a product of low water absorption. E. I. Du Pont de Nemours & Co.[105] have claimed the use of polyvinyl alcohol to cover the casting surface in the preparation of films from film-forming materials.

Processes for the preparation of polyvinyl acetals have been described by the Union Carbide & Carbon Corporation,[106] who carry out the acid hydrolysis of polyvinyl acetate in methanol solution in the presence of the aldehyde and in the initial absence of water to form a partial acetal, and by the Eastman Kodak Co.,[107] who carry out the acid hydrolysis in aqueous acetic acid solution in a process in which more water is added, followed by the aldehyde and sufficient solvent to keep the acetal in solution; a pure white product is claimed. Several processes for the stabilisation of polyvinyl acetate have been described. The Eastman Kodak Co.[108] have described electrolytic or catalytic hydrogenation of the polymer and the Wingfoot Corporation have claimed the use of 8-hydroxyquinoline[109] and of certain diamines, including ethylenediamine, and piperazines and their salts.[110]

The Monsanto Chemical Co.[111] have described the use of a dibenzyl or ditetrahydrofurfuryl ester of thiodiglycollic acid or a homologue as plasticisers for polyvinyl acetal when used as a safety glass interlayer, whilst the Eastman Kodak Co.[112] have described the use of tetrahydrofurfuryl oxalate and tetrahydrofuroate as plasticisers.

POLYAMIDES.

The formation of polyamides from piperazine and dicarboxylic acids has been studied by T. Lieser, H. Gehlen, and M. Gehlen-Keller.[113] Fibre-forming polymers were obtained from glutaric, pimelic, azelaic, sebacic, and higher acids, the quality of the fibres improving in that order. It was found when methyladipic acid was used that the side group caused a small lowering of the softening point of the polymer. Replacing a methylene group in the acid by a carbonyl group was detrimental to properties and polyamide formation, although this effect was less noticeable in long-chain dicarboxylic acids.

The formation of polyamides from adipic and sebacic acids and a series of diamines, including ethylene-, tetramethylene-, hexamethylene-, and decamethylene-diamine, has been investigated by V. V. Korschak and

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[104] B.P. 576,106; B., 1946, II, 215.
[105] U.S.P. 2,198,621; B., 1946, II, 22.
[106] U.S.P. 2,194,613; B., 1945, II, 388.
[107] U.S.P. 2,333,804; B., 1946, II, 392.
[108] U.S.P. 2,199,992; B., 1946, II, 136.
[109] B.P. 570,176; B., 1945, II, 350.
[110] B.P. 570,104; B., 1945, II, 350.
[111] U.S.P. 2,327,652; B., 1946, II, 96.
[112] U.S.P. 2,197,420; B., 1946, II, 99.
[113] *Annalen*, 1944, **556**, 114.

S. R. Rafikov[114]; hexamethylenediamine gave the products of the highest molecular weight, and it was found that the molecular weight was determined by the initial acid/diamine ratio and was inversely proportional to the acid excess. V. A. Zamiatina and V. V. Korschak[115] have studied the terminal groups of polyamides and by titration of these groups have calculated molecular weights which are in good agreement with those determined from viscosity measurements. With equivalent amounts of hexamethylenediamine and adipic acid the resulting polymer had an excess of amine groups probably due to the decarboxylation of the acid groups at the reaction temperatures. When an excess of diamine or acid was used in the reaction mixture, the end groups were predominantly those of the excess reactant. The same authors[116] have reported on the effect of acids and amines on the molecular weight and terminal groups of polyamides; when the polymer is heated in cresol solution with an excess of either reagent the polymeric chains are broken up and the reduction in molecular weight can be studied viscometrically or by titration of the end groups.

POLYETHYLENE AND DERIVATIVES.

Two translations of German reports have given interesting information on German research into the polymerisation of ethylene. The first of these, by Hopff and Goebel,[117] deals with the high-pressure polymerisation of ethylene and describes an experimental process for a continuous reaction; two plants are described, one operating at 200 atmospheres to give a product of low molecular weight used in compounding floor and shoe polishes, and the other operating at 2000 atmospheres. The second paper, by Hopff and Kern,[118] describes the emulsion polymerisation of ethylene using a persulphate catalyst and an alkaline aqueous phase; a continuous process was worked out. The products contained sulphur and had lower molecular weights than high-pressure polymers. The polymerisation of ethylene under pressure in an acidic aqueous medium in the presence of benzoyl peroxide has been described by E. I. Du Pont de Nemours & Co.[119] Polymerisation and copolymerisation of ethylene under pressure in inert organic solvents to give products of low molecular weight have been described by the General Aniline & Film Corporation.[120]

Derivatives of ethylene include polymers of α-chloro-α-fluoroethylene; these may be polymerised with other vinyl derivatives to give soluble products suitable for coating and impregnating, as described by the Monsanto Chemical Co.[121] Processes for the chlorination of polythene

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[114] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **48**, 35; B., 1946, II, 212.
[115] *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 480; C., 1946, 250.
[116] *Ibid.*, 609; B., 1946, II, 463.
[117] *Mod. Plastics*, 1946, **23**, *No.* 9, 141; B., 1946, II, 309.
[118] *Ibid.*, *No.* 10, 153; B., 1946, II, 309.
[119] B.P. 578,584; B., 1946, II, 391.
[120] U.S.P. 2,334,195; B., 1946, II, 296.
[121] U.S.P. 2,328,510; B., 1945, II, 388.

to give soluble products suitable for forming films, sheets, and tubes[122] and for use in paints and moulding compositions[123] have been described by Imperial Chemical Industries Ltd., who have also described processes for the production[124] and polymerisation[125] of nitroethylene.

Copolymers of ethylene described by E. I. Du Pont de Nemours & Co. include copolymerisation with vinylidene chloride[126] at elevated temperatures and pressure in organic solvent or water to give products having better properties than polymers of vinylidene chloride. The same company[127] have described film- and fibre-forming polymers obtained by partial hydrolysis of copolymers of ethylene and vinyl acetate and subsequent heating in solution with compounds such as dimethylolurea.

Papers on the structure of polythene have been presented by C. W. Bunn and T. C. Alcock[128] and by R. Houwink.[129] The former authors studied by means of X-ray photography the change from the mixed amorphous and crystalline state of polythene at normal temperatures to that of the wholly amorphous polymer which is reached at 123°; the proportions of the two states remained constant until 80° was reached, after which the amorphous state increased at the expense of the crystalline state. These authors have also concluded, from evidence obtained from the polarising microscope and from the electron microscope, that polythene has a spherulitic structure. Houwink considers that the properties of polythene indicate a branched-chain structure and has suggested that such a structure would account for its imperfect crystallinity, softness, rubber-like properties, and susceptibility to oxidation due to the presence of tertiary carbon atoms.

The phase relations between polythene and solvents have been studied by R. B. Richards,[130] who has presented data on the effect of polymer chain length and branching and solvent type on the solubility and swelling of polythene. J. G. Powles and W. G. Oakes[131] have investigated the dielectric behaviour of polythene at very high frequencies and have concluded that polythene is suitable for wave-lengths down to 1 cm. and probably lower.

The production of elastic filaments from polythene has been described by Imperial Chemical Industries Ltd.,[132] who have also described the coating of surfaces with a film of polythene by spraying[133] in atomised form with a blast of hot gas and by flowing[134] the molten polymer

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[122] B.P. 574,971 ; B., 1946, II, 175.
[123] B.P. 576,119 ; B., 1946, II, 257.
[124] B.P. 572,803 ; B., 1946, II, 30.
[125] B.P. 572,891 ; B., 1946, II, 30.
[126] B.P. 576,830 ; B., 1946, II, 296.
[127] B.P. 575,689 ; B., 1946, II, 256.
[128] *Trans. Faraday Soc.*, 1945, **41**, 317; A., 1945, I, 245.
[129] *Brit. Plastics*, 1946, **18**, 192; B., 1946, II, 293.
[130] *Trans. Faraday Soc.*, 1946, **42**, 10, 20 ; A., 1946, I, 183.
[131] *Nature*, 1946, **157**, 840; A., 1946, I, 374.
[132] B.P. 575,296 ; B., 1946, II, 204.
[133] B.P. 573,264 ; B., 1946, II, 183.
[134] B.P. 574,309 ; B., 1946, II, 138.

composition over the surface. Callender's Cable & Construction Co.[135] have described the expansion of polythene to a cellular state by dissolving carbon dioxide in the heated polymer under pressure and then releasing the pressure and cooling quickly.

The properties of a new polymer, polytetrafluoroethylene, have been described by M. M. Renfrew and E. E. Lewis[136] and others.[137] This polymer, which is already in small production, has extremely good resistance to heat and chemicals and at the same time also retains the electrical properties of polythene. The polymerisation of tetrafluoroethylene at elevated temperature and pressure in contact with an alkaline aqueous solution of a per-acid salt or inorganic peroxide has been described by E. I. Du Pont de Nemours & Co.,[138] who have also described[139] the polymerisation under similar conditions in the presence of an aqueous solution of a base or alkali.

Other Polymers.

A report, of German origin, on the preparation and properties of polyvinylpyrrolidine has been presented by Fikentscher and Herrle[140]; block and aqueous solution polymerisation methods have been worked out. The polymers are soluble in water and organic solvents; dilute solutions of the polymers have been used as a blood substitute and solutions can also be used as bonding agents and for sizing paper.

Several papers and patents have been published on the polymerisation and copolymerisation of allyl compounds. A general account of the polymerisation of allyl esters of dibasic acids and the use of these polymers in the preparation of laminated products has been given by N. H. Chamberlain.[141] W. Simpson[142] has studied the polymerisation of allyl phthalate. Initially, a linear polymer is formed, but after 25% conversion has been reached it is replaced by a cross-linked, three-dimensional polymer. Both the chains and bridges decrease in length as the reaction temperature is raised. Similar studies of the copolymerisation of allyl phthalate and ethylene maleate indicate that the product is mainly three-dimensional. The copolymerisation of allyl acetate and maleic anhydride in the presence of peroxides has been studied by P. D. Bartlett and K. Nozaki.[143]

The production of allyl alcohol and its esters from butane has been described by the Shell Development Co.,[144] and the American Cyanamid

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[135] B.P. 573,306 : B., 1946, II, 174.

[136] *Ind. Eng. Chem.*, 1946, **38**, 870; B., 1947, II, 21.

[137] *Mod. Plastics*, 1946, **23**. *No.* 10, 134; B., 1946, II, 340.

[138] B.P. 572,265; B., 1946, II, 54.

[139] B.P. 574,688; B., 1946, II, 174.

[140] *Mod. Plastics*, 1945, **23**, *No.* 3, 157; B., 1946, II, 109.

[141] *Plastics*, 1945, **9**, 622; B., 1946, II, 171.

[142] *J.S.C.I.*, 1946, **65**, 107; B., 1946, II, 293.

[143] *J. Amer. Chem. Soc.*, 1946, **68**, 1495; A., 1947, I, 55.

[144] B.P. 577,992; B., 1946, II, 361.

Co.[145] have claimed the polymerisation of allyl alcohol at elevated temperatures in presence of oxygen to give products suitable for use in the production of drying oils. The polymerisation of allyl halides has been described by the Shell Development Co.,[146] whilst Phillips Petroleum Co.[147] have described polymers obtained from sulphur dioxide and allyl cyanide.

The preparation and polymerisation of vinyl esters of halogeno-phenoxyaliphatic acids have been described by the General Electric Co.[148] (of America); the polymers vary from viscous liquids to hard solids, and copolymers with other olefinic compounds can be prepared. E. I. Du Pont de Nemours & Co.[149] have described polymers and copolymers of esters of vinyloxyacetic acid and[150] from vinyl trimethylacetate.

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[145] B.P. 573,757; B., 1946, II, 135.
[146] U.S.P. 2,331,869; B., 1946, II, 31.
[147] U.S.P. 2,198,936; B., 1946, II, 135.
[148] U.S.P. 2,335,651–2; B., 1946, II, 343, 323.
[149] B.P. 574,034; B., 1946, II, 134.
[150] B.P. 572,914; B., 1946, II, 136.

THERMOSETTING RESINS AND PLASTICS.

By C. A. Redfarn, B.Sc., Ph.D., F.R.I.C.,
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During the period under review, two important publications dealing with the structure of thermosetting resins have become accessible, namely, on phenol–formaldehyde resite and urea–formaldehyde resins; they will be considered under the appropriate headings. Apart from these two papers no outstanding contributions appear to have been published, but the usual large number of suggestions for modification of processes for preparing and compounding the various resins have been put forward.

Phenolic Plastics.

Constitution.

A. Zinke and E. Ziegler[1] have, as the result of original work and a survey of the literature, put forward the following views. In the formation of resite (*i.e.*, thermo-hardened phenol–formaldehyde resin made with an alkaline catalyst on a 1 : 1·5 mol. ratio) they state that the first stage is the production of phenol mono- and di-alcohols, which then react further with the loss of water to give di(hydroxybenzyl) ethers, o-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}OH$-6 : 1 : 2. On further reaction by heating, ether bridges are converted into methylene bridges by loss of formaldehyde, with the formation of diphenylmethane derivatives.

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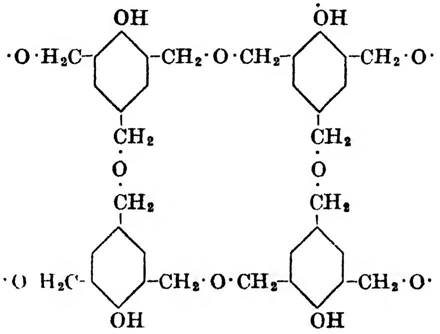
[1] *Wiener Chem.-Ztg., July,* 1944.

This conversion is stated to be rapid above 170° but will also take place on prolonged heating at lower temperatures: it is believed that the liberated formaldehyde is recombined. The initial formation of ether bridges followed by their conversion into methylene bridges is believed to be the principal reaction involved in building up the three-dimensional cross-linked structure of the final resite, which, it is stated, contains very few ether bridges. It is further suggested by Zinke and Ziegler that the various types of groupings occurring in resite are (*a*) ether linkings (to a small residual extent); (*b*) methylene bridges, aldehyde groups (in small amounts), methyl groups (in small amounts), and *o*-quinone-methide groups, all formed from the ether linkings, although the last-named are also derived direct from hydroxymethyl compounds; (*c*) ethylene and ethane linkings, both in small amounts and produced from *p*-quinone-methide groups. The authors claim that the presence of ether linkings, terminal aldehyde groups, and terminal hydroxymethyl groups has been demonstrated by experiment, and they give a structural picture of how the various groupings may occur in a resite. It must be confessed, however, that the paper is couched in somewhat obscure terms and it is, even in translation, sometimes difficult to follow how the authors relate their theories to their experimental work. In the writer's opinion, a good case has been made out for the initial formation of ether bridges which are subsequently converted into methylene bridges during the thermo-hardening. Although Zinke and Zeigler do not make the point, their ether bridge hypothesis does, in the writer's opinion, shed some light on the structure of cast phenolic resin, in which a phenol : formaldehyde ratio of 1 : 2 to 1 : 3 is used, about 1 : 2·3 being preferred. It would appear that 1 mol. of phenol does not combine with more than 3 mols. of formaldehyde.[2] It was impossible to accommodate products of the cast resin type in the old *o*-*o′*-*p* methylene bridge structural theory since on a 1 : 3 phenol : formaldehyde ratio all of the available reactive nuclear positions are already occupied. However, by accepting the formation of ether bridges, the following ideal structure for cast phenolic resin can be visualised:



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[2] *Inst. Plastics Ind. Booklet, Plastics Monograph* 4*a*, p. 13.

It will be noticed that, in agreement with experimental fact, such a structure will accommodate a phenol : formaldehyde ratio of 1 : 3.

Phenol–Formaldehyde Resin Production.

Further work is reported on the production of resinous products from phenol and formaldehyde in conjunction with oxidised rubber,[3] cashew nut oil,[4] naphthalene,[5] thiocyanates,[6] polyvinylal resin,[7] alkyd resin,[8] a solvent tar from petroleum products,[9] resorcinol,[10] and the lignin component of wet-hydrolysed lignocellulose.[11] The hardening properties of phenol–formaldehyde resin are stated to be improved by the addition of compounds such as sulphamic acid or a derivative, plus a little resorcinol.[12] A hardenable one-stage phenolic resin having a high degree of condensation is obtained by incorporating a primary or secondary aromatic amine, *e.g.*, aniline.[13]

A brief review is given of the development of resorcinol–formaldehyde resins for adhesives; resin formation can now be controlled to give a satisfactory commercial glueing process.[14]

An alkali-ion-absorbing resin is made by condensing phenol and formaldehyde to the gel stage with an excess of alkali as catalyst, grinding the gel, treating with acid, and washing before use.[15] Cation-exchange resins are made from an aminonaphtholsulphonic acid, a phenol, and formaldehyde.[16]

I. W. Ruderman has isolated *o*- and *p*-hydroxybenzyl alcohols by fractional crystallisation of the deposits in the exhaust stacks of the dryers in phenolic resin paper- or cloth-impregnating plants.[17]

Phenol–Formaldehyde Compositions.

Walnut shell flour is suggested as a filler for fast-setting phenolic casting resin.[18] Phenolic moulding compositions using such fillers as

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[3] Brit. Rubber Producers' Research Assoc., and F. J. W. Popham, B.P. 573,114; B., 1946, II, 99.

[4] A. F. Shepard, J. F. Boiney, and L. Sontag, Assrs. to Gen. Plastics Inc., U.S.P. 2,203,206; B., 1946, II, 178.

[5] E. B. Kester, Assr. to Koppers Co., U.S.P. 2,330,827; B., 1946, II, 100.

[6] F. Frank, Aspro Ltd., and Brit. Artificial Resin Co. Ltd., B.P. 572,989; B., 1946, II, 100.

[7] Scott, Bader & Co. Ltd., and H. C. Bryson, B.P. 573,437; B., 1946, II, 99.

[8] S. S. Gutkin, Assr. to Falk & Co., U.S.P. 2,329,045; B., 1946, II, 180.

[9] A. N. Sachanen and P. G. Waldo, Assrs. to Socony–Vacuum Oil Co. Inc., U.S.P. 2,198,318; B., 1946, II, 22.

[10] Bakelite Ltd., B.P. 576,745; B., 1946, II, 299.

[11] A. G. Hovey and T. S. Hodgins, Assrs. to Reichhold Chemicals Inc., U.S.P. 2,197,724; B., 1946, II, 179.

[12] Bakelite Ltd., B.P. 572,986; B., 1946, II, 58.

[13] Distillers Co. Ltd., J. D. Morgan, and B. Frenkel, B.P. 573,622; B., 1946, II, 100.

[14] P. H. Rhodes, *Mod. Plastics*, 1944, **22**, *No.* 4, 160; B., 1945, II, 383.

[15] Ocean Salts (Products) Ltd., B. A. Adams, and R. C. Barker, B.P. 573,116; B., 1946, II, 99.

[16] H. Wassenegger, U.S.P. 2,333,754; B., 1946, II, 392.

[17] *J.S.C.I.*, 1945, **64**, 204; B., 1945, II, 348.

[18] J. J. Pyle, E. F. Feidler, and T. V. Ferris, *Mod. Plastics*, 1945, **22**, *No.* 6, 132; B., 1945, II, 383.

keratin from feathers,[19] sawdust and waste wood,[20] glass fibre to give products of high impact strength,[21] and coconut shell flour to give improved heat- and moisture-resistance[22] are described. The use of 5% of graphite in moulding powder is recommended as a mould lubricant.[23]

Further descriptions are given of the production of phenolic resin–paper pulp materials.[24] A possible method for combining synthetic resins with paper directly on the paper machine has been discussed.[25] Pressed products of improved physical properties are stated to be obtained by impregnating the fibrous filler first with an aqueous solution and then with an alcoholic solution of a phenolic resin.[26] The production of moulding material from wood flour and solid, finely-divided phenol–formaldehyde resin is described.[27]

The process of "post-forming" of special phenolic laminated sheet material (cf. *Ann. Repts.*, 1945, **30**, 309) by heating and bending or drawing is described.[28] Low-density components such as tubes are made by impregnating paper or linen with a thermosetting phenolic resin, partly curing, and then coating with a thermoplastic resin such as polyvinyl acetate. Strips so treated are formed into tubes on mandrels and the edges sealed by softening the polyvinyl acetate with solvent and applying pressure. The tubes are assembled in blocks and the phenolic resin cure is completed.[29] A table of data on low-pressure laminating resins has been published,[30] and methods for low-pressure moulding have been described.[31]

The process for high-frequency preheating of thermosetting moulding compositions has been patented.[32] It is stated that improvements in the quality of the thermosetting mouldings result from the use of high-frequency preheating.[33] A process for resistance preheating of phenolic material containing graphite to make the material conducting is stated to be cheaper than infra-red heating.[34]

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[19] G. H. Brother, C. H. Binkley, and B. Brandon, *Mod. Plastics*, 1945, **22**, *No.* 7, 157; B., 1945, II, 381.

[20] F. Frank, B.P. 571,786; B., 1945, II, 384.

[21] Bakelite Ltd., and J. H. Bennitt, B.P. 570,990; B., 1946, II, 216.

[22] G. B. E. Scheueler, *Plastics*, 1946, **10**, 84; B., 1946, II, 339.

[23] Anon., *Canad. Plastics*, 1945, **3**, *No.* 11, 24; B., 1946, II, 339.

[24] S. L. Schwartz, J. C. Pew, and H. R. Meyer, *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 61; B., 1945, II, 347. H. C. Martin, *Plastics*, 1944, **8**, 520; B., 1945, II, 347. E. H. G. Sargent, B.P. 572,024; B., 1946, II, 58.

[25] R. H. Mosher, *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 233; B., 1946, II, 162.

[26] E. R. Dillehay, Assr. to Richardson Co., U.S.P. 2,198,805; B., 1946, II, 136.

[27] B.B. Chem. Co., B.P. 571,251; B., 1946, II, 216.

[28] F. Sullivan, *Met. & Alloys*, 1945, **21**, 392; B., 1945, II, 382. Anon., *Plastics*, 1946, **10**, 62; B., 1946, II, 255. B. Nash, *Mod. Plastics*, 1945, **23**, *No.* 1, 129; B., 1945, II, 382.

[29] Plasticrete Holdings Ltd., C. G. Wade, and A. Amigo, B.P. 578,603; B., 1946, II, 379.

[30] Anon., *Mod. Plastics*, 1946, **23**, *No.* 10, 144; B., 1946, II, 341.

[31] C. B. Hemming, *ibid.*, 1945, **23**, *No.* 2, 129; B., 1946, II, 93.

[32] Bakelite Ltd., B.P. 572,425; B., 1946, II, 56.

[33] A. R. Tinnerholm, *Mod. Plastics*, 1946, **23**, *No.* 8, 180; B., 1946, II, 338.

[34] C. G. Phillips, *Brit. Plastics*, 1945, **17**, 527; B., 1946, II, 93.

An aqueous dispersion of a coumarone resin or oil-soluble phenolic resin in a vulcanisable oil is used with cement to give a flooring composition.[35] Abrasive grains are worked into a sheet with phenolic resin and plasticisers, and this sheet is cut to shape and heat-hardened to give abrasive wheels.[36]

The hardness and shock-resistance of themosetting phenolic resins are improved by incorporating finely powdered, infusible, insoluble alkyd resin in the mix.[37]

A general survey has been given on the colouring of plastic materials and a list is given of the suitable dyes and pigments for the commoner plastic materials.[38]

Phenolic Coating Compositions.

Oil-soluble phenol–formaldehyde resins for coating compositions can be made from alkylated peat-tar phenols,[39] *o*-cresol and *o*- or *p*-hydroxydiphenyls,[40] *o*-cresol and *o*-*cyclo*hexylphenol,[41] *o*-cresol and *p*-cresol,[42] aromatic petroleum residue and cresylic acid,[43] cresol and acetaldehyde,[44] mixed xylenols and acetaldehyde,[45] *p*-*tert.*-butylphenol and rosin,[46] and an acid-catalysed phenol resin modified with raw soya-bean oil.[47] By the use of wetting agents it is stated that the reaction between *tert.*-butylphenol and formaldehyde can be carried out with weaker acids and at much lower acid catalyst concentration.[48]

For coating metal with resorcinol–formaldehyde resin the use of a polyvinyl resin undercoat and finishing coat is recommended.[49] Induction heating is recommended for hardening phenolic resins on steel piping.[50] A mixture of phenolic resin and coumarone resin is described as suitable for covering metal containers.[51]

[35] Semtex Ltd., F. G. Mottershaw, L. H. Griffiths, and P. H. Robin, B.P. 571,832; B., 1946, II, 23.

[36] Norton Grinding Wheel Co., B.P. 576,330; B., 1946, II, 300.

[37] G. S. Weith, Assr. to Bakelite Corp., U.S.P. 2,199,900; B., 1946, II, 180.

[38] C. R. M. Oehlcke, *J. Soc. Dyers & Col.*, 1945, **61**, 306; B., 1946, II, 93.

[39] A. J. Drinberg and P. P. Kretschko, *J. Appl. Chem. Russ.*, 1944, **17**, 458; B., 1945, II, 348.

[40] W. Charlton, J. B. Harrison, L. E. Perrins, and I.C.I. Ltd., B.P. 577,561; B., 1946, II, 345.

[41] *Idem*, B.P. 574,790–2; B., 1946, II, 179.

[42] W. Charlton, J. B. Harrison, and I.C.I. Ltd., B.P. 573,430; B., 1946, II, 99.

[43] E. F. MacTaggart and H. H. Chambers, B.P. 571,246 and 571,248–9; B., 1945, II, 388.

[44] Brit. Resin Products Ltd., J. D. Morgan, and B. Frenkel, B.P. 573,626; B., 1946, II, 99.

[45] Distillers Co. Ltd., J. D. Morgan, and B. Frenkel, B.P. 572,857; B., 1946, II, 100.

[46] I. Rosenblum, U.S.P. 2,338,543; B., 1946, II, 392.

[47] Bakelite Corp., B.P. 570,367; B., 1945, II, 351.

[48] J. V. Hunn, Assr. to Sherwin–Williams Co., U.S.P. 2,330,217; B., 1946, II, 58.

[49] E. I. Du Pont de Nemours & Co., and A. Hershberger, B.P. 574,168; B., 1946, II, 138.

[50] A. A. Mazzucchelli and R. E. Nicolson, *Iron Age*, 1945, **155**, *No.* 18, 46; B., 1945, II, 349.

[51] Vernis Duroux, B.P. 577,102; B., 1946, II, 300.

Film-forming materials are prepared from linseed oil fatty acids and an oil-soluble *p-tert.*-butylphenol–formaldehyde resin, which may also be esterified with an excess of glycerol and further heated with phthalic acid.[52] A quick-setting phenolic resin coating can be successfully applied by spraying the surface to be coated with the resin syrup and hardener from separate sprays so that the resin and hardener are mixed on the surface.[53]

The surface of phenolic material can be made hydrophilic, and hence more suitable for glueing, by treatment with fuming sulphuric or chlorosulphonic acid.[54]

Properties of Phenolic Materials.

Corrosion is liable to occur in metal inserts of wood flour-filled phenolic materials in the tropics; investigation has shown that acetic acid arising from the wood flour and ammonia from the hexamethylenetetramine are the chief causes of corrosion and a maximum of 0·18% of acetic acid and 0·015% of ammonia in the finished moulding is recommended.[55]

Further investigations have been carried out on the application of the voids theory to phenolic laminates and in general the results are in line with the theory, but the tensile strength of laminates of low resin content is less than was expected: the interlaminar shear strength has been found to be dependent on resin strength.[56]

The distortion of canvas-base laminated phenolic materials at elevated temperatures has been investigated and it is shown that the deformation rate increases sevenfold between 149 and 204°.[57]

The creep properties of phenolic plastics have been investigated and recorded[58,59]; the creep of materials containing inorganic fillers is less than that of materials with cellulosic fillers.[59]

AMINO RESINS.

Urea–Formaldehyde Resins.

A most interesting paper by C. S. Marvel, J. R. Elliott, F. E. Boett, and H. Yorke[60] deals with the structure of urea–formaldehyde resins. The new structure hypothesis is based on the view that urea acts as an amino-acid amide (*i.e.*, the amide of carbamic acid), which means that the two NH_2 groups are not equivalent. It is well known

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[52] H. S. Lilley, J. W. Dorling, and I.C.I. Ltd., B.P. 572,822-3; B., 1946, II, 138.

[53] R. J. Stevens and P. C. Major, B.P. 575,326; B., 1946, II, 218.

[54] Distillers Co. Ltd., J. J. P. Staudinger, and H. M. Hutchinson, B.P. 572,985; B., 1946, II, 98.

[55] H. Gerland, *Siemens Z.*, 1943, **23**, 23; *Plastics*, 1946, **10**, 137; B., 1946, II, 213.

[56] K. W. Pepper, F. T. Barwell, and D. K. Hale, *J.S.C.I.*, 1946, **65**, 153; B., 1946, II, 338.

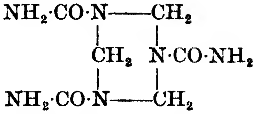
[57] J. Delmonte and E. Watkins, *Proc. Amer. Soc. Test. Mat.*, 1944, **44**, 1009; B., 1946, II, 172.

[58] W. N. Findley and W. J. Warley, *Mod. Plastics*, 1945, **22**, *No.* 10, 143; B., 1946, II, 255. *Idem, Proc. Amer. Soc. Test. Mat.*, 1944, **44**, 946; B., 1946, II, 254.

[59] W. J. Gailus and D. Telfair, *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 253; B., 1945, II, 348.

[60] *J. Amer. Chem. Soc.*, 1946, **68**, 1681; A., 1947, II, 110.

that urea reacts with formaldehyde to give mono- and di-methylolurea and it has been assumed that resinification takes place by the formation of linear polymers which then cross-link. According to Marvel *et al.* the amino-group in urea reacts with formaldehyde to give a methyleneimino-group, and this is followed by cyclisation to a 1 : 3 : 5-tricarbamylhexahydrotriazine (see annexed formula).



$$\begin{array}{lcl} NH_2\cdot CO\cdot N & \text{——} & CH_2 \\ \quad\quad\quad\quad | & & | \\ \quad\quad\quad\quad CH_2 & & N\cdot CO\cdot NH_2 \\ \quad\quad\quad\quad | & & | \\ NH_2\cdot CO\cdot N & \text{——} & CH_2 \end{array}$$

The formation of the thermoset urea resin is then believed to take place by reaction of the side-chain $\cdot CO\cdot NH_2$ of the trimer to give a highly cross-linked structure in which the triazine groups are joined by $\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot$ bridges. In the present writer's opinion, this new structural hypothesis is interesting, since the resemblance of the trimer to melamine is noteworthy, and the urea : formaldehyde resin structure postulated calls for a 1 : 1·5 urea–formaldehyde ratio : this is in line with the industrial conclusion arrived at empirically that the best results in urea–formaldehyde moulding powders are obtained on a 1 : 1·5 ratio. Some years ago G. Walter[61] put forward some distinctly tortuous structural hypotheses in order to account for the experimental data he obtained ; the Marvel hypothesis would appear to provide a better explanation of Walter's results.

Among the curing catalysts suggested for urea–formaldehyde resins are thio-β-naphthyl benzoate,[62] acetoxime *p*-toluenesulphonate,[63] glucono- or galactono-lactones, dibenzylhydroxamic acid and ethylene thiocyanate,[64] a nitro-hydroxy-paraffin and an acrylic aldehyde,[65] cyanothioformamide,[66] *N*-methylsaccharin,[67] the salt of a diamine with an aliphatic dicarboxylic acid,[68] the reaction product of hexamethylenetetramine and an aldehyde with a carboxylic acid or with a mixture of fatty acid and a mineral acid,[69] ammonium silico- or boro-fluoride,[70] ethylenediamine hydrochloride,[71] *NN'*-di(chloroacetyl)ethylenediamine,[72] and alkyl *p*-chloroacetamidobenzoates.[73]

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[61] *Trans. Faraday Soc.*, 1936, **32**, 377, 390, 402; *Farben-Chem.*, 1936, **7**, 69; Walter and M. Gewing, *Kolloid Beih.*, 1931, **34**, 163.

[62] N. A. Shepard, Assr. to Amer. Cyanamid Co., U.S.P. 2,331,862 ; B., 1946, II, 99.

[63] D. E. Cordier, Assr. to Plaskon Co., U.S.P. 2,203,772 ; B., 1946, II, 134.

[64] D. E. Cordier, Assr. to Plaskon Co., U.S.P. 2,203,773 ; L. S. Meyer, Assr. to Plaskon Co., U.S.P. 2,203,794 ; J. K. Simons, Assr. to Plaskon Co., U.S.P. 2,203,800 ; B., 1946, II, 175.

[65] C. Ellis, Assr. to Ellis Laboratories, U.S.P. 2,314,308 ; B., 1946, II, 101.

[66] D. E. Cordier, Assr. to Plaskon Co., U.S.P. 2,201,027 ; B., 1946, II, 175.

[67] E. H. Balz, Assr. to Plaskon Co., U.S.P. 2,201,021 ; B., 1946, II, 176.

[68] E. I. Du Pont de Nemours & Co., B.P. 572,245 ; B., 1946, II, 55.

[69] F. Nozicka, U.S.P. 2,335,440 ; B., 1946, II, 344.

[70] Amer. Cyanamid Co., Assees. of R. R. Harris, B.P. 576,995 ; B., 1946, II, 299.

[71] G. F. D'Alelio, Assr. to Gen. Electric Co., U.S.P. 2,334,545 ; B., 1946, II, 344.

[72] *Idem*, U.S.P. 2,337,313 ; B., 1946, II, 344.

[73] Brit. Thomson-Houston Co., B.P. 571,660 ; B., 1946, II, 22.

As plasticisers for urea–formaldehyde resins ammonium, sodium, or potassium lactate[74] and benzene- and *p*-toluene-sulphonhydroxyalkylamides[75] are recommended.

The production of resins from *NN*-di-(β-hydroxyethyl)-*N*-butylamine and *NN'*-di(alkoxymethyl)ureas,[76] the reaction product of urea and *N*-hydroxyethylurea with formaldehyde,[77] and from urea and pyruvic acid[78] is described. A resin with good compatibility with petroleum thinners is obtained by interaction of urea and formalin with an octanol such as 2-ethylhexanol in presence of methyl alcohol.[79]

Aqueous emulsions of alcohol-modified urea formaldehyde resins are made by compounding the resin with water-soluble cellulose ethers in the presence of an emulsifying agent.[80]

Solutions of urea–formaldehyde resins can be obtained by refluxing the crystalline diethers of dimethylolurea so that the polymeric ether of methyleneurea formed is dissolved in the liberated solvent.[81]

Further developments in the production of papers of high wet strength by the use of solutions of urea resins are described.[82]

A resin made from urea, phenol, and formaldehyde is recommended for casting[83] and a wood-finishing lacquer is made from an alcohol-modified urea–formaldehyde resin, a phenolic resin, and a fossil resin.[84]

Urea–Formaldehyde Adhesives.

A cold-setting urea–formaldehyde resin containing fish glue is stated to have high initial tack before acid polymerisation sets in.[85] A gap-filling adhesive is obtained by compounding the resin with comminuted cellulosic filler in presence of butyl alcohol.[86] Vetch and/or cockle meal may also be used as filler for urea–formaldehyde resin adhesive.[87] The theoretical aspects of adhesion have been discussed.[88]

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[74] W. Walker & Sons Ltd., J. R. Alexander, D. Burton, and F. Hausmann, B.P. 573,866; B., 1946, II, 180.

[75] D. E. Cordier, Assr. to Plaskon Co., U.S.P. 2,201,028; B., 1946, II, 179.

[76] E. I. Du Pont de Nemours & Co., B.P. 570,074; B., 1945, II, 351.

[77] J. F. Olin, Assr. to Sharples Chemicals Inc., U.S.P. 2,331,926; B., 1946, II, 218.

[78] A. G. Hovey and T. S. Hodgins, Assrs. to Reichhold Chemicals Inc., U.S.P. 2,195,570; B., 1946, II, 22.

[79] H. J. West, Assr. to Amer. Cyanamid Co., U.S.P. 2,327, 984; B., 1946, II, 179.

[80] W. J. Thackston, Assr. to Röhm & Haas Co., U.S.P. 2,196,367; B., 1945, II, 387.

[81] B. E. Sorenson, Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,201,926; B., 1946, II, 136.

[82] M. O. Schur, Assr. to Reconstruction Finance Corp., U.S.P. 2,338,602; B., 1946, II, 378. Wiggins, Teape & Co. (1919) Ltd., and S. R. H. Edge, B.P. 578,541; B., 1946, II, 378.

[83] K. Loos, U.S.P. 2,205,427; B., 1946, II, 260.

[84] E. F. Oeffinger and H. G. Stauffer, Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,201,914; B., 1946, II, 137.

[85] B. J. Balfe and I.C.I. Ltd., B.P. 573,887; B., 1946, II, 180.

[86] Aero Research Ltd., and E. L. R. Mowat, B.P. 574,095; B., 1946, II, 137.

[87] M. A. Bubeck-Wolfensberger and W. Dolder-Behn-Eschenburg, B.P. 570,357; B., 1945, II, 389.

[88] R. C. Rinker and G. M. Kline, *Mod. Plastics*, 1945, **23**, *No.* **2**, **153**; *No.* **3**, **164**; B., 1946, II, 93.

Urea–Formaldehyde Moulding Powders.

Further modifications in the production of cellulose-filled urea–formaldehyde moulding compositions are described.[89] It is claimed that the yellowing of moulded cellulose-filled urea–formaldehyde compositions is reduced by the incorporation of titanium oxide.[90]

Improvements in handling and the production of better castings are claimed as the result of using urea–formaldehyde resin binders in the preparation of sand-cores for light alloy casting.[91]

Melamine Resins.

Melamine resin for moulding powder is made by interaction of about 3 mols. of formalin with 1 mol. of melamine at pH 6·3 and then vacuum-distilling at a pH above 7.[92] Interaction of melamine under alkaline conditions with dimethylolurea in presence of chloroacetamide gives a resin used in moulding powders.[93]

Compounds such as *p*-toluenesulphonhydroxy-methyl- and -ethyl-amide[94] and a carbamidomethylaminobenzenesulphonamide[95] are recommended as plasticisers for melamine– and urea–formaldehyde resins, whilst halogenoketones are used as curing catalysts for melamine–formaldehyde resin.[96]

Among the miscellaneous triazine derivatives recommended for resin making are products made from diguanido sulphate, ethyl α-ethylhexoate (and similar esters), and formaldehyde,[97] 4 : 6-diamino-2-semicarbazido-1 : 3 : 5-triazine,[98] 1 : 3-diamino-5-carboxymethyltriazines (the NH_2 groups may be substituted),[99] bisdiaminotriazinyl cyanoalkylene disulphides,[100] and certain complex diazines, triazines, and their thio-derivatives.[101]

In a report on German synthetic resin manufacture[102] some details are given of the preparation of various complex triazines which give resinous products when condensed with formaldehyde.

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[89] L. Smidth, U.S.P. 2,338,464 and 2,329,172; B., 1946, II, 391, 216.

[90] C. R. Stock, Assr. to Amer. Cyanamid Co., U.S.P. 2,333,396; B., 1946, II, 299.

[91] F. G. Felske, *Mod. Plastics*, 1945, **23**, *No.* 2, 118; B., 1946, II, 93.

[92] Amer. Cyanamid Co., B.P. 574,016; B., 1946, II, 180.

[93] G. F. D'Alelio, Assr. to Gen. Electric Co., U.S.P. 2,328,424–5; B., 1945, II, 389.

[94] P. C. Schroy, Assr. to Amer. Cyanamid Co., U.S.P. 2,326,728; B., 1945, II, 351.

[95] G. F. D'Alelio, Assr. to Gen. Electric Co., U.S.P. 2,327,772; B., 1945, II, 387.

[96] *Idem*, U.S.P. 2,327,771; B., 1945, II, 387.

[97] Amer. Cyanamid Co., B.P. 569,363; B., 1945, II, 336.

[98] G. F. D'Alelio and J. W. Underwood, Assrs. to Gen. Electric Co., U.S.P. 2,335,846; B., 1946, II, 300.

[99] *Idem*, U.S.P. 2,338,492; B., 1946, II, 392.

[100] Brit. Thomson-Houston Co., B.P. 576,163; B., 1946, II, 392.

[101] G. F. D'Alelio and J. W. Underwood, Assrs. to Gen. Electric Co., U.S.P. 2,328,956–64 and 2,337,547; B., 1946, II, 6, 344. Brit. Thomson-Houston Co., B.P. 570,520 and 570,569; B., 1945, II, 351.

[102] R. W. Sudhoff, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXIV–21; B., 1946, II, 294.

Melamine–formaldehyde resins modified with butyl alcohol,[103] and melamine–formaldehyde resins in conjunction with oil-soluble phenolic resins[104] and Manila or kauri resin, are suggested for coating compositions.[105]

Melamine–formaldehyde resin is recommended as the hardening agent in Novolak resin moulding compositions,[106] and the mixing of partly condensed melamine–formaldehyde and phenol–formaldehyde resins is stated to give products resistant to boiling water.[107]

Melamine resins are recommended for use in the production of paper of high wet strength,[108] and for insulation.

Among the uses for melamine–dicyanodiamide–formaldehyde resins are laminating, electrical insulation, and adhesives,[109] impregnation of textiles,[110] and the production of polyamide fibre fabric laminates of improved impact strength.[111]

Miscellaneous Amino Resins.

The modification of aniline–formaldehyde resin by the addition of shellac[112] and dicyanodiamide[113] is reported. Resins for use in making grinding wheels are prepared from aniline–formaldehyde resins and the tri(monochloroacetate) of glycerol or of tri(hydroxymethyl)propane,[114] ethylene glycol di(monochloroacetate),[115] glycerol chlorohydrin chloroacetate,[116] and di-β-chloroethyl phthalate.[117] A cold-setting cement with good adhesive properties is made by compounding a dehydrating agent with a furfuraldehyde-soluble aniline resin, furfuraldehyde, and glycerol in presence of an acid.[118] A resin soluble in acetone and ethyl alcohol is prepared by fusing together equimolecular proportions of lactic acid and aniline.[119]

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[103] Brit. Industrial Plastics, Ltd., B.P. 572,239; B., 1946, II, 57. A. Hill and I.C.I. Ltd., B.P. 573,368; B., 1946, II, 101.

[104] R. C. Swain and P. Adams, Assrs. to Amer. Cyanamid Co., U.S.P. 2,331,774; B., 1946, II, 100.

[105] *Idem*, U.S.P. 2,329,663–4; B., 1946, II, 23.

[106] Amer. Cyanamid Co., B.P. 570,073; B., 1945, II, 351.

[107] Brit. Thomson-Houston Co., B.P. 570,956; B., 1945, II, 389.

[108] K. E. Youngchild, *Pacific Pulp and Paper Ind.*, 1945, **19**, *No.* 12, 54; B., 1946, II 162. C. G. Landes and C. S. Maxwell *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 51; B. 1945, II, 371. F. A. Strovink, *Paper Mill News*, 1945, **68**, *No.* 49, 28; B., 1946, II, 332.

[109] K. E. Ripper, Assr. to Amer. Cyanamid Co., U.S.P. 2,333,390; B., 1946, II, 299.

[110] *Idem*, U.S.P. 2,336,370; B., 1946, II, 391.

[111] Amer. Cyanamid Co., B.P. 572,301; B., 1946, II, 57.

[112] *Idem*, B.P. 577,182; B., 1946, II, 297.

[113] *Idem*, B.P. 572,829; B., 1946, II, 101.

[114] Norton Grinding Wheel Co., B.P. 577,021; B., 1946, II, 299.

[115] *Idem*, B.P. 576,880; B., 1946, II, 299.

[116] *Idem*, B.P. 576,881; B., 1946, II, 299.

[117] *Idem*, B.P. 576,882; B., 1946, II, 299.

[118] *Idem*, B.P. 578,412; B., 1946, II, 391.

[119] A. G. Hovey and T. S. Hodgins, Assrs. to Reichhold Chemicals Inc., U.S.P. 2,197,723; B., 1946, II, 101.

Ion-exchange resins for the removal of anions have been prepared from formaldehyde, *p*-phenylenediguanide, and guanidine.[120] Interaction of triethylenetetramine, formaldehyde, and a ketone gives an irreversible gel which has anion-exchange or acid-removing properties.[121]

Resins have also been reported as made from formaldehyde and 2 : 4-dimethylpyrrole or 4-hydroxy-2-thiolthiazole[122] and formaldehyde and *p*-sulphonamidophenyldiguanide[123]; this last compound also may be used to modify thermosetting amino resins.[124]

ANALYSIS AND TESTING OF THERMOSETTING MATERIALS.

Analytical procedures are reported for classifying resins into groups[125] and for determining the total solids in a resin solution.[126] A method of analysis of the phenolic resin glue line in yellow birch plywood is described.[127] Urea-formaldehyde resins may be detected qualitatively by using carbazole in concentrated sulphuric acid,[128] by precipitating dixanthylurea from aqueous hydrochloric acid extracts after digestion with acetic acid in presence of methyl alcohol,[128] and by means of the aniline test[129]; also combined urea in urea–formaldehyde resins can be determined quantitatively by refluxing with benzylamine.[129]

A method for determining the instantaneous hardness of plastic substances by dropping a weighted cone on to the surface is described[130]; the result is substantially independent of the height of drop and the weight of the cone. In a study of the indentation behaviour of soft metals and plastics on the Rockwell hardness tester it was found that the measurement based on the recovered depth is not a true measure of the resistance to indentation and a procedure has been developed for measuring indentation depth under major load.[131] The factors determining the amount of energy required to fracture a specimen under impact test have been examined; for many plastics the tensile strength varied linearly with the log of the stressing rate over a relatively wide range.[132]

Methods for the determination of thermal conductivity have been compared and the method of Erk, Keller, and Poltz is stated to be the most accurate.[133] The moisture content of moulding powders can be

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[120] Amer. Cyanamid Co., B.P. 575,266; B., 1946, II, 219.

[121] Permutit Co. Ltd., B.P. 572,836; B., 1946, II, 137.

[122] W. Zerweck and M. Schubert, U.S.P. 2,339,314; B., 1946, II, 344.

[123] G. F. D'Alelio, Assr. to Gen. Electric Co., U.S.P. 2,331,376; B., 1946, II, 97.

[124] *Idem*, U.S.P. 2,331,377; B., 1946, II, 97.

[125] J. H. Graff, *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 45; C., 1946, 169.

[126] C. D. McKinney, jun., E. Turk, and W. E. Shaefer, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 14; C., 1946, 93.

[127] C. A. Farrow, D. H. Hamly, and E. A. Smith, *ibid.*, 307: C., 1946, 226.

[128] F. P. Brennan, *Rayon Text. Month.*, 1944, **25**, 339; C., 1946, 23.

[129] C. P. A. Kappelmeier and W. R. van Goor, *Paint Tech.*, 1946, **11**, 7; C., 1946, 171.

[130] A. Cameron, *Trans. Faraday Soc.*, 1945, **41**, 583; C., 1946, 68.

[131] L. Boor, *Proc. Amer. Soc. Test. Mat.*, 1944, **44**, 969; C., 1945, 299.

[132] D. Telfair and H. K. Nason, *ibid.*, 993; C., 1945, 300.

[133] F. Gottwald, *Arch. Techn. Messen*, 1943; *Plastics*, 1944, **8**, 564; C., 1945, 287.

determined by the Karl Fischer reagent using a potentiometric endpoint for coloured moulding powders.[134]

A method for testing laminate adhesion of plastics is described[135] and a modification of the standard TAPPI procedure is given for obtaining accurate and reproducible results when preparing melamine resin-impregnated sheets for evaluation.[136]

[134] G. R. Cornish, *Plastics*, 1946, **10**, 99; C., 1946, 93.

[135] W. Weigel, *Kunststoffe*, 1944, **34**, 76; *Plastics*, 1945, **9**, 512; C., 1946, 68.

[136] C. G. Landes and C. S. Maxwell, *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 51; C., 1945, 241.

CELLULOSIC PLASTICS.

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Economic circumstances rather than technical problems to-day restrict the logical development of cellulosic plastics. The industry has now reached the stage where further progress depends on the production of new cellulose derivatives on a commercial scale and here raw material requirements pose the major problem. This situation is more readily appreciated when it is considered against the general background of cellulose plastics technology. In the manufacture of thermoplastic materials from cellulose there are, broadly speaking, three essential steps. They involve separation of the natural polymer from the different chemical species with which it is associated, conversion of cellulose into one of its organic solvent-soluble derivatives, and the subsequent plasticisation of this derivative by combination with permanently retained softening agents; this final step enables the composition to be moulded at temperatures which are low enough not to cause decomposition of the cellulose derivative.

Whilst it is true that work is currently in progress on problems associated with each of these three stages, it is the step of converting cellulose into its derivatives which holds greatest interest at the present time. This is because, apart from some common features, the properties of cellulosic plastics are determined by the nature of the substituent groups in the derivative. It is particularly true of such properties as rigidity, temperature- and water-sensitivity, and the resultant property of dimensional stability. Without improved performance in these respects, the characteristic property of toughness will not by itself enable the cellulosic materials as a group to widen their present fields of application.

It has been widely recognised that for plastics manufacture the cellulose esters and mixed esters of higher fatty acids, such as cellulose acetate butyrate, and ethers such as ethylcellulose, offer considerable advantages over the older established derivatives represented by cellulose nitrate and cellulose acetate. The non-availability of higher fatty acid anhydrides in suitable quantity and quality and at a reasonable cost has greatly retarded cómmercial development along the lines indicated by laboratory work. A case in point is cellulose propionate plastic, which was introduced in the United States towards the end of 1945. Although the ester, cellulose tripropionate, was first evaluated twenty years ago, its commercial production became possible only with the eventual development of a process for deriving propionic acid from petroleum raw materials.

Even in the United States, where ethylcellulose and cellulose acetate butyrate plastics have been commercially available for almost ten years, the production of cellulose acetate plastics, owing to the raw material position, still leads that of all others by a very large margin. Still less satisfactory is the position in this country. Apart from insignificant quantities of ethylcellulose plastics, production here is virtually confined to cellulose nitrate and acetate materials and there are no reports yet of the development of facilities for producing the newer products.

A more immediate difficulty is the shortage of cotton linters which, in common with America, we are experiencing as a result of competitive buying in the cottonseed oil industry. This situation has been followed inevitably by a sharp increase in the price of American linters which may necessitate making greater use of wood cellulose in future. If it becomes necessary to change over to Scandinavian wood pulp for part of our requirements, new plants will have to be built, and continuing high prices for linters may force the issue.

Plasticiser supply is also causing anxiety, with a widening gap between supply and demand. With cellulose derivatives, vinyl polymers, and alkyd resins all making large demands on the available phthalic anhydride, there is a danger that the production of phthalate plasticisers will not keep pace with increased facilities for producing the basic polymers.

Repeated editorial comments in the trade journals suggest that the plastics industry as a whole has viewed with some impatience the failure of the Government to produce authoritative production figures. The Board of Trade Census of Production may prove to be informative, but until this is published United States sources once again provide the only production estimates. Statistics compiled by the Tariff Commission[1] and the Bureau of Census[2] show an increase of 380% in the production of cellulosic plastics from 35 million lb. in 1940 to 133 million lb. in 1946. Total United States production of plastics and synthetic resins during 1946 was 729 million lb. Cellulosic plastics made up 18% of this total, and 39% of the total production of thermoplastic materials. There has so far been

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[1] *Chem. Eng.*, 1947, **54**, *No.* 2, 118.
[2] *Mod. Plastics*, 1947, **24**, *No.* 8, 234.

no disclosure of the individual contributions of the different cellulosic materials. Collectively, cellulose acetate and the mixed ester plastics represented approximately 77% of the total, cellulose nitrate plastics 13%, other cellulosics including ethylcellulose making up the remainder.

A further account[3] of investigations into the state of the German plastics industry at the end of the war contains interesting information on the position of cellulosic materials. Developments were greatly restricted by the shortage of cellulose in Germany, and the great demands made on available supplies by non-plastics applications such as smokeless powder, textiles, and paper for propaganda purposes. Large quantities of cellulose were also converted into water-soluble derivatives and used as soap extenders and thickening agents for food products. As a result the production of cellulosic plastics in Germany during 1943, and prior to dislocation by bombing, was only 7 million lb. compared with 85 million lb. fn the United States.[4] Nevertheless, a few new products were being manufactured on a limited scale. These included mixtures of cellulose tripropionate and acrylic polymers for artificial leathers and a rubber-like shoe sole material prepared by the interaction of cellulose xanthate with ethylene dichloride.

There is again a large volume of published material for review in the different sections of this Report which follow.

Cellulosic Raw Materials.

The production of chemical cellulose from annual crops other than cotton is an old problem and one of great potential interest to European users. Hitherto questions of yield and of the chemical and physical suitability of the cellulose obtained have always caused difficulty. Under the stimulus of çellulose shortage the practical aspects of this subject have been intensively studied in Germany in recent years. Details of the work carried out have now been given in the reports of technical teams which have investigated German progress with wood and cellulose research[5] and the use of materials other than wood and cotton as sources of cellulose.[6] Although the pulps from at least a score of annual plants had been evaluated, most of the projects never passed beyond the laboratory stage and only two such sources were being used commercially when the war ended. One of these was straw and the other *Arundo donax*, a reed which is prevalent in Northern Italy. Cellulose obtained from these materials had been used successfully for nitration but was apparently rejected as unsuitable for acetylation because of the high ash content.

Both in this country and in the United States attention has again been given to the improvement of industrial processes for purifying wood and

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[3] J. M. DeBell, W. C Goggin, 'and W. E. Gloor, "German Plastics Practice"; DeBell & Richardson, Springfield, 1946

[4] W. C. Goggin, *Plastics* (*Chicago*), 1946, **4**, 50.

[5] *Field Information Agency, Technical, Final Rept.* 450.

[6] *Ibid.*, 490.

cotton cellulose. A. Meller[7] has reviewed the literature of the last 20 years dealing with the hot alkaline purification of cellulose. Patents of the Cellulose Research Corporation describe the purification of wood pulp by extraction of highly swollen pulp with cold caustic soda solution,[8] and by chlorination of unbleached pulp with a subsequent alkaline boil.[9] Other patents in this field have described the production of chemical cellulose from wood pulp,[10] straw,[11] and cotton.[12]

Research investigations have covered several aspects of the chemical and physical properties of cellulose which have technological as well as academic interest.

Russian authors have contributed a series of studies[13,14] on the controlled oxidation of cellulose in cuprammonium solution. In these the products, mechanism, and possible consequences of depolymerisation by atmospheric oxygen have been considered. This work has an important bearing on current views on the degree of polymerisation of cellulose. Working under carefully controlled conditions, O. P. Golova and V. I. Ivanov[13] have found a direct relationship between the viscometrically determined degree of polymerisation and the quantity of oxygen present in the system. The sensitivity of cuprammonium solution to oxidative depolymerisation leads these authors to propose a truer value for degree of polymerisation obtained by the device of extrapolating to zero oxygen content. This method indicates a minimum value of 15,000 compared with the usual value of about 3000.

The mutual arrangement of glucose chains in the crystal lattices of native[15] and regenerated[16] cellulose has been discussed by F. T. Pierce, who has shown that a modification of the Meyer and Misch[17] lattice unit is in better accord with available evidence. *X*-Ray diffraction patterns are consistent with a slight distortion of the basic orthorhombic cell. In the case of native cellulose this distortion is considered to be maintained by the formation of a chelate bond between a primary alcohol group and two oxygen atoms in the same chain. In regenerated cellulose the planes of the glucose rings are turned from the lattice plane, in which they lie in native cellulose, towards the plane containing chains of alternate sense. The formation of hydrogen bonds between chains of opposite sense will

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[7] *Paper Trade J.*, 1945, **121**, *TAPPI Sect.*, 119; B., 1946, II, 9.

[8] L. M. Sheldon and L. E. Goff, U.S.P. 2,198,065; B., 1946, II, 13.

[9] L. M. Sheldon, L. E. Goff, D. A. Alderson, and G. N. Fisher, U.S.P. 2,198,706; B., 1946, II, 13.

[10] C. I. Haney and M. E. Martin, Assrs. to Celanese Corp. of America, U.S.P. 2,408,849.

[11] H. Dreyfus, B.P. 576,510; B., 1946, II, 333.

[12] Herculos Powder Co., B.P. Appl. 18,556/45.

[13] *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 279; A., 1946, I, 12.

[14] V. I. Ivanov and O. P. Golova, *ibid.*, 385, 492; B., 1946, II, 200; E. D. Kaverzneva and V. I. Ivanov, *ibid.*, 603; A., 1946, II, 646.

[15] *Trans. Faraday Soc.*, 1946, **42**, 545; A., 1946, I, 387.

[16] *Ibid.*, 560; A., 1946, I, 387.

[17] *Helv. Chim. Acta*, 1937, **20**, 232.

under these conditions maintain the required distortion of orthorhombic symmetry.

Several studies have been concerned with the crystalline structure of cellulosic materials in relation to fibre properties. Fibrillation by swelling in 70% nitric acid has been employed by L. M. Welch, W. E. Roseveare, and H. Mark[18] in the investigation of crystallinity in rayon fibres. They found that rayons which have a high degree of crystallite orientation separate into fibrils, whereas unoriented rayons show no evidence of a fibrillar structure. E. E. Berkeley and T. Kerr[19] have examined the structure and plasticity of undried cotton fibres. Using the *X*-ray diffraction method, they have followed the changes in molecular and micellar structure of cotton fibres during dehydration. Native cellulose fibres showed considerable plasticity in the undried state and crystallised under slight tension or on drying. By impregnating the fibres with glucose under different conditions the crystalline pattern was modified and an indication obtained that the layer of water separating the chains in crystalline regions may be only one or two molecules thick. In a further contribution on the physical structure of cellulosic materials R. F. Nickerson and J. A. Habrle[20] have extended their previous work[21] on the determination of amorphous cellulose by chemical accessibility measurements. Estimates have now been made of the quantities of amorphous, mesomorphous, and crystalline cellulose present in samples of mercerised and unmercerised cotton, purified wood pulp, and viscose rayon. The similarity in hygroscopic and hydrolytic behaviour between the mesomorphous and crystalline components has led these authors to suggest that they should be considered together in determining relations of properties to structure. The Nickerson accessibility method has also been used in conjunction with photomicrographic studies by E. L. Lovell and O. Goldschmid,[22] whose investigation of the crystallinity of regenerated cellulose filaments indicates that rayon crystallinity is determined primarily by the process of coagulation and regeneration, the effects of stretching and original cellulose crystallinity being small.

Another method for determining the percentage of crystalline component in cellulose fibres has been adopted by P. H. Hermans and his collaborators. These authors have adduced evidence from moisture sorption data to support the conclusion that density is a measure of the crystallinity of the fibre substance. They have emphasised the necessity for using indifferent liquids in measuring the density of cellulose fibres,[23] and their estimates of the percentage of crystalline matter in native and regenerated cellulose are based on accurate density determinations in a

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[18] *Ind. Eng. Chem.*, 1946, **38**, 580; B., 1946, II, 368.
[19] *Ibid.*, 304; B., 1946, II, 241.
[20] *Ibid.*, 299; B., 1946, II, 242.
[21] *Ibid.*, 1945, **37**, 1115; B., 1946, II, 116.
[22] *Ibid.*, 1946, **38**, 811; B., 1946, II, 415.
[23] P. H. Hermans and D. Vermaas, *J. Polymer Sci.*, 1946, **1**, 149; B., 1946, II, 369.

carbon tetrachloride medium.[24] These papers were contributed from the Institute for Cellulose Research at Utrecht which was opened in 1943. A fuller account of the fundamental work subsequently carried out by Dutch workers on the physics of cellulose fibres has been given elsewhere by P. H. Hermans.[25]

Further consideration has been given to the origin of the characteristic cloudiness, or haze, in solutions of wood cellulose derivatives. The correction of this fault is a problem of great technological importance, for haze severely limits the extent of the application of such derivatives in plastics manufacture. H. Dolmetsch, E. Franz, and E. Correns[26] have made the interesting suggestion that microscopic observation of the degradation of the spiral structure of wood cellulose fibre may provide an indication as to whether derivatives of the material will yield clear solutions. In attempting to correlate the morphological structure and behaviour of native cellulose, these authors observed microscopically the effect of strong swelling agents on fibrous celluloses isolated by different extraction processes. The nature of the fissures produced leads to the belief that characteristic morphological differences exist between alkali- and acid-degraded cellulose. Acid cooking processes yield celluloses which form transverse and longitudinal fissures on swelling, whilst celluloses isolated by alkaline cooking exhibit no fissures and their morphological structure is not attacked. This partial breakdown of the fibrous structure is thought to explain the generally greater reactivity of acid pulps in subsequent chemical treatment and will assist in releasing haze-forming constituents, which are associated with the layer containing the spiral structure. This layer is composed of non-cellulosic materials, probably pentosans, which yield insoluble derivatives. The subject has also been investigated by J. W. McKinney[27] in connexion with the cause of extreme haziness observed in solutions of cellulose acetate prepared from alkali-purified wood pulp. It was found that the introduction of a preliminary acid cook prior to alkaline cooking effectively reduced the amount of haze in the resulting derivative. The formation of anhydro-hemicelluloses during alkaline cooking is advanced as a possible explanation of haziness.

MANUFACTURE AND PROPERTIES OF CELLULOSE DERIVATIVES.

The literature in this section is very similar in general character to that of previous years. Information on technical problems associated with the preparation of cellulose derivatives is based mainly on patents, whilst numerous research investigations have been concerned with their properties.

Increased attention has been given to cellulose nitrate manufacture,

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[24] P. H. Hermans, J. J .Hermans, and D. Vermaas, *J. Polymer Sci.*, 1946, **1**, 162; B., 1946, II, 369.

[25] "Contribution to the Physics of Cellulose Fibres," Elsevier, London, 1946.

[26] *J. makromol. Chem.*, 1944, **1**, 167; B., 1946, II, 83.

[27] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 36; B., 1946, II, 201.

and in particular to the method of vapour-phase nitration which is of special interest because it yields a highly stable product. In this method esterification is accomplished with nitric acid vapour under reduced pressure. It avoids the introduction of unstable sulphate groups which occurs with the nitric-sulphuric acid mixture usually employed in liquid-phase reaction. With the aid of *X*-ray diffraction technique M. Mathieu[28] has shown that in the vapour phase nitration takes place rapidly and completely, the diffraction patterns passing through all stages from cellulose to the trinitrate. Using the same technique supplemented with an examination of solubility relationship, G. Champetier and M. Foëx[29] have differentiated between products of equivalent nitrogen content obtained by the two methods. The product of liquid-phase nitration differs in being homogeneous, whereas a heterogeneous product is obtained by vapour-phase nitration, which is regarded as a topochemical reaction. The effect of temperature, pressure, and other factors has been studied by M. Foëx[30] and by F. Trombe[31]; the reaction is exothermic and the rate of nitration increases with temperature, pressure having little effect provided the time is prolonged. These workers have also given an account[32] of vapour-phase esterification with carboxylic acids, as well as nitric acid, over a range of temperatures and pressures; the degree of esterification increased with the temperature and duration of exposure. It was suggested that under these conditions the reactive substances are the monomeric forms of the carboxylic acids and $HO{\cdot}NO_2$.

Of considerable interest in connexion with the mechanism of the nitration process is the work of G. M. Bennett, J. C. D. Brand, and G. Williams[33] on the nature of the nitration agent in nitric–sulphuric acid mixtures. The precise rôle of sulphuric acid has been a matter of speculation for many years and the evidence for the views of previous workers has been reconsidered. The hypothesis of Saposchnikov that nitrogen pentoxide is the nitrating agent is shown to be untenable. According to the view now advanced, the active species is the NO_2^+ cation formed when nitric acid is dissolved in sulphuric acid according to the equation $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$. Evidence for the existence of the nitronium ion is taken from the ultra-violet and Raman spectra of mixed acids, the vapour pressure of nitric acid over mixed acids, and from cryoscopy. The concept of the new ion is also shown to be in accord with the electronic theory of reactions, from which it may be argued that the positively charged NO_2^+ ion would be the most active of the possible nitrating agents.

Improvements disclosed in patents dealing with the manufacture of cellulose nitrate have been mainly concerned with methods for obtaining

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[28] *Compt. rend.*, 1941, **212**, 80; A., 1946, I, 9.
[29] *Bull. Soc. chim.*, 1941, [v], **8**, 115; A., 1945, I, 330.
[30] *Ibid.*, 381, 390; B., 1945, II, 369, 370.
[31] *Ibid.*, 1942, [v], **9**, 526; B., 1945, II, 370.
[32] G. Champetier and M. Foëx, *ibid.*, 711; B., 1945, II, 370.
[33] *J.C.S.*, 1946, 869, 875, 880; A., 1947, I, 24.

a more stable product. Thus G. V. Caesar[34] carries out the nitration process in the absence of sulphuric acid by using nitrogen pentoxide in a non-aqueous solvent in presence of phosphorus pentoxide. A stable product is also said to be obtained when nitration is accomplished by precipitating a viscose solution in the nitric–sulphuric acid bath,[35] whilst according to the proposal of R. E. Reeves and J. E. Giddens[36] nitrated cellulose is stabilised at room temperature by agitating in aqueous ammonia solution. The stability of cellulose nitrate has been discussed by C. Kullgren,[37] who distinguishes the effects of combined sulphate and bisulphate groups. Neutralisation of the acid sulphate radicals by metal ions, such as sodium, gives a more stable cellulose nitrate. Boiling, however, converts the acid ester into the neutral sulphate, which is difficult to remove by hydrolysis, and consequently boiled cellulose nitrate almost completely loses its cation-exchange ability. Details have also been given[38] of a method for the recovery of nitric acid by partial evaporation of the aqueous mixed acid produced in the drowning process.

Two investigations have been concerned with the technology of cellulose acetate manufacture. In the acetylation of cellulose in presence of sulphuric acid C. J. Malm, L. J. Tanghe, and B. C. Laird[39] have demonstrated that quantitative combination between sulphuric acid and cellulose occurs during the intermediate stages. At the point where all the hydroxyl groups are esterified, the combined sulphur content falls rapidly as the sulphate groups are replaced by acetyl. A further conclusion is that the formation of sulphoacetic acid in this type of acetylation is negligible, and that this substance is a very weak acetylation catalyst which does not combine appreciably with cellulose. The second paper is that of L. Clément and C. Rivière,[40] who have examined and described the effect of variations in the concentrations of acetic anhydride, sulphuric acid, and water on the rates of esterification and hydrolysis and the extent of chain degradation in the final product.

Patents dealing with cellulose acetate manufacture have described several miscellaneous improvements in methods for ripening[41] and stabilising the product. According to proposals of British Celanese Ltd., enhanced stability is obtained by the inclusion of a wetting agent in the stabilising medium,[42] by the addition of a polycarboxylic acid at the ripening stage,[43] or by a variation of the previously disclosed technique of high-temperature ripening.[44] Activation with acetic or formic acid

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[34] Assr. to Stein, Hall & Co. Inc., U.S.P. 2,400,287.

[35] H. von Kohorn, U.S.P. 2,410,319.

[36] U.S.P. 2,404,887.

[37] *Svensk Kem. Tidskr.*, 1944, **56**, 221.

[38] F. J. Bouchard, R. C. Gunness, and R. L. Stern, Assrs. to Hercules Powder Co., U.S.P. 2,403,493.

[39] *Ind. Eng. Chem.*, 1946, **38**, 77; B., 1946, II, 161.

[40] *Bull. Soc. chim.*, 1942, [v], **9**, 494; B., 1946, II, 10.

[41] British Celanese Ltd., B.P. 581,157; B., 1947, II, 52.

[42] B.P. 577,963; B., 1946, II, 333.

[43] B.P. 571,010; B., 1945, II, 341.

[44] J. W. Fisher, B.P. 574,106; B., 1946, II, 119.

followed by exhaustive extraction with a lower aliphatic alcohol has been proposed as a means for obtaining a high-clarity product.[45]

In regard to the manufacture of higher fatty acid esters and mixed esters there is very little to report. Methods for increasing the reactivity of cellulose towards this type of esterifying agent are being sought, but recorded improvements[46] have not gone beyond refinements in an essentially standard technique. The position is much the same with cellulose ether esters and ethers. Accounts have been given of the preparation and properties of a number of derivatives of cellulose which have not yet attained commercial importance. G. Champetier and F. Appell[47] have described the preparation of fully-substituted cellulose hydrogen phthalates by the interaction of cellulose and phthalic anhydride in pyridine. Two nitrogenous derivatives of some interest are β-aminoethyl- and β-cyanoethyl-cellulose acetate, which have been reported by T. S. Gardner[48]; these products are less soluble in the common organic solvents than ester and ether type cellulose derivatives, and exhibited marked affinity for acid dyes. The preparation of cyanoethylcellulose[49] and of methylcellulose *o*- and *p*-chlorophenylcarbamates[50] has also been described.

Further developments have been reported in connexion with the chemical modification of cellulose derivatives to obtain improved resistance towards heat and to the action of organic solvents. The methods put forward in the literature involve either the introduction of substituent groups which are capable of undergoing subsequent polymerisation, as with methallyl-[51] and ethylvinyl-cellulose,[52] or alternatively depend on cross-linking cellulose chains through the agency of added bifunctional substances such as bis(chloroalkyl) ethers of polymethylene glycols.[53] Typical of other miscellaneous proposals for this purpose are the use of *NN'*-bis(methoxymethyl)uron,[54] substituted melamines,[55] and partial esters of a polysilicic acid.[56]

Publications dealing with the properties of cellulose derivatives have been concerned mainly with the measurement of molecular shape and size by indirect physical methods. In this connexion P. M. Doty and H. Mark[57] have discussed the interpretation of results obtained by methods based on osmotic pressure, the ultracentrifuge, light-scattering, and

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[45] British Celanese Ltd., B.P. Appl. 22,472/45.

[46] *Idem*, B.P. 578,504; B., 1946, II, 377. B.P. Appl. 5198/46.

[47] *Bull. Soc. chim.*, 1944, [v], **11**, 136; A., 1946, II, 310.

[48] *J. Polymer Sci.*, 1946, **1**, 289; B., 1947, II, 11.

[49] L. H. Bock and A. L. Houk, Assrs. to Röhm & Haas Co., U.S.P. 2,332,049; B., 1946, II, 247.

[50] E. Dyer and K. L. McCormick, *J. Amer. Chem. Soc.*, 1946, **68**, 986; A., 1946, II, 527.

[51] W. J. Burke, Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,398,767.

[52] S. N. Uschakov, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, **1**, 35.

[53] P. V. Afanasiev and S. E. Bresler, *ibid.*, 1944, **2**, 120.

[54] Imperial Chem. Industries Ltd., B.P. 575,260; B., 1946, II, 216.

[55] *Idem*, B.P. 570,853; B., 1945, II, 341.

[56] R. E. Fothergill, J. W. Hill, and A. A. Johnson, Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,406,755.

[57] *Ind. Eng. Chem.*, 1946, **38**, 682; A., 1946, I, 313.

streaming birefringence. Optical methods for studying the shape of dissolved macromolecules are now receiving increased attention and several developments have been reported. One method depends on the observation and evaluation of the depolarisation of light scattered from polymer solutions ; the results do not yield information on exact molecular dimensions but they are proving useful in showing how the shape and size change with such variables as molecular weight, solvent, and concentration. P. Doty and H. S. Kaufman[58] have recently applied this method to fractionated cellulose acetate in acetone solution. They found that the degree of polymerisation was essentially independent of concentration, regardless of molecular weight, and concluded that until the degree of polymerisation exceeds a value of about 380 the molecules of cellulose acetate are rigid enough to be little affected by polymer–polymer interactions. Their observations suggested, however, that longer chains show an increasing tendency to coil up. Measurements of the angular distribution of the intensity of the scattered light have given similar results, indicating that the smaller molecules of cellulose acetate are fully extended in acetone solution.[59]

Fractionation on a molecular weight basis is a well-established method for deriving the characteristic molecular weight distribution curves of high polymers. In an experimental study of fractionation technique D. R. Morey and J. W. Tamblyn[60] have drawn attention to several interesting points of procedure. They have shown that the choice of solvent and precipitant can lead to marked differences in the degree of separation obtained in precipitation methods of fractionation. Their evidence leads these authors to conclude that the initial concentration of the polymer solution, providing it is dilute, has a minor effect on fractionation efficiency. Earlier workers have generally supported the opposite view. For some systems examined during the present work, particularly in the precipitation of cellulose acetate butyrate from acetone with *iso*propyl ether, solubility properties were independent of molecular weight. The importance of this observation is that it opens up the possibility of making solubility more directly dependent on some other property, permitting fractionation, for example, on the basis of degree of esterification. A comprehensive review of the literature on fractionation methods up to 1944 has been published by L. H. Cragg and H. Hammerschlag.[61]

Osmometric methods have been used for the determination of absolute values of the molecular weight of cellulose derivatives by A. Dobry,[62] and by I. Jullander and T. Svedberg,[63] who have described the adaptation of an analytical balance for the measurement of osmotic pressure in

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[58] *J. Physical Chem.*, 1945, **49**, 583 ; A., 1946, I, 117.

[59] R. S. Stein and P. Doty, *J. Amer. Chem. Soc.*, 1946, **68**, 159 ; A., 1946, I, 176.

[60] *J. Physical Chem.*, 1946, **50**, 12 ; A., 1946, I, 154.

[61] *Chem. Rev.*, 1946, **39**, 79.

[62] *J. Chim. phys.*, 1945, **42**, 114 ; A., 1946, I, 252.

[63] *Nature*, 1944, **153**, 523 ; C., 1945, 297. *Arkiv Kemi, Min., Geol.*, 1945, **21**, **A**, No. 8 ; B., 1946, II, 9.

solutions of much lower concentration than have previously been employed. Details of a convenient form of small osmometer have been given by B. H. Zimm and I. Myerson.[64] J. L. Riley and G. W. Seymour[65] have given an account of the apparatus and procedure used in their accurate determination of the viscosity of cellulose acetate in dioxan by the Ostwald method; in this work the variables of time, temperature, and pressure were so controlled that the coefficient of variation of the viscosity determination was reduced to 0·01%.

Thermal evidence of crystallinity in cellulose derivatives has been sought by W. O. Baker and C. S. Fuller,[66] who have studied the form of temperature–time curves obtained on cooling from a fluid state. Cellulose ethers, tributyrate, and acetate butyrate when examined in this way did not reveal the relatively sharp phase transitions obtained with more highly crystalline polymers, where the thermal effects are closely analogous to those observed in the crystallisation of ordinary molecules. It has been suggested in explanation of these results that the intrachain rigidity and high interchain forces of cellulose derivatives prevent co-operative growth into crystallites large enough to cause evident latent heat.

In the heterogeneous acid hydrolysis of secondary cellulose acetate in the presence of neutral salts, R. N. Haward and T. White[67] have reported a marked anionic effect, the rate of hydrolysis increasing in the order $I' > Br' > Cl'$. The lyotropic series is, however, in the opposite order to that previously reported for homogeneous hydrolysis, and it has been suggested that the reversal is due to the action of the ions in increasing the accessibility of the acetyl groups attached to the insoluble substrate.

PLASTICISERS AND SOLVENTS.

Studies in the mechanism of solvent action provide the principal material for review in this section. Employing the criterion of threshold concentration which he established in an earlier paper[68] as a measure of solvent power, A. K. Doolittle[69] has investigated the influence of the size and shape of the solvent molecule on the temperature-dependence of solvent ability. In a homologous series of solvents, small linear molecules become better solvents as the temperature rises, large linear molecules behaving in the opposite manner. For solvent molecules of the same molecular weight, the temperature coefficient of solvent ability is positive for compact molecules and negative for molecules containing extended chains. This inversion of the temperature coefficient for extended structures is greater with branched chains and increases with the extension of the branches. The well-known temperature-reversible sol–gel transformation in solutions of cellulose derivatives, in certain single and mixed solvents, is considered in terms of the relative viscosity and temperature

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[64] *J. Amer. Chem. Soc.*, 1946, **68**, 911; C., 1946, 311.
[65] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 387; C., 1946, 310.
[66] *Ind. Eng. Chem.*, 1946, **38**, 272; B., 1947, II, 120.
[67] *J.S.C.I.*, 1946, **65**, 63; A., 1946, I, 186.
[68] *Ind. Eng. Chem.*, 1944, **36**, 239; A., 1944, I, 170.
[69] *Ibid.*, 1946, **38**, 535; A., 1946, I, 246.

coefficient of solvent ability. The work reported in this paper has practical application in the preparation of gelable solutions for film casting and lacquer coating. According to conclusions published by G. Champetier and P. Clément[70] the absorption of indifferent organic liquids by films of cellulose acetate or nitrate is mainly of a lyophilic nature and the absorbed liquids can be completely removed by heating. If, however, absorption takes place in the presence of a gelatinising agent intermolecular penetration is facilitated and the organic liquids cannot subsequently be completely removed. The plasticisation of cellulose acetate by a non-solvent plasticiser such as triphenyl phosphate is considered to occur in this way. Similar investigations have been concerned with the absorption of camphor[71] and other solvents[72] by cellulose nitrate.

A significant recent advance in methods of plasticisation has been made possible by the commercial production of resinous polymeric plasticisers in the United States. The use of certain of these materials in cellulose nitrate films is claimed[73] to be particularly advantageous because they represent a practical compromise between the plasticising efficiency of the monomeric plasticisers and the high tensile strength, permanence, and durability typical of resinous plasticisers. The properties of polymer–plasticiser systems have been discussed in a useful paper by H. Jones[74]; although concerned primarily with the function of plasticisers in elastomeric compositions, the considerations of factors influencing miscibility and retention are generally applicable. Emphasis is placed on the importance of the viscosity–temperature relationship of a plasticiser in determining the physical properties of plastics at different temperatures.

In general, there is little information concerning new plasticisers and solvents outside the patent literature, but W. E. Gloor[75] has reported some German developments which are of interest. According to this source the triethylene glycol ester of long-chain fatty acids from Fischer–Tropsch synthesis, hexanetriol trichloroacetate, and butylene glycol diglycollate were included among the new products successfully used as plasticisers for cellulose acetate. Other novel features reported[76] in the course of investigation of the German plastics industry were the development of thiodibutyric esters of Fischer–Tropsch alcohols as dual-purpose acid-bonding stabilising plasticisers, and the extensive use of tetrahydrofuran as a solvent. The altogether wider variety of products available for plastics manufacture in Germany, as compared with this country and the United States, resulted from the development of specialised methods of synthesis which were designed to make maximum use of coal.

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[70] *Compt. rend.*, 1946, **222**, 563; A., 1946, I, 280. *Ibid.*, 92; *Chem. Abs.*, 1946, 3298.

[71] T. Petitpas and J. Desmaroux, *ibid.*, 1944, **218**, 785; *Chem. Abs.*, 1946, 3895.

[72] T. Petitpas, *Mém. Serv. Chim. l'Etat*, 1943, **20**, 201. S. N. Danilov and M. E. Dinkin, *J. Gen. Chem. Russ.*, 1945, **15**, 550; *Chem. Abs.*, 1946, 4583.

[73] H. L. Tuthill, *Paint, Oil Chem. Rev.*, 1945, **108**, *No.* 25, 7; *Chem. Abs.*, 1946, 1677.

[74] *Trans. Inst. Rubber Ind.*, 1946, **21**, 298; B., 1946, II, 265.

[75] *Amer. Paint J.*, 1945, **30**, *No.* 12, 95; *Chem. Abs.*, 1946, 1047.

[76] J. M. DeBell, W. C. Goggin, and W. E. Gloor, "German Plastics Practice," DeBell & Richardson, Springfield, 1946, p. 227 *et seq.*

The patent literature contains an unusually large number of proposals relating to new plasticisers or solvents for use with cellulose derivatives. No more than a selection can be given to indicate the varied nature of the many suggestions which have been put forward. Thus E. I. Du Pont de Nemours & Co. have been granted patents on the use of halogenated acrylic esters[77] and additive products of thiophenols and acrylic esters.[78] Other patents relate to the use of substituted dioxans,[79] esters of crotonic acid and polyhydric alcohols,[80] furfuryl- and tetrahydrofurfuryl-oxyacetic esters,[81] polyglycol acetate butyrates,[82] and esters of cyclic ketonic tetracarboxylic acids.[83] Branched-chain saturated C_{18-24} ketones,[84] alkyd resins,[85] esters of pentaerythritol acetate and ketals,[86] and acyloxy*cyclo*hexanes[87] have also been recommended as plasticisers. Proposals regarding new solvents include the use of condensation products[88] of tertiary aliphatic alcohols and formaldehyde, polymerisable allyl, methallyl, and vinyl esters,[89] and propargyl alcohol, which is stated[90] to be a solvent for cellulose triacetate.

MANUFACTURE AND MANIPULATION OF CELLULOSIC PLASTICS.

Since the range of cellulosic plastics was extended by the introduction of cellulose tripropionate towards the end of 1945, considerable interest has been shown in the new product. Cellulose propionate plastic was expected to afford a particularly satisfactory combination of low moisture-sensitivity and superior rigidity. These expectations, which appear to have been fulfilled, were based on previous knowledge of the relationship between these two properties and the number of carbon atoms in the esterifying acid. During the past year cellulose propionate moulding materials have been manufactured on a limited scale and evaluated in field trials.[91] An important observation is that the material gives satisfactory results over a wide range of injection temperatures, usually with

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[77] R. A. Jacobson, U.S.P. 2,195,712; B., 1945, II, 362.

[78] *Idem*, U.S.P. 2,199,799; B., 1946, II, 155.

[79] L. G. MacDowell and H. C. Chitwood, Assrs. to Carbide & Carbon Chemicals Corp., U.S.P. 2,331,993; B., 1946, II, 238.

[80] H. A. Bruson, Assr. to Röhm & Haas Co., U.S.P. 2,198,373; B., 1946, II, 4.

[81] J. B. Dickey and J. G. McNally, Assrs. to Eastman Kodak Co., U.S.P. 2,196,746; B., 1946, II, 12.

[82] W. E. Gloor, Assr. to Hercules Powder Co., U.S.P. 2,198,665; B., 1946, II, 32.

[83] H. A. Bruson, Assr. to Resinous Products & Chem. Co., U.S.P. 2,329,432; B., 1946, II, 5.

[84] F. A. Bent and F. G. Byrne, Assrs. to Shell Development Co., U.S.P. 2,327,007; B., 1946, II, 180.

[85] G. Alleman and J. H. Perrine, Assrs. to Sun Oil Co., U.S.P. 2,329,236; B., 1946, II, 180.

[86] British Celanese Ltd., B.P. 579,179; B., 1946, II, 409.

[87] L. P. Kyrides, Assr. to Monsanto Chem. Co., U.S.P. 2,331,329; B., 1946, II, 38.

[88] M. T. Harvey, Assr. to Harvel Research Corp., U.S.P. 2,333,927–9; B., 1946, II, 297.

[89] Pittsburgh Plate Glass Co., B.P. 574,606; B., 1946, II, 154.

[90] I.G. Farbenind., G.P. 741,551; *Chem. Abs.*, 1946, 464.

[91] J. J. Keville, jun., *Mod. Plastics*, 1947, **24**, *No.* 5, 127. *Plastics* (*Chicago*), 1946, **4**, *No.* 6, 32.

shorter moulding cycles. Mouldings show an extremely high polish, possess excellent machining qualities, and exhibit good dimensional stability and impact-resistance. Developments are expected from the application of cellulose propionate to production of sheets, films, and extrusions, which is still in an experimental stage. It is, however, reported that cellulose propionate is not quite equal to ethylcellulose in toughness and resistance to warping.

Several developments have been recorded in connexion with the manufacture of cellulose acetate in sheet form. Reference was made in last year's Report[92] to the production of material in continuous rolls by solventless extrusion at high temperature. Details have now been given of the process developed for this purpose by the Tennessee Eastman Co.[93] The material is extruded from a circular die operating in conjunction with a conventional extrusion machine, and the tube is split, flattened, and subsequently polished in one continuous operation. Expanded cellulose acetate sheet has been developed for use as a structural core material in low-density laminates. For this application unplasticised cellulose acetate is extruded in the form of multicellular boards,[94] which are readily built up into sheets combining high strength with low density. B. M. Axilrod and E. Koenig[95] have published a detailed comparison of the physical properties of cellular cellulose acetate with those of balsa, and other expanded plastics.

Finishing technique has been advanced by the development of some specialised processes for surface treatment. In a process devised by E. I. Du Pont de Nemours & Co.[96] the surface hardness of transparent plastics is improved by treatment with a partly hydrolysed ester of polysilicic acid. New methods have been introduced for applying metal coatings to plastics.[97] Apart from their purely decorative value, these metallic coatings improve the properties of treated materials and lead to increases in tensile strength, temperature-resistance, and dimensional stability. Metals have been applied for some years by spraying or electrodeposition, and recently the method of vacuum evaporation has been perfected. This last process is carried out in an enclosed chamber evacuated to pressures as low as 10^{-5} mm. Most metals can be evaporated over heated filaments under these conditions and the condensation of metal vapour produces a glossy metallic coating on articles placed several inches away. The process is of sufficiently short duration to prevent plastics materials becoming overheated.

There are no noteworthy developments to report in connexion with methods for the manufacture of films and moulding powders. Patents dealing with the process of extrusion have again been concerned mainly

[92] *Ann. Rcpts.*, 1945, **30**, 323.
[93] *Mod. Plastics*, 1946, **23**, *No.* 9, 132.
[94] R. E. Maier, *ibid.*, 96.
[95] *Plastics* (*Chicago*), 1946, **5**, *No.* 1, 68; B., 1946, II, 424.
[96] B.P. Appl. 7386/44.
[97] Anon., *Brit. Plastics*, 1946, **18**, 428.

with details of machine design. They include details of a series of unusual extruders[98] fitted with several intermeshing screws, an arrangement designed to enable plastics raw materials to be mixed and extruded by a single machine. Current practice in extrusion technique has been reviewed by R. B. Akin.[99]

The continued search for improved methods of increasing the resistance of cellulosic plastics towards degradation at high temperature and deterioration by ultra-violet light has provided a number of proposals for stabilising additions. In patents granted to the Eastman Kodak Co., cellulose nitrate is stabilised with aromatic hydroxy-compounds such as *p-tert.*-butylphenol,[100] whilst *NN'*-diphenylacetamidine[101] and 2-anilo-3-alkylbenzthiazolines[102] are recommended for use with cellulose fatty acid esters. Cellulose acetate compositions have been effectively stabilised with lactates of alkaline-earth metals.[103] New stabilisers proposed for ethylcellulose include organic sulphites[104] such as bis(triethyl citrate) sulphite, *N*-alkylated diamines,[105] citric esters,[106] and polyhydric phenols.[107]

Publications relating to the formulation of cellulose derivative have been rather limited in scope. M. Bentivoglio and B. E. Cash[108] have provided additional information concerning a series of mineral-filled high-acetyl acetate moulding powders designed primarily for flame-resistance; these materials are shown to possess the further advantage of good dimensional stability under adverse conditions of temperature and humidity. The inflammability of ethylcellulose compositions has been depressed by using heavy-metal oxalates as fillers,[109] and by using chlorinated plasticisers such as polychlorodiphenyl.[110] Dipping lacquers of conventional type for applying plastics coatings have been improved by the introduction of gelable lacquers, the properties of which have been described in some detail by C. J. Malm and H. L. Smith, jun.[111] These compositions possess the important property of undergoing a reversible change from viscous liquids to firm gels, merely with change in temperature. Gel lacquers are prepared by dissolving cellulose mixed esters in a carefully balanced mixture of solvents such as toluene, or xylene, and

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[98] S. P. A. Lavorazione Materie Plastiche, B.P. Appl. 13,326/46 and 13,329–30/46.

[99] *Mod. Plastics*, 1946, **24**, *No.* 2, 134.

[100] D. R. Swan and J. M. Calhoun, U.S.P. 2,407,209.

[101] D. R. Morey and J. W. Tamblyn, U.S.P. 2,393,802.

[102] *Idem*, U.S.P. 2,393,801.

[103] British Celanese Ltd., B.P. Appl. 34,612/45.

[104] B.P. Appl. 34,767/45.

[105] J. E. Jones, J. H. Sharphouse, and J. Downing, B.P. 575,073; B., 1946, II, 163.

[106] B.P. Appl. 34,770/45.

[107] J. H. Sharphouse and J. Downing, B.P. 580,359; B., 1946, II, 458.

[108] *Mod. Plastics*, 1946, **23**, *No.* 6, 119; B., 1946, II, 425.

[109] W. W. Koch, Assr. to Hercules Powder Co., U.S.P. 2,397,320.

[110] S. L. Bass and E. G. Hallonquist, Assrs. to Dow Chem. Co., U.S.P. 2,196,575; B., 1946, II, 45.

[111] *Ind. Eng. Chem.*, 1946, **38**, 937; B., 1947, II, 22.

*iso*propanol. They lend themselves to dipping more quickly, and deposit a coat much thicker than can be obtained with ordinary lacquers.

A current development in methods of manipulation and fabrication is the use of diamond-tipped tools[112] for machining plastics. Practically no frictional heat is developed when using these tools and the absence of distortion in the material permits extremely accurate machining. This technique is finding application where an improvement on normal moulding tolerances is necessary. An authoritative American publication[113] has assembled information on methods for cementing plastics. Thermoplastic materials have been welded and moulded by the application of frictional heat followed by pressure; the necessary heat is supplied by high-speed rotation of one of the surfaces against the other.[114]

PHYSICAL PROPERTIES AFD TESTING OF CELLULOSIC PLASTICS.

Research investigations on the properties of plastics materials have adopted the functional approach to an increasing extent. Underlying this trend is a recognition that the dependable performance of materials in a wide variety of applications can be assured only by a knowledge of their behaviour under all conditions likely to be encountered in service. Consequently much of the published work in this section is concerned with the accumulation of data on the performance of materials under varying environmental conditions.

A study of the mechanical properties of cellulose acetate moulding compositions over a wide range of atmospheric temperatures and humidities has been reported by W. E. Welch, R. F. Hayes, T. S. Carswell, and H. K. Nason.[115] Test specimens were injection-moulded from medium- and high-acetyl cellulose acetate compositions and the effects of varying atmospheric conditions on yield and ultimate strengths in tension, elongation, elastic modulus, and flexural and impact strengths were determined. Prolonged exposure of cellulosic plastics to sunlight, or to ultra-violet light, produces discoloration and deterioration in mechanical strength as a consequence of photochemical cleavage of the cellulose chains. The photochemical decomposition of cellulose acetate butyrate films has been investigated by R. L. Tichenor,[116] who concludes that the rate of reaction is independent of the mineral impurities present in the ester and the concentration of probable decomposition products, such as acetic and butyric acids; it was also found to be the same for fractions with different molecular weights. A. E. Brown[117] has dealt with the interesting subject of fungal growth on plastics. This problem became acute during the war in connexion with the tropical deterioration of

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[112] R. Maxfield, *Mod. Plastics*, 1946, **23**, *No.* 6, 131.

[113] "Cementing and Assembly of Plastics," Society of the Plastics Industry, New York, 1946.

[114] R. N. Freres, *Mod. Plastics*, 1945, **23**, *No.* 3, 142; B., 1946, II, 129.

[115] *Ibid.*, 1946, **23**, *No.* 12, 159; B., 1946, II, 464.

[116] *J. Polymer Sci.*, 1946, **1**, 217; B., 1946, II, 371.

[117] *Mod. Plastics*, 1946, **23**, *No.* 8, 189; B., 1946, II, 339.

military equipment. Owing to its recent origin and the limited extent of the investigations which have been carried out, differences of opinion exist on several fundamental questions. For instance, in some cases it is undecided whether the fungus grows on a nutrient supplied by the plastic itself or on a contaminating material on the surface. Even where it is established that the fungus is being nourished by the material there is doubt whether the properties or the composition of the material have been altered. The fungal resistance of plastics can now be estimated with some certainty from a knowledge of the susceptibility of their components. As a group the cellulose derivatives and the phthalate and phosphate plasticisers have been found to be quite resistant. Fungicides, such as phenyl mercuric salicylate, have been used successfully by incorporating them in plastics compositions but research is complicated by the difficulty of establishing satisfactory controls. Papers dealing with the evaluation of physical behaviour by accelerated methods include descriptions of a tropical testing chamber[118] and an ageing oven[119] for determining the volatility of plasticisers.

The relationship between impact and flexural tests for plactics has been considered by L. E. Welch and H. M. Quackenbos, jun.[120] Their conclusions are of interest although concerned primarily with the testing of thermosetting materials. The ability of the standard notched-bar impact tests to differentiate between materials with similar tensile and flexural strength properties is due to variations in notch-sensitivity in these materials. In such tests as much as 50% of the indicated breaking energy is absorbed by the machine and by the broken part of the specimen. These authors propose to avoid this complication by substituting values of true impact-resistance obtained from measurements of the flexural work in breaking notched and unnotched specimens. A. Bailey and O. W. Ward have described methods for determining the flexural[121] and impact strength[122] of materials when only small test specimens can be prepared. Other published work deals with the measurement of hardness,[123] abrasion-resistance,[124] and heat-distortion temperature[125] of plastics. The physical properties of thermoplastic laminates prepared by low-pressure combination of cellulose derivatives with fabrics have been determined by C. W. Eurenius, R. H. Hecht, W. Koch, and H. C. Malpass,[126] and information is given on the effects of using different types of fabric and filler in the lamination process.

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[118] T. F. Cooke and R. E. Vicklund, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 59 ; C., 1946, 142.

[119] D. K. Rider and J. K. Sumner, *ibid.*, 1945, **17**, 730 ; C., 1946, 142.

[120] *Trans. Amer. Soc. Mech. Eng.*, 1946, **68**, 547 ; B., 1946, II, 464.

[121] *Amer. Soc. Test. Mat.*, 1946, *Bull.* 138, 33.

[122] *Ibid.*, *Bull.* 140, 50.

[123] A. Cameron, *Trans. Faraday Soc.*, 1945, **41**, 583; C., 1946, 68. V. E. Lysaght, *Amer. Soc. Test. Mat.*, 1946, *Bull.* 138, 39 ; cf. C., 1946, 145.

[124] M. E. Marks and P. Conrad, *Mod. Plastics*, 1946, **23**, *No.* 6, 165.

[125] G. Lubin, *ibid.*, *No.* 7, 163 ; C., 1946, 226.

[126] *Ind. Eng. Chem.*, 1945, **37**, 959 ; B., 1946, II, 129.

The permeability of films of cellulose derivatives to gases and vapours has been widely studied in relation to the application of these materials in packaging. P. M. Doty[127] has dealt with the effect of plasticisation on the permeation of a polymer by water. From a study of the rate of permeation as a function of temperature he has deduced values for the entropy of solution, and interpreted these results as showing that water molecules dissolved in the unplasticised polymer possess much less freedom than when dissolved in a plasticised polymer. E. Rossmann and G. Schultze[128] have studied the vapour and liquid transmission of water through lacquer films of cellulose derivatives and other substances. They found that the liquid transmission was usually, although not always, the greater of the two. An examination of the effect of pigment and plasticiser over a large number of samples showed the existence of an optimum content of either ingredient for minimum transmission. For films of similar composition the permeability varied with the solvent used, and decreased with increase in mechanical strength. Details of apparatus and procedure have also been given for determining the permeability of wrapping materials to food odours[129] and to carbon dioxide.[130]

An account of the application of the Karl Fischer method to the determination of small amounts of moisture in moulding compositions has been given by G. R. Cornish.[131]

Density-gradient tubes have been used by R. F. Boyer, R. S. Spencer, and R. M. Wiley[132] in studying the physical properties of high polymers. The density-gradient tube is a special glass vessel in which a vertical linear density gradient can be maintained in a stable condition for prolonged periods by using liquids or solutions of the proper density. Whilst the work cited in this paper is not strictly relevant to this Report, it provides an example of the way in which the device can be applied in giving quick and accurate values of the density of polymer particles, and the procedure has some interesting potential uses.

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[127] *J. Chem. Physics*, 1946, **14**, 244 ; A., 1946, I, 251.

[128] *Korros. u. Metallschutz*, 1943, **19**, 13 ; B., 1946, II, 95.

[129] F. Kiermeier, *Chem. Technik*, 1943, **16**, 204 ; C., 1945, 242.

[130] J. D. Edwards and D. B. Strohm, *Mod. Packaging*, 1945, **19**, 157.

[131] *Plastics*, 1946, **10**, 99 ; C., 1946, 93.

[132] *J. Polymer Sci.*, 1946, **1**, 249 ; C., 1947, 51.

RESINS, DRYING OILS, VARNISHES, AND PAINTS.

NATURAL AND SYNTHETIC RESINS.

By D. H. Hewitt, M.A., A.R.I.C.,

Lewis Berger and Sons Ltd.

There are no major innovations to report in this branch of surface coating technology. The main items of interest continue to be the development of ethenoid polymers, formaldehyde resins, and silicones as recorded in previous years. Considerable attention continues to be paid to sources of resin-forming materials. J. I. Jones[1] has discussed exhaustively the utilisation of agricultural products, stressing the importance of continuity of supplies as contrasted with petroleum. F. C. B. Marshall[2] has dealt with the utilisation of coal in this industry, with some reference to research in this field.

Natural Resins.

Copals.—The main development continues to be the increasing use of large-scale equipment for heat-treatment. W. A. Mitchell[3] has described yet a further type of apparatus for this process.

The work of E. Mertens and L. Hellinckx on the constitution, heat-treatment, cracking, and esterification has been reviewed and extended in a series of publications[4] which have recently become available. Of particular interest in connexion with the latter is the production of hard stoving, elastic films from mixed esters of unrun copal, unsaturated fatty acids, hydroxy-acids, and glycerin.[5]

Armstrong Cork Co.[6] claim the esterification of unrun fossil resins with high-boiling mono- or di-hydric alcohols such as polyethylene glycols; the products are suitable as varnish resins or plasticisers. They also claim[7] similar reactions with high-boiling polyethyleneamines and amino-alcohols such as 2-aminobutanol.

Shellac.—Much of the work reported last year has been supplemented and extended. Considerable attention has been devoted to the modification of lac–glycol ether esters with unsaturated acids to yield oil-soluble products[8]; an alternative procedure is the interaction of glycerol with a mixture of lac and drying oil fatty acids.[9]

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[1] *Brit. Plastics*, 1945, **17**, 359, 419, 451.

[2] *J. Oil Col. Chem. Assoc.*, 1946, **29**, 3; B., 1946, I, 158.

[3] B.P. 572,258; B., 1946, II, 47.

[4] *Comm. Copal de l'Assoc. des Intérêts colon. Belges*, 1942, *No.* 1, 3, 4, and 5; B., 1946, II, 464, 465.

[5] L. Hellinckx, *Chim. Peint.*, 1941, **6**, 204.

[6] K. H. Weber, Assr. to Armstrong Cork Co., U.S.P. 2,394,731.

[7] *Idem*, U.S.P. 2,382,838.

[8] B. S. Gidvani and Indian Lac Cess Committee, B.P. 573,826; B., 1946, II, 136. See also B. S. Gidvani and N. S. Kamath, *London Shellac Res. Bur.*, 1945, *Tech. Paper* 28; B., 1946, II, 53.

[9] B. S. Gidvani and N. S. Kamath, *Paint Manuf.*, 1946, **16**, 242; B., 1946, II, 427.

American Cyanamid Co. claim[10] the modification of aniline–formaldehyde resins with shellac to provide fusible products which may be subsequently hardened.

Rosin and its Derivatives.—There is very little to report in this field. United States research appears to be concentrating rather on the development of new terpene materials. An interesting account[11] has, however, become available of the development of the naval stores industry in the Dutch East Indies

PHENOL–FORMALDEHYDE RESINS.

This subject continues to receive a very fair share of attention, particularly in British patent literature. Interest centres in varnish resins, in low-viscosity resins of the cold-hardening type, and in the use of cashew nutshell liquid. C. T. O'Connor[12] has summarised the current situation from the point of view of raw materials.

Developments in phenolic varnish resins in this country appear to aim at the replacement of at least a proportion of the *p*-alkyl- or *cyclo*alkyl-substituted phenols which are imported and relatively expensive by indigenous coal-tar fractions. Thus Imperial Chemical Industries[13] claim the use of mixtures of *o*-cresol with various more conventional *o*- and *p*-substituted phenols in the production from formaldehyde of resoles which have good solubility, mixtures of these substituted phenols alone may also be used.[14] In the production of thermo-hardening oil-soluble resins from cresols and xylenols J. D. Morgan and B. Frenkel adopt two methods of approach: in the earlier method[15] condensation with formaldehyde is effected in the presence of a primary or secondary arylamine and a catalyst; the alternative process[16] involves a first-stage condensation with acetaldehyde in the presence of an acid catalyst to form an oil-soluble thermoplastic resin, followed by interaction with formaldehyde or an amine to induce thermo-hardening properties while still retaining oil-solubility.

In a series of patents[17] conditions are described under which resorcinol can be made to yield reasonably stable, potentially hardening resin solutions, and even permanently fusible resins, with formaldehyde.

It is interesting to note further attention to cashew nutshell liquid by consumers in this country, as well as by Indian chemists. C. R. Pye and K. Parvin have provided a comprehensive review[18] of this subject. In the first of a series of papers, G. M. Ajmen and S. U. K. Gatkan[19]

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[10] B.P. 577,182; B., 1946, II, 297.

[11] W. Spoon and P. A. Rowaan, *Verfkroniek*, 1941, **14**, 212; B., 1946, II, 129.

[12] *Paint, Oil & Chem. Rev.*, 1946, **109**, *No.* 13, 24, 54.

[13] W. Charlton, J. B. Harrison, L. E. Perrins, and Imperial Chemical Industries, B.P. 573,430, 574,790, 577,561; B., 1946, II, 99, 179, 345.

[14] *Idem*, B.P. 574,791–2; B., 1946, II, 179.

[15] Distillers Co. Ltd., B.P. 572,857; B., 1946, II, 100.

[16] British Resin Products Ltd., B.P. 573,626; B., 1946, II, 99.

[17] Pennsylvania Coal Products Co., U.S.P. 2,386,370–4.

[18] *Paint Tech.*, 1945, **10**, 249; B., 1946, II, 90.

[19] *J. Indian Inst. Sci.*, 1944, **26A**, 11; B., 1946, II, 428.

describe the preparation of conventional cashew nutshell liquid–formaldehyde varnishes and their oil modification, whilst S. K. Ranganathan and K. G. Tandon[20] cover newer ground by describing the action of sulphur on the liquid at high temperatures at which dehydrogenation occurs.

AMINOPLASTS.

Urea- and Melamine–Formaldehyde Resins.—Considerable interest in melamine resins continues and H. M. Payne[21] has reviewed the current situation in this field. A variety of modifications in manufacture have been claimed,[22] but there do not appear to be any real innovations.

Efforts to improve the economics of urea–formaldehyde resins continue to be directed towards one-stage processes.[23] I.G. Farbenindustrie[24] have proposed a continuous process in which the components or their preliminary condensation products are passed through a column in which the vapour of monohydric alcohol is partly refluxed ; the aqueous alcohol is passed overhead and the solution of the condensation products collected from the bottom of the still.

Processes have been proposed for the modification of both melamine[25] and urea–formaldehyde[26] resins with ketone–formaldehyde condensation products.

Amide Resins.—A variety of amides is being explored from the point of view of reactivity with aldehydes. Thus Pittsburgh Plate Glass Co.[27] claim unsaturated ester-amides whilst the British Thomson-Houston Co.[28] claim the condensation of chloroacetylated aminobenzoic acid with formaldehyde.

ALKYD RESINS.

J. I. Lynas-Gray[29] has discussed graphical methods for formulating these resins by means of triangular diagrams.

The search for resin variations has been very widespread over the past years. Thus is has been proposed[30] to form the adduct from β-naphthol and maleic acid and to esterify in the normal way. The continued interest in maleic anhydride as an alkyd component is also revealed in a paper by A. J. Drinberg[31] on polyglycol maleates as varnish ingredients. Bell Telephone Laboratories[32] claim that such linear esters are hardened

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[20] *Paint Tech.*, 1946, **11**, 94; B., 1946, II, 295.

[21] *Paint, Oil & Chem. Rev.*, 1946, **109**, *No.* 6, 9; B., 1946, II, 341.

[22] British Industrial Plastics Ltd., B.P. 572,239; B., 1946, II, 57. A. Hill and Imperial Chemical Industries Ltd., B.P. 573,668; B., 1946, II, 101.

[23] Albert Chemische Werke, G.P. 741,331.

[24] G.P. 745,100.

[25] Ellis–Foster Co., U.S.P. 2,364,900.

[26] E. I. Du Pont de Nemours & Co., U.S.P. 2,389,682.

[27] B.P. 576,153; B., 1946, II, 218.

[28] B.P. 571,660; B., 1946, II, 22.

[29] *Paint Tech.*, 1946, **11**, 129; B., 1946, II, 341.

[30] Pinchin, Johnson & Co. Ltd. (Docker Bros.) and G. F. Wilkinson, B.P. 572,455; B., 1946, II, 57.

[31] *J. Appl. Chem. Russ.*, 1944, **17**, 606.

[32] U.S.P. 2,388,319.

and toughened by cross-linking with small percentages of organic peroxides. I.G. Farbenindustrie[33] claim the reaction of maleic anhydride with unsaturated glycols such as dipropenyl glycol to give fast-drying oils. Among other acid constituents which have been proposed are silicic acid[34] and complexes formed by interaction of fatty acids with phenol–formaldehyde resoles.[35] A novel polyhydric alcohol is obtained by condensing terpene alcohols with formaldehyde in presence of an acid catalyst.[36]

ETHENOID POLYMERS.

Activity in this field remains undiminished and the first comprehensive account of recent German work has become available.[37]

Resins from Unsturated Hydrocarbons and their Derivatives.—The usefulness of ethylene as an ingredient of coatings has been enhanced by the description of a number of important copolymers such as that with vinyl acetate.[38]

In a number of patents[39] British Thomson-Houston Co. describe the partial polymerisation and copolymerisation of divinylbenzene short of gelation and also claim the further reaction products of such "prepolymers."

The utilisation of styrene as a general rather than a specialised coating material has made considerable progress. Thus the author's laboratory have described and claimed[40] products obtained by copolymerisation with partly polymerised polyhydric alcohol mixed esters, including drying oils and drying oil-modified alkyd resins. Such resins are already in commercial production. A toluene-insoluble copolymer with oxidised linseed oil of high oil content has also been proposed as a linoleum cement.[41] The styrene–maleic anhydride reaction continues to offer attractive possibilities of polymeric polybasic acids for use in preparing alkyds. T. Alfrey and E. Lavin[42] have correlated mathematically the composition of the reaction mixture and the initial copolymer. E. I. Du Pont de Nemours & Co.[43] modify the reaction by the presence of terpenes to give products of lower molecular weight.

*cyclo*Pentadiene may be copolymerised with unsaturated glyceride oils

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[33] F.P. 898,257.

[34] E. I. Du Pont de Nemours & Co., B.P. 578,484; B., 1946, II, 392.

[35] H. S. Lilley, J. W. Dorling, and Imperial Chemical Industries Ltd., B.P. 572,822–3; B., 1946, II, 138.

[36] Harvel Research Corp., U.S.P. 2,383,791.

[37] G. M. Kline, J. H. Rooney, *et al.*, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 9 and 22, *File* XXIX–62 and XXXIII–23.

[38] E. I. Du Pont de Nemours & Co., B.P. 575,689; B., 1946, II, 256.

[39] B.P. 572,272; B., 1946, II, 57. B.P. 577,137, 577,288, 577,322, and 576,944; B., 1946, II, 298, 299.

[40] L. Berger & Sons Ltd., L. E. Wakeford, D. H. Hewitt, and F. Armitage, B.P. 573,809, 573,835; B., 1946, II, 134. *J. Oil Col. Chem. Assoc.*, 1946, **29**, 109; B., 1946, II, 342.

[41] Armstrong Cork Co., U.S.P. 2,382,212.

[42] *J. Amer. Chem. Soc.*, 1945, **67**, 2044; A., 1946, I, 120.

[43] U.S.P. 2,383,399.

under pressure at high temperatures in a continuous process.[44] *Dicyclo*pentadiene is also caused to react with similar oils under the influence of boron trifluoride[45]; such products are claimed to give quick-drying varnishes of good water-resistance. *Dicyclo*pentadiene may also be copolymerised with styrene to give useful resins.[46]

Among newer raw materials, J. I. Jones has discussed acenaphthylene as a raw material of polymers.[47]

Polymers from Unsaturated Acids.—C. H. Fisher and his colleagues have continued their work on the preparation of substituted acrylates[48] via the corresponding lactates but it seems likely that this approach will be outmoded by the Reppe process of direct synthesis from acetylene and carbon monoxide in presence of nickel carbonyl.[49]

A review of the chemistry of crotonic acid[50] is timely in view of the commercial availability of this material.

ALLYL POLYMERS.

In the period under review, this class has been the subject of probably greater activity than any other on the ethenoid group. D. H. Hewitt has reviewed the utilisation of allyl esters in surface coatings fairly exhaustively to date.[51]

The main items of development include a research by W. Simpson[52] on the polymerisation of diallyl phthalate with and without diethylene maleates; in the former case gelation occurs at approximately 25% of polymer, which is only slightly branched. Variations have been proposed in the preparation of polyallyl alcohol to give products having superior colour and greater hydroxyl value.[53] Considerable attention has been paid to the polymerisation and copolymerisation of allyl esters of silicic and boric acids, which are capable of giving extremely hard products.[54] Unsaturated polyesters of increasing complexity are being described in number.[55] W. S. Penn has reviewed the present position regarding allylstarch.[56]

SILICON POLYMERS.

Further reviews on the utilisation of silicones in surface coatings have

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[44] Pittsburgh Plate Glass Co., U.S.P. 2,381,895, 2,392,732, 2,393,140.

[45] *Idem.* U.S.P. 2,390,530.

[46] Dow Chemical Co., U.S.P. 2,371,499.

[47] *Brit. Plastics*, 1946, **18**, 286; B., 1946, II, 388.

[48] *J. Amer. Chem. Soc.*, 1945, **67**, 208; cf. B., 1945, II, 247.

[49] *Mod. Plastics*, 1945, **23**, *No.* 3, 162; cf. B., 1946, II, 406.

[50] P. W. Blaylock, *Paint Manuf.*, 1945, **15**, 367; B., 1946, II, 132.

[51] *Paint Tech.*, 1946, **11**, 215; B., 1946, II, 427.

[52] *J.S.C.I.*, 1946, **65**, 107; B., 1946, II, 293.

[53] American Cyanamid Co., B.P. 573,757; B., 1946, II, 135.

[54] E. I. Du Pont de Nemours & Co., B.P. 577,456; P. J. Garner and Imperial Chemical Industries, Ltd., B.P. 576,938, 576,716; B., 1946, II, 197.

[55] Pittsburgh Plate Glass Co., U.S.P. 2,384,115–26, 2,383,930–4.

[56] *Paint Manuf.*, 1946, **16**, 163.

appeared.[57] The patent position in this whole field is extremely confused, but notable advances include the preparation of unsaturated silicones[58] and particularly the direct, non-Grignard synthesis of organo-silicon halides from silicon and alkyl halides in presence of copper.[59] Another feature of interest is the tendency to replace chlorine atoms by ester groupings as the hydrolysable groups.

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[57] W. S. Penn, *Paint Manuf*, 1945, **15**, 364; Chicago Paint & Varnish Production Club, *Off. Digest*, 1945, *No.* 250, 424.

[58] D. T. Hurd, *J. Amer. Chem. Soc.*, 1945, **67**, 1813; A., 1946, II, 170. American Cyanamid Co., U.S.P. 2,388,161.

[59] British Thomson-Houston Co., B.P. 575,667–8, 575,673–4, B., 1946, II, 239.

DRYING OILS, DRIERS, AND VARNISHES.

By J. H. Greaves, B.Sc., A.R.I.C.,

Messrs. Younghusband, Barnes & Co. Ltd.

In the year under review the published literature lays almost equal emphasis on many different subjects, and at the same time avoids making any particular topic one of major interest. Although the production of conjugated double bonds during oxidation of methyl esters of drying oil fatty acids continues to be observed, the promise of immediate technical application is small.

Recent controversy concerning theories of polymerisation emphasises that much remains to be learned concerning the chemistry of the first stages of the formation of stand oil.

As has been the case since 1940, the majority of references comes from publications in the United States, a state of affiars due not only to war conditions still with us, including paper restrictions, but also to different attitudes concerning publication of research. In this connexion it is unfortunate that nearly all the work of the Paint Research Station continues to be confidential.

Drying Oils.

M. M. Piskur[1] has prepared an extensive review, including full references, of papers and patents dealing with all aspects of oils and fats for the year 1945, and another useful review is that of M. J. Van de Wal[2] for Dutch patents in the decade beginning 1929.

Increasing oilseed production has engaged attention in many countries, including the U.S.S.R.[3] W. J. Newman[4] states that linseed oil produced in New Zealand from flax grown primarily for linen passes the British Standards Specification, but is somewhat inferior to imported oils. In the Dutch Empire overseas the most interesting possibilities for future

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[1] *Oil and Soap*, 1946, **23**, 113, 151; B., 1946, II, 386.

[2] *Verfkroniek*, 1939, **12**, 142; 1940, **13**, 73, 97, 137; B., 1946, II, 20.

[3] A. M. Goldovskii, *Pischchevaya Prom.*, 1944, *No.* 11, 20; *Chem. Abs*, 1946, 479.

[4] *Paint Manuf.*, 1945, **15**, 316; B., 1946, II, 90.

development of the seeds of drying oils are stated by P. A. Rowaan[5] to be *Aleurites montana*, *Licania crassifolia*, and certain *Parinarium* oils. According to the Munitions Supply Laboratories, Melbourne,[6] it is hoped to be able to supply some hundreds of tons of candlenut oil (similar to linseed oil) from a plant (*Aleurites moluccana*) which grows wild in North Queensland.

Linseed Oil.—The fatty acids of this oil, which will without doubt be used in far greater quantities when glycerol is in better supply than at present, are described by R. Rosenbusch[7] with special reference to production and grades available in this country.

Tung Oil.—The investigations into the possibility of growing tung oil in various parts of the Empire continue to make progress. F. Major[8] finds that *Aleurites montana* fruits from the Sudan yield an oil conforming to the British Standards Specification. War-time conditions have enabled a study to be made of the characteristics of American and Chinese tung oils after long storage. As might be anticipated, it was usual for acid values to increase and gelation times to decrease, but the observation that during the gelation test the time between the first signs of polymerisation and complete gelation increased is less expected. To prevent skinning and accompanying gelation it is suggested that the oil should either be stored in an inert atmosphere or circulated by frequent transfer from one tank to another.

Trienol.—It is most satisfactory that the position concerning "Trienol," the so-called "synthetic tung oil," has been very much clarified. That tung oil and the samples of Trienol which were once distributed were remarkably similar has been known for some time; for example, it is extraordinary that any synthetic oil should have the same odour as the crude vegetable oil. A. Steger and J. van Loon[9] show that the patents concerned do not disclose a workable method of making Trienol, that this oil is indistinguishable from tung oil, and furthermore that it contains α-elæostearic acid, which occurs only in natural oils. T. P. Hilditch and M. L. Meara,[10] in confirming these last findings, comment that α-elæostearic acid could not possibly be produced at a high temperature in the presence of powerful chemical reagents. A. V. Blom[11] has admitted that the synthesis has not proved successful on a commercial basis.

Dehydrated Castor Oil.—This product, reviewed by R. Mansell,[12] continues to be used in ever-increasing quantities. The preparation and properties are now well investigated and there is little new to

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[5] *Verfkroniek*, 1941, **14**, 171; B., 1946, II, 16.
[6] *Chem. Trade J.*, 1946, **118**, 711.
[7] *Paint Tech.*, 1945, **10**, 281; B., 1946, II, 208.
[8] *Bull. Imp. Inst.*, 1946, **44**, 8; B., 1946, II, 385.
[9] *Fette u. Seifen*, 1944, **51**, 102.
[10] *Chem. and Ind.*, 1946, 158.
[11] *Paint Tech.*, 1946, **11**, 258.
[12] *Paint, Oil and Chem. Rev.*, 1946, **109**, 9; B., 1946, II, 337.

report. Universal Oil Products Co.[13] use a solid phosphoric acid specially prepared by calcination as a dehydration catalyst, whilst F. A. Bent and C. R. Ryan[14] prepare a varnish specially suitable as a baking finish for food and beverage containers by dehydrating in the presence of allyl phthalate. W. Charlton, H. A. Hampton, J. B. Harrison, and F. J. Siddle[15] claim the production of varnishes by heating the raw oil with an acidic resin which no doubt catalyses dehydration to some extent.

Oiticica Oil.—A concise yet very informatory account of the cultivation (in Brazil) and properties of this oil has been given by G. T. Bray.[16] Perhaps the greatest defect of the oil from the point of view of a film-forming material is poor durability due to rapid embrittlement. Scientific Oil Compounding Co.[17] claim that film elasticity, as well as bodying and gelation rates, are greatly increased by blowing with air for one hour at 350° F.

L. Huffman[18] gives practical instructions for varnish making using various alkyd and phenolic resins, usually in conjunction with other drying oils.

Tall Oil.—The literature relating to the preparation and use of this oil for surface coatings is now extensive. After the crude material has been refined one difficulty encountered is that resin acids may spontaneously crystallise, giving great trouble in handling on the manufacturing scale. A. V. Oliver and R. C. Palmer[19] stabilise the oil by partly neutralising with alkali and then heating at about 290°. Besides vacuum-distillation, described by O. Kress,[20] the mixture of fatty acids and resin acids can be conveniently separated by esterifying the fatty acids with methyl alcohol, leaving the resin acids unchanged: the resultant mixture can be treated in a variety of ways. R. G. Dressler, R. E. Vivian, and T. Hasselstrom[21] add an organic solvent and saponify the resin acids with aqueous alkali, obtaining two easily separated layers. T. Hasselstrom[22] heats the mixture with iodine, after which, on cooling, the crystallised resin acids are easily removable from the mother-liquor containing fatty acid esters. Alternatively, according to E. Segessemann,[23] the resin acids may be esterified with glycerol, and the methyl esters distilled off under vacuum. The Chemical Foundation[24] describes a direct separation into fatty and resin acids by countercurrent extraction with liquid propane.

[24] U.S.P. 2,388,412; *Oil and Soap*, 1946, 62.

[13] U.S.P. 2,380,720; *Chem. Abs.*, 1945, 5095.

[14] Assrs. to Shell Development Co., B.P. 576,316–7; B., 1946, II, 254.

[15] With Imperial Chemical Industries, B.P. 571,051; B., 1946, II, 183.

[16] *Bull. Imp. Inst.*, 1946, **44**, 15.

[17] U.S.P. 2,388,257; *Chem. Abs.*, 1946, 1327.

[18] *Amer. Paint J.*, 1945, **29**, *No.* 50, 48; B., 1946, II, 94.

[19] Assrs. to Newport Industries, Inc., U.S.P. 2,330,792; B., 1946, II, 17.

[20] *Paint, Oil and Chem. Rev.*, 1945, **108**, *No.* 21–22, 60; B., 1946, II, 127.

[21] U.S.P. 2,396,646; *Oil and Soap*, 1946, 173.

[22] U.S.P. 2,396,651; *Oil and Soap*, 1946, 173.

[23] Assr. to Nat. Oil Products Co., U.S.P. 2,199,653; B., 1946, II, 127.

Dealing with paint-making properties of tall oil stand oil made by esterifying refined oil with glycerol, N. C. Otte[25] finds that the tall oils available in Denmark do not give such good performance as has been claimed in the German literature. General uses for paints and varnishes are discussed by P. Kirjakka.[26] H. Nihlen,[27] in a report of work carried out in Sweden on analytical methods for crude and distilled tall oil, briefly describes methods for determination of resin acids, fatty acids, unsaponifiable matter, water, ash. water-soluble acids, and acids insoluble in light petroleum.

Other Oils.— For different varieties of American sunflower and safflower acids and oils, R. T. Milner, J. E. Hubbard, and M. B. Wiele[28] give a wide range of analytical figures, namely, for the seeds, ash, protein, sugar, and oil; for the oils, free acids, unsaponifiable matter, refractive index, iodine value, thiocyanogen value, and fatty acid composition; the iodine value of any one variety of sunflower-seed oil was found to vary widely (up to 20 units) according to location. C. L. Lundell[29] describes the oil obtainable from the genus *Garcia*, closely allied to *Aleurites* (tung); though known sources of the seed would provide only about 5 tons of oil annually, the oil is so similar to tung oil as to arouse very great interest. A. Steger and J. van Loon[30] have given an analysis of po-yoak oil (41% of coupeic acid, 31% of elæostearic acid), and, with H. P. Kaufmann,[31] of allemantia oil, similar in composition to linseed oil. Grape-seed oil is frequently discussed as a drying oil substitute in literature[32] published on the Continent, but is really of little importance in this country. Highly unsaturated oils have been described by C. R. and T. P. Mehta[33] (*Ocimum canum*, iodine value 179·8) and by V. I. Esafov, V. L. Glikina, and M. A. Panjukova[34] (*Lappula echinata*).

MODIFIED OILS.

Modified oils and other developments in the drying oil field during the last few years have been reviewed by H. R. Touchin,[35] J. H. Greaves,[36] and E. H. Valance.[37]

According to S. E. Freeman[38] the more highly unsaturated better

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[25] *Farve og Lak*, 1944, *No.* 19, 10; B., 1946, II, 126.

[26] *Suomen Kem.*, 1943, **16**, **A**, 28; B., 1946, II, 295.

[27] *Svensk Papperstidn.*, 1945, **48**, 345; *Chem. Abs.*, 1945, 4755.

[28] *Oil and Soap*, 1945, **22**, 304; B., 1946, II, 208.

[29] *Wrightia*, 1941, **1**, 1; B., 1946, II, 126.

[30] *Rec. trav. chim.*, 1940, **59**, 955; B., 1946, II, 291.

[31] *Fette u. Seifen*, 1941, **51**, 1; *Paint, Oil and Chem. Rev.*, 1946, **109**, *No.* 1, 20.

[32] R. Arzens, *Chim. Peint.*, 1941, **4**, 22, 65, 120, 194; V. Charrin, *Peint, Pig. Vernis*, 1946, **22**, 89; R. Viollier and E. Iselin, *Mitt. Lebensm. Hyg.*. 1942, **33** 298; B., 1946, II, 51.

[33] *Current Sci.*, 1943, **12**, 300; B., 1946, II, 16.

[34] *J. Appl. Chem. Russ.*, 1945, **18**, 175; *Chem. Abs.*, 1945, 5515.

[35] *Paint Manuf.*, 1946, **16**, 186; B., 1946, II, 337.

[36] *Oil Col. Tr. J.*, 1946, **109**, 410, 506; B., 1946, II, 209.

[37] *Off. Digest*, 1946, *No.* 255, 183; B., 1946, II, 337.

[38] Assr. to Pittsburgh Plate Glass Co., U.S.P. 2,200,390-1; B., 1946, II. 127, 170,

drying fractions of drying and semi-drying oils can be separated by extraction with furfuraldehyde or furfuryl alcohol at normal temperatures, or at lower temperatures by certain oxygen-containing solvents typified by ethyl acetoacetate.

Conjugation of double bonds in fatty acids by heating with excess of alkali, reviewed by J. L. Boyle[39] along with other methods of producing conjugation, has reached an almost stationary situation. D. E. Terry and D. H. Wheeler[40] describe two *iso*linoleic acids, obtained by alkali treatment of linoleic acid, only one of which is conjugated, and conclude that it should be possible to separate this acid on a commercial scale by using a suitable fractionating column.

E. I. Du Pont de Nemours & Co.[41] replace one of the fatty acid radicals in linseed triglyceride by a lower acid by interaction of linseed diglycerides with, for example, cinnamic acid.

J. D. Brandner, R. H. Hunter, M. D. Brewster, and R. E. Bonner[42] describe the drying oils made by heating linseed fatty acids and sorbitol. The conditions for optimum esterification are that the fatty acids are added to molten sorbitol (4·5 mols. to 1 of acid) firstly at 200° and later at 250° in an inert atmosphere; a calcium acetate-barium acetate mixture is suggested as catalyst. Drying time, hardness, and water-resistance are all equal to or better than the corresponding pentaerythritol, mannitol, and glycerol esters.

Oxidation, Polymerisation, and Drying.

The formation of conjugated double bonds during oxidation of alkyl esters of unsaturated fatty acids continues to be observed and described. F. D. Gunstone and T. P. Hilditch,[43] when following the autoxidation of the methyl esters of oleic, linoleic, and linolenic acids by changes in peroxide and iodine values, show that the development of conjugated diene unsaturation to a maximum with subsequent decline is parallel with formation of peroxide. In the light of α-methylenic oxidation of methyl linoleate followed by a rearrangement to a mixture of 9 : 11- and 10 : 12-conjugated unsaturated esters, S. Bergstrom[44] has discussed the reactions which occur when linseed oil is blown and boiled.

In a comprehensive critical review of work done since 1930 on polymerisation of drying oils, E. Sunderland[45] includes a discussion on various postulated structures for dimers of fatty acids. C. P. A. Kappelmeier,[46] in correspondence with E. Sunderland, points out that this review omits his postulate of a Diels–Alder diene reaction taking part in stand oil

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[39] *Paint Manuf.*, 1946, **16**, 50.
[40] *Oil and Soap*, 1946, **23**, 88; B., 1946, II, 383.
[41] B.P. 574,680–2; B., 1946, II, 170.
[42] *Ind. Eng. Chem.*, 1945, **37**, 809; B., 1946, II, 51.
[43] *J.C.S.*, 1945, 836; A., 1946, II, 64.
[44] *Arkiv Kemi, Min., Geol.*, 1946, **21**, A, *No.* 14; A., 1946, II, 417.
[45] *J. Oil Col. Chem. Assoc.*, 1945, **28**, 137; B., 1946, II, 16.
[46] *Ibid.*, 1946, **29**, 229.

formation, a postulate for which certain experimental support has been given by G. Champetier and J. Petit.[47] Evidence of a somewhat indirect nature for the formation of an intrapolymer during polymerisation of linseed oils has been found by H. E. Adams and P. O. Powers.[48] The technical side of oil polymerisation, namely stand oil manufacture, has been reviewed by H. Feinberg,[49] and also by I. R. Priester,[50] who discusses pre-oxidised stand oils. T. S. Russell[51] prefers stainless steel equipment and vapour-phase heating for bodying oils and varnishes, and describes chemical engineering factors involved. Rapid-bodying linseed oil, E. A. Lasher[52] claims, is produced by addition of inter-halogen compounds which are stated to be polymerisation catalysts.

V. J. Frilette[53] finds from determinations of acid value on oil and varnish films that except for a modified phenolic varnish showing a minimum value, acidity increases rapidly in the first month of life. Alkali-resistance of films as shown by the periods of immersion required for wrinkling and disintegration is determined by this development of acidity; initial acidity has little effect. The acids originate from decomposed peroxides and not from ester hydrolysis.

DRIERS.

G. Fearnley[54] has abstracted 44 recent accounts of various aspects of driers and gives some constructive criticism for each one. P. L. Gordon, R. Aronowitz, and B. Cohen[55] find vanadium linoleate a less effective drier than a lead–cobalt combination; from exposure tests these authors suggest that a vanadium drier may be suitable in paints for tropical conditions and in wrinkle finishes. The addition of between 1 and 10% of sorbitol is claimed by Ferro Enamel Corporation[56] to stabilise a solution of a drier in a non-polar solvent.

VARNISHES.

A scheme for the layout of buildings and production equipment is suggested by the Montreal Club.[57] Some of the factors influencing dispersion of pentaerythritol–rosin resins in drying oils have been investigated by G. F. Oswald[58]; whereas the viscosity of linseed stand oil varnishes increased with age, that of dehydrated castor oil varnishes prepared by bodying the oil, checking back with a little of the resin,

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[47] *Bull. Soc. chim.*, 1945, [v], **12**, 689; B., 1946, II, 208.

[48] *J. Appl. Physics*, 1946, **17**, 325; B., 1946, II, 384.

[49] *Off. Digest*, 1946, *No.* 254, 112; B., 1946, II, 337.

[50] *Verfkroniek*, 1943, **16**, 108; B., 1946, II, 342.

[51] *Off. Digest*, 1946, *No.* 252, 19; B., 1946, II, 169.

[52] Assr. to California Flaxseed Products Co., U.S.P. 2,335,520; B., 1946, II, 292.

[53] *Ind. Eng. Chem.*, 1946, **38**, 493; B., 1946, II, 342; C., 1946, 172.

[54] *Off. Digest*, 1945, *No.* 244, 132; B., 1946, II, 131.

[55] *Amer. Paint J.*, 1945, **30**, *No.* 3, 26; B., 1946, II, 173.

[56] U.S.P. 2,390,830; *Chem. Abs.*, 1946, 1327.

[57] *Amer. Paint J., Conv. Daily*, 1945, **30**, *No.* 6B, 7; B., 1946, II, 130.

[58] *Off. Digest*, 1946, *No.* 254, 122; B., 1946, II, 340.

and then blending the remaining resin in the cold showed a reduction of viscosity on storage. The various methods of clarifying varnishes with special reference to filtration processes have been fully described and compared by W. Meyer,[59] K. Kölln,[60] and F. von Artus.[61]

ANALYTICAL METHODS.

Statisticians and research workers in many fields have for a long time held the view that statistical analysis is necessary for proper design and interpretation of experiments. W. N. W. Wallace[62] discusses the advantages of applying statistical methods to detect significant deviations among analytical results with special reference to the reliability of routine chemical analysis ; the accuracy of an analysis may be assessed, the effect on analyses of changing the operator is derived, and tests are given for faulty sampling and for the detection of deterioration in accuracy.

F. R. Cropper[63] reviews modern technique dealing with the potentiometric titration of weak bases in glacial acetic acid solution, ultra-violet spectrometry as applied to drying oils, and infra-red spectrometry as applied to many polymers. V. G. Frilette[53] determines acid values of dried oil and varnish films by titrating slowly in benzene–alcohol with 0·01N-sodium hydroxide, using Victoria Blue as indicator; the titration takes about one hour. Constructional details and the operating procedure for the micro-determination of the saponification value of oils are given K. Marcali and W. Rieman III[64]; three methods are described, all depending on the back-titration of excess of alkali used for saponification, according to whether 5, 50, or 500 mg. of oil are used. A. N. N. Trenité[65] finds that if an ordinary determination of saponification value is carried out with 30 mg. of oil then carbon dioxide is absorbed from the atmosphere and the results are vitiated ; the use of a sealed tube is recommended. It is emphasised by G. K. Jones[66] that determination of iodine value by Wijs' method requires rigid control of acetic acid concentration (99·0%), time of reaction, temperature, proportion of reagent to sample, and concentration of reagent; the differences that changes in the last two of these factors make in the apparent iodine value of a treated linseed oil are illustrated graphically. In rapid determinations of iodine value P. S. Skell and S. B. Radlove[67] find that the mercuric acetate catalyst gives anomalous results with methyl ricinoleate due to the free hydroxyl group. The room temperature method for determination of peroxide values by the use of potassium iodide in acetic acid–chloroform solution

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[59] *Farben-Chem.*, 1940, **11**, 56; B., 1946, II, 295.
[60] *Ibid.*, 53; B., 1946, II, 295.
[61] *Ibid.*, 60; B., 1946, II, 295.
[62] *J. Proc. Austral. Chem. Inst.*, 1945, **12**, 243; C., 1946, 144.
[63] *J. Oil Col. Chem. Assoc.*, 1945, **28**, 207; C., 1946, 60.
[64] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 144; C., 1946, 91.
[65] *Verfkroniek*, 1943, **16**, 97; C., 1946, 257.
[66] *Paint Manuf.*, 1945, **16**, 58; C., 1946, 91.
[67] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 67; C., 1946, 84.

has been investigated by C. B. Stuffins and H. Weatherall,[68] who find that an inert atmosphere is necessary.

In a general description of chromatography applied to analysis of fatty oils, K. A. Williams[69] includes the separation of free fatty acids, carotenes, xanthophylls, and oxidised acids. The use of the Karl Fischer reagent for the determination of water content of oils is described by M. M. Acker and H. A. Frediani[70]; emphasis is placed on the necessity for rigid adherence to detail and the schedule of (potentiometric) titration. C. P. A. Kappelmeier and W. R. van Goor[71] have given details of a method for determination of the oil content of varnishes based on saponification of the non-volatile organic medium followed by esterification of the liberated resin acid–fatty acid mixture with methyl alcohol using sulphuric acid as catalyst; the unesterified resin acids are extracted with alkali and the methyl esters of the fatty acids are weighed. Fair accuracy is obtained for varnishes based on linseed or tung oil with rosin, ester gum, or modified phenolic resins, but about 20% of the acids of run Congo copal are esterified by the methyl alcohol under the experimental conditions described.

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[68] *Analyst*, 1945, **70**, 403; C., 1946, 22.
[69] *Ibid.*, 1946, **71**, 259; C., 1946, 220.
[70] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 793; C., 1946, 90.
[71] *Verfkroniek*, 1943, **16**, 68; C., 1946, 172.

SOLVENTS.

BY H. L. HOWARD, B.SC., M.I.CHEM.E., F.R.I.C.

SHORTAGES continue to dominate the trend of advance during the year. Owing to the serious coal position the developments of the past 20 years in the hydrogenation of coal to produce petrol and the efforts to utilise coal as a raw material for chemical industry threaten to be swamped, and the main effort has been rather in the direction of dehydrogenation of petroleum, in an effort to make good the shortage of aromatic solvents. A large proportion of British patents have been taken out by American interests to cover these developments.

The production of toluene figures prominently in these activities. Thus Shell Development Co.[1] claim the dehydrogenation of methyl*cyclo*hexane by means of chromium oxide catalyst in the vapour phase and the conversion of dimethyl*cyclo*pentane into methyl*cyclo*hexane[2] and thence into toluene as above. Standard Oil Development Co.[3] catalytically reform naphtha, and by treatment with phenol as extractive obtain a product containing 62% of toluene. In other patents[4,5] they

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[1] Assees of R. C. Archibald and G. S. Greensfelder, B.P. 572,251; B., 1946, II, 35.
[2] Shell Development Co., B.P. 570,651; B., 1945, II, 333.
[3] B.P. 571,913; B., 1946, II, 4.
[4] Standard Oil Development Co. and A. Arnold, B.P. 572,323; B., 1946, II, 4.
[5] Standard Oil Development Co., B.P. 572,089; B., 1946, II, 35.

describe apparatus for the extraction of toluene of 99% purity by means of liquid sulphur dioxide and claim modifications that permit the production of benzene and other aromatic hydrocarbons in a similar way. The same company[6] cover the use of alumina in conjunction with molybdenum and other metals as dehydrogenation catalysts.

Again, the methylation of benzene by means of methyl alcohol or dimethyl ether in the vapour phase at atmospheric pressure with the aid of silica–phosphoric acid catalyst has been covered[7] and W. M. Kutz and B. B. Corson[8] achieve the redistribution of alkyl groups by passing a mixture of benzene and polyalkylbenzenes over silica alumina, whereby an increased yield of monoalkylated benzenes is obtained. The cracking of αβ-diphenylethane at high temperature and pressure in the presence of hydrogen to yield toluene is claimed by L. Schmerling.[9] The use of zirconium–chromium hydroxides as fluid bed catalyst for the continuous production of aromatic products is claimed by H. Fehrer.[10]

The Gas Light & Coke Co. with R. H. Griffith[11] catalytically hydrogenate *o*-phthalic acid and the same company with R. H. Griffith and J. H. G. Plant[12] treat naphthalene and its homologues in the presence of tin to produce toluene.

In the ethylation of benzene by the Friedel–Crafts reaction, A. W. Francis and E. E. Reid,[13] in a comprehensive review of the yields obtained in 60 previous investigations, claim to have obtained 15% higher yield than any previously reported, and to have achieved a hundred-fold increased reaction rate over that of many commercial processes. H. F. Oxley, E. B. Thomas, and F. S. Nichols,[14] by increasing pressure and temperature so that the benzene is maintained in the liquid phase, claim improved yields and decreased catalyst consumption. V. N. Ipatieff and L. Schmerling[15] claim 80% conversion in a single pass at 325° and 40 atmospheres.

Terpenes.—B. L. Davis, L. A. Goldblatt, and S. Palkin[16] report high yields of isoprene from turpentine, using a hot-wire heater immersed in the liquid. Dipentene yields 60% of isoprene. Many previous claims by different workers have not been confirmed. Temperature is shown to be the most important factor controlling the polymerisation of myrcene

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[6] B.P. 577,171 and Addn. B.P. 577,282; B., 1946, II, 277.

[7] Standard Oil Development Co., B.P. 574,738; B., 1946, II, 155, also Gas Light & Coke Co., A. R. Morcom, W. B. S. Newling, and J. H. G. Plant, B.P. 577,314; B., 1946, II, 277.

[8] *Ind. Eng. Chem.*, 1946, **38**, 761; B., 1946, II, 407.

[9] Assr. to Universal Oil Products Co., U.S.P. 2,338,973, B., 1946, II, 363.

[10] Assr. to Process Management Co. Inc., U.S.P. 2,336,783; B., 1946, II, 277.

[11] B.P. 577,816; B., 1946, II, 320.

[12] B.P. 577,818; B., 1946, II, 320.

[13] *Ind. Eng. Chem.*, 1946, **38**, 1194.

[14] B.P. 576,432; B., 1946, II, 277.

[15] *Ind. Eng. Chem.*, 1946, **38**, 400; B., 1946, II, 271.

[16] *Ibid.*, 53; B., 1946, II, 149.

according to W. J. Runckel and L. A. Goldbaltt,[17] who report no appreciable change in monomeric myrcene stored for 12 months at 3°. At temperatures up to 25°, the addition of 0·1% of *p*-nitrosodimethylaniline or *p*-*tert.*-butylpyrocatechol suffices to inhibit polymerisation.

The presence in turpentine from the Coulter pine of *n*-heptane and *n*-undecane has been reported by N. T. Mirov[18]; the presence of aliphatic hydrocarbons in turpentine is rare, the occurrence of the former having been noticed in only two species and the latter in three. A. B. Anderson[19] points out that resins form no integral part of wood structure and that their presence degrades high-class lumber. In a later publication,[20] he draws attention to the possibility of combining their extraction by means of acetone with the simultaneous removal of moisture, thereby combining a seasoning effect on the wood as well as obtaining valuable by-products.

Nitro-Derivatives.—In the production of nitro-paraffins, higher conversion with less risk of oxidation and explosion are obtained by passing a gaseous mixture of paraffin and nitric acid over silicate glass capillary tubes containing arsenic or antimony according to N. Levy and Imperial Chemical Industries Ltd.[21] In other patents[22] the use of lead glass as well as aluminium turnings[23] as catalysts is covered. Nitration in the liquid phase in the presence of a reducing catalyst (sulphur or carbon) is the subject of a patent claim by M. Senkus.[24]

The production of β-nitroethyl alcohol and β-nitroethyl nitrate by the reaction of dinitroethane with methyl alcohol is described by A. E. W. Smith, R. H. Stanley, C. W. Scaife, and Imperial Chemical Industries Ltd.,[25] and the same authors claim[26] the production of β-nitroethyl ethers in similar manner, via nitroethylene. E. F. Degering and A. Sprang[27] describe the preparation of unsaturated nitro-alcohols by the addition of nitromethane to crotonaldehyde and its homologues in presence of methyl alcohol and potassium carbonate. J. T. Thurston, C. Cob, and D. W. Kaiser[28] have patented the preparation of β-nitroalkyl esters of α-hydroxy*iso*butyric acid.

Esters, Ethers, and Polyhydric Alcohols.—The aromatic esters of α-hydroxy*iso*butyric acid,[29] halogenated derivatives of tetrahydrofuroic

[17] *Ind. Eng. Chem.*, 1946, **38**, 749; B., 1946, II, 405.

[18] *Ibid.*, 405; A., 1946, III, 616.

[19] *Ibid.*, 450; A., 1946, III, 699.

[20] *Ibid.*, 759; B., 1946, I, 335.

[21] B.P. 575,733; ;B., 1946, II, 233.

[22] M. Appleby and Imperial Chemical Industries Ltd., B.P. 578,044; B., 1946, II, 360.

[23] K. W. Gee and Imperial Chemical Industries Ltd., B.P. 576,129; B., 1946, II, 233.

[24] Assr. to Commercial Solvents Corporation, U.S.P. 2,332,491; B., 1946, II, 233.

[25] B.P. 575,604 and 575,618 (Addn. to B.P. 572,949); B., 1946, II, 233.

[26] B.P. 573,872; B., 1946, II, 111.

[27] Assrs. to Purdue Research Foundation, U.S.P. 2,332,482; B., 1946, II, 234.

[28] Assrs. to Amer. Cyanamid Co., U.S.P. 2,336,318; B., 1946, II, 317.

[29] J. T. Thurston, C. Cob, and J. M. Grim, Assrs. to Amer. Cyanamid Co., 2,336,317; B., 1946, II, 317.

acid,[30] and 4-keto-2-methyl-1 : 3-dioxolan[31] are all claimed as solvents or plasticisers, the last-mentioned being susceptible to polymerisation in presence of mineral acids or boron trifluoride. B. H. Wojcik[32] claims the production and use of the halogenated alkyl carbonates for the purpose of making flame-resistant materials. The production of a number of chlorinated di- and tetra-hydropyran derivatives is covered by P. A. Hawkins, N. Bennett, and Imperial Chemical Industries Ltd.,[33] and in another patent these same authors[34] describe the preparation of 5 : 6-dihydropyran-3-carboxylic glycol ester and related derivatives. E. I. Du Pont de Nemours & Co.[35] describe the production of pentaerythritol in 89% yield by the hydrogenation with Raney nickel at 100 atm. of alkaline mixtures of formaldehyde and acetaldehyde, and of related polyhydric alcohols from propaldehyde. Similarly, W. E. Hanford and R. S. Scheiber[36] condense aldol alone or with acetaldehyde to produce trihydroxyhexane and tetrahydroxyoctane. M. T. Harvey[37] describes the preparation of condensation products of *tert.*-amyl, -butyl, and -hexyl alcohol with formaldehyde, which are solvents for cellulose derivatives and polyvinyl esters. According to H. S. Holt,[38] *cyclo*hexene oxide may be condensed with monohydric alcohols, glycols, or polyhydroxydialkyl ethers to yield a series of ethers and esters of value as plasticisers. T. W. Evans and E. F. Bullard[39] describe the preparation of glycidol *sec.*-butyl ether, which is said to be a good solvent for nitrocellulose. W. A. Woodcock[40] suggests that butyl acetate may advantageously be replaced by a mixture of methyl *iso*butyl ketone and methylamyl acetate together with a small amount of *iso*propyl alcohol or acetate, which permits higher solids at equal viscosity in nitrocellulose lacquers with substantially higher diluent content and lower cost; similarly, a mixture of 85% of methylamyl acetate and 15% of butyl acetate has equal evaporative rate to amyl acetate itself at 25% lower cost.

Mechanism of Solvent Action.—The extensive literature on the nature of dissolution is confined almost entirely to investigations of aqueous solutions. The lack of systematic knowledge of the nature of dissolution in non-aqueous solvents is a serious handicap to workers in this field, precluding in many cases systematic investigation into many pressing problems. A. K. Doolittle,[41] in an endeavour to fill an obvious gap,

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[30] J. B. Dickey and R. A. Corbitt. Assrs. to Eastman Kodak Co., U.S.P. 2,333,771; B., 1946, II, 235.

[31] E. I. Du Pont de Nemours & Co., B.P. 573,087; B., 1946, II, 80.

[32] Assr. to Hooker Electrochem. Co., U.S.P. 2,337,172, B., 1946, II, 317.

[33] B.P. 571,265; B., 1945, II, 367.

[34] B.P. 570,974; B., 1945, II, 367.

[35] B.P. 576,842; B., 1946, II, 273.

[36] Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,334,761; B., 1946, II, 274.

[37] Assr. to Harvel Research Corp., U.S.P. 2,333,927–9; B., 1946, II, 297.

[38] Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,197,105; B., 1946, II, 79.

[39] Assrs. to Shell Development Co., U.S.P. 2,197,467; B., 1946, II, 31.

[40] *Off. Digest*, 1946, *No.* 255, 172; *Paint Ind. Mag.*, 1946, **61**, 124; B., 1946, II, 463.

[41] *Ind. Eng. Chem.*, 1946, **38**, 535; A., 1946, I, 246.

presents a working theory which may prove of value to investigators of reversible sol–gel transformations, so important in the lacquer industry. Solvent ability is dependent on the size and shape of the solvent molecule, and the temperature coefficient of solvent ability is defined as the negative fractional rate of change of threshold concentration per degree; the coefficient may be positive or negative, a positive value implying the usual liquefaction of the gel with rise of temperature. In general, solvent molecules of compact shape exhibit positive coefficients, whereas molecules of the extended type may possess negative coefficients. Conditions where the inverted type of solubility–temperature relation can occur may be forecast from a consideration of the plots of relative viscosity against reciprocal concentration as determined at two or more different temperatures. Converging curves will, if they intersect, define the conditions under which sols will gelate with rise in temperature. Several instances are given of two- and three-component systems containing cellulose nitrate or acetate where such conditions obtain. Application of these principles to the formulation of gel-lacquers suitable for application by the new gel-lacquer technique of C. J. Malm and H. L. Smith, jun.[42] (see p. 420), would imply that curves exhibiting marked divergence would be favourable conditions especially suitable for this development. It is also shown that in the case of linear molecules possessing multiple solvating groups, the position of these groups influences the dependence of solubility on temperature, the inversion being the greater the further removed the active groups are from the ends of the chain.

Distillation.—Any discussion of general principles and of recent advances in this field is outside the scope of this section, but several items of interest in connexion with solvents may be mentioned. J. Griswold and C. F. Van Berg[43] report the successful fractionation of the well-known solvent Skellysolve C (a narrow C_7 hydrocarbon fraction of boiling range 190—233° obtained from mid-continent natural gas) into 14 components, the precise boiling points of which are given; the *n*-heptane fraction obtained was of a high degree of purity (99·47 mol.-%). According to R. F. Marschner and W. P. Cropper,[44] benzene forms azeotropes with all paraffins and naphthenes boiling within the range 60—100°. Data for known azeotropes as well as for six hitherto unknown azeotropes are given; *trans*-1 : 2- and *trans*-1 : 3-dimethyl*cyclo*pentane do not form azeotropes with benzene. Nomographs connecting vapour pressure and temperature with the boiling points at atmospheric pressure for pure liquids over the range −50° to 550° have been constructed by S. B. Lippincott and M. M. Lyman[45]; from these, if any two factors are known, the third may be obtained by a single setting of a straight-edge. The use of a shield of the type prescribed for the Standard distillation apparatus

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[42] *Ind. Eng. Chem.*, 1946, **38**, 937; B., 1947, II, 22.
[43] *Ibid.*, 170; B., 1946, II, 229.
[44] *Ibid.*, 262; A., 1946, I, 206.
[45] *Ibid.*, 320; A., 1946, I, 202.

(A.S.T.M. and B.S.S.) is criticised by D. Williams.[46] Superheating of the vapour occurs to an appreciable degree, causing errors in all probability greater than those likely to be due to draughts in a properly designed laboratory; it is better to insulate the flask separately from the source of heat, and the use of a formed-in-place heater of the type described by Krantz and Hufford[47] is to be preferred.

Analysis and Testing.—A. G. Keenan[48] has described the estimation of ethyl acetate in the presence of inert solvents by means of the violet colour developed on treatment with hydroxylamine hydrochloride in acid solution followed by ferric chloride; an accuracy of 1 to 2 p.p.m. is possible in the range of 10—200 p.p.m. R. C. Reincke and E. N. Luce[49] determine $\alpha\beta$-propylene glycol in the presence of ethylene glycol by periodate oxidation; the acetaldehyde and formaldehyde formed are aspirated through sodium bicarbonate solution containing glycine by means of a stream of carbon dioxide and the former is converted into the bisulphite compound. B. Warschowsky and P. J. Elving,[50] using a similar oxidative procedure, determine the aldehyde polarographically after simple distillation. P. W. Morgan[51] has explained the failure of earlier attempts to apply the Zeisel method to the estimation of ethylene glycol, ethylene being formed, thus leading to low results; by absorbing this in bromine water and correcting for the amount so found satisfactory results may be obtained. The author claims by this procedure to have determined the correct degree of substitution in hydroxyethylcellulose for the first time. In the iodometric estimation of peroxides, K. Nozaki[52] has shown that by using acetic anhydride as solvent in place of acetic acid, precautions against oxidation may be omitted and more rapid liberation of the iodine occurs. Removal of peroxides from ether and other solvents may be expeditiously effected by means of activated alumina according to W. Dasler and C. D. Bauer[53]; this method has the advantage that no water need be added, and may be employed in the case of water-soluble solvents. R. B. Pollak[54] draws attention to the effect of different metals on the ignition temperatures of solvents. In a case where cellulose lacquers were being forced-dried in an electrically heated stove fitted with iron trays the ignition temperature was 180—190°; when aluminium trays were substituted no ignition occurred up to 300°. The significance of this fact in the case of hitherto inexplicable fires occurring should not be overlooked. Flash-point apparatus is commonly constructed in copper or brass and attention to this aspect might be kept in mind.

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[46] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 157; C., 1946, 160.
[47] *Ibid.*, 1940, **12**, 752.
[48] *Canad. Chem.*, 1945, **29**, 857; C., 1946, 84.
[49] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 244; C., 1946, 160.
[50] *Ibid.*, 253; C., 1946, 160.
[51] *Ibid.*, 500; C., 1946, 248.
[52] *Ibid.*, 583; C., 1946, 249.
[53] *Ibid.*, 52; C., 1946, 84.
[54] ***Paint, Oil and Chem. Rev.***, **1945, 108,** ***No.*** **20, 14; B., 1946, II, 294.**

CELLULOSE ESTER AND ETHER LACQUERS.

By H. L. Howard, B.Sc., M.I.Chem.E., F.R.I.C.

Very few developments of a spectacular character have occurred during the year; rather has the progress made been towards consolidation and extension of our knowledge of the properties of the materials already in use and more searching investigation and correlation of these properties with those of the films produced.

W. Koch, H. C. Philipps, and R. Wint,[1] continuing investigations already reported (*Ann. Repts.*, 1945, **30**, **345**), conclude that cellulose nitrate of 30—35 centipoise viscosity may be used in furniture lacquers without sacrifice of cold check-resistance provided suitable resins (*e.g.*, Glyptal 2477) and plasticisers (dioctyl phthalate) are employed. A new technique is put forward by C. J. Malm and H. L. Smith, jun.,[2] by which unusually heavy coatings are obtained by dipping of cold (if necessary pre-cooled to 40° F.) articles in solutions of 40% solid content at temperatures up to 120° F., whereby the rapid cooling promotes gelation of the liquid film and ensures a smooth finish. Film thicknesses up to 0·015 in. per dip are thus possible and may be satisfactorily applied to wood, metal, paper, glass, and moulded plastic articles; cellulose acetate propionate and acetate butyrate are used with *iso*propanol–toluene solvent. The removal of excess of lacquer from dipped articles by means of an electrostatic field is claimed by Brush Development Co. and C. K. Gravley[3] to be particularly suitable for the coating of piezo-electric units, increased thickness being thus obtainable on the edges. Prevention of mildew formation on aircraft fabrics by the incorporation of naphthenates of copper,[4] zinc, or mercury in aircraft dopes is covered by patents.[5] The incorporation of silicon esters modified by the addition of alkaline-earth chlorides and ammonium phosphate into solutions of cellulose esters or ethers to yield non-inflammable dopes is claimed by C. Shaw.[6] In the finishing of leather H. M. Goppelt[7] claims that the addition of pentaerythritols to nitrocellulose lacquers produces bright scuff-free films; also vinyl copolymers dispersed in nitrocellulose solutions improve flexibility, and coloured emulsions so made remain stable for six months. Further claims using the phase reversal technique already reported for the dispersing of pigment–water pastes in nitrocellulose lacquers are made by H. Jennett and S. Meeker.[8] The paste index of a pigment is

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[1] *Ind. Eng. Chem.*, 1946, **38**, 518; B., 1946, II, 343.

[2] *Ibid.*, 937; B., 1947, II, 22.

[3] B.P. 570,552; B., 1945, II, 390.

[4] L. Roon, Assr. to Roxalin Flexible Finishes Inc., U.S.P. 2,330,998; B., 1946, II, 15.

[5] Roxalin Flexible Finishes Inc., B.P. 572,165 and 572,196; B., 1946, II, 50.

[6] B.P. 574,548; B., 1946, II, 156.

[7] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 245; B., 1946, II, 354.

[8] Assrs. to Interchem. Corp., U.S.P. 2,198,669; B., 1946, II, 138.

defined by J. F. H. van Eijnsbergen[9] as the number of grams of plasticiser required to convert 100 g. of pigment into paste; he considers that this corresponds to the point of maximum consistency during grinding. The same author points out[10] that in lacquers of high pigment concentration the properties of plasticisers tend to be masked, whereas with lower concentrations hardness decreases regularly with increasing plasticiser content.

The moisture-permeability of lacquer films has been shown by E. Rossmann and G. Schultze[11] to be very sensitive to pigment and plasticiser content, minimum transmission occurring at an optimum content in each case; the solvent used also influences the result, presumably by affecting the type of film structure produced. No correlation between vapour and liquid transmission rates could be established, though the former are in general less than the latter; for films of similar composition those possessing greater mechanical strength generally show lower transmission rates. W. König[12] finds that the development of anisotropy under mechanical stress in detached films is, in general, parallel with other evidence of internal strain; the coefficients of linear expansion of various films were of the order of 10^{-4} cm. per cm. per sec. J. S. Gourlay[13] has investigated the strain energy relationship of a number of cellulose derivatives, using the Rayleigh equation, $T = (-\alpha P + k_0)w + \beta P$, where the tension T produced by the pressure P, using a weight w of colloid per unit area, enables the constant k_0 characteristic of the colloid under test to be determined; α and β are constants vanishing at zero pressure. The constant k_0 is thus a measure of the strain energy content of the deposited colloid, and arises from the method of deposition on the substrate (linen). In the case of cellulose derivatives it is shown that this constant is not a function of the degree of nitration, acetylation, or esterification of the cellulose, nor is it a function of the molecular weight of the derivative. It is assumed, therefore, that it derives from the inability of the linear molecules to attain a condition of minimum potential energy owing to the viscosity of the liquid film exceeding a certain threshold value before alignment is possible. In the case of thermoplastic materials increase of temperature facilitates alignment and k_0 is permanently reduced. Under conditions of increasing humidity k_0 is reduced, but this change is reversible. The addition of plasticiser reduces the value of the constant, as might be expected.

The investigations of the Chicago Club (see *Ann. Repts.*, 1945, **30**, 348) on the properties of 49 plasticisers have been extended; in the second part of this investigation[14] the water-solubility, developed acidity, influence on the static charge and electrical properties of the film, ultra-violet

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[9] *Chim. Peint.*, 1942, **5**, 4; B., 1946, II, 390.
[10] *Ibid.*, 1943, **6**, 134; B., 1946, II, 390.
[11] *Korros. u. Metallschutz*, 1943, **19**, 13; B., 1946, II, 95.
[12] *Ibid.*, 5; B., 1946, II, 94.
[13] *J. Oil Col. Chem. Assoc.*, 1946, **29**, 94.
[14] *Off. Digest*, 1946, *No.* 262, 488.

transmission, and colour changes are recorded. Benzyl butyl phthalate is found to be inferior to tricresyl phosphate in respect of adhesion, elasticity, and scratch-hardness by J. F. H. van Eijnsbergen.[15] In another communication the same author[16] records data for diamyl and diheptyl phthalates. At low temperatures, tri-2-ethylhexyl phosphate maintains flexibility substantially unaltered, and a new linear type ester actually develops increased flexibility according to W. A. Woodcock.[17] R. A. Jacobson[18] claims the use of methyl β-p-tolylthiolpropionate and similar addition products of thiphenols and acrylic esters as plasticisers suitable for the manufacture of cinema film. The condensation of *cyclo*pentanone and similar ketones with acrylonitrile to form tetracarboxylic acids, the esters of which are suitable plasticisers for nitrocellulose and ethylcellulose, is claimed by H. A. Bruson,[19] whilst the Pittsburgh Plate Glass Co.[20] have covered a series of hydroxy-carboxylic esters prepared from monohydroxy-acids (*e.g.*, lactic) and unsaturated alcohols (*e.g.*, vinyl) followed by esterification with polybasic acids, their anhydrides, or acid chlorides. The use of crotonic acid as a raw material for use in coating compositions is reviewed by P. W. Blaylock.[21] H. L. Tuthill[22] points out the fallacy of relying on the loss at 150° as a criterion for the ageing characteristics of plasticisers; correlation of this loss with decreasing extensibility and increasing tensile strength of films after stoving enables a more satisfactory assessment of the performance to be made. In this way Paraplex G.20 and G.25 show advantages not otherwise noticed. The same author (*loc. cit.*) has examined the flexibility of films at low temperatures by determining the angle of droop over the range —60° to 20°; within this range Plasticisers 35 and 36 (amides of synthetic fatty aids) prove to be superior to dibutyl phthalate. Methyl*cyclo*hexyl acetate and methyl*cyclo*hexanone possess advantages over butyl acetate in respect of evaporative rate, dilution ratio, and lowered viscosity of nitrocellulose solutions and may be used in replacement of the latter up to 40% in admixture with toluene according to D. Cannegieter and A. Kooiker.[23]

As the result of a plea for the more systematic evaluation of resins for use in nitrocellulose lacquers put forward by E. A. Bevan,[24] R. J. Ledwith[25] has reported preliminary results obtained on 20 modified alkyd resins; each resin was incorporated into two standarised lacquers of 0·23 and 0·5 resin/nitrocellulose ratio, the amount of plasticiser (tricresyl phosphate) being adjusted in each case so that films just passed a bend test over

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[15] *Chim. Peint*, 1942, **5**, 320; B., 1946, II, 390.
[16] *Ibid.*, 270; B., 1946, II, 390.
[17] *Amer. Paint J. Conv. Daily*, 1945, **30**, *No.* 6B, 10; B., 1946, II, 131.
[18] Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,199,799; B., 1946, II, 155.
[19] Assr. to Resinous Products & Chem. Co., U.S.P. 2,329,432; B., 1946, II, 5.
[20] B.P. 574,606; B., 1946, II, 154.
[21] *Paint Manuf.*, 1945, **15**, 367; B., 1946, II, 132.
[22] *Ibid.*, 1946, **16**, 132.
[23] *Verfkroniek*, 1943, **16**, 105; B., 1946, II, 342.
[24] Cf. J. B. G. Lewin, *J. Oil Col. Chem. Assoc.*, 1946, **29**, 247; B., 1947, II, 85.
[25] *Ibid.*, 214.

a ⅛-in. mandril at 0°. The resultant films were examined for gloss, polishing, scratch-hardness, and solvent-resistance. If some such procedure can be adopted on a more general scale over a much wider field, comparable results will become available which will ultimately enable a proper assessment of any component to be made in a systematic manner, and it is to be hoped that co-operation between manufacturers and users will enable this to be done in the very near future.

W. A. Woodcock[26] has suggested a similar procedure for the evaluation of the relative efficiency of plasticisers in cellulose nitrate lacquers. A standard flexibility test of 12·5 alternate bending cycles at 20° before rupture of the film was adopted and the amount of plasticiser per 100 lb. of cellulose nitrate (½-sec.) required to attain this degree of flexibility was taken as the inverse measure of the efficiency of the plasticiser. Dioctyl phthalate and trioctyl phosphate exhibit marked superiority, the smaller amount of plasticiser required to produced films of equal flexibility enabling considerably higher tensile strengths to be obtained.

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[26] *Off. Digest*, 1946, *No.* 255, 172; *Paint Ind. Mag.*, 1946, **61**, 124; B., 1946, II, **463**.

PIGMENTS AND PAINTS.

By L. J. Brooks, A.R.I.C.,

Messrs. Henry Clark & Sons, Ltd.

As in recent years there has been a steady increase in the application of fundamentals to practice, shown, for example, by the continued promotion of schemes for co-operative investigation in this country and America, mainly designed to clarify the present confusing state of information on many points of simple technique. The problem of antifouling has revealed in a conspicuous manner the desirability of studying first principles, most evident in the notable American contributions to this subject.

Much activity is being devoted to the rheological problems of consistency, and attempts have been made to elucidate the peculiarities of paint flow and to define its optimum characteristics in manufacture and application. In the field of plant and equipment, it is not altogether improbable that the continued study and application of supersonic waves in other industries may one day render obsolete the present massive machinery of pigment grinding and dispersion.

The state of transition observed in the previous Report continues. Under the stimulus of war, certain fields were cultivated intensively while others were neglected. To-day there is a more even distribution of activity but a corresponding stimulus is lacking and will be so while the prevalent shortages and restrictions continue.

PIGMENTS.

There are few notable developments to report in the field of pigment manufacture. The conspicuous energy applied to titanium pigments during the war years has diminished, although various minor modifications in nucleaton and in coated particle types continue to appear; it is probable that underlying this apparent quiescence much effort continues to be directed towards evolving a fine-particle rutile type of superior whiteness.

In the production of hydrous titanium oxide, which may be converted into rutile titanium oxide at high temperature, A. T. McCord and H. F. Saunders[1] describe the preparation of γ-titanic acid by precipitation from an aqueous solution of a titanium fluoride compound with ammonia; this may be used as the nucleating agent in the hydrolysis of the main titanium sulphate solution. The Sherwin–Williams Co.[2] advocate the use of small quantities of zinc, calcium, or magnesium resinates when titanium oxide is pulverised in an air stream to reduce particle size and to improve texture and wetting properties.

Methods of manufacture of antimony oxide have been reviewed by M. Schofield,[3] who considers the fume method to be the most usual, although the precipitate from antimony fluoride solutions yield a good though expensive product. The use of 5% of zinc oxide in preventing yellowing due to the formation of antimonious sulphide, and the use of antimony oxide in preventing chalking of titanium oxide, are confirmed. Its use in fire-resistant coatings is well known, and it is established that this is due to the formation of antimonides on the metal surface under great heat. It is considered to have greater protective power than any other white pigment, and acts as a negative catalyst in film breakdown due to actinic agencies.

There is continued interest in the production of pigments from the alkaline earths and lead salts of the complex inorganic acids, *i.e.*, silicates, titanates, plumbates, and molybdates. In particular, a recent patent[4] describes the preparation of alkaline-earth orthoplumbates, such as those of calcium and barium, claiming that effective anticorrosive primers can be prepared which have good opacity and vary in colour from the white–brown calcium orthoplumbate to the black barium salt; the manufacture consists of heating a mixture of the alkaline-earth hydroxide or carbonate with litharge in air at 700—750° for 8 hours. L. E. Barton[5] describes the preparation of lead silicate pigments and indicates their use in paints, claiming that the basic lead silicate has greater resistance to checking and chalking, and better durability, than the more acidic varieties, but is more susceptible to light. A range of lead silicates may be manufactured by

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[1] Assrs. to Sherwin–Williams Co., U.S.P. 2,333,660; B., 1946, I, 131.

[2] U.S.P. 2,386,885; *Chem. Abs.*, 1946, 477.

[3] *Paint Manuf.*, 1946, **16**, 288; B., 1947, I, 23.

[4] Goodlass Wall & Lead Industries Ltd., and N. J. Read, B.P. 574,826; B., 1946, II, 219.

[5] U.S.P. 2,391,118; *Chem. Abs.*, 1946, 1325.

varying the proportions of lead oxide and silica, which are heated together below the fusion point. It is claimed[6] that a leaded zinc oxide may be prepared by treating an aqueous suspension of zinc oxide and zinc sulphate or zinc sulphite, with lead hydroxide, lead carbonate, basic lead sulphate, basic lead silicate, or preferably litharge; the product is filtered off and dried without calcination.

The significance of certain physical characteristics of both pigments and extenders in determining paint behaviour is shown by R. L. McCleary.[7] A definite relationship is considered to exist between the intrinsic properties of the pigment and the rheological properties of the pigmented paint. It is claimed that, in a given medium, the properties of consistency, suspension, levelling, sagging, and also the retention of tint and gloss may be related in a simple manner to the oil absorption, the pH, and the conductivity (*i.e.*, degree of ionisation and "soluble salts") of the pigment or extender; consideration of these critical factors therefore determines the selection of suitable extenders for paints. Flushing experiments are used to study the relative wetting properties of a number of common pigments and extenders.

K. Vettewinkel[8] discusses the influence of basic pigments on paint durability, in particular the behaviour of white lead sulphate and white lead carbonate of varying PbO content. The main function of basic pigments is to stabilise the film and prevent softening, by forming solid soaps with the low-molecular liquid carboxylic acids which are among the decomposition products of linseed oil films. Two types of white lead sulphate are indicated, the sublimed material in which the PbO content varies from 15% to 20%, and the precipitated variety with a PbO content of 25—27%. Exposure tests show that the more uniform and more reactive precipitated type has much better durability. The low PbO content of the sublimed variety resulted in excessive chalking and poor adhesion. That these properties are associated with the amount of lead soaps formed in the film is confirmed by microscopic examination. It is considered that the presence of reactive pigment is indispensable if stability and film integrity are required, but due consideration should also be given to the type of basic pigment used.

E. J. Dunn., jun.,[9] has studied the physical and chemical properties of red lead in simple oil paints. In comparison with primers prepared from zinc chromate, zinc dust, zinc oxide, aluminium, iron oxide, or lead chromate, it is shown that its specific permeability and water absorption are very low. Determinations of void spaces and oil absorption are also found to give relatively low values for read lead, and it is considered that a more compact film results from the heterogeneous size and shape of its

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[6] R. L. Hallows and V. C. Walker, Assrs. to Eagle-Picher Lead Co., U.S.P. 2,330,050; B., 1946, II, 137.

[7] *Off. Digest*, 1946, *No.* 258, 291.

[8] *Paint Ind. Mag.*, 1946, **61**, 64.

[9] *Off. Digest*, 1946, *No.* 260, 375.

particles. Its exceptional protective properties are, furthermore, identified with its basic character, which renders any water which does penetrate harmless to steel. Zinc chromate films were found to be swollen, and iron oxide films wrinkled, but red lead films were unaffected by immersion. New types of protective pigments are under test for use above and below the water-line ; these include barium potassium chromate and chromatised red lead ; the latter has the advantage over red lead of non-whitening on exposure to the atmosphere, and therefore providing a primer and finishing coat in one application. The stoicheiometry of lead oxides has been examined by A. Byström,[10] who has made an *X*-ray study of the non-stoicheiometric compounds believed to be formed in the decomposition of PbO_2, and shows that the range of homogeneity is in fact very limited, and probably non-existent. It is shown that PbO_2 cannot be less than $PbO_{1\cdot95}$; α-PbO_x is very nearly Pb_3O_5, and β-PbO_x almost exactly corresponds to Pb_2O_3.

Zinc yellow, or basic potassium zinc chromate, was widely used during the war in anticorrosive primers. W. F. Spengeman[11] discusses its peacetime applications, and indicates the principles on which correct formulation should be based. Primers for many different purposes are considered, and the need for a suitable means of evaluating them is discussed ; it was found that accelerated laboratory tests must be interpreted very conservatively, and it is considered that the only reliable means of rating anticorrosive paints are the outdoor fence and raft tests. The importance of considering factors other than the primer is clearly shown by panel photographs indicating the effect of clean and rusted steel, and the effect of different thicknesses of application. For marine primers, representing the most severe conditions of weathering, the zinc yellow content should be 40—60% of the total, and for less severe conditions it may be 20—40%. Durable, impermeable vehicles should be used, and it is stressed that no free oil should be present in primers for marine purposes.

The activities of the Marine Corrosion Sub-Committee of the Iron and Steel Institute on the problem of antifouling have been described in a comprehensive report by J. E. Harris and W. A. D. Forbes.[12] The salient features of this report, on the basis of an advanced issue, were given in last year's Report[13] and should require only a brief recapitulation here. The report presents a detailed marine biological description of fouling conditions in British waters. It is shown that the effect of bacterial slime on the development of fouling is less than hitherto suggested, and it is considered that the presence of rosin increased slime. It is confirmed that 10 mμg. per sq. cm. per day of copper provides an adequate leaching rate, and that even less suffices when mercury is present. A detailed

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[10] *Arkiv Kemi, Min., Geol.*, 1945, **20**, **A**, *No.* 11 ; A., 1946, I, 53. *Nature*, 1946, **158**, 275.

[11] *Paint Ind. Mag.*, 1946, **61**, 160 ; B., 1946, II, 466.

[12] *Oil & Col. Tr. J.*, 1946, **109**, 796; *J. Iron and Steel Inst.*, 1946, **154**, 297P; B., 1947, II, 122.

[13] *Ann. Repts.*, 1945, **30**, 359.

description of the leaching rate apparatus, based on the American method, is given. It is considered that mercury oxide suppresses the rate of leaching of cuprous oxide and that the leaching rate of cuprous oxide is roughly proportional to its concentration and increases with the acidity of the medium. A mortality index of numerous organic poisons is given; it is important, in this connexion, that the organic poison should be insoluble in the paint solvent, otherwise it may be brought to the surface and rapidly washed away. The most efficient in actual antifouling tests, especially in co-operation with cuprous oxide, were: organic arsenicals, *e.g.*, diphenylarsenious oxide; thiocarbamic acid derivatives, *e.g.*, ferric dithiocarbamate and tetramethylthiuram monosulphide; ethyl bromoacetate; derris extract; and mercury phenyl compounds. Attempts have also been made[14] to prepare a combined antifouling and anticorrosive paint, based on metallic zinc and an organic poison in an aqueous cementiferous medium.

The only other major investigation of an official character has been recorded in a series of cotributions throughout the year by the team of investigators working at the Woods Hole Oceanographic Institute and reported below. As an initial approach to the more general problem, and on the assumption that the efficiency of an antifouling film depends ultimately on the controlled dissolution of its toxic ingredients in sea-water, it is considered desirable to obtain exact information on the solubility of those components. J. D. Ferry and D. E. Carritt[15] determined the rate of dissolution of cuprous oxide in oxygen-free sea-water under various conditions of pH, temperature, salinity, ionic strength, and agitation. It was shown that, under conditions of high agitation, the rate of dissolution of cuprous oxide is proportional to the hydrogen-ion concentration, and is a linear function of the square of the chloride-ion concentration, at constant ionic strength. The mechanism of dissolution is not simple, and its theoretical elucidation is discussed in detail. It is considered that the rate-determining step in dissolution involves the complex ions $CuCl_2'$, and $CuCl_3''$, and only a very minor contribution is made by a process which does not involve Cl' ions. The process $\frac{1}{2}Cu_2O + H^{\cdot} + 2Cl' = CuCl_2 + \frac{1}{2}H_2O$ is the rate-determining step. The opinion advanced is supported by the good agreement between the observed values and those calculated from the energy data; the effect of temperature on the rate of dissolution shows, after correction for changes in the pH with temperature, good agreement with the Arrhenius relation. Natural sea-water has only a slightly depressant action on the rate of dissolution, and it is thus permissible to use artificial solvents in tests of leaching rate. The effect of oxygen is somewhat obscure, but is not considered to affect the rate of dissolution, apart from oxidising copper actually in solution to the insoluble basic oxychloride.

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[14] L. A. Jordan, P. J. Gay, and L. Whitby, B.P. 573,079; B., 1946, II, 58.

[15] *Ind. Eng. Chem.*, 1946, **38**, 612; B., 1946, II, 341.

As a complementary contribution to the above work, J. D. Ferry and G. A. Riley[16] extended the study of solubility to other compounds of copper, and to mercury chloride and mercury oxide. It is considered that the solubility of cuprous oxide, 5·4 μg. of Cu per c.c. in sea-water, is an optimum value which explains its general utility, *i.e.*, it is high enough to be effective, but not so high that its leaching rate from antifouling paints is too difficult to control. The solubility of cupric oxide and cupric hydroxide is negligible and may be computed from the energy data and dissociation constants. Basic cupric carbonate is of interest because of its formation as a by-product in the dissolution of antifouling films; its analysis shows considerable variation between different investigators. It is suggested that the composition of this complex varies with conditions and with ageing; the general tendency appears to be a gradual transition from basic carbonate to oxychloride. Further to the development of a leaching rate method by B. H. Ketchum, J. D. Ferry, A. C. Redfield, and A. E. Burns, jun.,[17] it is shown that the extremely high solubility of copper citrate provides a basis for an accelerated control test. It is of interest that the considerable development of green by-product on the film should be associated with antifouling efficiency as observed in certain exposure tests[18] in the sea off Miami.

The proportion of toxic substance in the paint formulation, the come position of the matrix, and the effect of these variables on leaching rate and the mechanism of antifouling action under different conditions are discussed in succeeding papers of this series. J. D. Ferry and B. H. Ketchum[19] consider, in the first instance, the case of antifouling paints formulated with insoluble and impermeable matrices, and show that adequate release of poisons may be maintained over a prolonged period by close packing of the film with a high concentration of cuprous oxide. When a cuprous oxide paint formulated in this way with a vinyl polymer medium is leached in sea-water containing sodium citrate, the film becomes completely denuded of cuprous oxide and only the insoluble and inerodible matrix remains. The proportion of solid must exceed 30% by volume and antifouling coatings of this type have the advantage of being effective when applied as thin films with good resistance to erosion. Ketchum, Ferry, and Burns[20] then consider the maintenance of leaching rate in an antifouling paint formulated with a soluble matrix, *i.e.*, one containing acidic resins, which loses both toxic and matrix simultaneously as a result of saponification of the media in the slightly alkaline sea-water, viz., on the so-called "exfoliation" principle; this has the advantage of gradually exposing stores of poisons originally buried deep in the film. It is shown

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[16] *Ind. Eng. Chem.*, 1946, **38**, 699; B., 1946, II, 389.

[17] *Ibid.*, 1945, **37**, 456; C., 1945, 184.

[18] Bakelite Corp., *Off. Pub. Bd., Rept. P.B.* 12.149, 1942; *N.P.V.L. Abs.*, **1946**, 115, 121.

[19] *Ind. Eng. Chem.*, 1946, **38**, 806; B., 1946, II, 427.

[20] *Ibid.*, 931; B., 1947, II, 22.

that the substitution of neutral or insoluble resins may destroy the ability of the paint to maintain an effective leaching rate. It is stated that the dominant factors to be considered in devising a suitable antifouling paint are the solubility of the matrix and the solubility of the poisons. In the case of an insoluble matrix, the optimum conditions are provided by a maximum concentration of poison in a thin film, and other things being equal in the case of a soluble matrix, the converse should hold good, *i.e.*, a minimum concentration and increased thickness of film.

The mechanism of blister formation and adhesion in under-water metal-protective paints has been studied by W. W. Kittelberger and A. C. Elm.[21] A paint system consisting of one coat of zinc chromate primer and one coat of a low-gloss alkyd hull paint was applied to various materials, which were immersed in distilled water and in solutions of sodium chloride of varying osmotic strength, the variation being introduced by the addition of sucrose. It was shown that blistering decreases with increasing osmotic strength of the bath, and it is indicated that water is transferred through the face of the paint film under the influence of, and at a rate determined by, the difference in osmotic pressure of the bath and the solution formed within the paint system by the absorbed water. The minimum osmotic pressure of the external solution required to prevent blistering varied with the nature of the substrate, and it is therefore suggested that this fact provides a basis for measuring the adhesion level of the test coating for a given surface. A more fundamental study of the process of water absorption and permeability has been presented by C. F. Drake and H. W. Keenan.[22] The method described is an elegant adaptation of Stock's micro-balance for the determination of vapour density, and represents an important contribution to current apparatus used in permeability studies. The method is a dynamic one, and determines the actual weight of water passing through unpigmented rosin and metal rosinate fims. The transfer of water may be continuously observed by the increase in weight (due to the absorption of water vapour) of phosphorus pentoxide carried on one arm of an electromagnetic microbalance, connected to a diffusion cell by means of a Pyrex glass sleeve. Paper films of rosin, copper, zinc, magnesium, and cadmium rosinates, and rosin plasticised with polyvinyl butyrate resin, and a mixture of boiled linseed oil and hydrogenated methyl abietate, were examined. It was found that the permeability of the rosin soaps differed little from that of the normal rosin, but the effect of plasticising the film was very marked and is of special significance in antifouling studies. A mathematical treatment of the results is given. Consideration of the energy data shows that the exponential change of permeability with temperature is governed by the activation energy of the diffusion process, and the heat of dissolution of water in the substance of which the membrane is composed.

The evaluation of paint consistency continues to be the subject of much

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[21] *Ind. Eng. Chem.*, 1946, **38**, 695; B., 1946, II, 389.

[22] *J. Oil Col. Chem. Assoc.*, 1946, **29**, 273; B., 1947, II, 121.

activity. H. Green and R. N. Weltman[23] consider the practical implications of consistency changes arising from thixotropic breakdown during the manufacture of paint, and particularly the effect of momentary breakdown on the delicate synchronisation of the printing ink process.

The long held view that there is some intimate relation between pigment wetting and paint structure continues to gain acceptance. H. Mills[24] applies the classical technique of surface physics to pigment surface, and shows how real may be the association between the surface forces of the discrete particles and the rheological behaviour of the particles in bulk. The existence of sigmoid curves and the presence of the element of time, as features common to measurements of surface physics and paint rheology, are considered to indicate a common origin of disturbance, *i.e.*, the separation of a phase; here, the phase is considered to be an absorbed envelope or skin of medium surrounding the particle, and in accordance with the concept of absorption, differing in the concentration of its constituents from that of the bulk of free liquid. The size of the micelle of enveloped pigment is considered to affect the mobility of the paint, and it is shown that there is a close correlation between the activity of pigment surface and the phenomena of paint rheology, which lends support to the theory of thixotropy advanced. W. Carr,[25] in a clear and comprehensive description of the flow properties of pigment–oil mixtures, shows how, from the originally cruder concept of "false body" and the even more loosely applied term "thixotropy," there has emerged the possibility of identifying and controlling the familiar characteristics of paint: sagging, brushmarks, levelling, and storage properties, in terms of certain clear and unequivocal structural nomenclature. Experiments are described using the Pryce-Jones viscometer where with increasing pigmentation a true fluid may be made to pass through the series: true fluid → anomalous fluid → excessive anomaly; the process may be reversed or controlled by judicious use of wetting agents.

The wetting theory is at present much in favour as it appears to explain the facts, especially the action of surface-active agents. Nevertheless, support for the less widely accepted electro-mechanical theory of thixotropy has been provided[26] by the reported variation of dielectric constant of oil and pigment mixtures with disturbance and rest in a manner exactly analogous to that of viscosity with shear and time.

While respecting the need for a fundamental study of paint flow, the requirements of works control justify a more pragmatic approach. The attractive simplicity of the Ford cup and the palette knife continues to appeal to the practical man requiring a quick and ready means of evaluating consistency. H. G. Rains[27] indicates the need to standardise

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[23] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 167; C., 1946, 222.

[24] *J. Oil Col. Chem. Assoc.*, 1946, **29**, 128; B., 1946, II, 342.

[25] *Ibid.*, 47; B., 1946, II, 294.

[26] A. Parts, *Nature*, 1945, **155**, 236; B., 1946, II, 215.

[27] *Paint Manuf.*, 1946, **16**, 37.

consistency-measuring instruments, and illustrates the difference in size, shape, and length of orifice between the British and American No. 4 Ford these differences, in presumably identical instruments, are contrary to cup; Poiseuille's law. It is shown that if the Ford cup is redesigned to provide a steeper angle of cone (64° against 39—40°) and a variable bush, it is then capable of dealing with thin paints, treacly paints, and paints of ordinary consistency. Provision for constant temperature, and a protective skirting around the orifice, are also advocated. F. K. Daniel and P. Goldman[28] describe a simple and rapid technique for the evaluation of dispersions and dispersing agents. A palette knife, a glass plate, and a burette are the tools which form the basis of this method, which is, however, reinforced by a sound theoretical interpretation of the results. The test comprises mixing the dry powder with the dispersing solution and measuring the amount of liquid required to produce two characteristic and reproducible consistencies and observing the rheological phenomena of the mixture. These two consistencies are represented by a "wet point" and a "flow point." It is shown that liquid-powder systems can exist in three distinct and recognisable rheological groups : dull putty-like flocculates, plastic in behaviour and representing poor dispersions; good dispersions, showing at first great resistance to sudden pressure or kneading, and than a few moments later flowing readily into a glossy pool; fair dispersions in which the liquid gradually combined with the pigment, the resultant mixture appearing dull as in flocculates, yet when gently tapped it becomes glossy and begins to flow, but ceases to do so as soon as the disturbance ends. A good dispersion displays active dilatancy at high powder concentration; a poor one never shows any flow characteristics, and a fair dispersion displays passive dilatancy at high concentration and visible thixotropy at lower pigment concentrations.

R. Buchdahl and M. F. Polglase[29] present two attractive methods for the determination of covering power and film thickness of printing ink and paint films. Both depend on the use of tracer materials; in one case a dye which may be Soxhlet-extracted and the transmission coefficient at a given wave-length measured, and in the other case, a trace of radioactive isotope of phosphorus, as pentachloride, preferably a liquid isotope, is introduced into the printing ink or paint, and the activity of the print or film determined against background activity due to cosmic radiation using a conventional Geiger counter.

P. F. Luft[30] has studied existing methods for the determination of hiding power and submits a new method which is claimed to express this value in absolute units, and to be more closely related to practical performance of paint than conventional determinations of hiding p of The standard method of measuring hiding power based on the amown to paint required to obliterate a given black and white contrast

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[28] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 26; C., 1946, 135.
[29] *Ibid.*, 115; C., 1945, 241; 1946, 172.
[30] *Ibid.*, 484; C., 1947, 15.

have no practical significance, since the paint must be applied in abnormal thickness; it is considered, therefore, more useful to determine what contrast may be obliterated by a single normal coat, rather than which thickness should be applied to obliterate a given contrast. The paint is applied on test charts which have both black and white backgrounds provided with graduated scales of grey shades. The hiding power, or better the contrast-obliterating power, is ascertained by two constants numerically equal to the contrast between the black and white backgrounds; it may be defined as the negative log of the ratio of light reflexions of background and grey spots. The practical results are confirmed by a mathematical treatment based on the Kubelka–Munk[31] theory, based on reflectance ratio constants derived by D. B. Judd, E. F. Hickson, and A. J. Eickhoff.[32] The method is said to be superior to standard methods as it does not require a standard paint, is independent of colour and finish, and may be carried out in a single simple operation using the naked eye, on both fresh and dry films.

The problem of examining and assessing paint sediments has been studied by A. Hancock and T. F. Brown,[33] who have evolved a new and simple type of penetrometer, which comprises a steel plunger tipped with a steel hemisphere, and connected to a can supplied with water from a constant-head reservoir; the method permits the relative hardness of the various stratified layers to be computed. The familiar difficulties of correlating accelerated weathering tests with practical performance are discussed by R. N. Wheeler,[34] who concludes that it is in fact very difficult to find any exact correlation between durability and humidity or salt-spray tests although their utility as general sorting-out tests is confirmed. The problem of recording the performance of paint exposure panels has been examined by N. B. Garlock and E. W. McMullen,[35] who have devised a nomograph based on characteristic paint failures, which is claimed to provide a systematic and universal rating.

A number of marked improvements in the use of silicone resins are described in a progress report by J. R. Patterson.[36] At present, however, the commercial use of silicones is restricted to stoving enamels and heat-resisting finishes, and this subject is comprehensively reviewed in a series of contributions by R. L. Frost.[37]

ANALYSIS.

I. Baker and R. S. Gibbs[38] have examined the problem of determining metallic copper in cuprous–cupric oxide mixtures, and show that the

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[31] *Z. tech. Physik*, 1931, **12**, 593.
[32] *J. Res. Nat. Bur. Stand.*, 1937, **19**, 287.
[35] *Pain* *Col. Chem. Assoc.*, 1946, **29**, 155; C., 1946, 315.
[36] *Off.* 71; B., 1947, II, 22.
[37] *Paint* *Diges* *ag.*, 1946, **61**, 88; *Off. Digest*, 1946, *No.* 253, 88; B., 1946, II, 214.
[38] *Ind.* *Manuf.*, *No.* 258, 281; *No.* 261, 439.
Eng. Chem. **16**, 294, 356, 382.
1946, **18**, 124; C., 1946, 147.

influence of particle size and shape provided difficulties in earlier methods which their method obviates.

E. R. Wright and R. H. Delaune[39] describe the separation of calcium in the presence of excess of magnesium by an oxalate method.

N. S. Bayliss and R. W. Pickering[40] determine small amounts of cobalt in presence of other metals, by a preliminary extraction of the thiocyanate complex, before determination by other microchemical methods, viz., the nitroso-R-salt method of H. R. Marston and D. W. Dewey.[41]

H. Barnes[42] describes a simple method of determining copper and mercury in antifouling compositions when present together in small samples of antifouling paint, viz., the dry film of small panels exposed to the leaching rate tests of the Marine Corrosion Sub-Committee, and also paint scrapings from ships in service.

A more recent alternative to diphenylthiocarbazone in the colorimetric determination of small quantities of mercury in organic material is advocated by J. Cholak and D. M. Hubbard.[43] This reagent is the analogue, di-β-naphthylthiocarbazone, of which the mercury complex is considered to be more stable. The process is similar to the dithizone procedure as described by Barnes (*loc. cit.*), except that the digestion is effected with sulphuric and nitric acid, and the influence of copper is suppressed by means of sulphuric acid and sodium thiosulphate.

W. Pugh[44] suggests the use of mercurous perchlorate as volumetric reagent for the determination of iron.

H. Crossley,[45] in a brief but excellent survey, describes the peculiar difficulties of paint analysis. A number of useful points of technique and several modern methods are indicated. The determination of small quantities of volatile metals, or those difficult to centrifuge, such as mercury or antimony, is best effected by the method of "wet oxidation." Small quantities of metallic soaps, *e.g.*, the napthenates of cobalt, manganese, lead, copper, zinc, may be accurately determined by extracting a solution of the soaps in white spirit with the appropriate hot acid. Reference is made to the method of A. D. Whitehead[46] in the microscopic investigation of paint failure. The method of centrifuging is advocated for the separation and analysis of competitors' paints, and the need to ignite the separated pigments is stressed; an exception is red lead, which is decomposed by traces of organic matter. The increasing difficulties of analysing the organic portion of the paint are described, but reference is made to methods for determining phthalic and maleic acids simultaneously present, and of identifying phenolic resin by using 2 : 6-dibromobenzoquinonechloroimide.

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[39] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 426; C., 1946, 232.

[40] *Ibid.*, 446; C., 1946, 241.

[41] *Austral. J. Exp. Biol.*, 1940, **18**, 343.

[42] *Analyst*, 1946, **71**, 578; C., 1947, 56.

[43] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 149; C., 1946, 197.

[44] *J.C.S.*, 1945, 588; C., 1945, 244.

[45] *J. Oil Col. Chem. Assoc.*, 1946, **29**, 292; C., 1947, 73.

[46] *Ibid.*, 1939, **22**, 139.

INDIARUBBER AND ALLIED MATERIALS.

By D. F. Twiss, D.Sc.

The past year has seen a remarkable contrast in the outlook of some of the contributions to the applied chemistry of rubber and rubbery materials. In the first place there has been a considerable flow of details on the methods of production and purification, the properties and processing, and the storage and polymerisation or copolymerisation of various intermediate products,[1] particularly butadiene, *iso*butene, styrene, acrylonitrile, and cyanobutadiene, used in the manufacture of synthetic rubbers. This is explained partly by the post-war release of information from America but arises largely from reports which have resulted from official interviews of technical representatives of the Allies with German chemical technologists and from visits of the former to Germany for investigation of war-time developments, in particular those arising from the extreme shortage of natural rubber and the consequent dependence on synthetic rubbers.

The emergency pooling of technical information inside various industries also appears to have led since to greater freedom of publication, and accounts have been made available of many war-time measures, some of which mark improvements on older processes.

The enforced search for alternative materials to plantation *Hevea* rubber has now given rise to the publication of details concerning attempts to obtain rubber of passable quality, and by economically reasonable methods, from plant sources ; most of these sources were known previously but their characteristics and practical possibilities had not been investigated so systematically. To guayule,[2] which had already received much scientific attention, must now be added *Cryptostegia grandiflora*, from which the rubber can be extracted by bacterial[3] and/or chemical[4] treatment of the leaves, and of which the characteristics of the latex and rubber,[5] even derived from various parts of the plant,[6] have been recorded. Trial has also been made of this rubber prepared from plants grown in

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[1] The publications on these points, including papers and patents, are so numerous, totalling the best part of one hundred, if not more, that consideration of space prevents their detailed record.

[2] H. Tint and J. M. Cumming, *India Rubber World*, 1946, **113**, 509 ; B., 1946, II, 220.

[3] J. Naghski, J. W. White, jun., S. R. Hoover, and J. J. Willaman, *J. Bact.*, 1945, **49**, 563 ; B., 1946, II, 436. S. R. Hoover, T. J. Dietz, J. Naghski, and J. W. White, jun., *Ind. Eng. Chem.*, 1945, **37**, 803 ; B., 1945, II, 391.

[4] C. E. Linscott and J. McGavack, *Rubber Age*, 1946, **59**, 441 ; B., 1946, II, 436. S. S. Bhatnagar, Karimullah, and U. Shanker, *J. Sci. Ind. Res., India*, 1946, **4**, 654 ; B., 1946, II, 347.

[5] A. K. M. Pillai, *Current Sci.*, 1946, **15**, 73 ; B., 1946, II, 393; *Trans. Inst. Rubber Ind.*, 1945, **21**, 242 ; B., 1946, II, 263. R. H. Siddiqui and S. A. Warsi, *Indian J. Pharm.*, 1945, **7**, 75, 117 ; B., 1946, II, 139, 346.

[6] R. Blondeau and J. T. Curtis, *Rubber Age*, 1946, **59**, 57 ; B., 1946, II, 436.

various parts of India.[7] Cultivation of *Taraxacum kok-saghyz* has been the subject of extensive experiment in the United States[8] and, under the abnormal conditions then obtaining, showed considerable promise. Other plants or trees investigated include *Lobelia excelsa* and *Chonemorpha macrophylla*,[9] the common milkweed,[10] *Euphorbia cespitosa*[11] root, *Castilla*,[12] and *Solidago leavenworthii*[13] (goldenrod). A wide range of Indian latex-bearing plants has also been investigated.[14]

The change in the world position with respect to the availability of supplies of plantation *Hevea* rubber has reduced much of the above work to the level of historic interest. The unexpected discovery that the rubber plantations had suffered relatively little permanent damage while in Japanese hands, coupled apparently with a remarkably rapid easing of the labour position on the plantations, has led to an early prospect of renewed large supplies of *Hevea* rubber. From November 18, 1946, permission was granted for resumption of private trading in rubber and for the re-establishment of the London Rubber Market. For the next year or so, during replenishment of stocks and change-over of manufacturing processes to *Hevea* rubber, there will probably be a ready sale for deliveries of natural as well as of synthetic rubber. In 1946 the respective totals of natural and synthetic rubber consumed were probably approximately equal but the proportion of the former will increase rapidly and by 1948 a surplus of total raw rubber may be possible. The less economical ethanol process for the production of butadiene has already been discontinued in the United States and other of the less economical synthetic plant-units are likely to be eliminated gradually.

A striking reply to the claims frequently made earlier to the effect that synthetic rubbers, because of their controlled method of production, would be remarkably uniform in quality and show less variability than the plantation product is implicit in a report that commercial rubbers of the Buna S type show considerable variability[15] both in the raw and in the vulcanised condition; such variation, moreover, is in accord with evidence from the infra-red spectra for synthetic rubbers of the Buna N type as to irregularity in the proportions of 1 : 2 and 1 : 4 polymerisation coupling.[16]

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[7] K. L. Budhiraja, *Current Sci.*, 1943, **12**, 154; B., 1946, II, 220.

[8] Anon., *Rubber Age & Synthetics*, 1946, **27**, 50; B., 1946, II, 220. R. K. Eskew, *India Rubber World*, 1946, **113**, 117; B., 1946, II, 220. *See also* J. McGavack and P. J. Faulks, *Rubber Age*, 1945, **58**, 204; B., 1946, II, 139. A. A. Drobkov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **47**, 362; B., 1946, II, 59.

[9] R. H. Siddiqui and S. A. Warsi, *J. Indian Chem. Soc., Ind. Ed.*, 1945, **8**, 63; B., 1946, II, 220.

[10] R. V. Tomkins and N. H. Grace, *Canad. J. Res.*, 1946, **24**, **F**, 146; R. W. Watson and N. Levitin, *ibid.*, 95; B., 1946, II, 302.

[11] R. Nico, *Rev. Fac. Cienc. Quim., La Plata*, 1943, **18**, 7; B., 1946, II, 302.

[12] E. M. Blair and T. F. Ford, *Ind. Eng. Chem.*, 1945, **37**, 760; B., 1945, II, 392.

[13] M. L. Rollins, T. L. W. Bailey, jun., and I. V. de Gruy, *India Rubber World*, 1945, **113**, 75; B., 1946, II, 139.

[14] K. L. Budhiraja and R. Beri, *Forest Res. Inst. Dehra Dun, Indian Forest Leafl.* 70, 1944; B., 1946, II, 102.

[15] G. Salomon and C. Koningsberger, *J. Polymer Sci.*, 1946, **1**, 366.

[16] H. W. Thompson and P. Torkington, *J.C.S.*, 1944, 597; A., 1945, I, 45.

That the best types of synthetic rubbers have given valuable service to the contestants on both sides[17] during the war years is acknowledged and, except possibly for purposes making the most exacting demands on the material, *e.g.*, in large heavy-duty tyres, the results have been gratifying.

After the troubles attendant on the conversion of the manufacturing industry from natural rubber to synthetic rubber, it seems almost paradoxical that the inverse reconversion to natural rubber, because of new labour and modified processing methods introduced during the synthetic-rubber period, must also similarly be attended by considerable manufacturing troubles and difficulties.

Regret must be admitted that during the past seven years, with conditions so favourable to the establishment of a synthetic-rubber-producing industry, circumstances in Great Britain, except for an apparently isolated case of large-scale production of Thiokol plastic in solid and latex form, prevented any substantial manufacture of synthetic rubber.

RUBBER LATICES.

On account of the need to supplement supplies of natural latex, the literature dealing with aqueous emulsions of rubber has been increased by contributions concerning various types of artificial dispersions of reclaimed rubber, as well as of synthetic rubbers.

From the Department of Rubber Science at Delft there has appeared during the year a doctorate thesis by J. H. E. Hessels recounting a systematic investigation into the "polydispersity" of *Hevea* latex, covering the relation between the size of the latex particles and the composition and structure of the rubber. Careful centrifugal fractionation of preserved latex enables the separation of a number of fractions in which the average particle size ranged from 1·1 to approximately 0·15 μ. In accordance with expectation, the increased total surface per unit of weight of rubber leads to an increased proportion of adsorbed serum substances in the rubber from the latex with smaller particles; particle size therefore is found to have a considerable influence, directly and indirectly, on the composition of the rubber. The evidence also suggests that increase in the degree of polymerisation is greater in the larger particles.

Other publications of some general interest in connexion with latex relate to a rapid estimation[18] of the rubber content of guayule, and possibly other forms of, latex by a count of the particles under the microscope; to the formation of Liesegang rings[19] when zinc chloride solution is allowed

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[17] Anon., *Rubber Age*, 1945, **57**, 565, 692; **58**, 210; B., 1946, II, 141. *See also* E. W. Pittman, G. O. Trenchard, M. J. Tierney, and W. C. Asbury, *India Rubber World*, 1946, **113**, 647; B., 1946, II, 302. *Combined Intelligence Objectives Sub-Commee.*, 1944, *Items* 2 and 22, *File* V–30 and XII–18; B., 1946, I, 309. *Ibid.*, 1945, *Item* 22, *File* VII–8; B., 1946, II, 352.

[18] R. T. Whittenberger and B. A. Brice, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 209; C., 1946, 172.

[19] G. T. Verghese and M. A. G. Rau, *J. Sci. Ind. Res., India*, 1945, **4**, 11; B., 1945, II, 392.

to diffuse into latex; to a viscometer permitting measurements during thixotropic recovery with compounded latex[20]; and to storage conditions which proved effective in keeping centrifuged *Hevea* latex in good condition over the period 1941–45, the content of rubber and of ammonia, the pH, "KOH number," mechanical sterility, and odour all remaining satisfactory.[21]

Comparison of *Hevea*, *Castilloa*, and *Cryptostegia* latices[22] indicates that although the particles of all three appear to have a protein covering, the last, from their electrophoretic behaviour, appear to have only a partial covering, the particle surface consisting mainly of exposed rubber hydrocarbon. This difference is also reflected in the coagulation behaviour.

A process has been elaborated for the separation of crystalline quebrachitol from the serum obtained in coagulation of *Hevea* latex.[23] An improved method of recovery of the small proportion of rubber remaining in the "skim" which is obtained in large volumes in the creaming or centrifuging of latex has also been described; the method is based on initial separation of the rubber from the skim by flocculation and then washing, and the product has a protein content comparable with that of acid-coagulated rubber from ordinary latex. In a modified method for the production of preserved *Hevea* latex with a low "KOH number," fresh latex containing no preservative, or only a non-alkaline one such as formaldehyde, has its carbon dioxide content first reduced by passage of moist air free from carbon dioxide before raising the pH to at least 7·5 by addition of ammonia.[25]

Pectin extracted from the seeds of the coral wood tree (*Adenanthera pavonina*) is effective as a creaming agent for latex.[26] Another method[27] for applying vegetable material to raising the concentration of latex is by bringing the former in discrete portions, *e.g.*, as seeds, in contact with the latex so that water is removed by absorption; this procedure avoids substantially the introduction of soluble impurities into the latex but large-scale operation may be inconvenient.

Amongst German war-time developments is a method, based on a new principle, for raising the concentration of synthetic-rubber latex from an initial value of 25 or 30% to about 50%; the process is applicable to Buna S latices but not to Buna N. The Buna S latex (Igetex S or SS) is cooled to its "Stockpunkt," at which a pasty consistency is attained, and is then beaten to a fluid mass from which a concentrated cream

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[20] M. Mooney, *J. Colloid Sci.*, 1946, **1**, 195; B., 1946, II, 348; C., 1946, 222.

[21] J. McGavack, *India Rubber World*, 1946, **113**, 808; B., 1946, II, 263.

[22] W. Seifriz, *ibid.*, 1945, **112**, 587; B., 1945, II, 391. *Ibid.*, 729; B., 1946, II, 139. *See also* A. K. M. Pillai, *Trans. Inst. Rubber Ind.*, 1945, **21**, 242; B., 1946, II, 263, 392. R. Blondeau and J. T. Curtis, *Rubber Age*, 1946, **59**, 57; B., 1946, II, 436.

[23] B.P. 572,128; B., 1946, II, 60.

[24] B.P. 574,266; B., 1946, II, 141.

[25] B.P. 572,134; B., 1946, II, 60.

[26] G. T. Verghese, *Current Sci.*, 1945, **14**, 200; B., 1946, II, 25.

[27] U.S.P. 2,332,902; B., 1946, II, 265.

separates on standing.[28] Mention at this point may be made of methods adopted by the German industry for the heat-sensitisation[28] of most Buna latices for dipping or moulding operations. Not only is use made of the addition of calcium chloride in the presence of a protective agent (*e.g.*, Emulphor O, an additive product of ethylene oxide and oleyl alcohol) on well-known lines, but heat-sensitisation is also, alternatively, effected by adding an aqueous solution of polyvinyl methyl ether (so-called Igevin M50), which becomes insoluble when the temperature is raised above 85°.

Methods which have been published for modifying latex in other ways cover preservation by alkali plus a small proportion of quinoline,[29] heat-sterilisation,[30] purification of formaldehyde-preserved latex by a flocculation and creaming process,[31] thickening with an alkali-soluble acid cellulose acetate dicarboxylate,[32] and the raising of surface tension[33] by adding up to 5% of a sparingly soluble salt of an alkaline-earth metal, *e.g.*, calcium carbonate.

Several useful communications have been made on some of the uses to which rubber latex was increasingly applied during the war period. L. H. Griffiths[34] has reported on the use of synthetic latices as substitutes for natural latex in latex–casein–hydraulic cement mixtures for flooring etc., considerable light also being thrown on the general principles. GR-S latex and even artificial dispersions of reclaimed rubber can be used but are inferior; Neoprene latex is applicable satisfactorily whilst polyvinyl acetate dispersions, in that they give non-sticky dirt-repellent surfaces, have an advantage even over natural latex. This problem of finding war-time alternatives for natural latex for general purposes has also been discussed by S. D. Sutton.[35] GR-S latex was not good enough for dipped goods although it gave reasonable service in the treatment of rayon cord for tyres. Neoprene 571 latex was applicable almost generally except for surgeons' gloves and for very thin dipped goods. Utilisation of dispersions of Thiokol was limited because of the tendency of this material to cold flow and because of its odour. A somewhat different type of latex–cement composition from that mentioned at the commencement of this paragraph, intended as a self-setting flexible adhesive, comprises a mixture of unvulcanised and vulcanised latex with sodium silicate and aluminous cement.[36]

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[28] *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXII–21; B., 1946, II, 350. *Brit. Intelligence Objectives Sub-Commee.*, *Final Rept.* 349, *Item* 22; B., 1946, II, 347. *See also* S. D. Sutton, *Trans.-Inst. Rubber Ind.*, 1946, **22**, 163; B., 1947, II, 90.

[29] U.S.P. 2,327,940; B., 1945, II, 393.

[30] U.S.P. 2,327,939; B., 1945, II, 394.

[31] U.S.P. 2,327,115; B., 1945, II, 353.

[32] U.S.P. 2,326,956; B., 1945, II, 353.

[33] U.S.P. 2,203,866; B., 1946, II, 184.

[34] *Trans. Inst. Rubber Ind.*, 1946, **22**, 170; B., 1947, II, 90.

[35] *Ibid.*, 161; B., 1947, II, 90.

[36] U.S.P. 2,335,104; B., 1946, II, 306.

Advances in the use of rayon cord for tyres have led to increased need of latex for treatment of the cord, thereby ensuring a good bond with the rubber of the tyre carcase. M. M. Heywood has surveyed this method of rayon treatment[37]; the most popular bath for the purpose comprises latex (natural or GR-S) with a resorcinol–formaldehyde resin which is still in the soluble condition; alternative baths contain latex, reclaim dispersion, and casein, or latex, reclaim dispersion, and hæmoglobin. A comparative investigation of the tyre-cord dipping characteristics and behaviour of preserved natural latex, GR-S latex types 2 and 3, and a dispersion of whole-tyre reclaim has been published by H. H. Gillman, R. Thoman, and D. Chalmers.[38] In the shoe industry also the problem of finding a satisfactory substitute for natural latex as an adhesive for assembling purposes has been acute. Although dispersions of selected reclaims, with added tackifying agents, can be used the only really satisfactory alternative[39] to natural latex appears to be Neoprene latex with added tackifier.

Early days in the compounding of latex, and of its applications to the production of moulded goods, are recalled by V. H. Wentworth's account of experiments and the successful emergency methods eventually adopted, in the difficult conditions of a prisoners' of war camp in Singapore, to meet the need of unfortunate captives for the repair and replacement of ebonite dentures.[40]

Quite naturally much information has been forthcoming on a wide variety of artificial or synthetic latices, dealing with such aspects as their formation, characteristics and their modification, and uses. Amongst the types may be mentioned the formation of aqueous dispersions from natural rubber[41]; the formation of latices of GR-S, Buna N type rubber,[42] and polybutadiene[43] by emulsion polymerisation, and the emulsification of preformed GR-S[44] or poly*iso*butene.[45] Polyvinyl acetate dispersions may be made by emulsion polymerisation or by artifically dispersing the preformed polymer.[34] Interesting information has also been published on the various types of GR-S latex,[46] Buna S latex[47] (Igetex), and Thiokol[48] latices and on their characteristics. The method of applying Neoprene latex to the production of flexible moulds has also been

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[37] *Trans. Inst. Rubber Ind.*, 1946, **22**, 159; B., 1947, II, 90.

[38] *Rubber Age*, 1946, **58**, 591; B., 1946, II, 263.

[39] L. E. Puddefoot, K. J. George, and A. M. Hall, *Trans. Inst. Rubber Ind.*, 1946, **22**, 167; B., 1947, II, 90.

[40] *Ibid.*, 149; B., 1947, II, 91.

[41] B.P. 575,284; B., 1946, II, 223.

[42] B.P. 576,157: B., 1946, II, 224.

[43] L. W. Rainard, *India Rubber World*, 1946, **114**, 67; B., 1946, II, 349.

[44] B.P. 576,665; B., 1946, II, 266.

[45] U.S.P. 2,330,504: B., 1946, II, 21.

[46] F. S. Conover, *Rubber Age*, 1945, **58**, 207; B., 1946, II, 140.

[47] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 349, *Item* 22; B., 1946, II, 347.

[48] B.P. 572,830; B., 1946, II, 61. B.P. 578,656; B., 1946, II, 431.

described.[49] Judged by practical experiences with the application of electro-deposition to the manufacture of rubber goods from latex, the electro-deposition of vinyl plastics from emulsions[50] is unlikely to have important industrial consequences. Application by dipping or spreading is likely to be more encouraging, as indeed is indicated by experiments with vinylidene chloride latices.[51]

Unvulcanised Rubbers.

On account of the bewildering number of materials and the smallness of the steps in the scale of physical properties which have to serve for distinguishing adjacent members, a general sharp classification of rubber and synthetic plastics is very difficult. Furthermore, descriptions in many patents are insufficient to enable an outside judgment as to whether the products are to prove of importance in the rubber field, in the plastic field, or in both fields or in neither. A recent suggestion[52] from Germany that capacity for vulcanisation should be regarded as the distinguishing characteristic of so-called elastophors (as opposed to plastophors), of which rubbers form the predominant members, although falling far short of ideal, does at least provide a possible temporary working basis.

In view of the large number of plant materials which have been examined in the last few years as possible sources of rubber, it is of practical interest that examination of a range of these hydrocarbon products, by their light absorption in the 12 μ. region, shows them to be rubber or gutta-percha and never a mixture of the two.[53]

The precipitation value[54] of natural rubbers, particularly goldenrod, *i.e.*, the proportion of ethanol required under standard conditions to cause incipient precipitation or clouding from clear benzene solutions, is increased when the rubber has been degraded and its viscosity reduced, *e.g.*, by irradiation or heating. Measurement of this value, however, does not provide a trustworthy index of quality. Extension[55] of this work to fractional precipitation of goldenrod and *Hevea* rubbers shows that the precipitation value is lowest for the first rubber fractions separated by addition of methanol to the benzene solutions and that the distribution of molecular weight in various fractions can be used for estimation of the proportion of *Hevea* rubber in a mixture of *Hevea* and goldenrod rubbers. Comparative fractionation has also been carried through with *Cryptostegia* and guayule rubbers using a fractional extraction or diffusion method into hexane[56]; the results indicate very different distribution of molecular

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[49] H. H. Abernathy and R. H. Walsh, *Rubber Age*, 1945, **58**, 349; B., 1946, II, 222.

[50] M. Feinleib, *Trans. Electrochem. Soc.*, 1945, **88**, *Preprint* 6; B., 1946, II, 19.

[51] G. W. Stanton and W. A. Henson, *Ind. Eng. Chem.*, 1946, **38**, 468; B., 1946, II, 293.

[52] A. Schwarz, *Kautschuk*, 1940, **16**, 34; B., 1946, II, 305.

[53] S. B. Hendricks, S. G. Wildman, and E. J. Jones, *Arch. Biochem.*, 1945, **7**, 427; B., 1946, II, 24.

[54] E. L. Skau, W. J. Runckel, F. B. Kreeger, and M. A. Sullivan, *J. Physical Chem.*, 1945, **49**, 281, 295; B., 1946, II, 24.

[55] *Ibid.*, 304; B., 1946, II, 24.

[56] E. A. Hauser and D. S. le Beau, *India-Rubber J.*, 1946, **110**, 601; B., 1946, II, 263.

weight in the two and the inferior quality of both relative to *Hevea* rubber. E. A. Hauser and his co-workers have also applied fractional dissolution in hexane to the separation of *Hevea* rubber[57] into fractions representing different viscosities and molecular weights; the degree of chemical unsaturation throughout was approximately uniform, as also was the rate of vulcanisation with the exception of that of the residual gel rubber. The more rapid vulcanisation of the last-named is not surprising ; what is more surprising is the observation that the number of sulphur atoms required to enter into combination for the removal of each double bond is greater for the gel rubber than for the rubber in the sol fractions. Molecular weight distribution has also been investigated by a fractional precipitation method for *Hevea* rubber, Buna S, and a polyvinyl butyl ether, the distribution curves being normal for the first two materials but showing an abnormal occurrence of two maxima with the third material.[58]

Using dilatometric measurement of the change in volume as a quantitative index to the extent of crystallisation, L. A. Wood and N. E. Bekkedahl[59] have studied the effect of temperature on the crystallisation of smoked sheet rubber. Crystallisation is not observed below −50° or above 15°, the maximum rate being at about −25°. The rate is influenced by the conditions of preparation. In view of the polymolecular character of rubber the observed facts that melting of the crystals occurs over a considerable range of temperature and that it is possible, by appropriate selection of the crystallisation temperature, to produce crystals melting at any temperature between −40° and 45° are less surprising than they might at first appear.

Determination of the specific heat by means of a modified adiabatic type calorimeter shows that for *Hevea*, GR-S, and GR-I (*i.e.*, "Butyl") rubbers, and for their compounded stocks, the specific heat even of the vulcanisates[60] is in good accordance with that calculated from the proportions and known specific heats of the constituents.

Considerable attention has been given to the structural changes suffered by rubber under the action of disruptive agents. Although oxidation is already known to be an important factor in the mastication process,[61] no appreciable loss in chemical unsaturation as normally measured is discernible in natural rubber, even if mastication is fairly prolonged.[62] Ultramicroscopic examination of films obtainable from masticated rubbers of the *Hevea*, GR-S, GR-S 10, and Neoprene GN types, however, appears in some cases to give indications of structural alteration caused by milling.

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[57] E. A. Hauser, D. S. le Beau, and Y. Shen, *Rubber Age*, 1945, **58**, 59 ; B., 1946, II, 183. See also W. C. Carter, R. L. Scott, and M. Magat, *J. Amer. Chem. Soc.*, **1946**, **68**, 1480; A., 1947, I, 8.

[58] H. Naidus and H. Mark, *India Rubber World*, 1945, **131**, 229 ; B., 1946, II, 183.

[59] *J. Appl. Physics*, 1946, **17**, 362 ; B., 1946, II, 393.

[60] W. H. Hamill, B. A. Mrowca, and R. L. Anthony, *Ind. Eng. Chem.*, 1946, **38**, 106 ; B., 1946, II, 221.

[61] See W. S. Penn, *India-Rubber J.*, 1945, **109**, 741 ; B., 1946, II, 102.

[62] D. S. le Beau and E. A. Hauser, *Rubber Age*, 1946, **59**, 67 ; B., 1946, II, 437.

The early stages of thermal, oxidative, and photochemical breakdown have been the subject of a series of refined investigations. J. L. Bolland and W. C. Orr[63] find that comminuted purified rubber is not chemically altered by temperatures below 200°. At 220—270° the rubber gradually softens and melts with little or no loss in chemical unsaturation as indicated by the iodine value. Some dipentene and isoprene, however, are formed concurrently. On longer heating, the molten product becomes more viscous and finally sets to a benzene-insoluble, soft, non-sticky solid. Whatever the initial or intermediate scission products, secondary reactions must also occur and no completely satisfactory explanation of the processes involved is yet possible. From study of the autoxidative changes with olefinic compounds, E. H. Farmer[64] has indicated that the initial products with these, and probably with rubber, are peroxidic substances formed by addition at double-bond centres, chain reactions then leading to α-methylenic peroxides which themselves undergo further changes. Irradiation of natural rubber by a mercury arc has been shown by L. Bateman[65] to lead to rapid development of insolubility accompanied by a steady slow formation of gaseous products of which, by volume, hydrogen is the chief, the remainder being condensible at − 80° and between − 80° and − 180°. Unlike the changes undergone in thermal degradation, these photochemical effects appear to be predominantly due to C–H fission.

The observations of H. P. Stevens on the photogelation of rubber solutions have been extended by him[66] and also by R. Buckingham and C. V. Planer.[67] The positive although mild activating effect of small proportions of antioxidants and of pro-oxygenic substances indicates that this is independent of oxidising or reducing properties. The rate of the photogelation process can be followed by viscosity measurements with the solutions in a sealed apparatus; the shape of the reaction curves accords, as expected, with a three-dimensional polymerisation.

In devising ways and means of producing rubber of improved properties or for increasing the length of the rubber molecular chains, many research workers must have pondered the possibility of increasing the molecular length by effecting a "copolymerisation" of natural rubber with a polymerisable monomer. No very optimistic claims in that direction have yet been made but it is of interest that two independent sets of observations have indicated the possibility of this type of copolymerisation using the rubber in latex form. By polymerising methyl methacrylate in the presence of *Hevea* latex, conversion of the rubber into a heat-, solvent-, and oxygen-resistant product has been claimed.[68] In an investigation

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[63] *Trans. Inst. Rubber Ind.*, 1945, **21**, 133; B., 1946, II, 103.

[64] *Ibid.*, 122; B., 1946, II, 103.

[65] *Ibid.*, 118; B., 1946, II, 103.

[66] *J.S.C.I.*, 1945, **64**, 312; B., 1946, II, 60; cf. B., 1945, II, 228.

[67] *Ibid.*, 1946, **65**, 6; B., 1946, II, 139. *Trans. Inst. Rubber Ind.*, 1945, **21**, 175; B., 1946, II, 221. C. V. Planer, *Ind. Chem.*, 1946, **22**, 291; B., 1946, II, 264.

[68] B.P. 573,062; B., 1946, II, 96.

covering polymerisation of a wide range of vinyl compounds,[69] *e.g.*, acrylonitrile, styrene, or acrylic acids or esters, products of diverse properties were obtained, the acrylonitrile copolymer being almost insoluble in ordinary rubber solvents. The product obtained by milling maleic anhydride into natural rubber is believed to be of similar type.

Before passing to information on synthetic rubbers, a paper by E. A. Hauser and D. S. le Beau[70] may be recorded in which ultramicroscopic examination of the structure of films of gutta or balata (prepared from xylene solutions) indicates the *trans*-configuration of this hydrocarbon and the presence of two modifications which may be inter-convertible by alteration of temperature.

As has been remarked already, a very large number of publications, mainly patents, has appeared recently claiming new or modified polymerisation methods for the production or the improvement of synthetic rubbery products of many different types.

Turning to the more general accounts of progress of the applied chemistry of synthetic rubbers, it is of interest to note T. R. Dawson's judgment, which is supported by a wide review of the literature, that the believed resistance of many elastomers to attack by bacteria, fungi, and insects arises (like earlier assumptions as to their necessarily greater uniformity of quality) merely from lack of contrary evidence.[71] An informative table of the commercial synthetic rubbery materials produced in America and indicating their chemical nature and leading characteristics has been published by H. A. Winkelmann.[72]

G. R. Vila and M. D. Gross have given an interesting account of statistical methods applied to experimental data accumulated in the bulk production of GR-S for the more uniform control of continuous manufacturing operations.[73] Details have also been published[74] of an investigation of the influence of the proportion of the benzene-insoluble fraction, or "gel," in GR-S on its physical and processing qualities. Distinction is drawn between the "A gel" which disappears on light mastication and is relatively innocuous and the more persistent "B gel" which adversely affects the processing behaviour (extrusion possibly excepted) and the quality of the vulcanised product. Considering the forced rate of development of its production and the distracting circumstances generally, the American GR-S synthetic rubber has proved very serviceable. Comparative tests reported on the products from fifteen different copolymer plants show a reasonable degree of uniformity.[75]

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[69] P. Compagnon and J. le Bras, *Compt. rend.*, 1941, **212**, 616; B., 1946, II, 59. *Bull. Soc. chim.*, 1944, [v], **11**, 553; B., 1945, II, 352.

[70] *India-Rubber J.*, 1946, **111**, 453; B., 1946, II. 470.

[71] *J. Rubber Res.*, 1946, **15**, 1; B., 1946, II, 141.

[72] *India Rubber World*, 1946, **114**, 680; B., 1946, II, 473.

[73] *Rubber Age*, 1945, **57**, 551; B., 1945, II, 353.

[74] L. M. White, E. S. Ebers, G. E. Shriver, and S. Breck, *Ind. Eng. Chem.*, 1945, **37**, 770; B., 1945, II, 393.

[75] R. E. Morris and A. E. Barrett, *Rubber Age*, 1945, **57**, 425; B., 1945, II, 353.

One of the difficulties in the manufacture of products from synthetic rubbers has been the relative lack of tackiness so necessary for assembling the various pieces. Various remedial substances have been tried by incorporation or surface application but none has proved really satisfactory. Unfortunately, the quality of tackiness is difficult of assessment except by manufacturing trial.[76]

News on the production and use of German synthetic rubbers has seemed more spectacular probably on account of the collective, as well as detailed character of the reports received, *e.g.*, from various manufacturing centres. The reports from the I.G. synthetic rubber laboratory at Leverkusen[77] include also details of "I.-Gummi," a thermoplastic product of glycol–adipic acid polyester type, the properties of which have been raised by treatment with a dicarbimide and which was expected to serve as a leather substitute; it approximated to Perbunan in oil-resistance but was inferior in electrical qualities. Plasticisers for synthetic rubbers include dibutyl thioacetate and methylenethioacetate, and also thiodipropionitrile. In addition to a considerable number of rubbers of Buna S type, others of Buna N type and copolymers of butadiene with methyl acrylate and methacrylate were also under large-scale investigation. The production of various forms of Buna S and Buna N and the corresponding latices at Leverkusen forms the subject-matter of separate reports.[78,79] Other reports cover methods used for production of butadiene, and the various necessary intermediates,[80] and also of the Buna S rubber[81] at Schkopau, details being included of the plant. The aim at Schkopau was maximum production of Buna S and this attained a rate even exceeding 6000 tons per month. Yet other reports describe production of Buna S at Hüls,[83,84] where, as at Leverkusen, potassium persulphate was used as polymerisation catalyst with di*iso*propylxanthogen disulphide as "modifier." The reports also cover procedure[85] (including details of the vaunted Koresin tackifier) and plant[86] at Ludwigshafen. Poly*iso*butene manufacture at Oppau[87] is also detailed. A condensed version of the synthetic rubber record in Germany has also been prepared by E. R. Weidlein, jun.[88]

Individual subjects investigated during the year include the preparation

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[76] W. F. Busse, J. M. Lambert, and R. B. Verdery, *J. Appl. Physics*, 1946, **17**, 376. B., 1946, II, 396.

[77] *Combined Intelligence Objectives Sub-Commee., Item* 22, *File* XXV–34; B., 1946, II, 184, 396.

[78] *Ibid., Item* 22, *File* XXXI–76; B., 1946, II, 473.

[79] *Ibid., Item*, 22, *File* XXIII–4; B., 1946, II, 351.

[80] *Ibid., Item* 22, *File* XXII–20; B., 1946, II, 310.

[81] *Ibid., Item* XXII–22; B., 1946, II, 350.

[82] *Ibid., Item* 22, *File* XXVIII–13; B., 1946, II, 397.

[83] *Ibid., Item* 22, *File* XXII–21; B., 1946, II, 350.

[84] *Ibid., Item* 22, *File* XXXI–75; B., 1946, II, 473.

[85] *Ibid., Item* 22, *File* XXII–7; B., 1946, II, 351.

[86] *Ibid., Item* 22, *File* XIX–1; B., 1946, II, 396.

[87] *Ibid., Item* 22, *File* XXVI–76; B., 1946, II, 424.

[88] *Chem. Eng. News*, 1946, **24**, 771; B., 1946, II, 350.

and properties of rubbery polymers of butadiene or isoprene or dimethylbutadiene with benzoyl peroxide or diazoaminobenzene as catalyst, the latter being not only a good catalyst but giving rise to decomposition products favourable to good ageing[89]; butadiene copolymers of *αp*-dimethylstyrene or vinyl fatty esters[90]; and the effect of varying the monomer ratio and the conversion ratio, in the preparation of GR-S, on the character of the product obtained.[91] In the last case the indications are that lowering the conversion and raising the butadiene proportion are advantageous for GR-S to be used in tyres.

Study also has been made of the rubbery polymers obtained from methylpentadiene alone or with butadiene, indications being observed of the possibility of products which when incorporated in GR-S impart some degree of improved ageing and tackiness.[92]

The effect of molecular weight and molecular weight distribution in Butyl rubber and of the proportion of cross-linkings introduced by vulcanisation on various physical properties of the vulcanisates prepared from a number of fractions separated by graded acetone precipitation from benzene solution have been studied.[93] In order to deal with the small quantities available a special technique of small-scale compounding and testing was necessary.

The remarkable developments arising from the pioneering work of F. S. Kipping on organic silicon compounds have become a popular press item and silicone rubbers continue to command considerable attention, particularly because of the novelty of some of their characteristics.[94,95] Little new information, however, is forthcoming. Rubbery materials so little affected by wide temperature changes cannot other than appeal for special and exceptional applications[96,97] but for use in normal circumstances they are unlikely to be of much practical interest.

VULCANISATION.

Most of the publications reaching this country concerning vulcanisation relate to the preparation and use of various organic compounds for acceleration purposes and are chiefly in the patents literature. Few, if any, really novel accelerators have been described recently and practically all can be regarded as modifications or variants of known types, *e.g.*,

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[89] C. Koningsberger and G. Salomon, *J. Polymer Sci.*, 1946, **1**, 200; B., 1946, II, 388

[90] P. O. Powers, *Ind. Eng. Chem.*, 1946, **38**, 837; B., 1946, II, 437.

[91] E. D. Maher and T. L. Davies, *Rubber Age*, 1946, **59**, 557; B., 1946, II, 437.

[92] F. M. McMillan, E. T. Bishop, K. E. Marple, and T. W. Evans, *India Rubber World*, 1946, **113**, 663; B., 1946, II, 304.

[93] P. J. Flory, *Ind. Eng. Chem.*, 1946, **38**, 417; B., 1946, II, 303.

[94] W. S. Penn, *Plastics*, 1945, **9**, 273; *India-Rubber J.*, 1945, **109**, 625; B., 1945, II, 381; 1946, II, 60.

[95] W. R. Collings, *Chem. Eng. News*, 1945, **23**, 1616; B., 1945, II, 381.

[96] P. C. Servais, *India Rubber World*, 1946, **114**, 657; B., 1946, II, 472.

[97] J. Marsden, *Rubber Age*, 1946, **59**, 691; B., 1946, II, 473.

diazole, thiazole,[98] or thiazoline derivatives,[99] dithiocarbamate compounds and derivatives,[100] thiuram[101] and other organic[102] sulphides or disulphides, amines[103] or amine salts[104] of various of the preceding or other classes of organic compounds. To these may be added resinous products of the diarylguanidines,[105] and various sulphenamides,[106] this last class being one which has been growing steadily for some years. The effects claimed for such accelerators are almost as varied as their character.

The most spectacular use of accelerators is seen in their application to bring vulcanisation of natural rubber down to room temperature. For this purpose zinc *iso*propylxanthate has been frequently used, activated with a subsidiary accelerator. A recent report indicates that diethylammonium diethyldithiocarbamate is the best secondary accelerator for this purpose and that the fastest vulcanisation at 25° is given by the use of 1—2% of a 3 : 1 mixture of the xanthate and dithiocarbamate together with 1½—2% of sulphur.[107] The zinc diethyldithiocarbamate customarily used previously as the secondary accelerator is less effective.

Other interesting investigations cover the joint use of triethanolamine or other amines and magnesium oxide for accelerating the vulcanisation of GR-S and butadiene–acrylonitrile copolymers,[103] and the effect of moisture in GR-S stock on its rate of vulcanisation.[108] In the latter case the effect which may arise by activation of the thiazole accelerator is not sufficient for normal variation in the moisture content of GR-S, or of the carbon black used, to cause an appreciable effect.

Evidence has been adduced by A. P. Stubbs and C. R. Johnson[109] that, in mixed GR-S and natural rubber stocks, vulcanisation leads to an abnormally high modulus relative to the individual unmixed stocks; addition of an amine soap as activator for the dibenzthiazyl disulphide accelerator appears to lead to better balanced behaviour of the two rubbers in the mixture, the modulus exaltation being less and any tendency of the natural rubber to reversion on prolonged heating being suppressed.

From the behaviour of appropriate mixings, M. H. Keck and L. E.

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[98] U.S.P. 2,334,042; B., 1946, II, 266. U.S.P. 2,337,680; B., 1946, II, 306.

[99] U.S.P. 2,327,052; B., 1946, II, 394. U.S.P. 2,331,995; B., 1946, II, 239. U.S.P. 2,334,630; B., 1946, II, 306. U.S.P. 2,336,217; B., 1946, II, 306. U.S.P. 2,335,429; B., 1946, II, 306.

[100] U.S.P. 2,199,105; B., 1946, II, 62. U.S.P. 2,333,468; B., 1946, II, 265. U.S.P. 2,337,802; B., 1946 II, 306. B.P. 578,540; B., 1946, II, 361.

[101] B.P. 572,669; B., 1946, II, 38. U.S.P. 2,326,984; B., 1945, II, 364.

[102] U.S.P. 2,325,735; B., 1945, II, 354. U.S.P. 2,196,707; B., 1945, II, 367. U.S.P. 2,203,090; B., 1946, II, 142.

[103] J. Breckley, *India Rubber World*, 1946, **114**, 663; B., 1946, II, 472.

[104] U.S.P. 2,331,749; B., 1946, II, 81. U.S.P. 2,335,059; B., 1946, II, 306. B.P. 576,271; B., 1946, II, 353.

[105] U.S.P. 2,340,833; B., 1946, II, 433.

[106] B.P. 575,074; B., 1946, II, 156. U.S.P. 2,339,552; B., 1946, II, 353. U.S.P. 2,339,002; B., 1946, II, 362.

[107] Imperial Chem. Industries, Ltd., 1946, *Rept.* R52.

[108] I. C. Rush, *Ind. Eng. Chem.*, 1946, **38**, 58; B., 1946, II, 184.

[109] *Rubber Age*, 1946, **59**, 567; B., 1946, II, 437.

Cheyney[110] are led to believe that vulcanisation of "Buna S" involves two concurrent chemical changes, one being combination with sulphur, which is primarily responsible for development of tensile strength, and the other being disappearance of double bonds presumably by polymerisation, which is related to the former and continues on over-vulcanisation.

Zinc oxide is necessary as an activator if the full effect of organic accelerators is to be exerted but zinc carbonate replacing the oxide in equivalent proportion is at least as effective and gives much more transparent vulcanisates.[111] On the other hand, premature vulcanisation of neoprene can be prevented by incorporating an alkali salt of a C_1—C_7 fatty acid with dissociation constant below 1×10^{3}, such as sodium acetate.[112]

Knowledge of the newer types of non-sulphur vulcanising agents has been usefully reviewed and extended[113] by T. Alfrey, J. G. Hendricks, R. M. Hershey, and H. Mark, whose treatment includes benzoyl peroxide, quinones (and the related imines and oximes), polynitrobenzenes, and mixtures of mono- or di-hydric phenols, or aromatic amines, with an oxidising agent. Vulcanisation, like polymerisation, is believed to involve formation of, or reaction with, free radicals whereby the cross-linking necessary for vulcanisation is eventually effected. The vulcanising effect of benzoquinone dioxime[114] towards Butyl rubber has been shown to need lead dioxide for its full development,[115] vulcanisation being caused by the resulting *p*-dinitrosobenzene, which is also capable of vulcanising natural rubber; a reaction mechanism is proposed. It is also suggested that the vulcanisation of natural rubber by polynitro-compounds is dependent on partial reduction of these to nitroso-compounds. Saturated acrylic elastomers obtained by copolymerisation of ethyl acrylate and bromoethyl acrylate are also rapidly vulcanisable by benzoquinone dioxime in presence of red lead.[116]

The di- or poly-*iso*cyanates (di- or poly-carbimides) which also have the power of producing cross-linkings between rubber molecules, and therefore of effecting a sort of vulcanisation, receive more specific mention later under "Bonding."

COMPOUNDING.

As a natural consequence to the shortage of rubber, consideration has been given to a wide range of possible inorganic and organic materials to enable reduction of the proportion of new rubber demanded for manufacturing purposes, fillers, diluents, substitutes, extenders, and reinforcing agents representing more or less different ways of approach to the problem.

[110] *Ind. Eng. Chem.*, 1945, **37**, 1084; B., 1946, II, 105.

[111] C. H. Birkitt, *J. Rubber Res.*, 1946, **15**, 157; B., 1946, II, 394.

[112] B.P. 575,549; B., 1946, II, 225.

[113] *India Rubber World*, 1945, **112**, 577, 738; 1946, **113**, 653; B., 1946, II, 139, 302.

[114] For formation of these dioximes, see U.S.P. 2,336,941; B., 1946, II, 323.

[115] J. Rehner, jun. and P. J. Flory, *Ind. Eng. Chem.*, 1946, **38**, 500; B., 1946, II, 303.

[116] W. C. Mast, T. J. Dietz, and C. H. Fisher, *India Rubber World*, 1945, **113**, 223; B., 1946, II, 171.

R. G. Newton and J. R. Scott have shown that the problem is capable of partial solution and that fine tyre-tread crumb has attractive features as an extender.[117] Choice of extender must, however, be decided largely by circumstances.[118] Although many of the emergency compounding measures will doubtless be dropped as soon as conditions permit, it is likely that the advantages accruing to a few will be sufficient to justify their retention.

"Naftolen," a hydrocarbon by-product of the refining of oil, has received considerable attention as to its possible use in GR-S for tyres[119]; a tabulated compilation of compounding results involving various proportions of it and of natural rubber, GR-S, whole-tyre reclaim, and carbon black has also been published.[120] Other extenders, modifiers, and diluents which have been under consideration include synthetic rubbers themselves,[121] various synthetic plastic materials[122] and resins,[123] lignosulphonates,[124] and terpene polymers. As extenders may serve also other purposes and give desirable incidental effects, classification is not always easy. Some plasticisers, also, may be incorporated in such generous proportions as to be additionally diluents.

Softeners or plasticisers, protected or otherwise described during the year, have included tall oil,[125] dibutyl sebacate, thiodipropionic esters,[126] phenoxypropionic and similar esters,[127] ketone–hydroxyamine products,[128] nitrosoarylguanidines,[129] and an acetylene–*tert.*-butylphenol condensation product.[130] Some of these, like the last, which is the much-publicised "Koresin," have some tackifying action also. A useful discussion of the physical characteristics necessary in a good plasticising agent has been presented by H. Jones.

There have been, as usual, reports on relatively coarse or cheaper fillers such as ground limestones,[132] strontium sulphate,[133] clays, and whitings, sometimes prompted by local needs.[134]

[117] *J. Rubber Res.*, 1946, **15**, 188, 193; B., 1946, II, 471.

[118] See L. E. Ludwig, D. V. Sarbach, B. S. Garvey, jun., and A. E. Juve, *India Rubber World*, 1945, **112**, 731; B., 1946, II, 140. J. S. Hunter, *India-Rubber J.*, 1945, **109**, 353; B., 1945, II, 392. J. F. Powell, *ibid.*, 271; B., 1945, II, 392.

[119] W. H. Grote and F. S. Rostler, *Rubber Age*, 1945, **57**, 685; B., 1946, II, 141.

[120] F. Rostler and K. Rostler, *India Rubber World*, 1946, **114**, 509; B., 1946, II, 397.

[121] Cf. U.S.P. 2,332,194; B., 1946, II, 225.

[122] H. A. Winkelmann, *India Rubber World*, 1946, **113**, 799; B., 1946, II, 254.

[123] J. W. Ferguson, *ibid.*, **114**, 218; B., 1946, II, 352. H. H. Irvin, *ibid.*, 660; B., 1946, II, 472; cf. U.S.P. 2,330,353; B., 1946, II, 142.

[124] L. J. D. Healy, *Rubber Age*, 1945, **57**, 701; B., 1946, II, 141.

[125] W. I. Harber and C. S. Yoran, *Ind. Eng. Chem.*, 1945, **37**, 953; B., 1946, II, 104.

[126] B.P. 575,541; B., 1946, II, 223.

[127] B.P. 575,137; B., 1946, II, 223.

[128] B.P. 575,134; B., 1946, II, 225.

[129] B.P. 575,609; B., 1946, II, 237.

[130] *Combined Intelligence Objectives Sub-Commee., Item* 22, *File* XXII–7; B., 1946, II, 351. *See also* U.S.P. 2,337,464; B., 1946, II, 306.

[131] *Trans. Inst. Rubber Ind.*, 1946, **21**, 298; B., 1946, II, 265.

[132] U.S.P. 2,323,550; B., 1946, II, 262.

[133] J. R. Scott, *J. Rubber Res.*, 1945, **14**, 159; B., 1945, II, 392.

[134] H. F. Whitworth, *Trans. Inst. Rubber Ind.*, 1946, **22**, 25; B., 1946, II, 393.

Several useful investigations have been directed at specific compounding problems such as the compounding of GR-S for tyres[135] and of Butaprene N[136] (a butadiene–acrylonitrile copolymer) for oil- or heat-resistance; comparison of the effect of various mineral "pigments" in GR-S[137]; improvement of the mechanical properties of GR-S compounded with hydrated calcium silicate by additional presence of polar compounds such as water or an alcohol or preferably a glycol or glycerol[138]; increase of the resistance of rubber to swelling by the presence of suitable fillers[139] and the influence of mineral fillers on the tensile strength of swollen rubber.[140]

The reinforcement of rubber by various agents, of which carbon black is the most effective, has long been more or less definitely attributed to adsorptive effects at the surface of the particles; this conception has received further support from G. Goldfinger[141] and F. B. Menadue.[142] The most marked advances in our knowledge of reinforcement, however, have resulted from investigation of the behaviour of the various forms of carbon black when incorporated in natural and synthetic rubbers.

Although the exceptional reinforcing effect of carbon black for rubber was first realised about 1904 (interesting details of the discovery have been unearthed by H. J. Stern[143]), wide extensions of its use for rubber compounding coincided with each of the war periods 1914–18 and 1939–45. The latter extension was related in part to the growing consumption of synthetic rubbers as well as to the increased production of numerous new grades of carbon black. Two timely reviews of the manufacture of the various forms of carbon black and their application in the rubber industry have appeared.[144]

Before passing to contributions of more fundamental importance, references may be given to suggestions for increasing the ease of incorporation in rubber by a preliminary forming of the black into a mother-stock in some soft absorbent such as poly*iso*butene[145]; or by raising the temperature of incorporation and ensuring access of air or even of ozonised air[146]; or by chemical pre-treatment of the black with hydrogen chloride.[147] Mention should also be made of the supplementing of natural gas or acetylene for the production of carbon black by hydrocarbon-enriched

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[135] J. G. Hendricks, *India Rubber World*, 1946, **114**, 60; B., 1946, II, 351.

[136] R. H. Crossley and C. G. Cashion, *Rubber Age*, 1945, **58**, 197; B., 1946, II, 141.

[137] R. E. Morris, R. R. James, and E. R. Evans, *ibid.*, 331; B., 1946, II, 222.

[138] F. W. Gage, *ibid.*, 343; B., 1946, II, 223. *India Rubber World*, 1945, **112**, 590; B., 1945, II, 393.

[139] J. R. Scott, *J. Rubber Res.*, 1946, **15**, 109; B., 1946, II, 348.

[140] E. Jutasi, *Trans. Inst. Rubber Ind.*, 1945, **21**, 227; B., 1946, II, 263.

[141] *J. Polymer Res.*, 1946, **1**, 58; B., 1946, II, 304.

[142] *India-Rubber J.*, 1945, **119**, 617; B., 1946, II, 60.

[143] *Rubber Age & Synthetics*, 1945, **26**, 268; B., 1946, II, 139.

[144] A. Speedy, *Chem. and Ind.*, 1946, 354. W. H. Cadman, *J. Soc. Arts*, 1946, **94**, 646.

[145] U.S.P. 2,330,698; B., 1946, II, 21.

[146] U.S.P. 2,199,099; B., 1946, II, 61.

[147] U.S.P. 2,331,199; B., 1946, II, 61.

producer gases,[148] this measure having been adopted successfully in Germany and elsewhere.

Results of practical importance have been obtained on the modification produced by various proportions of different carbon blacks in the physical characteristics of rubber,[149,150] and neoprene,[150] the effect of particle size of the black and the possible influence of structure development in the rubber–black system. A similar investigation has been made for acetylene black in Butyl rubber.[151]

Still more definite evidence of the formation of the reinforcing agent into structural or reticular aggregates in the surrounding rubber-medium has been obtained by examination of the electrical conductivity of the compounded products. Acetylene black is known to impart electrical conductivity to rubber or plastics in which it is incorporated, its exceptional effect in this direction being attributed to its inherent special character and to clustering of the particles.[152] The originally postulated clustering can be positively demonstrated by electron micrographs.[153] A conprehensive study of the electrically conductive rubber produced by compounding with carbon black is in accord with these views and shows, further, that electrically conducting ebonite is also obtainable.[154] Cluster formation of the carbon particles and the resulting electrical conductivity are probably associated with the existence of two types of molecular motion in rubber and two distinct "viscosity" values, a macro-viscosity of high magnitude controlling the movement of whole molecules while a micro-viscosity controls the vibratory movement of individual sections of the molecules.

CHEMICAL DERIVATIVES.

Halogenated rubbers, particularly chlorinated rubber, still receive considerable attention and several modifications in their conditions of preparation have been described[155] as also has their production by chlorination of rubber hydrochloride.[156] Preparation of chlorinated derivatives of other high-molecular hydrocarbons such as poly*iso*butene[157] and polythene[158] has also been the subject of patents. New methods of use for chlorinated rubber in protective coatings have been reported[159] and an account has been given of methods for the utilisation of chlorinated

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[148] Z. Baranek, *Rubber Age and Synthetics*, 1946, **27**, 290.

[149] D. Parkinson, *Trans. Inst. Rubber Ind.*, 1945, **21**, 7 ; B., 1945, II, 393.

[150] J. M. Buist and S. Mottram, *Trans. Inst. Rubber Ind.*, 1946, **22**, 82 ; B., 1946, II, 471. J. M. Buist and O. L. Davies, *ibid.*, 68 ; B., 1946, II, 471.

[151] R. H. Hall, *Canad. Chem.*, 1945, **29**, 858 ; B., 1946, II, 184.

[152] R. H. Hall, B. P. Buckley, and T. R. Griffith, *ibid.*, 587 ; B., 1945, II, 393.

[153] G. Benson, *Rubber Age*, 1946, **58**, 461 ; B., 1946, II, 220.

[154] D. Bulgin, *Trans. Inst. Rubber Ind.*, 1945, **21**, 188 ; B., 1946, II, 222.

[155] B.P. 573,988 ; B., 1946, II, 143. B.P. 573,536 ; B., 1946, II, 105. B.P. 574,834–5 ; B., 1946, II, 186. U.S.P. 2,331,985 ; B., 1946, II, 224. U.S.P. 2,198,973; B. 1946, II, 63.

[156] U.S.P. 2,331,237 ; B., 1946, II, 63.

[157] U.S.P. 2,327,517 ; B., 1945, II, 385.

[158] B.P. 576,119 ; B., 1946, II, 257.

[159] U.S.P. 2,328,566–7 ; B., 1945, II, 389.

rubber in paints.[160] The sensitiveness of the otherwise remarkably stable chlorinated rubber to some organic bases[161] such as piperidine is rather surprising.

Isomerised rubbers obtained by the action of such chemical agents as stannic chloride have been applied as compounding ingredients for deproteinised rubber[162] for further improvement of its water-resistance, and for synthetic rubbers of the butadiene–acrylonitrile type[163] to improve the processing qualities. As butadiene–styrene synthetic rubbers are less reactive than natural rubber towards such isomerising agents, it is possible to produce, by treatment of natural rubber containing a proportion of such synthetic rubber, chemically treated or isomerised products in which the substantially unaltered synthetic rubber serves as a softening agent or plasticiser.[164]

New oil-resisting rubbers have been obtained by the vulcanisation of incompletely hydrochlorinated, and therefore unsaturated, rubber hydrochloride,[165] and by heating or vulcanising various hydroxylated, acylated, or oxido-derivatives[166] of rubber. Oxidation products of rubber of better known types, or even oxidised reclaimed rubber,[167] can be further converted, by modification and elaboration of earlier methods of chemical treatment, such as condensation with phenol, formaldehyde, and maleic acid, into thermoplastic and thermosetting materials.[168] "Rubber sulphones,"[169] obtained by the action of sulphur dioxide on deresinated rubber in presence of a solvent and with lithium nitrate as catalyst, are additions to the chemical derivatives of rubber. Application of the highly reactive di- or poly-carbimides to the chemical and physical modification of rubber and of other rubber derivatives is a not unexpected recent development.[170]

PROPERTIES OF VULCANISED RUBBER.

In view of the uses to which rubber is commonly applied, its ageing and weathering are phenomena which justify continuous attention. As usual, claims have been made during the year for a considerable number of rubber-antioxidant agents but their relative assessment from the descriptions in the patents literature is difficult and detailed reference appears to be unnecessary.

A rather unusual aspect of the ageing of rubber, but of serious practical consequences, occurs in the damage to fire hose by sulphuric acid formed

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[160] J. F. H. van Eijnsbergen, *Paint Tech.*, 1945, **10**, 319; B., 1946, II, 214.
[161] A. Jarrijon and F. Lepetit, *Chim. et Ind.*, 1945, **54**, 404; B., 1946, II, 104.
[162] B.P. 571,494; B., 1946, II, 185.
[163] B.P. 571,495; B., 1946, II, 186.
[164] B.P. 580,155; B., 1946, II, 475.
[165] B.P. 572,730; B., 1946, II, 62.
[166] B.P. 572,575; B., 1946, II, 62.
[167] B.P. 573,050; B., 1946, II, 63.
[168] B.P. 572,828; B., 1946, II, 58.
[169] B.P. 572,574; B., 1946, II, 63.
[170] B.P. 574,901; B., 1946, II, 185.

by the action of sulphur-oxidising bacteria on the sulphur from the rubber; the acid frequently causes rotting of the fabric reinforcement unless preventive measures are taken.[171]

J. Crabtree and A. R. Kemp[172] have made a valuable study of the major factors, viz., light, oxygen, and ozone, in the weathering of vulcanised rubbers and of the effects of humidity, elongation, thickness, antioxidants, wax, and fillers on the rate of oxidation (increase in weight). The work confirms that the multiple cracking of stretched rubber exposed out of doors is caused by ozone, but unless the rubber is stretched even relatively high concentrations of ozone have no apparent action. The paper, which includes details of apparatus for subjecting rubber to controlled concentrations of ozone, covers synthetic rubbers as well as natural rubber and repays careful reading. Weathering and ageing of rubber generally have recently been popular subjects for investigation. Useful contributions include the weathering of vulcanised GR-S and protective methods for GR-S proofings,[173] the changes in physical properties during the heat-ageing of GR-S vulcanisates,[174] and the kinetics of the oxidation of GR–S as studied by the volumetric absorption of oxygen.[175] The mechanism of exposure cracking of rubber has been the subject of two other papers dealing respectively with identification of ozone as the active agent[176] and with the reasons for the initiation and preferential extension of the deeper cracks.[177]

Investigation relative to an Admiralty specification for rubber-insulated cables indicates that the ageing qualities of V.I.R. cable insulation are not affected appreciably by the proportion of zinc oxide present.[178] Also although basic fillers such as chalk and litharge may assist in checking surface deterioration of ebonite in sunlight, they are not invariably able to effect neutralisation of the deleterious sulphuric acid as fast as it is formed.[179]

Other studies dealing with electrical rubbers relate to the influence of variation of the rubber–sulphur ratio, and of the period of vulcanisation, on the composition, density, and thermal expansion of the resulting ebonite,[180] and to a comparison of natural rubber and various Buna synthetic rubbers as to their suitability for use in electrical cables,[181] consideration being given more particularly to specific resistance, ageing,

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[171] A. C. Thaysen, H. J. Bunker, and M. E. Adams, *Nature*, 1945, **155**, 322; B., 1946, II, 395.

[172] *Ind. Eng. Chem.*, 1946, **38**, 278; B., 1946, II, 348; C., 1946, 172.

[173] H. C. Harrison, *Trans. Inst. Rubber Ind.*, 1945, **21**, 93; B., 1946, II, 104.

[174] J. R. Scott, *ibid.*, 78; B., 1946, II, 104.

[175] J. R. Shelton and H. Winn, *Ind. Eng. Chem.*, 1946, **38**, 71; B., 1946, II, 184.

[176] R. G. Newton, *Trans. Inst. Rubber Ind.*, 1945, **21**, 113; B., 1946, II, 103; 1945, II, 229.

[177] E. F. Powell and V. Gough, *ibid.*, 102; B., 1946, II, 103.

[178] *J. Rubber Res.*, 1946, **15**, 19; B., 1946, II, 222.

[179] H. F. Church, L. H. N. Cooper, and H. A. Daynes, *ibid.*, 1945, **14**, 155; B., 1945, II, 392.

[180] H. F. Church and H. A. Daynes, *ibid.*, 165; B., 1946, II, 59.

[181] H. Roelig, *Kautschuk*, 1940, **16**, 26; B., 1946, II, 304.

dielectric properties, and permeability to moisture. At this point stress sohuld be laid on the adaptability of rubber, which according to the system of compounding adopted may provide products with excellent electrical-insulating properties or products with reasonably good electrical conductivity. Conditions for satisfactory measurement of the conductivity of electrically conducting rubbers have been elaborated by R. G. Newton.[182]

Various other characteristics of rubber are dealt with in other papers. Evaluation of the physical properties of vulcanised rubbers at low temperatures can be usefully indicated by the two temperatures at which the torsion modulus is respectively twice and ten times as great as at 20°.[183] The curves showing the effect of temperatures, between −40° and 10°, on the resilience of natural and synthetic rubbers have a characteristic form and are different for a mixture of two polymers and for a copolymer of the same total composition.[184] The behaviour of black-compounded natural rubber and GR-S under repeated stressing suggests that semi-reinforcing blacks impart better fatigue-resistance than the channel blacks, the reinforcing effect of the latter being more than off-set by their high hysteresis loss.[185] The contact potential of natural rubber (relative to steel) increases less rapidly than that of GR-S with rise of temperature, which may account for the difference in loss in tensile strength and may provide some confirmation of the electrostatic contact-potential theory of the action of reinforcing agents.[186] The tensile–temperature relationship of stretched vulcanised rubber indicates a predominant amorphous phase with embedded crystallites; this accords with some *X*-ray results, and the main factor responsible for tensile strength is orientation rather than increased crystallisation.[187] The permanent set in natural or synthetic rubber vulcanisates stretched at elevated temperatures appears to arise from simultaneous chain scission and cross-linking induced by atmospheric oxygen and this view permits derivation of a mathematical equation for the calculation of permanent set.[188] From consideration of the tensile strength of natural rubber, Butyl rubber, or neoprene in a single type of compound it can be argued that the tensile strength stands in a definite relation to the proportion of the polymer in the main chain.[189]

Although the gutta-percha hydrocarbon swells more slowly than rubber in a number of organic liquids no evidence appears to exist that either vulcanised or unvulcanised gutta can provide a satisfactory oil-resistant

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[182] *J. Rubber Res.*, 1946, **15**, 35; C., 1946, 173.

[183] L. Mullins, *ibid.*, 10; *Trans. Inst. Rubber Ind.*, 1945, **21**, 247; B., 1946, II, 140.

[184] L. Mullins, *J. Rubber Res.*, 1946, **15**, 60; B., 1946, II, 221.

[185] D. Parkinson and J. L. Bloxham, *Trans. Inst. Rubber Ind.*, 1945, **21**, 67; B., 1946, II, 104.

[186] R. S. Havenhill, H. C. O'Brien, and J. J. Rankin, *J. Appl. Physics*, 1946, **17**, 33; B., 1946, II, 395.

[187] A. J. Wildschut, *ibid.*, 51; B., 1946, II, 394.

[188] R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *ibid.*, 352; B., 1946, II, 396.

[189] J. C. Williams, *India-Rubber J.*, 1946, **113**, 805; B., 1946, II, 264.

alternative to rubber.[190] For production of ebonite,[191] butadiene–styrene or –acrylonitrile copolymers are less satisfactory than natural rubber. Comparison of a number of "foamed" plastics shows each to have its own advantages and disadvantages but cellular ebonite is outstanding in its low electrical conductivity as well as having good chemical resistance.[192]

Since measurement of the physical properties of vulcanised rubber is generally associated with the preparation of moulded test-specimens, any anisotropy in these is capable of introducing serious errors. W. A. Gurney and V. E. Gough[193] have reported on the unexpectedly frequent occurrence of anisotropy, even to an extent exceeding the well recognised calender grain, caused by movement of the rubber in the moulds after it has acquired some degree of vulcanised structure.

BONDING.

The structural association of metals and rubber has provided a big war-time problem for the contestants on both sides and the firm bonding of rubber to metal has never before received such intensive scientific study.

Following previous practice, chlorinated rubber[194] has found application in Germany as a bonding agent. Cyclised rubbers of the "Vulcalock" type, on the other hand, appear to fall short of the bonding strength needed for more drastic conditions of service and an attempt has been made to improve them by treatment with a cross-linking agent, or vulcanising agent, such as a quinoneimine or a halogenoquinone.[195]

Much interest has centred around the long-known brass-plating method for securing strong attachment of rubber to metals. W. G. Messenger[196] has provided a useful classified summary of previously published information.

Study of the reaction between sulphur and copper in paraffin at 120° indicates that the detrimental influence of vulcanisation accelerators on the rubber–brass bond may be explained by their interference not only with the combination of rubber and sulphur but also with the copper–sulphur[197] reaction. Furthermore, not only is the composition of the brass important, but its structure is also, as well as the composition of the rubber "compound" used and the conditions of moulding and of vulcanisation.[198] From observations at temperatures from 21° to –75°, S. Buchan and J. R. Shanks[199] conclude that bond strength is independent of rubber

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[190] T. R. Dawson, R. N. Johnson, and J. R. Scott, *J. Rubber Res.*, 1946, **15**, 26 ; B., 1946, II, 221.

[191] G. G. Winspear, D. B. Hermann, F. S. Malm, and A. R. Kemp, *Ind. Eng. Chem.*, 1946, **38**, 687 ; B., 1946, II, 394.

[192] B. M. Axilrod and E. Koenig, *Plastics (Chicago)*, 1946, **5**, 68 ; B., 1946, II, 424.

[193] *Trans. Inst. Rubber Ind.*, 1946, **22**, 132 ; B., 1947, II, 91.

[194] *Combined Intelligence Objectives Sub-Commee., Item* 22, *File* XXIII–5 ; B., 1946, II, 351.

[195] U.S.P. 2,329,852 ; B., 1945, II, 389.

[196] *J. Rubber Res.*, 1946, **15**, 181 ; B., 1946, II, 472.

[197] C. M. Blow and G. Hopkins, *J.S.C.I.*, 1945, **64**, 316 ; B., 1946, II, 60.

[198] W. A. Gurney, *Trans. Inst. Rubber Ind.*, 1945, **21**, 31 ; B., 1945, II, 393.

[199] *Trans. Inst. Rubber Ind.*, 1945, **21**, 266 ; B., 1946, II, 264.

strength although it is probably related to a physical phenomenon in the rubber phase; there are probably two types of rubber–metal bond, one involving chemical linkage, as between brass and rubber, and another, as probably exemplified by the ebonite or chlorinated (or cyclised) rubber bond, arising from fixation of surface-tension forces. In a further investigation, S. Buchan and W. D. Rae[200] find that rubber stocks giving good bonding are characterised by low formation of sulphide at the metal surface and it is suggested that bond development results from initial formation of cuprous sulphide and chemical attachment of this at points of unsaturation in the rubber molecules.

Although the brass-plating method was applied satisfactorily in Germany[201] it was discontinued there in favour of the "Desmodur" or polycarbimide process in spite of the critical drying time and experienced handling which this demands.[202]

The polycarbimide[203] process is applicable to rubber-to-fabric adhesion as well as to bonding rubber to metal. The favoured polycarbimide in German practice was Desmodur R, a tricarbimide of the formula $CH(C_6H_4{\cdot}NCO)_3$. Conversely but probably with less convenient results, the bonding of rubber to fabric by the brass-plating process has been described.[204]

For attaching rubber to metal, the polycarbimide, dissolved in methylene chloride or mixed freshly with rubber solution, is applied to the metal or to the rubber surface.[205] The bonding effect is doubtless associated with the cross-linking action of the polycarbimide on the rubber at its surface of contact with the metal. In the bonding of rubber to textile material, such as cotton, rayon, or nylon, the polycarbimide is reactive to both textile and rubber and presumably provides a molecular linking. Joint use of a dicarbimide and a cyclised rubber to enhance the adhesion of rubber to rubber or to rayon has also been described.[206]

It is of course possible to increase the adhesion of rayon to rubber by pretreatment of the former with a mixture of an aqueous dispersion of rubber with a solution of an incompletely formed resorcinol–formaldehyde resin or of casein or hæmoglobin[37,207] It has also been proposed to incorporate casein[208] or the resorcinol–formaldehyde resin[209] in the rayon fibre during its manufacture.

[200] *Trans. Inst. Rubber Ind.*, 1945, **21**, 323; B., 1946, II, 264.

[201] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 349, *Item* 22; B., 1946, II, 347.

[202] *Ibid., Final Rept.* 702, *Item* 22.

[203] For a method of preparation of such compounds, see B.P. 574,222; B., 1946, II, 112, also *Combined Intelligence Objectives Sub-Commee., Item* 22, *File* XXII–16; B., 1946, II, 359.

[204] B.P. 577,291; B., 1946, II, 306.

[205] *Combined Intelligence Objectives Sub-Commee., Item* 22, *File* XXIII–3; B., 1946, II, 347. *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 349, *Item* 22; B., 1946, II, 347. See also B.P. 574,898 and 574,903; B., 1946, II, 186.

[206] B.P. 578,233; B., 1946, II, 396.

[207] B.P. 572,232; B., 1946, II, 61. B.P. 577,985; B., 1946, II, 398.

[208] B.P. 580,776; B., 1946, II, 474.

[209] B.P. 582,210; B., 1947, II, 66.

A convenient historical and technological review[210] of the various methods for effecting the adhesion of rubber to other surfaces has been prepared by J. A. Merrill.

RECLAIMING.

The recent extreme need for materials to eke out the inadequate supplies of rubber, whether natural or synthetic, has again brought reclaiming and the use of reclaimed rubber into the list of important economic considerations. Doubt had been expressed as to whether the war-time measures in the substitution of natural rubber by synthetic rubbers and by extenders might gradually lower the quality of scrap vulcanised rubber available and render it unsuited to treatment by reclaiming operations. Tests on this point, however, and on the quality of reclaim have been reassuring.[211] The reclaiming of GR-S vulcanisates is more difficult than that of natural rubber vulcanisates[212] and several modifications have been described to prevent the hardening which commonly occurs when GR-S vulcanisates are heated, such as combining the heat-treatment with mechanical working[213] and/or with an intensified amount of concurrent oxidation.[214]

Other features in the recently published literature include the increasing use of mercaptans[215] of higher molecular weight, *e.g.*, the so-called Renacits,[201] and of hydroxyaryl sulphides[216] as peptising or softening agents to assist the reclaiming process, and also a number of modified methods for dealing with cellulose-containing scrap rubbers.[217] Reclaiming by mechanical treatment so as to effect "cold" replasticisation, which was extensively practised in Germany during 1914–18, has again become of interest[218] but has the disadvantage that the necessary milling equipment is a costly factor.

TECHNOLOGICAL, TESTING, AND ANALYTICAL.

Possibly because its pioneers were frequently men of remarkable judgment, the methods instituted in the early days of the rubber industry have withstood well the tests of time and thereby may have contributed unjustifiably to an impression that the industry has been exceptionally conservative. There are now, however, signs of approaching innovations

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[210] *Rubber Age*, 1946, **59**, 313; B., 1946, II, 341.

[211] J. M. Ball and R. L. Randall, *India Rubber World*, 1946, **114**, 368; B., 1946, II, 349.

[212] H. H. Gillman, *Rubber Age*, 1946, **58**, 709; B., 1946, II, 265.

[213] D. Comes and F. H. Banbury, *ibid.*, **59**, 563; B., 1946, II, 436. B.P. 577,829; B., 1946, II, 397.

[214] B.P. 572,269; B., 1946, II, 62. B.P. 573,053; B., 1946, II, 62. B.P. 580,051; B., 1946, II, 475. U.S.P. 2,338,427; B., 1946, II, 399.

[215] U.S.P. 2,333,810; B., 1946, II, 266. U.S.P. 2,338,427; B., 1946, II, 399.

[216] B.P. 572,268; B., 1946, II, 62. B.P. 575,545–6; B., 1946, II, 224. B.P. 575,547; B., 1946, II, 259.

[217] B.P. 573,054; B., 1946, II, 62. U.S.P. 2,333,810; B., 1946, II, 266.

[218] L. J. D. Healy, *India Rubber World*, 1946, **114**, 70; B., 1946, II, 352. B.P. 577,868; B., 1946, II, 398. B.P. 578,482; B., 1946, II, 399.

such as the application of high-frequency heating[219] and the introduction of new systems of moulding such as transfer- and injection-moulding[220] and the use of light, easily fabricated, non-metallic moulds.[221]

For facilitation of the industrial processing of rubber, a new test has been described in which a so-called "rugosimeter" measures the roughness of calendered material by the resistance to air-flow between the calendered sample and a superposed plane test-surface.[222] Study of the various types of difficulties encountered in factory processes has led to the suggestion that four tests may prove adequate for laboratory determination of processing properties, viz., filler-stiffening, plasticity, length-shrinkage, and rugosity.[223]

Publications concerning specific types of manufactured product include the conditions and requirements in the use of rubber equipment for dairies,[224] an abrasion test for soling material, swelling and other tests for the assessment of jointing materials,[225] *e.g.*, for gas- and water-mains, and the evaluation of rubberised raincoat material.[226] Motor tyres have received consideration from the behaviour of sections under torsional hysteresis tests[228]; the elastic properties,[229] and the magnitude and the effects of the moisture content, of the cords of various types used in tyre construction have also been discussed. A notable feature relating to the manufacture of hard and soft sponge rubber is the number of new "blowing" agents which have been described for this purpose, *e.g.*, a reaction product of zinc oxide and ammonium carbonate,[230] ferrous oxalate,[231] an azo*iso*butyronitrile ("Porofor N"),[232] a biuret–urea mixture,[233] a salt of diguanyl disulphide,[234] and a pentazdiene compound $\mathrm{NR{:}N{\cdot}NX{\cdot}N{:}NR}$ ($\mathrm{R} = \text{aryl}$).[235] A helpful review of the

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[219] V. L. Smithers, *India Rubber World*, 1946, **113**, 505; B., 1946, II, 221. G. P. Bosomworth, *Rubber Age*, 1946, **59**, 429; B., 1946, I, 349.

[220] S. Buchan, *Trans. Inst. Rubber Ind.*, 1946, **22**, 41; B., 1946, II, 394.

[221] B.P. 579,119; B., 1946, II, 438.

[222] M. Mooney, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 514; C., 1946, 67.

[223] L. M. White, E. S. Ebers, and G. E. Shriver, *Ind. Eng. Chem.*, 1945, **57**, 767; B., 1945, II, 392.

[224] W. G. Whittleston, *New Zealand J. Sci. Tech.*, 1945, **26**, A, 223; B., 1946, II, 140; C., 1945, 300.

[225] T. R. G. Lewis, *Trans. Inst. Rubber Ind.*, 1946, **21**, 375; B., 1946, II, 303; C., 1946, 173.

[226] J. W. W. Dyer, *J. Rubber Res.*, 1945, **14**, 173, 180; B., 1946, II, 25, 103.

[227] Kehren, *Textilber.*, 1940, **21**, 299; C., 1946, 89.

[228] H. Wakeman, E. Honold, and E. L. Skau, *J. Appl. Physics*, 1945, **16**, 388; B., 1946, II, 158.

[229] H. Wakeman, E. Honold, and H. Portas, *India Rubber World*, 1946, **113**, 659; B., 1946, II, 302.

[230] U.S.P. 2,200,473; B., 1946, II, 142.

[231] B.P. 574,320; B., 1946, II, 185.

[232] *Combined Intelligence Objectives Sub-Commee.*, *Item* 22, *File* XXIII–25; B., 1946, II, 312, 408. *Brit. Intelligence Objectives Sub-Commee.*, *Final Rept.* 349, *Item* 22; B., 1946, II, 347.

[233] H. F. Schwarz, *India Rubber World*, 1946, **114**, 211; B., 1946, II, 348.

[234] U.S.P. 2,195,623; B., 1946, II, 185.

[235] U.S.P. 2,337,680; B., 1946, II, 306.

literature on the manufacture and properties of porous ebonites of various types has been given by T. R. Dawson and E. A. M. Thomson.[236]

The good service which has been rendered by the microscope in the study of inorganic compounding ingredients is rapidly being supplemented by the use of the electron microscope[237]; the type and limitations of the results obtainable with each have been usefully compared by D. L. Tilleard and N. D. P. Smith.[238]

A micro-combustion method for the estimation of sulphur which is applicable to rubber has been described[239] in which the sulphate ion produced is measured by conductometric titration; such a micro-method is both expeditious and accurate.

Useful contributions to the knowledge of other analytical processes relating to rubber and allied materials include investigations of the degree of unsaturation of Butyl rubber[240] and of vulcanised rubber,[241] the determination of peroxides in synthetic rubbers,[242] and an account of qualitative tests for identification of rubber polymers[243] based on various colour reactions given by their pyrolysates with *p*-dimethylaminobenzaldehyde.

J. E. Field, D. E. Woodford, and S. D. Gehman[244] have published an account of the value of infra-red spectra for revealing the structure of rubber polymers and copolymers, *e.g.*, the relative proportions of 1 : 2 and 1 : 4 coupling, and the nature of subsequent structural chemical changes. A helpful record of the general principles of this powerful research weapon has also been given by H. W. Thompson.[245] Recent important developments in the chemical analysis of rubber along more usual lines have been opportunely reviewed by W. C. Wake.[246]

Small-scale methods for compounding and physical testing, needing as little as 10 g. of material, have been used in examining various fractions of Butyl rubber, separated by fractional precipitation[93]; such methods could probably be extended with advantage especially where economy of material is imperative. Two interesting descriptions have been given of practical procedure for the production, from latex by spreading and dipping respectively, of satisfactory specimens of rubber for test purposes[247,201]; the latter of these is especially convenient and gives test rings of standard dimensions in a simple manner.

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[236] *J. Rubber Res.*, 1945, **14**, 179; B., 1946, II, 102.

[237] D. L. Tilleard and N. D. P. Smith, *J.S.C.I.*, 1946, **65**, 305; B., 1947, I, 59.

[238] *Ibid.*, 261.

[239] H. L. Pedersen, *Dansk Tidsskr. Farm*, 1944, **18**, 1; C., 1946, 152.

[240] J. Rehner, jun., and P. Gray, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 367; C., 1945, 245.

[241] G. F. Bloomfield, *J.S.C.I.*, 1945, **64**, 274; B., 1946, II, 60.

[242] R. F. Robey and H. K. Wiese, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 425; C., 1945, 246.

[243] H. P. Burchfield, *ibid.*, 806; C., 1946, 94.

[244] *J. Appl. Physics*, 1946, **17**, 386; B., 1946, II, 396.

[245] *Analyst*, 1945, **70**, 443; C., 1946, 54.

[246] *Trans. Inst. Rubber Ind.*, 1945, **21**, 158; C., 1946, 94.

[247] C. R. Peaker, *Rubber Age*, 1945, **57**, 423; C., 1945, 245.

Plasticity testing is represented during the past year by descriptions of an improved type of shearing-cone plastimeter,[248] a high-pressure extrusion plastimeter,[249] [250] an account of precautions necessary for accurate working of the Mooney viscometer,[250] and recommendation of GR-I synthetic rubber as a comparative material for standardising this instrument.[251]

Apparatus has also been described for testing the soundness of motor tyre covers by means of ultrasonic vibrations,[252] for an accelerated "weathering" test[172] for soft rubbers generally, and—an important detail in tearing tests—for the accurate cutting of the initiatory nick.[253]

An attempt has also been made to develop a satisfactory quantitative test for measurement of the property of tackiness[254]; this characateristic, so important in the factory behaviour of rubber stocks, is realised to be influenced by a variety of factors.

Finally, the nature of a considerable proportion of the physical tests customarily applied to rubber justifies every serious attempt to ensure strict comparability of results from different laboratories. A systematic study of tensile tests from sixteen laboratories[255] shows a gratifying standard of accuracy but reveals a possibility of improvement by further careful standardisation of methods.

[248] G. H. Piper and J. R. Scott, *J. Sci. Instr.*, 1945, **22**, 206 ; C., 1946, 67.

[249] H. K. Nason, *J. Appl. Physics*, 1945, **16**, 338 ; C., 1946, 142.

[250] R. H. Taylor, *India Rubber World*, 1945, **42**, 582 ; C., 1945, 298.

[251] J. M. Buist, *India-Rubber J.*, 1945, **109**, 484 ; B., 1946, II, 25 ; C., 1946, 65.

[252] B.P. 571,817 ; C., 1946, 66.

[253] J. M. Buist and R. L. Kennedy, *India-Rubber J.*, 1946, **110**, 809 ; B., 1946, II, 352 ; C., 1946, 173.

[254] W. F. Busse, J. M. Lambert, and R. B. Verdery, *J. Appl. Physics*, 1946, **17**, 376 ; B., 1946, II, 396.

[255] B. D. Porritt and J. R. Scott, *J. Rubber Res.*, 1945, **14**, 93 ; C., 1945, 245. R. G. Newton, *ibid.*, 113 ; C., 1945, 299.

LEATHER.

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COLLAGEN.

K. H. GUSTAVSON[1] has compared the reactivities of mammalian and fish collagen. Both calf and cod collagen have the same acid-combining capacity, but the fish collagen has a low shrinkage temperature (44—45°) and is rapidly dissolved by tryptic enzymes, acids, or alkalis. Calf collagen is resistant to these reagents but is more rapidly attacked by calcium chloride solution. Cod collagen shows much greater affinity for vegetable tannins, and for chromium compounds of high molecular weight, than does calf. It is postulated that the salt link is the dominant type of internal linking in fish collagen, while in mammalian collagen the main cohesion is through co-ordination valency forces (hydrogen bonds) between polypeptide chains, supplemented by salt links. This view that salt linking is relatively unimportant in mammalian collagen is developed in a second paper[2] giving the effect of irreversible inactivation of salt links by naphthalene-2-sulphonic acid. This treatment lowers the shrinkage temperature by 11°, whereas potassium thiocyanate, which causes irreversible breakdown of co-ordinate cross-links, partially gelatinises the collagen. Collagen, denatured by moist heat, shows an increased uptake of co-ordination-active chromium compounds, and of vegetable tannins, due to the groups liberated by rupture of co-ordinated hydrogen bonds during heat-denaturation.

A large number of papers has been published on the determination of amino-acids in proteins, and a critical survey of methods has been made by A. C. Chibnall.[3] It was pointed out that before confidence can be felt in the determined values of any amino-acid unit in the molecule, results obtained by two different methods must show concordance; secondly, the only way of knowing how much of the molecule is still evading the analyst's skill is to record the results on the basis of the percentage of total nitrogen. However, in the analyses of proteins which contain labile nitrogen (for example, the amide nitrogen of collagen, which may be lost during alkaline treatment) it is also necessary to record the nitrogen content of the sample under analysis. This enables the amino-acids to be calculated as per cent. of the protein, if results in this form are required. The appended table sums up present opinions on the constitution of collagen and gelatin. Except where otherwise stated, the figures are those given by Chibnall or calculated from his values.

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[1] *Svensk Kem. Tidskr.*, 1942, **54**, 74; B., 1946, II, 26.

[2] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 47; B., 1946, II, 225.

[3] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 1; C., 1946, 121.

AMINO-ACID COMPOSITION OF GELATIN AND COLLAGEN.

	Gelatin.		Collagen.	
	N as % total protein N.	g. amino-acid per 100 g. protein.	N as % total protein N.	g. amino-acid per 100 g. protein.
% N content of protein, moisture- and ash-free	18·0	—	17·9	—
Glycine	27·5	26·5	27·0	25·9
Alanine	8·1	9·3	8·0	9·1
Valine	2·5	3·8	2·2	3·3
Leucine . . . . *iso*Leucine	3·1	5·2	3·2	5·4
Proline	10·0	14·8	9·9	14·6
Hydroxyproline . .	8·7	14·7	8·5*	14·2*
Tyrosine	0·0	0·0	0·0	0·0
Tryptophan . . .	0·0	0·0	0·0	0·0
Phenylalanine . .	1·2	2·6	1·9	4·0
Serine	2·3	3·1	2·3	3·1
Threonine	1·4	2·1	1·5	2·3
Cystine	—	—	—	—
Methionine . . .	0·6	1·2	0·5*	1·0*
Arginine	15·3	8·6	15·3	8·5
Histidine	1·0	0·7	1·2	0·8
Lysine	4·6	4·3	4·4	4·1
Hydroxylysine . .	1·2	1·3	1·3	1·3
Glutamic acid . .	3·1	5·9	3·1	5·8
Aspartic acid	2·0	3·4	2·0	3·4
Amide nitrogen . .	0·5	—	—	—
Total	93·1		92·3	

* From J. H. Bowes, *Ann. Repts.*, 1943, **28**, 324.

Chibnall points out that whereas old methods of gravimetric isolation of amino-acids required 10—100 g. of pure protein and took weeks of work, new methods may require only 25 mg. and are very quick. However, accuracy must be considered as well as convenience of working, and a method giving results to within 10% may be satisfactory for some nutritional investigations, whereas workers on protein structure require results within 2% of the correct values.

Chibnall surveys the newer methods for protein analysis, and points out their individual advantages or disadvantages. Glycine is a particularly suitable subject for biological methods as there is no question of racemisation; biological methods are specific to the natural stereoisomer. There is still no accurate method for determining hydroxyproline.

GELATIN AND GLUE.

W. M. Ames,[4] continuing his work on the preparation of gelatin, treated the collagen with lime suspensions for increasing periods of time, and

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[4] *J.S.C.I.*, 1945, **64**, 242; B., 1945, II, 355.

carried out formol titrations on the resulting gelatins. In liming for sufficient time to convert collagen completely into gelatin of good quality, loss of ammonia appears to be of greater significance than the rupture of peptide linkings. Ames' description[5] of the laboratory evaporator for solutions liable to degradation by heating led to the suggestion of alternative designs.[6]

The gelatin reactions supposed to be those of an aldehyde or sugar[7] are shown by A. Steigmann[8] to be those of nitrate or nitrite.

J. Kinet and R. Coutrez[9] have dialysed and measured properties of samples of gelatin from bones from different sources pretreated with alkali and with acid. They conclude that dialysis not only removes ions from gelatin but also modifies its structure. The significance in the titration curves of various groups is considered, and it is concluded that the dissociation constant K_{NH_2} is the same for all samples of gelatin irrespective of their origin.

Plasticisers suggested for gelatin or glue are reaction products of sodium bisulphide on a monosaccharide such as glucose or invert sugar.[10] W. C. Griffin[11] describes a technique for measuring the water intake of glue at various humidities, and records data for glue, glycerol, sorbitol, and their mixtures. Data for the effect of sorbitol and glycerol on the viscosity and gel and tensile strengths of glues are given by W. C. Griffin and E. G. Almy,[12] who recommend a mixture of equal parts of each plasticiser. An exterior tanning of gelatin capsules with benzoquinone gives increased tensile strength and water-resistance.[13]

Patents cover extraction[14] and drying[15] of glue and an apparatus for the rapid determination of gelling temperature.[16]

Raw Materials and Storage.

H. Anderson[17] has studied the adaptation of various bacteria to growth in the presence of sodium chloride; unfortunately, those organisms showing greatest adaptation to salt are strongly proteolytic. The salt adaptation of *B. subtilis* was studied in detail by experiments with two strains of this organism; these tests showed that salt tolerance of up to 25% could be built up by culturing in the presence of increasing concentrations of salt, and that this adaptation is a temporary property of the strain

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[5] *Chem. and Ind.*, 1946, 194; C., 1946, 223.

[6] B. N. Reavell, *ibid.*, 254, 366, G. S. Muirhead, *ibid.*, 326; C., 1946, 312.

[7] A. Steigmann, *J.S.C.I.*, 1943, **62**, 206; B., 1944, II, 27.

[8] *Ibid.*, 1945, **64**, 220; B., 1945, II, 355.

[9] *Bull. Soc. chim. Belg.*, 1941, **50**, 195; A., 1945, I, 304.

[10] N. R. Pike, P. H. Kelm, and G. A. McLaren, U.S.P. 2,322,736; B., 1946, II, 67.

[11] *Ind. Eng. Chem.*, 1945, **37**, 1126; B., 1946, II, 107.

[12] *Ibid.*, 948; B., 1946, II, 66.

[13] H. Hurst and J. H. Schulman, B.P. 573,678; B., 1946, II, 108.

[14] D. P. Grettie, U.S.P. 2,327,185; B., 1945, II, 355. A. Hoeren, U.S.P. 2,339,405; B., 1946, II, 354.

[15] E. H. Hoelscher and R. S. Tour, U.S.P. 2,198,617; B., 1946, II, 27.

[16] C. R. Fordyce and H. F. Vivian, U.S.P. 2,336,238; C., 1946, 214.

[17] *J. Soc. Leather Trades' Chem.*, 1945, **29**, 215; B., 1946, II, 26.

which is readily lost by culturing in salt-free media. These results add weight to the condemnation of the employment of used salt for the preservation of hides and skins.

M. E. Robertson[18] has shown that putrefaction is checked by hydrogen sulphide : samples of raw hide were kept for a week at 37° and a month at 20° in atmospheres of hydrogen sulphide. A patented softening treatment for dried hides consists of treatment with aqueous hydrogen sulphide, formed, for example, by acidification of an alkali sulphide.[19]

Fellmongering and Depilation.

An investigation of fellmongering by the sweating process has been made in Australia,[20] where in the past 20% of the skins fellmongered have been damaged or discarded. Sweating chambers are kept at a selected temperature between 16° and 26°, and the relative humidity at near saturation. The "depilation load" required to detach a standard wool staple is brought to nearly zero before a skin is ready for pulling. The most important contribution to wool freeing is made by an atypical strain of *Proteus vulgaris,* but damaged pelts contain an unduly large proportion of anaërobes. The time for a skin to become ready for pulling diminishes rapidly with increase in temperature over the range 10—22°, and less rapidly from 22° to 40°, cooling after partial sweating retards the process. Ammonia is evolved from sheepskins during sweating, but plays no major part in the process. The effect of a variety of chemicals on the depilation load is considered, but none is suitable for fellmongering purposes, nor do soaking experiments hold promise that modifications will accelerate sweating. The wool from pieces of skin trimmed from the neck and flanks is recovered after "pieing," that is, piling the pieces in a warm place. In this process anaërobic bacteria are present in greater numbers than in the sweating process. Two alternative treatments are considered hopeful and are to be further investigated : in the first the pieces are shrunk at 65° and then digested at 40° in a neutral solution of a protease obtained by culturing *Aspergillus flavus-oryzæ* on steamed bran ; the second process involves digestion with papain at 65°. During sweating, the cells of the wool root sheath and a portion of the bulb are digested, the wool root becoming tapered, and thus the wool-holding structures are largely eliminated. When the wool fibre is pulled from fresh skins, the papilla and root sheath are everted.

B. M. Das and M. Chaudhuri[21] recommend the use of sodium hydroxide in the unhairing of skins intended for box sides ; they suggest 1% sodium hydroxide and 2% sodium sulphide on the lime solution.

Bulk trials of amines in pit liming have been carried out at three

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[18] *Nature,* 1945, **155**, 395; B., 1946, II, 400.

[19] J. Pfannmuller, U.S.P. 2,326,798; B., 1945, II, 355.

[20] F. G. Lennox, M. E. Maxwell, and W. J. Ellis, *Counc. Sci. Ind. Res. Australia,* 1945, *Bull.* 184; B., 1946, II, 65.

[21] *J. Sci. Ind. Res., India,* 1946, **4**, 512; B., 1946, II, 267.

tanneries[22] and in general show little difference from the standard lime plus sulphide treatment. A mixture of sulphide with dimethylamine is more effective than either reagent used alone. Methylamine limes give leather showing more fine-splitting of the fibre bundles, and in certain cases leather yields exceed that of controls processed by normal methods.

BATING.

A valuable contribution to the theories of bating has been made by H. Anderson,[23] who has carried out experiments with purified enzymes on the following proteins : collagen, from the centre split of a limed, delimed, dehydrated goat skin ; elastin from the ligamentum nuchae of a goat ; involuntary muscle from the uterus of a goat ; interfibrillary protein extracted by salt solution from skins which had been limed and delimed. Solutions of chymotrypsin, and enzymes from *Clostridium sporogenes hæmolyticum*, *Clostridium histolyticum*, and papain were prepared and standardised with gelatin. When used to digest the proteins enumerated above, and in practical bating trials, it was shown that the bating activity of an enzyme ran parallel to its ability to digest muscle protein. Anderson suggests that the action of bating in giving a smoother grain is due to digestion of the points of attachment of the erector pili muscles, so that subsequent muscle contraction cannot distort the grain. The "fallen" feel of a bated pelt is probably due to mild peptisation of the collagen fibres, as effective bating enzymes attack collagen. The greater activity of the old dung puers compared with modern bates in which the enzyme is adsorbed on wood flour is associated with the particle size of the adsorbing material. The solid particles in a dung puer hold the enzyme in active form and, unlike wood flour, are sufficiently small to penetrate the hair follicles and so carry the enzyme into intimate contact with one end of the erector pili muscle.

K. H. Gustavson[24] compared the effect of trypsin on fish collagen tanned with a variety of materials. The enzyme does not attack chrome-tanned fish collagen ; formaldehyde or vegetable tanning confers considerable resistance, but the syntans examined did not increase the resistance to attack by trypsin. This low stability conferred by syntans remains unaltered after heavy vegetable retannage.

DEGREASING.

H. M. Davies and R. F. Innes have published two papers on grease in the light leather industry. The first[25] surveys some factors affecting the paraffin degreasing of sheepskins, and explains why opinions of this process vary so widely ; the proportion of total grease removed by paraffin varied from 10·5% to 75% in different tanneries. The amount of grease

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[22] D. Burton, J. G. Gray, E. W. Merry, W. B. Pleass, and W. L. Williams, *J. Soc. Leather Trades' Chem.*, 1946, **30**, 26 ; B., 1946, II, 187.

[23] *Ibid.*, 1945, **29**, 209 ; B., 1946, II, 26.

[24] *Svensk Kem. Tidskr.*, 1942, **54**, 249 ; B., 1946, II, 106.

[25] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 65 ; B., 1946, II, 267.

removed is a function of the paraffin uptake, which in turn depends on the water content of the pickled pelt. Paraffin uptake increases rapidly as the moisture content falls below 55%, and for best results the moisture content should be between 35 and 45%. Recovery of paraffin by steam-distillation is advocated.

The second paper[26] concerns the study of causes and prevention of greasiness in glazed kid, a trouble affecting 13% of total output and especially prevalent where dry-salted skins are processed. Greasiness of the finished leather is liable to develop if the original skin contains more than 1% of fatty acid; neutral triglycerides are unimportant in grease problems. Grease may be removed from the raw pelts by pickling and then paraffin degreasing, either after partial drying or with accessory agents (such as heavily sulphated oils) added to the paraffin to increase its affinity for wet pelts.

VEGETABLE TANNING.

The technology of extraction of tanning materials has received attention, particularly in the United States of America. F. P. Luvisi and I. D. Clarke[27] steeped leaf material from one Sicilian and three domestic (U.S.A.) species of sumac in water, the time and temperature of treatment being varied. Tannin extraction increases, but the quality of the extract decreases, with increase in steeping time. No limits for commercial extraction could be set; manufacturers must balance conditions to give an economic yield of reasonable quality. I. D. Clarke and H. Hopp[28] carried out drying tests on leaves from dwarf sumac (*Rhus copallina*, L.). Leaves dried while attached to the stems have a significantly higher tannin content than detached leaves similarly dried; slow-drying methods give material of higher tan to non-tan ratio and higher pH, but leather tanned with slowly dried leaves has poorer colour. I. D. Clarke, C. W. Mann, and J. S. Rogers[29] have tanned sheepskin skivers with sumac of three U.S.A. varieties, and with Sicilian sumac; all made satisfactory leather of commercial quality. Air-elutriation of the leaves, to remove petioles and rachises, raises the tan content and gives leather of better colour.

C. W. Beebe, T. C. Cordon, and J. S. Rogers[30] have developed a centrifugal filtration method for tannin extraction which can be operated on materials such as canaigre (*Rumex hymenosepalus*, Torr.) which are difficult to leach by normal methods; the material is ground or crushed, agitated with water at suitable temperature for half-an-hour, and then centrifuged through a filter cloth. The efficiency of the process with various materials is higher than that obtained by usual procedures, and varied up to 118%. Extraction efficiencies of greater than 100% indicate either defects in

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[26] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 104; B., 1946, II, 307.
[27] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 98; B., 1946, II, 267.
[28] *Ibid.*, 1945, **40**, 363; B., 1946, II, 26.
[29] *Ibid.*, 1946, **41**, 59; B., 1946, II, 226.
[30] *Ibid.*, 161; B., 1946, II, 267.

the analytical method, or solubilisation during bulk extraction of material not so altered by the analytical method.

Thermal density coefficients and hydrometer correction tables have been worked out by M. G. Blair and E. L. Peffer[31] for quebracho, oak bark, hemlock bark, chestnut, and mangrove bark extracts, for a density range of 1·00—1·12 and a temperature range of 50—100° F.; from the results obtained, a single equation is derived which is applicable to all the extracts, and from the tables, observations taken at any temperature between 50° and 100° F. can be directly converted into values at the standard temperature of 60° F.

W. Wiegand[32] gives physical methods for determining the conditions in a commercial extractor for tanning materials; diagrams make it possible to calculate the effects on the plant of changes in temperature, quantity of water, and extraction time. Extraction of spruce bark with sodium sulphite and alkali was shown by V. Kubelka and L. Masner[33] to give up to 12·5% more extract than water alone. The resulting extract differs from that produced by water; it is redder in colour, produces more sludge, and shows more rapid penetration of hides, but less ready fixation.

R. E. Liesegang[34] followed the effect of tanning agents on the diffusion of methylene-blue solution into strips of gelatin-impregnated paper; treatment with aluminium sulphate increased diffusion rate, whilst potassium dichromate, followed by exposure to light, retarded it.

The interest in new sources of vegetable tanning materials, begun by war-time shortages, has continued. Indian raw materials are surveyed by R. L. Badhwas, A. C. Dey, and M. V. Edwards,[35] who have divided 300 native plants into two main groups, those of known tan content, and those of negligible or unknown tan content. Those of practical interest include dhawa leaf (*Anogeissus* spp.), divi-divi pods (*Cæsalpinia coriaria*), and mangrove bark (*Ceriops* and others). Babul[36] (*Acacia arabica*) yields 5 tons of bark per acre from modern canal-bank plantations, but is felled extensively as timber and fuel, and bark is likely to be in short supply; pods should be prepared by seed removal and powdering. Mimosa plantations[37] necessitate the complete eradication of grass, and transplants are much better than direct sowings. Failure is caused by wind on the most exposed sites in southern India; damage by cottony cushion scale insect may be biologically controlled by the introduction of the ladybird.

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[31] *J. Res. Nat. Bur. Stand.*, 1944, **33**, 341; B., 1946, II, 26.

[32] *Collegium*, 1942, 249; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 98; B., 1946, II, 144.

[33] *Collegium*, 1943, 33; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 120; B., 1946, II, 65.

[34] *Collegium*, 1941, 209; *J. Soc. Leather Trades' Chem.*, 1944, **28**, 288; B., 1946, II, 106.

[35] *Forest Res. Inst., Dehra Dun*, 1944, *Indian Forest Leafl.* 72; B., 1946, II, 106.

[36] M. V. Edwards, *ibid.*, 1945, *Leafl.* 74; B., 1946, II, 266.

[37] *Idem*, *ibid.*, *Leafl.* 76; B., 1946, II, 266.

M. Nierenstein[38] draws attention to an error in nomenclature applied to the Hottentot fig by T. Y. Hum and R. Pratt[39]; this plant should be called *Mesembryanthemum acinaforma* L. and it contains tannin in the bark and leaves.

Possible means of reducing the consumption of vegetable tanning materials in Hungary were considered by J. Jány,[40] who concluded that reduction of degrees of tannage, the increased replacement by synthetics, or attempts to reduce losses in process were all dangerous procedures to be avoided if possible.

The soluble material and tannin content of 14 Brazilian plants are recorded by B. L. Primo[41]: tan contents up to 32% were found. The age of the plant was not found to have an appreciable effect on tan content.

A Alpaut[42] shows that tannin formation in galls depends on the stimulus causing gall formation, and not on the tree itself; some galls from the Pamuklu Valley near Ankara showed high tannin content although the trees on which they had formed were low in tannins, whilst some trees noted for their high tannin content gave galls of low tan content.

Mixtures of oak bark, or spruce bark extract, with syntans gave leather of chemical and physical properties varying considerably with the chemical composition of the syntan.[43]

T. D. Braunschweig[44] treated quebracho by varying the pH at equal and increasing rates of sulphur dioxide addition. His results show that the solubilising process is a function of pH and sulphur dioxide content, higher pH of treatment giving a more soluble product for a given sulphur dioxide content. Treated extracts showed considerable differences in buffer capacity which are important from the viewpoint of practical tanning. The mechanism of bisulphiting is interpreted on the basis of a suggested hypothetical formula of an olated quebracho catechin. The (U.S.A.) official tannin analysis does not disclose existing differences between various extracts treated with the same amount of sulphur dioxide; new analytical methods suggested are outlined below in the section on analysis.

SYNTANS.

Patented production methods[45] use as raw materials wood distillation products, natural resins, and sulphite cellulose lye as well as naphthalene-formaldehyde condensates.

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[38] *J. Soc. Leather Trades' Chem.*, 1945, **29**, 168; B., 1945, II, 395.

[39] *Ibid.*, 93; B., 1945, II, 66.

[40] *Collegium*, 1943, 223; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 197; B., 1946, II, 143.

[41] *Anais Assoc. Quim. Brasil*, 1945, **4**, 117; B., 1946, II, 267.

[42] *Collegium*, 1942, 417; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 97; B., 1946, II, 65.

[43] F. Stather, H. Herfeld, and O. Gottlieb, *Collegium*, 1941, 297; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 24; B., 1946, II, 106.

[44] *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 185; C., 1945, 246.

[45] Aktieb. Statens Skogsindustrier, B.P. 571,595; B., 1945, II, 395. E. Koch, U.S.P. 2,335,947; B., 1946, II, 308. O. A. Muller, B.P. 571,916; B., 1946, II, 146. A. Russell and J. W. Copenhaver, U.S.P. 2,204,512; B., 1946, II, 146.

F. Stather and H. Herfeld[46] have shown that the addition of up to 50% of syntan to vegetable tanning material does not adversely affect the stability of the resulting leather after storage for 3—8 years.

The most interesting publications on synthetic tanning materials have been the British Intelligence Objectives Sub-Committee reports on the German syntans and related chemicals[47]; these give the chemical composition of proprietary products with details of the manufacture and use. The reports are largely in the form of recipes and cannot be satisfactorily summarised, those interested in the subject are referred to the original texts.

MINERAL TANNING, FAT-LIQUORING, AND STUFFING.

R. W. Green[48] has examined the vapour pressure of basic chromium sulphate systems, and found that the moisture content of the basic sulphate is a continuous function of the vapour pressure. It is assumed that the solid phase consists of two or more definite hydrates in solid solution. At constant vapour pressure, the water content of basic chromium sulphate decreases with increasing basicity. The water content of chrome leather is slightly greater than the sum of that associated with basic chromium sulphate of the same basicity and the untanned protein, but is strongly influenced by the method of preparing the sample prior to conditioning. Green describes a new humidity-conditioning apparatus in which air is continually passed through a saturated solution of the appropriate salt to adjust humidity, and then over the sample of material under test.

T. A. Pressley[49] has shown that a small quantity (less than 0·5%) of free fatty acid is an essential constituent of the untanned pelt for the production of normal non-wetting chrome leather; water-resistance is affected by the chromium fixed by the protein and not merely by that attached to the fatty acid, so the simple explanation that the non-wetting is conferred by the film of chrome soap is insufficient to explain the facts.

E. R. Stern[50] claims to produce a non-crocking (that is, fast to rubbing) dyed suede by dyeing chrome leather and then after-treating with iron tannate and vegetable tanning materials. A titanium tannage in the presence of an organic acid, such as lactic, is said to produce a white leather of high quality.[51] Compounds formed by the interaction of aluminium salts with organic hydroxy-acids in the presence of alkali are stated to be useful for tanning and for treating chrome-tanned leather.[52]

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[46] *Collegium*, 1941, 211; *J. Soc. Leather Trades' Chem.*, 1944, **28**, 288; B., 1946, II, 106.

[47] C. F. Payan, *Brit. Intelligence Objectives Sub-Committee*, 1946, *Final Rept.* 157, *Item* 22; B., 1946, II, 400. W. Baird, *ibid.*, *Final Rept.* 240, *Item* 22; B., 1946, II, 400. M. P. Balfe, T. Redfern, C. G. Turner, and S. G. A. Wise, *ibid.*, *Final Rept.* 762, *Item* 22.

[48] *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 378; B., 1946, II, 27.

[49] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 94; B., 1946, II, 308.

[50] U.S.P. 2,204,262; B., 1946, II, 187.

[51] J. V. Vaughan, U.S.P. 2,195,715; B., 1945, II, 395.

[52] J. G. Niederoorn and W. O. Dawson, U.S.P. 2,327,815; B., 1945, II, 396.

German properietary substitutes for the normal fat-liquoring oils and stuffing greases have been investigated by H. Herfeld, F. Stather, and C. Reiss[53]; one of the types of compound, produced by condensing a secondary alcohol with an aromatic hydrocarbon in the presence of oleum, is recommended for soaking and degreasing as well as for fat-liquoring. L. Masner and K. Míček[54] have followed the fat balance in upper leathers, and found that little more than half the total grease is removed by solvent extraction; the remainder combines with the hide substance. Further fixation is caused by hard drying of chrome leather and by ironing during the finishing process. Drying vegetable-tanned leather results in the formation of hydroxy-fatty acids which are not removed by light petroleum but can be extracted by carbon tetrachloride. In fat-liquoring, only 2% of the oil used is discarded with the spent liquor, but curried leather may lose 14% of the added grease in finishing processes such as whitening.

PROPERTIES OF LEATHER.

An important contribution to knowledge of the cause and prevention of atmospheric degradation of vegetable-tanned leather was made by A. Cheshire.[55] It is known that leathers such as upholstery or book-binding leathers sometimes develop high acidity and deteriorate on ageing under industrial conditions, sulphur dioxide from the atmosphere forming sulphuric acid.[56] Cheshire postulates that leather in the moist state (the "bound water" is sufficient) and containing a strong acid presents an active surface on which hydrogen peroxide is formed catalytically from atmospheric oxygen; the peroxide so formed is decomposed by the catalytic effect of traces of ionic iron, and the oxygen so liberated brings about direct oxidation of the hide substance : this results in loss of fibre structure. Any material which will suppress the catalysis by iron, *e.g.*, by holding iron in insoluble, and therefore inactive, form, will have a protective action on leather; for example, treating leather with oxalic acid followed by calcium acetate will prevent deterioration. Existing accelerated ageing tests are criticised, and a 6-day bomb test employing 1 atmosphere of sulphur dioxide and 7 atmospheres of oxygen is described.

The internal surface of hide or leather has been determined by R. G. Mitton[57] using an air-permeability method, and by A. C. Zettlemoyer, E. D. Schweitzer, and W. C. Walker,[58] who measured the nitrogen adsorbed at the temperature of liquid nitrogen. The results of both sets of experiments are of the same order. Mitton's figures for specific surface of chrome-tanned leather are 1·24—1·60 × 10^4 sq. cm. per c.c.;

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[53] H. Herfeld, *Collegium*, 1943, 176; F. Stather and H. Herfeld, *ibid.*, 1942, 81, 121, 313; C. Reiss, *ibid.*, 269; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 240, 95, **94**; B., 1946, II, 144, 145.

[54] *Collegium*, 1942, 182; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 93; B., 1946, II, 145.

[55] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 134; B., 1946, II, 353; C., 1946, 262.

[56] R. F. Innes, *ibid.*, 1930, **14**, 624; 1931, **15**, 480; B., 1931, 130, 1109.

[57] *Ibid.*, 1945, **29**, 255; B., 1946, II, 107.

[58] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 253; B., 1946, II, 353.

the American workers found 1·0 × 10^4 sq. cm. per g. for formaldehyde-tanned collagen, and 4·8 × 10^4 for untanned hide.

H. Herfeld,[59] working with pots containing water and covered with diaphragms of the material under test, showed that water-vapour-permeability bears some relationship to water absorption but not to air-permeability; materials impervious to air may still pass water vapour. F. F. Marshall and D. Williams[60] constructed boxes of leather and of vinyl plastic material and compared the relative humidity inside and outside the box; water vapour was readily lost from a sole leather box but not from a plastic box.

R. G. Mitton[61] tested some physical properties of hide bellies and of goat skins. Hide bellies have a much greater density (probably due to their grease content) and low air-permeability and lastometer distension at grain crack than have goat skins; density, air-permeability, and water absorption show much greater variation between skins than is shown by different parts of the one skin.

The chemical, physical, and microscopical properties of chrome calf of American, British, and Continental origin have been thoroughly examined.[62] The characteristics may be summarised as follows: American leathers are thin, minimum shrinkage after 1 minute in boiling water, low pH, high grease content (2·9%), high melting point of grease, low chrome content (3·84% Cr_2O_3). British leathers are in many ways intermediate between American and Continental; they have low or medium distension at grain crack when tested on the lastometer, they are more compact in weave, and show less fine splitting than Continental samples. Continental leathers show low shrinkage temperatures, high distension at grain crack, full feel, low grease content (2·0%), and high chrome content (5·6% Cr_2O_3). In general, shrinkage temperature rises with chrome content to 4·5% Cr_2O_3, and after that shows closer correlation with fineness of splitting in the fibre structure. High chrome content is associated with low grease and vice versa.

R. M. Koppenhoefer[63] used tensile strength as a criterion of the suitability of various lubricants for vegetable-tanned belting leather; he concludes that the replacement of saponifiable oils or greases by mineral oils is in no way detrimental to the character or service life of the belting.

Two simple tests for rigidity of sole leather are described by P. White and F. G. Caughley.[64] In the knife-edge test, samples of leather are suspended on two knife edges and depression is produced by adding weights

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[59] *Collegium*, 1941, 65; *J. Soc. Leather Trades' Chem.*, 1944, **28**, 249; B., 1946, II, 107.

[60] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 6; B., 1946, II, 226.

[61] *J. Soc. Leather Trades' Chem.*, 1945, **29**, 269; B., 1946, II, 145.

[62] G. O. Conabere, D. Jordan Lloyd, and E. W. Merry, *ibid.*, 1945, **29**, 246; B., 1946, II, 107. G. O. Conabere, *ibid.*, 232; B., 1946, II, 107. E. W. Merry, *ibid.*, 223; B., 1946, II, 107.

[63] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 19; B., 1946, II, 226.

[64] *J. Soc. Leather Trades' Chem.*, 1945, **29**, 148; B., 1945, II, 395; C., 1945, 246.

to a pan suspended by a third knife edge from the centre of the sample. In the bow test, force is applied to the ends of a strip until it has bent to a degree such that tangents drawn from the ends of the strip meet at right angles. Changes in rigidity on wetting may be positive or negative. The dry rigidity is largely increased by water-soluble tans, whilst the predominating factor producing rigidity in wet leather is the presence of insoluble matter on or between the fibres. Increase in rigidity resulting from rolling may be accounted for by decrease in thickness.

C. E. Weir[65] has carried out experimental work on the compression of leather, and shown that compression-decompression curves exhibit large hysteresis loops; data show that in tannery rolling the leather is subjected to pressures of 2000—3000 lb. per sq. in.

Increased wear and reduced water penetration were obtained by F. Stather and H. Herfeld[66] for vegetable-tanned sole leather impregnated with mixtures of wood resin and paraffin wax, mineral waxes, and various proprietary preparations; stearin, paraffin wax, or montan wax increased only the wear-resistance, and aluminium soaps only the water-resistance. The influence of soil solutions on the wear of vegetable-tanned sole leather was investigated by R. L. Moore,[67] who soaked sheepskin, tanned with a variety of tanning materials, in different solutions including an infusion of farm soil. He concludes that wear-resistance is largely a function of the buffer index of the leather; the major injurious effects of soil solutions on the wet wear of leather are due to a rise in pH of the leather and the precipitation of the hydrolysed tannins by soluble calcium salts. W. T. Roddy[68] describes an experimental track for wear evaluation of sole leather, on which tests indicated that wear on the track did not simulate or parallel normal civilian wear.

R. G. Mitton and T. R. G. Lewis[69] have made a systematic study of the abrasion of leather, using a machine in which conditions were under close control. Variations were made in the pressure between the specimens and the abrasive, the air flow used for removing abraded material, the fineness of the abrasive, and the amount of abrasion each part of the abrasive must perform before being replaced; the hardness of the specimens was also measured. Using statistical methods, it is shown that (*a*) at low loads and with coarse abrasive, the rates of abrasion are determined almost entirely by the hardness of the specimens; (*b*) at higher loads or with finer abrasives, the hardness becomes relatively unimportant and other properties of the leather determine the rate of abrasion. It is suggested that as loading is increased, a cutting action by abrasive particles is replaced by a tearing or teasing out of fibres. The hardnesses of various leathers in the dry state are closely correlated with those of

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[65] *J. Res. Nat. Bur. Stand.*, 1945, **35**, 257; B., 1946, II, 226.

[66] *Collegium*, 1941, 247; *J. Soc. Leather Trades' Chem.*, 1944, **28**, 289; B., 1946, II, 107.

[67] *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 303; B., 1946, II, 27.

[68] *Ibid.*, 300; C., 1946, 68.

[69] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 74, 113; B., 1946, II, 307.

the same leathers measured in the wet state. The results of duplicate abrasion tests are seldom in exact agreement; the coefficients of variation of abrasion of specimens from two leathers were estimated as about 4·5 and 7·5%, respectively. The inherent inhomogeneity of the leather is the chief cause of this variability : lack of uniformity of the abrasive may be a contributory factor.

R. G. Mitton[70] has also investigated the mechanical properties of individual vegetable-tanned leather fibres. The rigidity modulus of the fibres decreases as the amount of adsorbed water increases. Changes in fibre length are complicated by plastic flow, but if the initial extension due to this is removed by a load, further changes in length caused by humidity are reversible. Length change from dryness to saturation approximates to 2% and is almost independent of load. At constant humidity, fibres obey Hooke's law approximately. High humidities increase extension, but the extension–load curve is independent of temperature in the range 15 – 100° Fibres dried under tension do not retract fully, and internal stresses remain; these cause a further retraction when the fibre is brought into an atmosphere of higher humidity. Calculations show that the tensile strength of the fibres examined is consistent with the view that leather specimens break by rupture of their fibres rather than because they slip.

C. W. Mann[71] has measured scuff-resistance on a modified Tinius Olsen stiffness tester, which gives results similar to those of alternative machines in a much shorter time. Scuffing-resistance is greater in the direction leading into the hair follicles, and differences due to direction of testing are greater than those due to the position of sampling the skin.

ANALYSIS AND TESTING.

P. Wenger and R. Duckert[72] give two lists of reagents for chromium cations: one concerns recommended reagents and gives references, sensitivity limits, and reaction characteristics of recommended reagents; the second list gives those not recommended because of lack of sensitivity or specificity. S. G. Shuttleworth,[73] replying to criticism by D. Burton and P. N. Taylor[74] of his conductometric method for the analysis of chromium sulphate liquors, describes an electron beam indicator circuit for increasing the sensitivity of the Mitcham measuring bridge type GM 4104 C; using this bridge, chrome basicity and neutral salt content can be obtained accurately in 30 minutes.

The final report of the British Section of the International Society of Leather Trades' Chemists' Committee on the determination of the colour of vegetable tanning solutions has been published.[75] This compares

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[70] *J. Soc. Leather Teades' Chem.*, 1945, **29**, 169; B., 1946, II, 26;

[71] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 121; B., 1946, II, 267, C., 1946, 173.

[72] *Helv. Chim. Acta*, 1944, **27**, 1839; C., 1946, 78.

[73] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 120; C., 1946, 152.

[74] *Ibid.*, 1941, **25**, 152; B., 1941, II, 285.

[75] D. Burton, *J. S Leather Trades' Chem.*, 1946, **30**, 48; C., 1946, 95.

the transmission curves of vegetable tan liquors, determinations being made with the Bolton and Williams colorimeter using as heat-removing filter (*a*) a 1% solution of copper sulphate, and (*b*) a glass heat-removing filter of the type usually employed in the Spekker absorptiometer. As the copper sulphate solution gives higher transmission figures and cuts off more sharply in the region of 600—700 mμ., it is concluded that a copper sulphate solution should be an integral part of filter combinations. Provided this is done, any instrument giving percentage transmission at specified wave-lengths can be used, and transmission converted to Lovibond units by the Forsyth–Pound formula. W. Kirkbride[76] determined the colour of vegetable tannin solutions with a Spekker absorptiometer, using a more sensitive galvanometer than that normally provided, and with a 1-cm. cell of 3% copper sulphate solution as heat-removing filter; the results obtained were in good agreement with those of a Bolton and Williams instrument using a 2-in. filter cell containing 1% copper sulphate solution.

A colorimetric estimation of tannins in spruce bark extract has been developed by F. Vorsatz,[77] who treats the tannin with nitrous acid followed by alkali; a red colour is produced from chlorogenic acid present, and this is compared with the shade developed from standard tannin solutions. The error caused by excessive dilution of vegetable tannin extracts prior to determining the acid and salt content has been studied by D. Burton and G. Lee.[78] Dilution of liquors prior to titration for total acid yields higher values for intitial pH and lower values for total acid. For determining salts, the equivalent of not more than 1 c.c. of N-sodium chloride solution should be passed through 15 g. of base-exchange resin before regeneration. The method of determining sulphur dioxide in the volatile acids by oxidation with hydrogen peroxide and precipitation of barium sulphate is shown to give high results. G. H. d'Orville[79] has shown the prime importance of the concentration of the analytical solution in the determination of tanning material in syntans and spruce bark extract by the filter bell method.

A modification of the Atkin–Thompson method[80] for determining the pH of vegetable-tanned leather is suggested by G. A. Bravo[81] to overcome the difficulty of the graph relating the three pH values to the logarithm of dilution not being a straight line.

F. Feigl and H. E. Feigl[82] give a qualitative test for tannins in solutions such as the dilute ammoniacal extract of leather; in the presence of tannins and ammonia, a reagent consisting of 0·25 g. of 2 : 2′-dipyridyl

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[76] *J. Soc. Leather Trade' Chem.*, 1946, **30**, 124; C., 1946, 209.
[77] *Collegium*, 1942, 424; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 97; C., 1946, 24.
[78] *J. Soc. Leather Trades' Chem.*, 1946, **29**, 204; C., 1946, 24.
[79] *Collegium*, 1942, 55; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 94; C., 1946, 24.
[80] *J. Soc. Leather Trades' Chem.*, 1929, **13**, 300; B., 1929, 865.
[81] *Collegium*, 1942, 241; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 97; C., 1946, 24.
[82] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 62; C., 1946, 95.

and 0·146 g. of crystalline ferrous sulphate in 50 c.c. of water gives a violet precipitate.

The alleged shortcomings of the U.S.A. official tannin analysis in examining sulphited quebracho have led T. D. Braunschweig[44] to suggest new methods of analysis, including solubility in organic solvents, and fractional salting-out of tannin solutions by varying concentrations of aqueous sodium chloride.

W. Hausam,[83] in his laboratory examination of curing salts, simulates practical conditions of skin storage by piling 20-cm. squares of skin on an inclined plate, weighting with a 1-kg. weight, and covering the whole with a bell jar.

Work on the laboratory evaluation of bating materials has been published by A. K. Vlček and V. Mansfeld,[84] who followed the fall in viscosity of a gelatin solution. G. D. McLaughlin and H. R. Wilson[85] evaluate bates by treating 100-g. samples of limed skin in jars rotating in a thermostat, and comparing the solubilised nitrogen; a control is run with no enzyme, and allowance is made for the nitrogen content of the ammonium salts present. Results agree with those of practical bating trials, whereas methods involving substrates other than pelt do not.

C. Valencien and J. Deshusses[85] suggest a tentative method for determining *o*-toluidine in leather dyes by steam-distillation and subsequent titration of the distillate. J. Deshusses[87] has improved the final stage of this determination by a bromometric determination using potassium bromate in solutions strongly acidified with hydrochloric acid.

The fourth of a series of papers by S. Glicher[88] on sulphated oils deals with analysis; tests are given for water content, ash content, acid value, saponification value, iodine value, acetyl value, total fat, saponifiable and unsaponifiable matter, oxidised fatty acids, and total and inorganic sulphate.

A. Colin-Russ[89] has modified his synthetic perspiration formula,[90] a simpler form giving the same loss of sulphate from leather; his present suggestion is 1 g. of urea, 5 c.c. of lactic acid, 1 c.c. of 10% disodium hydrogen phosphate, and 100 c.c. of N-sodium chloride, diluted with water to form 500 c.c. of stock solution, which is further diluted at the rate of 35·55 c.c. to form 100 c.c. of test material. G. A. Brown[91] has reviewed leather-testing methods and developed a machine which flexes leather and applies to it an artificial perspiration; 20% of the normal damage in service shoes occurred in the insoles.

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[83] *Collegium*, 1942, 377, *J. Soc. Leather Trades' Chem.*, 1945, **29**, 97; C., 1946, 24.
[84] *Collegium*, 1942, 42; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 94; C., 1946, 95.
[85] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 155; C., 1946, 173.
[86] *Mitt. Lebensm. Hyg.*, 1940, **31**, 57; C., 1946, 166.
[87] *Ibid.*, 1941, **32**, 176; C., 1946, 87.
[88] *Petroleum*, 1945, **8**, 130, 145; C., 1946, 23.
[89] *J. Hygiene*, 1945, **44** 53; C., 1945, 246.
[90] *Ibid.*, 1935, **35**, 199; A., 1936, 882.
[91] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 158; C., 1946, 173.

German work on physical tests included a waterproofness test of upper leather devised by G. Otto,[92] which consists of determining the height of a water column required to force water through a leather sample, pressure increase being at the rate of 1 cm. per minute; high waterproofness is coupled with low air-permeability and vice versa. The method is compared with that of F. Stather and H. Herfeld.[93]

A simple test for the mould-resistance of leather is given by M. Dempsey,[94] who suspended samples in bottles containing damp cotton wool and maintained them at 30°; satisfactory leather remained almost mould-free after four weeks. R. Ganday[95] gives a method for determining *p*-nitrophenol in full-chrome leather by extracting with ether, evaporating, and dissolving the residue in light petroleum, extracting this solution with water, and determining the phenols in the aqueous solution by the bromate–bromide method.

A. C. Chibnall's paper[3] on the estimation of amino-acids in proteins has been dealt with in the section on the constitution of collagen. Various modifications of the Kjeldahl method for the determination of nitrogen have been suggested, and results with varying catalysts[96] and improvements to apparatus[97] have been described.

MISCELLANEOUS.

Practical aspects of drying full-chrome gloving leather have been studied by C. J. Pittard.[98] Preliminary setting-out by a well-kept machine removes more than 50% of the total moisture present in a skin, and leads to maximum area yield. High temperatures and humidities with an upward air flow are recommended for the small drying cabinets considered; recirculation of air results in a reduction of at least 50% in the heat required for the plant. Automatic controls are very satisfactory provided they are given some attention. A patented freeze-drying process[99] is stated to give plump skins of increased area; there is no migration of soluble matter to the surface, and the usual conditioning and staking processes for chrome leather are unnecessary.

Present-day leather finishes are discussed by H. M. Goppelt,[100] whose chief points are the use of calcium and aluminium salts of casein, the use of new synthetic plasticisers for casein, and the development of emulsions of cellulose lacquers and synthetic resins; nitrocellulose is now

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[92] *Collegium*, 1941, 158; *J. Soc. Leather Trades' Chem.*, 1944, **28**, 289; C., 1946, 25.

[93] *Collegium*, 1935, 13; B., 1935, 323.

[94] *J. Soc. Leather Trades' Chem.*, 1945, **29**, 133, C., 1945, 246.

[95] *Ibid.*, 143; C., 1945, 246.

[96] L. Miller and J. A. Houghton, *J. Biol. Chem.*, 1945, **159**, 373; C., 1946, 49. I. A. Kaye and N. Weiner, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 397; C., 1945, 234. R. S. Dalrymple and G. B. King, *ibid.*, 403; C., 1945, 273. A. E. Beet, R. Belcher, and A. L. Godbert, *ibid.*, 746; C., 1946, 121. J. O. Cole and C. R. Parks, *ibid.*, 1946, **18**, 61; C., 1946, 136. R. Jonnard, *ibid.*, 1945, **17**, 246; C., 1945, 278.

[97] R. Jonnard, *loc. cit.* T. J. Potts, *ibid.*, 1946, **18**, 78; C., 1946, 136. M. Meneghini, *ibid.*, 1945, **17**, 672; C., 1946, 136.

[98] *J. Soc. Leather Trades' Chem.*, 1945, **29**, 199; B., 1946, II, 27.

[99] United Shoe Machinery Corp., B.P. 572,367; B., 1946, II, 66.

[100] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 245; B., 1946, II, 354.

frequently modified with resins to give improved properties. Emulsions of resins may be of two types: either a solvent-free dispersion made by polymerising emulsified monomer, or solvent-base types in which a solution of the resin in a non-aqueous solvent is emulsified; each type offers certain advantages. E. Chadwick[101] reviewed the application of synthetic resins to leather, especially the thermoplastic types which possess greater flexibility than the thermosetting resins; the possibilities of using resins for impregnation as well as for coating are pointed out, the possible adverse effect on ventilating properties being noted. A patented leather finish[102] gives a japanned leather in which the top coat is based on a urea–formaldehyde resin; the undercoat is on the more usual lines of japanners' oil or nitrocellulose.

A. Colin-Russ[103] records the principles of formulation and the physical properties of his leather resinoids; seven grades are described, ranging from a syrup to a hard, resilient gel. Compounding with materials such as polyvinyl chloride or synthetic rubber GR-S gives a product suitable for shoe soles or linoleum manufacture.

German leather board manufacture during the war years followed lines similar to those of this country. A. Miekeley[104] describes the use of polyacrylic esters in place of rubber latex as binder, and chrome leather scrap is found to be superior to vegetable-tanned material; the importance of pH control during the distribution of binder prior to precipitation with aluminium salts is stressed.

W. Hausam and E. Liebscher[105] report damage to leather by insects seldom considered in this respect, viz., the giant wood wasp (*Sirex gigas*) and common wood wasp (*S. juvencus*); a beetle (*Stephanopachys substriatus*, Payk.) caused considerable damage to spruce bark in stock.

Corrosion properties of 56 different metals and alloys were determined by A. H. Winheim and R. A. Mills,[106] who measured weight loss of samples suspended in the principal tannery liquors.

A. Gansser[107] surveyed prehistoric tannages employed for fur skins in palæolithic times; fat tannage (brain material and oil) was used, sometimes aftertreated with smoke, in which formaldehyde is the active agent. Chinese leathers were tanned by smoke from burning bones and fleshings; Mongolian leathers were treated with sour milk and common salt.

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[101] *J. Soc. Leather Trades' Chem.*, 1946, **30**, 53; B., 1946, II, 267.

[102] D. E. Edgar and P. Robinson, U.S.P. 2,201,892, M. B. Walker and P. W. McWherter, U.S.P. 2,204,520; B., 1946, II, 146.

[103] *Brit. Plastics*, 1946, **18**, 256; B., 1946, II, 401.

[104] *Collegium*, 1941, 257; *J. Soc. Leather Trades' Chem.*, 1944, **28**, 288; B., 1946, II, 107.

[105] *Collegium*, 1943, 65; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 146; B., 1946, II, 145.

[106] *J. Amer. Leather Chem. Assoc.*, 1945, **40**, 441; B., 1946, II, 145.

[107] *Collegium*, 1943, 1; *J. Soc. Leather Trades' Chem.*, 1945, **29**, 121; B., 1946, II, 144.

Mould growth on leather is reviewed in a literature survey by A. J. Musgrave.[108] Experiments on mould growth on vegetable-tanned strap leather were carried out by J. R. Kanagy, A. M. Charles, E. Abrams, and R. F. Tener,[109] who exposed samples in tropical rooms, soil burial beds, and a humidity cabinet. They report that mould growth results in loss of tensile strength and decrease in stretch at breaking point, weakening of the grain, and increased stiffness. There was loss of grease and soluble material. Samples impregnated with oil containing *p*-nitrophenol and pentachlorophenol showed no mould after 12 weeks under the above conditions. Methods of estimating mould-resistance[94] and for determining *p*-nitrophenol in chrome leather[95] have been dealt with under analysis and testing.

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[108] *Chem. and Ind.*, 1946, 226; B., 1946, II, 354.
[109] *J. Amer. Leather Chem. Assoc.*, 1946, **41**, 198; B., 1946, II, 354.

AGRICULTURE AND HORTICULTURE.

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The practice adopted in these Reports in recent years, namely, that of selecting a number of subjects for consideration, rather than of surveying the whole field of literature, again seems to render the more useful service.

The choice of subjects in this Report has been decided partly by an assessment of their general interest and partly by the amount and kind of published literature available : it has been limited to some extent by the calamity, from a scientific viewpoint, of restrictions on the use of paper.

The chemistry of soils and fertilisers is of fundamental importance and the periodical review of developments in these matters is almost a routine necessity. The potato is approaching the status of a corner-stone in the structural fabric of the nation's nutrition and as such demands consideration.

Of the chemistry of insecticides not hitherto introduced into these Reports a general review would not be commensurate with the available space. It seems desirable at this time to devote attention to the most startlingly successful insecticide in the history of this aspect of agricultural chemistry.

ORGANIC MATTER IN SOILS.

Nature and Formation of Humic Materials.

In the period under review the literature relating to soil organic matter has concerned its relation to soil conditions and crop production, and the formation and maintenance of suitable proportions in the soil, rather than the finer points of its composition. Among the relatively small proportion of reported investigations of the latter complex problem, the general acceptance of the view that humus consists largely of lignin–protein complexes has tended to focus attention on the properties of lignin and related substances. Thus J. Sieberlich[1] draws a distinction between lignin in the form of lignocellulose in green plants and that separated from cellulosic material following the chemical or microbiological decomposition of plant residues in the soil. The former, "protolignin," is much the more active, chemically, and is capable of conversion into dark-coloured, amorphous polymers ; the latter has become more resistant to both chemical and biological change and has assumed an acidic character, thus tending to become more soluble and capable of combining with proteins. A study of these changes in the composition of lignin, which

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[1] *Northeastern Wood Util. Counc.*, 1945, *Bull.* 7, 49 ; B., 1946, III, 251.

occur progressively as cellulosic and pectinous matter is stripped from the original "protolignin," would probably afford an explanation of the observed differences in the capacities of organic manures, green manures, etc. to build up a humus reserve in soils. Sieberlich has examined the sulphite-waste lignin from paper mills from this angle and finds it much less effective than lignin separated, chemically or biologically, from plant material, *e.g.*, "Scholler lignin." It would appear that during the pulping process the lignin has undergone changes in character which lower its value as a humus-forming material. According to W. A. Bollen,[2] the application of sulphite waste liquor in moderate amounts to soil stimulates microbiological activity. Sugars and other degradation-products of cellulose offer an immediately available source of energy, and it is suggested that the fixation of atmospheric nitrogen may be favoured thereby. The lignin, presumably in the form of sulphonic acid products, undergoes slow decomposition. The response of soil micro-organisms to the sulphite liquor is said to be similar to that evoked by the incorporation of straw etc. with soil.

Further evidence that the value of lignin as a soil component is dependent on its source and previous history is afforded by the work of E. Bennett.[3] In an examination of lignin from maize cobs it is shown that the base-exchange capacity of the freshly-isolated material largely disappears on drying, but returns after a form of rehydration effected by dissolution in alkali and subsequent purification. The purified lignin exhibits many of the properties of soil humus and has a base-exchange capacity of the order of 150 milli-equivalents per 100 g. and is sufficiently reactive to absorb calcium from calcite; it possesses a marked buffer capacity, notably in the pH range 4·5—6·5. The exchange capacity further increases after partial oxidation. H. Perrenoud[4] records that oxidation of lignin is also associated with a lowering of the pH (4·0—5·0) at which dispersion occurs. Pedological aspects of the distribution of organic matter in soil profiles are of interest in this connexion. A review of recent literature concerning the influence of lignin on soils and crops is given by V. Sanchelli.[5]

Among recent investigations of the chemical constituents of soil organic matter may be noted that of A. G. Norman and W. V. Bartholomew.[6] These authors report that in a number of profiles (prairie soils, podsols, etc.) 10—15% of the organic matter in surface soils may be present as uronides. In general, the proportion of uronide-carbon tends to increase with depth, and in podsol profiles, in which movement of organic matter is so characteristic a feature, there is a well-defined accumulation of uronides in the *B*-horizon.

[2] *Pacific Pulp and Paper Ind.*, 1942, **16**, *Dec.*, 30; B., 1943, III, 93.
[3] *Soil Sci.*, 1943, **55**, 427; B., 1944, III, 2.
[4] *Mitt. Lebensm. Hyg.*, 1943, **34**, 327; B., 1946, III, 165.
[5] *Amer. Fert.*, 1946, **104**, *No.* 3, 7; B., 1946, III, 85.
[6] *Soil Sci.*, 1943, **56**, 143; B., 1944, III, 57.

Phytin derivatives appear in considerable amounts in the alkali-soluble fraction of soil organic matter. C. A. Bower[7] records 26—35% of the organic matter and 11—14% of the organic phosphorus in a number of soils examined to be in this form. The insoluble nature of the calcium and ferric salts of these compounds (which seem to include inositol phosphate components) suggests that the phytin derivatives may be concerned in the movement and distribution of organic matter and phosphorus in soil profiles.

Maintenance of Humus Reserves in Soil.

The provision of an adequate supply of humus in soils is often regarded as one of the primary long-term objectives in crop production. That the contributions made by crop residues to the reserve of organic matter is not inconsiderable is emphasised by S. Gericke,[8] who calculates that the annual addition of organic matter by this means on arable soils may amount to approximately 1 ton per acre. I. V. Tiurin[9] indicates a much larger proportion (more, in fact, than results normally from customary applications of animal manure), of which he states 25% may be derived from the decomposition of micro-organisms. The production of "humic acid" from cellulose is examined by C. Enders,[10] who suggests that this transformation is effected not by living organisms but by the enzyme systems of autolysed bacterial cells. The influence of soil temperature and moisture content on the extent to which crude organic matter is converted into humic acid is said to operate primarily through its effect on the rate of autolysis of soil bacteria. On the other hand, V. A. Kirsanova,[11] in a study of enzyme activity in decomposing grass and clover, concludes that part at least of the amylase, cytase, and peroxidase actively concerned in the decomposition of organic matter in soil is derived from plant materials.

The nature of plant residues and the manner in which they are incorporated with soil are important factors in humus production. In Trinidad sugar-cane soils F. Hardy[12] observes that cane trash, *i.e.*, waste aërial parts of the plants, yields approximately double the amount of humus resulting from cane roots. Moreover, the addition of the trash to the soil surface is more effective, under Trinidad conditions, than is ploughing in below the surface, probably by providing greater accessibility to air and moisture. Decomposition of the roots in soil may even be accompanied by a temporary toxic effect. Under normal working conditions the return of crop residues provides less humus than is lost by oxidative processes. Cultivation and cropping tend, almost inevitably, towards a gradual decline in the organic matter content of soils. The rate at which this

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[7] *Soil Sci.*, 1945, **59**, 277; B., 1946, III, 62.
[8] *Chem.-Ztg.*, 1943, **67**, 277; B., 1945, III, 1.
[9] *Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **51**, 311; B., 1946, III, 249.
[10] *Biochem. Z.*, 1943, **315**, 259; A., 1945, III, 894.
[11] *Biochimia*, 1946, **11**, 227; A., 1946, III, 982.
[12] *Trop. Agric.* [*Trinidad*], 1944, **21**, 203; B., 1946, III, 89.

occurs clearly will depend on the cropping system, *i.e.*, on the amount and kind of plant matter returning to the soil in normal practice. In general farming, crop rotations adopted have as one of their objectives the minimising of this loss of organic matter in any one cycle of operations. Studies of the effect of particular rotations in this respect are numerous, a typical example being that of W. H. Metzger[13] on various cereal-legume rotations. Marked differences in the total organic matter and organic nitrogen contents of soils occur following different crops and different rotations, for details of which the original publication needs to be consulted. It is noted, incidentally, that the use of artificial fertilisers, while not involving direct additions of organic matter to soil, nevertheless maintained larger proportions of organic nitrogen in soil than occurred in unmanured land. A similar observation is made by J. Elson[14] and is an interesting comment on the view, prevalent in some quarters, that the use of artificial fertilisers accelerates the natural decline in the humus content of soils.

Sewage as a Soil Amendment.

The decline in supplies of animal manures has for many years stimulated enquiry into other sources of suitable organic wastes. None stands out in greater prominence than sewage, the loss of nitrogen from which was described many years ago as the greatest error in our agricultural economy. The problem of producing sewage sludges in a form suitable for transport and easy application to soil, free from matter injurious to plants or soils, at an economic price is a complex one. Although great strides have been made towards its solution, the ideal product is yet to be produced. War conditions again brought this problem to the forefront and, indeed, almost necessitated the use of sewage material regardless of its condition. Sludges may contain 15—50% of organic matter besides the principal plant nutrients. The general position has been discussed by, among many others, C. C. J. Bullough,[15] A. H. Bunting,[16] and J. Finch.[17] The manurial value, in terms of nitrogen, potash, and phosphate, may exceed that of farmyard manure[18,19] although the potash content is normally smaller. E. M. Crowther and A. H. Bunting[20,21] describe cropping experiments which demonstrate the high manurial value of sewage sludge. With crops of high potash requirement the sludge needs to be supplemented with potash fertilisers. The sludge, used alone, may have very little effect on potato yields, but with appropriate potash supplements

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[13] *Kansas Agric. Exp. Sta.*, 1939, *Tech. Bull.* 45; B., 1945, III, 238.

[14] *Soil Sci.*, 1943, **56**, 235; B., 1944, III, 82.

[15] *J. Inst. Sewage Purif.*, 1942, 277; B., 1944, III, 79.

[16] *J. Min. Agric.*, 1945, **53**, 123; B., 1946, III, 62.

[17] *J. Proc. Inst. Sewage Purif.*, 1941, 98; B., 1943, III, 3.

[18] K. G. Joshi, *Current Sci.*, 1942, **11**, 465; B., 1943, III, 141.

[19] W. Rudolfs and H. W. Gehm, *New Jersey Agric. Exp. Sta.*, 1942, *Bull.* 699; B., 1945, III, 83.

[20] *J. Inst. Sewage Purif.*, 1942, 13; B., 1944, III, 58.

[21] *J. Proc. Inst. Sewage Purif.*, 1944, 46; B., 1946, III, 167.

has increased yields to almost the same extent as does double the application of farmyard manure. For spinach-beet the sludge is at least as effective as farmyard manure. The availability to the plant of the nitrogen of activated sludge is greater than that of raw sludge. Digested sludges contain a relatively larger proportion of the resistant types of nitrogenous organic matter, the utilisation of which by crops is spread over a relatively long period. Such sludges, however, are likely to contain injurious constituents, and according to A. M. Rawn[22] are preferably applied to grassland and fruit trees: they are more readily dried for transport than are activated sludges. In glasshouse practice, in which the rate of availability of nitrogenous manures is a particularly important factor, H. A. Lunt[23] records that digested sludges are not very efficient.

The preliminary rotting of sewage sludges, either alone or composted with straw or other waste vegetable matter, is now receiving greater attention. H. T. Cranfield[24] describes the partial drying of sludge in lagoons followed by rotting in heaps. He records no appreciable loss of nitrogen by this process. The final product contains approximately 50% of water and compares favourably with farmyard manure in its effects although its distribution in the field is more difficult. A method and suitable plant for drying sludge (to 10% of moisture), described by W. A. Dundas and C. P. McLaughlin,[25] involves preliminary conditioning with ferric chloride and filtration. The press-cake (80% of water) is mixed with a proportion of previously dried material and passed through a flash-dryer. The manurial value of the organic matter is not affected appreciably by the drying process. The composting of sludge with straw is shown by F. H. Ransome[26] to yield a material very similar to farmyard manure in many respects, but containing more nitrogen and less potash than the natural manure. P. T. H. Pickford, J. O. Jones, and J. C. Todd[27] also describe satisfactory composting of sludge and straw whereby a serviceable substitute for farmyard manure, having similar nitrogen and phosphorus contents, is obtained. Interesting possibilities are suggested by a paper by S. V. Desai and S. C. Biswas[28] describing a small-scale plant for the anaërobic fermentation of a mixture of sewage sludge and cow dung, a lake-bottom mud providing suitable micro-organisms. From 1 lb. of dry matter from the dung an effective manure and 5·3 cu. ft. of gas (500—640 B.Th.U.) are obtained.

The composting of sewage sludges with town refuse offers a further means of utilising valuable waste, and has received much attention in recent years. The high-temperature fermentation of such materials,

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[22] *Water Works and Sewerage*, 1941, **88**, 186; B., 1943, III, 3.
[23] *Sewage Works J.*, 1946, **18**, 46; B., 1946, III, 127.
[24] *J. Proc. Inst. Sewage Purif.*, 1941, 223; B., 1943, III, 3.
[25] *Proc. Amer. Soc. Civil Eng.*, 1943, **69**, 80; B., 1943, III, 119.
[26] *J. Proc. Inst Sewage Purif.*, 1944, 143; B., 1946, III, 168; also *J. Min. Agric.* 1944, **51**, 202; B., 1944, III, 202.
[27] *Ann. Rept. Agric. Hort. Res. Sta., Long Ashton*, 1944, 110; B., 1946, III, 40.
[28] *Indian Farming*, 1945, **6**, 67; B., 1946, III, 4.

favoured in warmer climates and where sanitary conditions are more primitive, is as yet less popular in this country. The ordinary composting process is in more general use. The handling of certain materials, *e.g.*, disintegration, mixing, turning, aëration, etc., seems to offer scope for large-scale mechanical processes. A report of a symposium on this subject by W. Scott *et al.*[29] and a review by A. R. P. Walker[30] afford useful information on the process of composting and the use of the product. G. C. Dymond[31] reports on a successful South African process operating with night-soil and various waste products of the sugar-cane industry. As an indication of commercial interest in the composting process may be cited a patent granted to the Mitchell Engineering Co. and C. C. Bullough,[32] covering a method and machinery for impregnating comminuted salvage with sewage sludge, turning and stacking the material, and controlling its fermentation. Another patented process[33] involves admixture of sewage sludge with absorbent matter, *e.g.*, dried sludge, soot, chalk, peat, etc., and subsequent drying, the process of adding sludge and drying being repeated several times, to yield a product of adequate nitrogen, potash, and phosphate content, and of suitable physical condition. Another variation of the process[34] includes incorporation of partly dried (40% of water) sludge with peat, straw, or sawdust, and, after a short period of aërobic fermentation, heating the mixture sufficiently to pasteurise it.

An anaërobic fermentation process for the production of humic material referred to in the patent literature[35] operates by addition of nutrient salts and ferric chloride to a mixture of cellulosic waste and sewage sludge, together with sufficient alkali to maintain pH 7—10; the product is said to contain soluble iron humates.

FERTILISERS.

Prevention of Hygroscopicity.

The increasing use of ammonium nitrate in fertiliser mixtures brings with it the need for additional care in avoiding the ill-effects of hygroscopicity and the resulting caking of the mixtures. According to J. O. Hardesty, J. Y. Yee, and K. S. Love[36] this may be dealt with by ensuring sufficient moisture content in the mixture to dissolve added ammonium nitrate, in excess of that used in standard mixtures of earlier years, and by avoiding incompatible mixtures. Suitable mixtures of fertiliser salts with ammonium nitrate showing minimum hygroscopic effects are noted by A. M. Smith.[37] The problem is also discussed by F. W. Parker

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[29] *J. Inst. Sewage Purif.*, 1942, 196; B., 1944, III, 79.

[30] *J. Proc. Inst. Sewage Purif.*, 1943, 186; B., 1945, III, 181.

[31] *Proc. 18th Congr. S.Afr. Sugar Tech. Assoc.*, 1944, 77; B., 1945, III, 54.

[32] B.P. 563,897; B., 1944, III, 254.

[33] C. J. Allday, B.P. 553,435; B., 1943, III, 176.

[34] Holford Processes Ltd., B.P. 572,171; B., 1946, III, 6.

[35] E. F. Grether, U.S.P. 2,313,434 and 2,317,990; B., 1945, III, 38, 98.

[36] *Ind. Eng. Chem.*, 1945, **37**, 567; B., 1945, III, 201.

[37] *Chem. Eng. News*, 1943, **21**, 2100; B., 1944, III, 83.

and W. H. Ross,[38] who recommend the addition of kaolin or kieselguhr to avoid caking in mixtures of high ammonium nitrate content. A more elaborate method is described by P. Miller, G. A. Lenaeus, W. C. Saeman, and M. N. Dokken.[39] The nitrate is treated with a preparation of liquid paraffin, resin, and paraffin wax followed by a coating of kaolin, plaster of Paris, talc, or kieselguhr (approximately 4%). The finished product may be stored in waterproofed paper bags. A patented process[40] involves incorporation, during drying, of 3—10% of an anti-caking material, specifically calcined gypsum or an accelerated anhydrous calcium sulphate, the accelerator being a sulphate or bisulphate of an alkali metal, ammonium, copper, zinc, iron, or aluminium or their double sulphates. Organic materials, *e.g.*, ground-nut shell meal, tobacco stems, etc., have been used with considerable success in preventing the caking of mixtures. The risk of spontaneous ignition in such mixtures containing ammonium nitrate is avoided, according to R. O. E. Davis and J. O. Hardesty,[41] by treatment with 2·5% of ammonia; the incorporation of lime or chalk does not obviate the fire risk. A patented method involving the use of ammonia to prevent caking is described by J. Y. Yee and R. O. E. Davis[42]; approximately 5% of powdered peat is thoroughly mixed with the fertiliser, which may include ammonium nitrate, in an atmosphere containng 20 vol.-% of ammonia at less than 1 atm. pressure and the mixture is subsequently heated to release absorbed ammonia.

The examination of the hygroscopic properties of fertiliser mixtures has now become an almost essential routine operation in many factories; J. E. Chenevey[43] describes the construction of an air-conditioned testing chamber for this purpose.

Phosphate Fertilisers.

Introduced mainly as an economy measure, "serpentine" superphosphate aroused considerable interest, notably in Australasia. The product is obtained by mixing hot superphosphate (3 parts) with ground serpentine (1 part); this admixture causes a partial reversion of the superphosphate and probably neutralises free acidity. Some workers, *e.g.*, L. J. H. Teakle and H. G. Cariss,[44] disapprove the introduction of the magnesium silicate inasmuch as it produces no improvement in the efficiency of the fertiliser although, on an equal-phosphate basis, the mixture is as effective as superphosphate for wheat. L. J. Wild[45] and A. G. Elliott[46] record that the serpentine superphosphate compares favourably with standard superphosphate for a variety of crops, *e.g.*, pasture, wheat, potato, and *Brassicæ*,

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[38] *Chem. Met. Eng.*, 1943, **50**, *No.* 9, 109; B., 1944, III, 3.
[39] *Ind. Eng. Chem.*, 1946, **38**, 709; B., 1946, III, 213.
[40] G. W. Ettle, B.P. 571,080; B., 1945, III, 245.
[41] *Ind. Eng. Chem.*, 1945, **37**, 59; B., 1945, III, 117.
[42] U.S.P. 2,307,252; B., 1944, III, 176.
[43] *Chem. Met. Eng.*, 1945, **52**, *No.* 8, 115; B., 1945, III, 239.
[44] *J. Dept. Agric. W. Australia*, 1944, **21**, 143; B., 1945, III, 138.
[45] *New Zealand J. Agric.*, 1944, **69**, 1; B., 1946, III, 38.
[46] *Ibid.*, 27; B., 1946, III, 38.

on New Zealand soils. The new material does not lessen the need for lime on deficient soils and the effect of lime used in conjunction with it is similar to that with ordinary superphosphate. A routine method for determining the proportion of magnesium in serpentine as a measure of its suitability for the purpose is described by J. J. S. Cornes.[47] A summary of the development of serpentine superphosphate is given by R. L. Andrew.[48]

Reports of the British Intelligence Objectives Sub-Committee give information regarding the German manufacture of Rhenania phosphate and a sintered phosphate fertiliser. The former,[49] prepared by heating rock phosphate with sand and sodium carbonate of 1100—1250° in a kiln or furnace, contains 92—95% of its total phosphorus content (23—31%) in a citrate-soluble condition. By sintering in a rotary kiln a mixture of mineral phosphate, sodium sulphate, and lignite, a product having 95—100% citrate-solubility is obtained.[50] In cropping trials the sintered phosphate proves as efficient as the Rhenania type and is especially suitable for use on acid soils. E. M. Crowther and F. M. Lea[51] record field trials with a silicophosphate fertiliser prepared by heating mineral phosphate with soda ash and sand in presence of steam. The fertiliser approaches superphosphate in efficiency on acid soils and is slightly superior on soils of pH exceeding 5·5. Its composition renders it unsuitable as a substitute for superphosphate in many mixed fertilisers. A means of using native mineral phosphate deposits in County Clare, Ireland, by heating with sodium carbonate is examined by P. H. Gallagher and T. Walsh[52]; when thus treated the mineral becomes almost as effective as superphosphate, although to obtain maximum results the proportion of sodium carbonate used appears to need adjustment in accordance with the character of the soil to which the fertiliser is applied. M. Comyn[53] develops another method for utilising this and similar phosphatic minerals, whereby a mixture of the mineral and shale, together with chalk, sand, and sulphur if necessary, is heated nearly to the melting point.

Calcium metaphosphate, to which reference was made in an earlier Report,[54] may be prepared, according to a patent granted to H. A. Curtis[55] by heating rock phosphate with sufficient phosphoric acid to produce dicalcium phosphate; the mixture is further heated at 1000—1200° to form the molten metaphosphate. The product is stated to be more available to plants than is dicalcium phosphate.

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[47] *New Zealand J. Sci. Tech.*, 1945, **26**, B, 188; C., 1945, 155.

[48] *Ibid.*, 1942, **23**, B, 208; B., 1944, III, 38.

[49] J. R. Hawes and F. M. Lea, *Brit. Intelligence Objectives Sub-Commee.*, 1945, *Final Rept.* 94, *Item* 22; B., 1946, III, 214.

[50] *Idem, ibid., Final Rept.* 107, *Item* 22; B., 1946, III, 213.

[51] *J. Min. Agric.*, 1946, **53**, 102; B., 1946, III, 168.

[52] *Econ. Proc. Roy. Dublin Soc.*, 1943, **3**, 172; B., 1945, III, 35.

[53] B.P. 559,238; B., 1944, III, 91.

[54] *Ann. Repts.*, 1943, **28**, 341.

[55] U.S.P. 2,173,826; B., 1944, III, 91.

Granulation of Fertilisers.

The production of fertilisers in a granular from[56] continues to find favour as a means of ensuring ease of drilling, minimising caking, restraining the accessibility of fertiliser salts to young seedlings (thus avoiding seedling injury), and of prolonging the period of action of very soluble or reactive fertilisers. In practice the use of granular material also permits the economy of sowing the fertiliser with the seed without risk of germination injury. This aspect of granulation is commented on by T. T. Demidenko[57] and beneficial effects are demonstrated in field trials.

A process for granulating superphosphate or mixed fertilisers is described by Sturtevant Engineering Co.[58] The ground mineral phosphate and sulphuric acid are mixed to form a slurry, which is passed through a cylindrical rotary dryer in which the granules are formed. In a second cylinder the granules are hardened and finally graded, any fine material being returned to an appropriate stage of the process. The basic idea of granulation is carried a stage further by A. E. Badger and R. H. Bray,[59] who suggest the incorporation of potassic and phosphate fertilisers into a glass-like material. A vitreous product can be obtained by fusing rock phosphate with potassium carbonate and sand at 1100° and from this both potash and phosphate can be leached by water. By grading the sizes of granules, and thus the surface area exposed, the rate of dissolution of the fertiliser components in the soil water may be controlled. The same fundamental idea finds expression in a somewhat novel process developed by H. J. Heasman[60] in which the fertiliser mixture is moulded into pellets which are coated with a material insoluble in water. Apertures are formed through which wicks may be inserted. The blocks or pellets are buried in the soil, which receives a gradual supply of nutrients by this means.

An informative review of modern developments in the manufacture of fertilisers, especially of superphosphate, is given by P. Parrish.[61]

POTASH, THE SOIL, AND THE PLANT.

To establish the chemical status of potash in soils in relation to its availability to the plant is an old-standing problem of the soil chemist. Empirical methods of assessing the availability of soil-potash have long been in use and for many practical purposes give extremely valuable information. Nevertheless, such methods yield relative rather than absolute data and, unless interpreted by an experienced worker in the light of previous observations, may not give accurate information in all cases. It is generally accepted that potash exists in soils largely in the form of relatively refractory minerals, partly in an exchangeable condition

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[56] *Ann. Repts.*, 1943, **28**, 337.
[57] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **48**, 207; B., 1946, III, 127.
[58] B.P. 559,482; B., 1944, III, 91.
[59] *Chem. Met. Eng.*, 1945, **52**, *No.* 4, 112; B., 1945, III, 137.
[60] B.P. 573,166; B., 1946, III, 46.
[61] *Chem. and Ind.*, 1944, 198; B., 1944, III, 145.

and partly in an intermediate state from which it is released to plants only slowly. Probably a further amount exists in some form of organic combination. Each form may contribute its quota to the crop during the growing season. The weight of evidence now favours the view that there is an equilibrium or perhaps a series of equilibria between the different forms. It is clear, therefore, that the critical factor, viz., the rate at which the plant can obtain supplies of potash, notably at the stage of maximum intake, is a function of the make-up of the individual soil and also of the nutritional physiology of the individual plant. Any attempt therefore to assess availability, as a general routine procedure, by treating the soil with an extractant solution can give only an incomplete picture of the true position. It is known that nearly the whole of soluble potash fertiliser salts added to soils remains in a condition which resists easy leaching by water. Not all of it can be traced in an exchangeable state; much of it "reverts" to a form in which it is less readily accessible to plants. The ability of plant species to obtain potash from different sources varies widely. Thus, under many conditions ground felspar would be a poor source of potash for most crops yet, according to S. A. Wilde and R. O. Rosendahl,[62] certain pine seedlings, *P. banksiana* and *P. resinosa*, were able to utilise it in sand-cultures.

In discussing the general problem O. de Vries and C. W. G. Hetterschij[63] emphasise the impossibility of separating the various forms of potash in soil by routine analytical means and suggest that useful information additional to that yielded by single-extraction methods might be obtained by repeated extractions with different extractants. It is pointed out that soils which have received no potash fertiliser for many years continue to yield potassium in repeated water extractions. Presumably such repeated extractions afford a measure of the ability of the soil to maintain a supply of potassium during the period of continuous removal by the growing crop—a fundamental point in establishing the productivity of a soil. In a survey of the capacity of some New Jersey soils to provide potash for lucerne crops F. E. Bear, A. L. Prince, and J. L. Malcolm[64] record that although the best index of potash-supplying power is the exchangeable potash content, the rate at which the crop is able to obtain potash from this source varies widely from soil to soil. E. E. De Turk, L. K. Wood, and R. H. Bray[65] have investigated the "fixation" of soluble fertiliser potash, *i.e.*, the transformation into insoluble forms not associated with the base-exchange complex. The authors present the view that an equilibrium exists between the "fixed" and exchangeable forms, and that removal of soluble potash by plants is followed by transition not only from exchangeable into soluble forms, but also from the "fixed" into the exchangeable condition. By this indirect route a considerable

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[62] *J. Forestry*, 1945, **43**, 366; B., 1946, III, 62.
[63] *Rec. trav. chim.*, 1940, **59**, 789; B., 1946, III, 250.
[64] *Soil Sci.*, 1944, **58**, 139; B., 1944, III, 242.
[65] *Ibid.*, 1943, **55**, 1; B., 1943, III, 200.

proportion, though not all, of the fixed potash may become available during the growth of the crop. The extent to which fixation can occur was very large in the soils examined; the limit of fixation was not reached by additions of potassium chloride equivalent to 20 tons per acre. It would appear also that the form in which potash is added to the soil influences the amount fixed, higher proportions entering the fixed state from potassium phosphate than from any other salts examined. That the colloids are, in part, concerned in the fixation process is indicated by the observation that separated soil clays themselves absorbed appreciable amounts of potassium in forms not soluble in 5N-nitric acid. According to C. Hurwitz and H. W. Batchelor[66] the incorporation of plant material with soil may result in the fixation of potash in non-leachable forms in amounts up to 200 lb. per acre. In soils thus treated a periodic variation in the amount of leachable potash was observed. This suggests a possible microbiological rhythm in the potash transformations of soils. It is noteworthy that no corresponding "fixation" of calcium occurred as a result of such treatment. A rather different association of organic matter with soil-potash is recorded by W. E. Worsham and M. B. Sturgis,[67] who, in examining the general association of high base-exchange capacity in soils with high available potash content, also establish that the presence of organic matter and high water contents in soil are conducive to high availability and leachability of soil-potash. This is possibly linked up with the phenomenon, noted by I. W. Wander and J. H. Gourley,[68] that the heavy mulching of orchard soils at the time of applying fertilisers facilitates the downward movement of potash into the soil, penetration to 8 in. in 4 months being recorded; in ordinary (unmulched) conditions surface applications of potash fertiliser would have remained "fixed" in the immediate surface layers.

Potash Nutrition of Crops.

The vital relationship between potash intake and the carbohydrate metabolism of plants, together with the interrelation between the carbohydrate and nitrogen metabolism, imposes a dual significance on the potash nutrition of plants since both quality and quantity of crop are fundamentally affected. The literature provides numerous examples of this aspect of potash nutrition. Among recent publications bearing on this subject may be noted that of T. T. Demidenko[69] concerning sugar-beet. In this crop, at the stage of the development of the 7th to 10th leaves, there is a period of rapid formation of sugar. Insufficiency of potassium in the plant prior to this period restricts the growth and final yield of the crop; insufficiency at later stages results in an increased proportion of colloids in the sap and a greater content of soluble nitrogen in the roots, a commercially undesirable condition. The indirect

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[66] *Soil Sci.*, 1943, **56**, 371; B., 1944, III, 83.

[67] *Proc. Soil Sci. Soc. Amer.*, 1942, **6**, 342; B., 1943, III, 3.

[68] *Proc. Amer. Soc. Hort. Sci.*, 1945, **46**, 21; B., 1946, III, 62.

[69] *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **47**, 215; A., 1946, III, 75.

influence of potash on nitrogen metabolism, common to all green plants, is examined in detail, in the case of wheat, by O. Eckstein,[70] who shows that the influence of potash manuring on carbon assimilation, transpiration, and protein synthesis may be positive or negative according to the level of nitrogen supply. G. T. Nightingale,[71] in an investigation of the mineral nutrition of pineapple, observes that deficiency of potash not only affects, adversely, the normal balanced growth of the plant but also restricts the intake of nitrogen from the soil. A detailed examination of the potash nutrition of *Ananas comosus* by C. P. Sideris and H. Y. Young[72] affords a further instance of the multiple effects of this element on the growth and composition of plants. It is demonstrated that the influence of different levels of potash feeding on the nitrogen metabolism and therefore on the growth of the plant varies according to the nature of the nitrogen source (nitrate or ammonium salt), the relative beneficial effect on the gross weight of the plant being greater when the plants receive ammonium salts. Further evidence of the influence of potassium is afforded by differences on the ratio of protein to soluble nitrogen compounds in the tissues, a measure of the efficiency of the nitrogen metabolism, in the two cases. A further physiological point brought out by these authors is that the production of reducing sugars by the plant proceeded almost normally with very low supplies of potash. Carbohydrate metabolism is apparently restricted at this stage by inadequate potash feeding, since the contents of non-reducing sugars and starch were relatively low. This is obviously a matter of importance in the quality of fruit crops. A similar effect is noted by W. R. Roy[73] in oranges, in which the ratio of reducing to non-reducing sugars was higher in fruit from unmanured trees than in that from trees receiving potash fertilisers. It is noted also that potash deficiency is associated with a lower concentration of ascorbic acid in the fruit. In tobacco, also, lack of potash diminished the ability of the leaves to accumulate starch.[74] A. V. Vladimirov[75] records similar observations on the nutrition of tobacco, and also demonstrates that the effect of potash on leaf quality may be different in nitrate- and in ammonium-fed plants: it is also dependent on the form of the fertiliser used, chloride-containing fertilisers tending generally to produce higher citric acid and organic nitrogen and lower sugar contents in the leaves than do sulphate-containing mixtures. In the case of the rubber-bearing plant, kok-saghyz, potassium sulphate produced higher rubber contents than did the chloride.

The ability of sodium to serve as a partial substitute for potassium, or at least to facilitate the action of potassium, in plant nutrition is demonstrated, in the barley plant, by W. R. Mullison and E. Mullison.[76] Visual

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[70] *Plant Physiol.*, 1939, **14**, 113; A., 1944, III, 309.
[71] *Bot. Gaz.*, 1942, **104**, 191; B., 1945, III, 7.
[72] *Plant Physiol.*, 1945, **20**, 609, 649; 1946, **21**, 218; A., 1946, III, 327, 979.
[73] *J. Agric. Res.*, 1945, **70**, 143; B., 1945, III, 138.
[74] D. Day, *Plant Physiol.*, 1940, **15**, 367; A., 1944, III, 83.
[75] *Soil Sci.*, 1945, **60**, 377; A., 1946, III, 1093.
[76] *Plant Physiol.*, 1942, **17**, 632; A., 1944, III, 440.

symptoms of potash deficiency appear much earlier in the absence than in the presence of an adequate supply of sodium salts. It is concluded that, at least in the early stages of growth, sodium can partly replace potassium in the plant economy.

Determination of Potassium in Soils, Plants, and Fertilisers.

Analytical methods for potassium are notoriously time-consuming and, in the case of some micro-methods, are subject to experimental variations beyond that desirable for many types of agricultural investigation. Recent publications on this subject are, therefore, of very general interest, and, even when they relate to methods devised for other than agricultural purposes, may offer serviceable suggestions.

Suggested variations of the cobaltinitrite method are numerous. In adapting the photoelectric colorimeter to this purpose W. H. Garman[77] records that values obtained by this means for the exchangeable potassium in soils agree well with those yielded by standard gravimetric methods. G. F. Hauser,[78] who favours the use of Krauss' solution for the extraction of potassium from soils, records that cobaltinitrite precipitates formed in presence of this solution are more uniform than when other extracts are employed. The capillary centrifuge tube method is utilised by this author, who introduces corrections for temperature errors and irregularities in capillary tubes, and compiles tables of relative accuracy for different amounts of potassium present. A modification, originally designed for urine analysis, of the Blanchetière–Pirlot method, based on the green colour produced by dissolution of the double cobaltinitrite in hydrochloric acid and adding excess of sodium bicarbonate, is described by A. A. Albanese and D. L. Wagner.[79] R. A. Cantani[80] examines the permanganate titration of the cobaltinitrite precipitate on a semi-micro-scale (0·01—0·1 milli-equiv. of K) and records that the method gives satisfactory results in presence of very large proportions of sodium (Na : K = 100 : 1). Moreover, the relation between the permanganate used and that of potassium present is a stoicheiometric one. This is contrary to the views of Kramer and Tisdall, who originally developed the method. The silver cobaltinitrite method is modified by P. A. Kometiani and S. Dolidze[81] by adding gelatin and ammonium sulphide and determining colorimetrically the sulphides produced ; the effective range of the method is said to be 0·075—0·2 mg. of potassium in 5 ml. of solution.

The method involving the precipitation of potassium as phosphotungstate, $K_5H(PO_4,12WO_3)_2,6H_2O$, is further developed by D. D. Van Slyke and W. K. Rieben.[82] The precipitate is separated centrifugally

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[77] *Soil Sci.*, 1943, **56**, 101 ; C., 1946, 284.
[78] *Z. anal. Chem.*, 1942, **124**, 327 ; B., 1943, III, 230.
[79] *J. Lab. clin. Med.*, 1945, **30**, 280 ; C., 1946, 119.
[80] *Anais Assoc. Quim. Brasil*, 1944, **3**, 131 ; C., 1945, 211.
[81] *Biochimia*, 1946, **11**, 29 ; C., 1946, 230.
[82] *J. Biol. Chem.*, 1944, **156**, 743 ; C., 1946, 130.

and determined volumetrically by the Toennies–Elliott[83] procedure. The preliminary removal of calcium, magnesium, iron, and phosphate, unless present in very high proportions, is unnecessary. In the preparation of samples (plant or soil) for analysis by digestion with sulphuric acid and ignition at 480°, it is noted that if silica dishes are used in place of platinum a correction for the loss of potassium is necessary. By use of silica centrifuge tubes the whole process may be carried out in these without transference. Alternatively the precipitate may be washed, dried, and weighed in the centrifuge tubes.[84]

The photometric determination of potassium as the chloroplatinate is shown by M. F. Adams and J. L. St. John[85] to give very satisfactory results with amounts of potassium as small as 0·2 mg. (accuracy 2%). This method is preferred by the authors to the iodoplatinate procedure, which, although more sensitive, gives less uniform results.

A more recent development in methods for determining potassium, namely, by precipitation with the sodium salt of 4 : 6-dinitrobenzfurazan 1 : 3-oxide in 30% alcohol, is examined by H. Rathsburg and A. Scheurer.[86] The potassium salt has a solubility in water of 0·22% at 16°, in 90% potassium sulphate solution or in alcohol, of 0·08%. It is stated that potassium in 10^{-5}N-potassium chloride solution may be detected by this method, which is also applicable to micro-analytical work.

A general review of methods, including the cobaltinitrite, chloroplatinate, dipicrylamine, phosphotungstate, and 6-chloro-5-nitrotoluene-3-sulphonate procedures, is recorded by F. Burton.[87]

MANGANESE IN SOIL AND IN PLANT NUTRITION.

Manganese Deficiency in Plants.

The rôle of manganese as a factor in soil and plant metabolism continues to attract increasing attention from research workers. Serious disturbances in plant growth and the occurrence of physiological diseases in plants, with associated loss of yield and/or deterioration in quality, have been attributed to the deficiency or excess of manganese in soils. Since this subject was last referred to in these Reports,[88] accounts of many new investigations have appeared and demand some further consideration here. Deficiency of manganese in soil, which causes grey speck disease in oats, is now shown to produce similar symptoms in other cereals. P. H. Gallagher and T. Walsh[89] state that the sensitivity of wheat, barley, and rye to this disorder decreases in the order named and in all cases is less than that of oats. Different varieties of wheat also exhibited

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[83] *J. Biol. Chem.*, 1935, **111**, 61 ; A., 1935, 1356.

[84] *Ibid.*, 1944, **156**, 743 ; C., 1945, 130.

[85] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 435 ; C., 1945, 222.

[86] *Chemie*, 1943, **56**, 123 ; C., 1946, 1.

[87] *Metallurgia*, 1946, **34**, 105 ; C., 1946, 230.

[88] *Ann. Repts.*, 1941, **26**, 374.

[89] *J. Agric. Sci.*, 1943, **33**, 197 ; B., 1944, III, 59. See also *idem*, *Proc. Roy. Irish Acad.*, 1943, **49**, B, 187 ; B., 1944, III, 3.

differences in susceptibility. All affected cereals recovered after spraying with a 1% solution of manganese sulphate and produced an increased number of tillers: subsequently ear formation and ripening were accelerated. In water-cultured wheat A. Kaltia[90] observes an increase in number and size of grains following small additions of manganese to the culture solution. In soil cultures manganese-treated plants were less susceptible to mildew. The sensitivity of grass species to deficiency of manganese varies considerably and according to T. Walsh[91] different strains of the same species vary somewhat in this respect.

The failure of onion crops on shallow peat soils overlying marl is attributed to lack of manganese and J. E. Knott[92] finds that applications of sulphur to increase the soil pH or the application of manganese sulphate at the rate of 100 lb. per acre affords a satisfactory remedy. Although a high pH in soil is commonly the cause of immobilisation of manganese, R. L. Cook and C. E. Millar[93] find that dressings of 100 lb. of manganese sulphate per acre correct the deficiency in oats and beans even on highly calcareous soils. T. Walsh and S. J. Cullinan[94] also find that on an alkaline medium loam marsh-spot in peas is prevented or cured by application of 0·5 cwt. of manganese sulphate per acre. Spraying with 1% solution of manganese sulphate at the flowering period was also effective and caused no appreciable foliage injury. Differences in the susceptibility of peas to the deficiency are attributed to differences in actual manganese requirement rather than to different capacities for the absorption of manganese from the soil. It is noted that the manganese contents of healthy and spotted peas in the same pod were similar and spraying increased the values in both to similar extents.

A chlorotic condition of bracken reported by J. G. Hunter[95] is ascribed, in part, to manganese deficiency although it is not prevented by late-season (September) spraying with manganese sulphate solution. The chlorosis is accentuated by high calcium concentrations in the tissues causing immobilisation of iron, and is probably dependent on a manganese/iron balance in the plant, such as has been observed in other species.

The control of manganese deficiency in fruit trees is not always so easily or rapidly effected as in the case of annual crops. Spraying with manganese sulphate solution or a manganese sulphate–lime suspension is fairly generally successful, *e.g.*, in citrus trees showing mottling due to interveinal chlorosis examined by E. C. Levitt and R. I. Nicholson[96] and also by E. R. Parker and R. W. Southwick,[97] in walnut by O. L.

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[90] *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 383; B., 1944, III, 21.
[91] *Nature*, 1945, **155**, 429; B., 1946, III, 39.
[92] *Proc. Amer. Soc. Hort. Sci.*, 1940, **37**, 803; B., 1943, III, 233.
[93] *Proc. Soil Sci. Soc. Amer.*, 1942, **6**, 224; B., 1943, III, 5.
[94] *Proc. Roy. Irish Acad.*, 1945, **50**, B, 279; B., 1946, III, 232.
[95] *Nature*, 1942, **150**, 578; A., 1943, III, 72.
[96] *Agric. Gaz. New South Wales*, 1941, **52**, 283; B., 1942, III, 9.
[97] *Proc. Amer. Soc. Hort. Sci.*, 1942, **39**, 51; A., 1943, III, 538.

Braucher and R. W. Southwick[98] and by A. P. Vanselow[99] and in other fruits by T. Wallace and J. O. Jones[100] and by E. Epstein and O. Lilleland.[101] The last-named workers obtain satisfactory results by injection of solid or aqueous solutions of manganese salts directly into the tree trunks. Injection methods used by J. B. Duggan[102] are recorded as successful when solids but unsatisfactory when solutions were employed. Injected solids probably become effective in the following season. According to Wallace and Jones (*loc. cit.*[100]) soil treatments with manganese sulphate, alone or in conjunction with sulphur, were ineffective for fruit trees although sulphur, used alone, prevented deficiency symptoms in beet grown in the same soil.

Some Chemical Aspects of Soil-Manganese.

Manganese sulphate added to soils of alkaline reaction (pH 7·4—7·8) is shown by R. L. Wain, B. J. Silk, and B. C. Wills[103] to be converted into insoluble forms in 7—14 days, although in one instance the immobilised manganese was released subsequently. Water-logging and steam-sterilisation of soil tended to increase the readily-extractable manganese content. According to P. H. Gallagher and T. Walsh,[104] grey speck disease in oats may be prevented by adding acid materials, *e.g.*, formalin, tartaric acid, or acid peat mould, to the soil and by maintaining an adequate moisture content therein. Potash fertilisers tended to increase the severity of the disease.

Manganese deficiency is not limited to soils of alkaline reaction. J. E. de Parva Netto,[105] in an examination of Brazilian coffee soils, shows that the leaching of manganese from soils of pH below 5·0 is sufficiently rapid to create a deficiency. Fixation of manganese occurs when the pH exceeds 6·5. As a means of testing soils for manganese status, extraction with 0·001N-nitric or -sulphuric acid is found to give data corresponding to the response of coffee plants. The available or active manganese in soils may exist, according to G. D. Sherman, J. S. McHargue, and W. S. Hodgkiss,[106] in three distinct forms, namely, water-soluble, exchangeable, and easily reducible. These may be determined by extraction with water, N-ammonium acetate, and N-ammonium acetate containing 2% of quinol, respectively. It is concluded that manganese-deficiency symptoms are likely to occur in neutral or alkaline soils if the easily-reducible manganese dioxide content falls below 25 p.p.m. Very acid soils containing less than 25 p.p.m. of active manganese probably become deficient

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[98] *Proc. Amer. Soc. Hort. Sci.*, 1942, **39**, 133; B., 1943, III, 144.
[99] *Ibid.*, 1945, **46**, 15; A., 1946, III, 331.
[100] *Ann. Rept. Agric. Hort. Res. Sta. Long Ashton*, 1942, 18; B., 1944, III, 108.
[101] *Proc. Amer. Soc. Hort. Sci.*, 1942, **41**, 11; B., 1943, III, 209.
[102] *J. Pomology*, 1943, **20**, 69; B., 1944, III, 4.
[103] *J. Agric. Sci.*, 1943, **33**, 18; B., 1943, III, 93.
[104] *Proc. Roy. Irish Acad.*, 1941, **46**, B, 143; B., 1942, III, 164.
[105] *Anais Assoc. Quim. Brasil*, 1942, **1**, 159; A., 1943, III, 74.
[106] *Soil Sci.*, 1942, **54**, 253; B., 1943, III, 118.

after liming. Deficient soils generally have a high capacity for oxidising manganous salts. In a survey of soils and crops of Illinois, H. J. Snider[107] notes an inverse relationship between available manganese contents and pH, and shows that the actual uptake of manganese by the crop is influenced by fertiliser treatment as well as by pH. For example, on a soil of pH 6·0 liming diminished and application of superphosphate increased the manganese intake of maize. That manganese deficiency symptoms are not entirely dependent on soil-pH is also indicated by some investigations of W. A. Albrecht and N. C. Smith.[108] On a prairie soil of pH 5·5 leguminous crops were poor. Admixture of lime with the whole of the soil used in pot-culture trials further depressed growth and the intake of manganese. Surface applications of chalk, however, increased the manganese intake. Additions of calcium phosphate increased manganese absorption and growth to parallel extents, leaving the manganese concentration in the plants unchanged. Treatment with a mixture of chalk and calcium phosphate increased the proportion of manganese in the plants.

Manganese and Plant Physiology.

Interrelationships between manganese and calcium in plant nutrition are indicated by the work of T. R. Swanback,[109] who demonstrates that when potassium is the dominant base in the nutrient, manganese retards both the intake of calcium and its subsequent utilisation by tobacco plants. On the other hand with nutrients in which calcium predominates, manganese has a beneficial effect. A relationship between manganese in plants and their photosynthetic activity has frequently been suggested. In the case of tung foliage W. Reuther and F. W. Burrows[110] find that "frenched" leaves of manganese-deficient trees showed no increased photosynthesis after treatment with manganese sulphate solution; chlorotic and green leaves have the same photosynthetic efficiency. The effect of manganese deficiency is to diminish leaf size and, in that manner, the total photosynthesis in the tree. R. D. Dickey and M. Drosdoff[111] indicate that the action of manganese sulphate on "frenched" leaves was not intensified by simultaneous application to the soil of magnesium sulphate. On the other hand aluminium sulphate used with the manganese salt, or even if used alone, had a beneficial effect. Probably this action is attributable to the diminution in soil-pH produced.

An influence of manganese on ascorbic acid formation in plants is indicated by Y. B. Rangnekar.[112] In pot-cultured *Amaranthus* plants small additions of manganese sulphate to the soil (0·05—0·1 g. per 6 lb. of soil) raised the ascorbic acid content of the leaves; larger supplements,

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[107] *Soil Sci.*, 1943, **56**, 187; B., 1944, III, 81.
[108] *Bull. Torrey Bot. Club*, 1941, **68**, 372; A., 1944, III, 378.
[109] *Plant Physiol.*, 1939, **14**, 423; A., 1944, III, 309.
[110] *Proc. Amer. Soc. Hort. Sci.*, 1942, **40**, 73; A., 1943, III, 538.
[111] *Ibid.*, 1943, **42**, 74; B., 1944, III, 250.
[112] *Current Sci.*, 1945, **14**, 325; A., 1946, III, 513.

although further increasing the manganese content of the leaves, tended to suppress ascorbic acid formation. M. N. Rudra[113] records larger proportions of ascorbic acid in leaves of *Phaseolus radiatus* resulting from soaking the seed, before sowing, in manganous chloride solution. Improved germination and subsequent growth of a number of crops following presoaking for not more than 24 hours is also reported by T. L. Loo and Y. W. Tang.[114] J. S. McHargue[115] summarises researches on the agricultural rôle of manganese in Kentucky.

MAGNESIUM DEFICIENCY IN SOILS AND CROPS.

Magnesium and the Plant.

The significance and extent of magnesium deficiency in crops has been the subject of much under investigation since it was last under consideration in these Reports.[116] Visible symptoms of the deficiency seem, in some respects, to lack specificity and, consequently, are not always easy to discern or even to describe. In many instances deficiencies of only moderate severity result merely in rather indifferent growth, poor yield, and perhaps decline in the quality of products. In the absence of striking visible symptoms, the disorder tends to pass unnoticed. There is reason to believe, however, that partial deficiency of magnesium is more general than is ordinarily believed. The close association of magnesium with chlorophyll and photosynthesis in plants serves to explain the effects of mild deficiencies of this element. More severe symptoms include marginal blotching or scorching and possibly premature leaf-fall and an enhanced susceptibility to invasion by pathogenic fungi. For example, in the case of pea-nuts examined by R. W. Bledsoe, H. C. Harris, and W. B. Tisdale,[117] the earlier leaf discoloration is followed by outbreaks of leaf-spot disease due to the fungus *Mycosphaerella arachidicola*. The disease appears to result from deficiency of magnesium and not from that of any other nutrient element examined. According to A. L. Sommer and A. Baxter[118] the deficiency affected the nut yield much more than it did leaf growth. These authors also record that crimson clover and cotton were moderately susceptible to magnesium deficiency, whereas turnip suffered only under more extreme conditions. Further investigations of the deficiency in tomatoes at Long Ashton[119] suggest that a criterion of deficiency is a decline in the magnesium content of tomato leaves to less than 0·5% (dry basis). Direct applications of magnesium sulphate to soil are less effective in correcting the deficiency than is spraying 3—4 times with a 2·5% solution of the salt, the amounts required in the two cases

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[113] *Nature*, 1944, **153**, 743; A., 1946, III, 782.

[114] *Amer. J. Bot.*, 1945, **32**, 106; A., 1946, III, 329.

[115] *Soil Sci.*, 1945, **60**, 115; B., 1946, III, 252.

[116] *Ann. Repts.*, 1943, **28**, 352.

[117] *Plant Physiol.*, 1946, **21**, 237; A., 1946, III, 1093.

[118] *Ibid.*, 1942, **17**, 109; A., 1944, III, 228.

[119] J. O. Jones, D. J. D. Nicholas, T. Wallace, and A. Jefferies, *Ann. Rept. Agric. Hort. Res. Sta., Long Ashton*, 1944, 61; B., 1946, III, 41.

being 10 cwt. and 1—5 cwt. of magnesium sulphate per acre respectively. A number of American publications relate to the occurrence of the deficiency in apple orchards. Thus D. Boynton[120] reports that applications of dolomitic limestone to the soil are only slowly effective and that several years may elapse before leaf-scorch is completely eliminated. Spraying with a solution of magnesium sulphate with or without addition of lime is more efficient. J. A. Chucka, J. H. Waring, and O. L. Wyman,[121] E. B. Kidson, H. O. Askew, and E. Chittenden,[122] and also L. Southwick and colleagues[123] arrive at similar conclusions and further record that soil treatment with magnesium sulphate or calcined kieserite gave satisfactory results in clean-cultivated orchards although not in old-standing grass orchards. The effect of potash fertilisers in intensifying the symptoms of deficiency is observed by Southwick (*loc. cit.*) and also by D. Boynton, J. C. Cain, and J. V. Gelume.[124] The latter workers find that the effect of lime on the deficiency symptoms is the reverse of that of potash. In another publication D. Boynton and A. B. Burrell[125] note that symptoms of magnesium deficiency may be induced in apple trees grown on soils of low base-exchange capacity by the repeated use of potash fertilisers, the gradual displacement of magnesium in the exchange complex by potassium being accompanied by similar changes in leaf ash composition and by increasing severity of leaf-scorch. In tung trees also, potash fertilisers accentuate the effects of magnesium deficiency.[126] Some relations between potash manuring and the occurrence of magnesium deficiency symptoms are examined by T. Walsh and T. V. O'Donohoe.[127] In potatoes heavy applications of potassium sulphate (5 cwt. per acre) cause the appearance of magnesium deficiency symptoms, concomitant low concentrations of magnesium and calcium in the leaves, and increased severity of blight. Application of magnesium sulphate to the deficient crop increases the intake of magnesium and lowers that of sodium. In sugar-beet the diminution of magnesium intake caused by potash manuring was less marked than in potatoes. On some Irish soils examined cereals were only slightly susceptible to lack of manganese, potash manuring effecting only a moderate degree of deficiency in barley and none in wheat. As an index of the critical level of magnesium in plant leaves, marking the border between adequacy and insufficiency, the following values are given : potato 0·17—0·38, tobacco 0·06, sugar-beet 0·05, barley 0·05, mangold 0·22—0·43% (dry matter).

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[120] *Proc. Amer. Soc. Hort. Sci.*, 1945, **46**, 1 ; B., 1946, III, 63.

[121] *Ibid.*, 13 ; B., 1946, III, 63.

[122] *New Zealand J. Sci. Tech.*, 1943, **25**, A, 31 ; B., 1944, III, 86.

[123] L. Southwick, *Proc. Amer. Soc. Hort. Sci.*, 1943, **42**, 85 ; L. Southwick and J. K. Shaw, *ibid.*, 1944, **44**, 8 ; L. Southwick and C. T. Smith, *ibid.*, 1945, **46**, 6 ; B., 1944, III, 247 ; 1945, III, 4 ; 1946, III, 64.

[124] *Ibid.*, 1943, **42**, 95 ; A., 1944, III, 247.

[125] *Soil Sci.*, 1944, **58**, 441 ; B., 1946, III, 6.

[126] M. Drosdoff and A. L. Kenworthy, *Proc. Amer. Soc. Hort. Sci.*, 1944, **44**, 1 ; B., 1945, III, 7.

[127] *J. Agric. Sci.*, 1945, **35**, 254 ; B., 1946, III, 127.

An earlier investigation by G. Michael[128] in which rye and maize were used as test plants leads to the conclusion that magnesium deficiency is more prevalent in acidic than in limed soils. The intake of magnesium by the crops tends to diminish with increase in supplies of calcium and vice versa although the ratio of water-soluble to total magnesium in the leaves changes but little with age or level of magnesium supply. The amount of magnesium concerned in chlorophyll is relatively small and reaches 20—30% of the total leaf-magnesium only in cases of actual deficiency. It is also recorded in these investigations that the formation of carotene, xanthophyll, and protein in these plants is restricted by lack of magnesium.

Soil-Magnesium.

It would seem that the appearance of magnesium-deficiency symptoms in plants may result from absolute deficiency in the soil or from ionic interactions which modify the actual intake by the plants. Neither condition is common in soils of normal type unless these have received some rather extreme treatment. The degree of saturation of soils with magnesium is usually lowered to some extent by liming, and W. A. Albrecht, W. J. Pettyjohn, and E. O. McLean[129] find that a similar effect may be produced by phosphatic manuring. Under conditions examined by these authors, soils are subject to severe erosion and the intensive growth of field and cover crops, practiced to prevent this, results in a fairly extensive magnesium deficiency. Indeed, the prolonged intensive growth of crops under any conditions may increase the magnesium requirement of soils to levels comparable with those for the major plant nutrients.

An investigation of the behaviour of magnesium in the colloid complex of soils is recorded by H. P. Cooper,[130] who recommends the use of dolomitic limestone at the rate of 1 ton per acre every few years, or, for quicker results on soils of pH exceeding 7, "potash salts" (potassium magnesium sulphate).

For the determination of magnesium in soils and plants the 8-hydroxyquinoline method is very commonly utilised. A. J. Metson[131] describes a technique suitable for exchangeable magnesium in which the ammonium acetate leachate is treated to remove iron, aluminium, and calcium prior to precipitation of magnesium; the 8-hydroxyquinoline precipitate is dissolved in acid and magnesium is determined iodometrically after addition of potassium bromide–bromate. A colorimetric adaptation of this method is recorded by M. E. Weeks and J. R. Todd,[132] who utilise the green colour produced by dissolving the 8-hydroxyquinoline precipitate in a ferric chloride–acetic acid reagent. For determining the available

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[128] *Bodenk. Pflanzenernähr.*, 1941, **25**, 65; B., 1944, III, 40.

[129] *Soil Sci.*, 1943, **55**, 447; B., 1944, III, 2.

[130] *Ibid.*, 1945, **60**, 107; B., 1946, III, 252.

[131] *New Zealand J. Sci. Tech.*, 1940, **22**, **B**, 125; B., 1941, III, 250.

[132] *Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 297; A., 1943, III, 704.

magnesium in soil W. H. Garman and F. G. Merkle[133] adopt a rapid method involving extraction of the soil with 0·25N-ammonium acetate (pH 5·0) followed by the colorimetric Titan-yellow procedure; the method is sufficiently reliable to distinguish deficient soils in routine advisory work.

E. B. Kidson[134] has developed an interesting method for detecting magnesium (and also potassium) deficiency by leaf diagnosis, using an ashing technique whereby a complete ash "skeleton" leaf is obtained. The undisturbed ash is sprayed with 0·5N-sodium hydroxide followed by 0·05% Titan-yellow. The intensity and distribution of the transient pink colur are observed. Potassium is determined similarly by spraying with cobaltinitrite reagent.

SOME CHEMICAL ASPECTS OF POTATO CULTURE.

The importance which the potato crop has assumed in our national economy in recent years and the significance which now attaches to the production of heavy crops of good-quality tubers render it appropriate that some reference be made in this Report to the very considerable chemical literature concerning this vegetable, which has come to hand during the past two or three years.

"Seed" Treatment.

At all stages from "seed" to stored tubers the potato has been the subject of much chemical investigation. Early shooting of planted seed is desirable primarily to avoid premature decay, especially if the seed tubers have been cut, and in many cases to ensure that the plant reaches a stage of development enabling it fully to utilise the period of optimum growth conditions and be harvested under good weather conditions. These matters are of importance where late spring and early autumn frosts are prevalent or in warmer climates where two crops can be produced annually.

Decay on cut seed pieces is largely avoided in practice by planting immediately after cutting in warm, moist soil, thus favouring early shooting.[135,136] Tubers in which the dormant period is unduly long (possibly because of unsuitable conditions at harvest or in storage) may be stimulated into activity by chemical means, thus improving yields and minimising premature decay.[137] Perhaps the best known of such treatments is that with ethylene chlorohydrin, extensively examined by F. E. Denny.[138] Subsequent treatment with sodium thiocyanate or urea is also recommended. In later work Denny[139] shows that still better

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[133] *Soil Sci.*, 1942, **53**, 15; B., 1942, III, 162.

[134] *New Zealand J. Sci. Tech.*, 1943, **24**, B, 140; A., 1944, III, 156.

[135] J. E. Krauss and G. W. Woodbury, *Proc. Amer. Soc. Hort. Sci.*, 1943, **43**, 262; B., 1945, III, 2.

[136] H. B. Cordner and N. Ward, *ibid.*, 1940, **37**, 874; B., 1943, III, 231.

[137] H. B. Cordner, *ibid.*, 879; B., 1943, III, 231.

[138] *Amer. Potato J.*, 1943, **20**, 171; B., 1944, III, 3.

[139] *Contr. Boyce Thompson Inst.*, 1945, **14**, 1; B., 1945, III, 241.

effects are obtained with a mixture of ethylene chlorohydrin, ethylene dichloride, and carbon tetrachloride (7 : 3 : 1 by volume). According to N. C. Thornton[140] the dormancy of early-harvested potatoes may be broken in 7—9 days by exposure to an atmosphere of low oxygen content ($N_2 : O_2 = 98 : 2$) under dry storage conditions or to one containing 5—10% of oxygen under moist conditions. In pure nitrogen, sprouting occurs in approximately 18 days. The treatment also has the effect of obliterating the normal tendency for apical buds ("eyes") to sprout at the expense of others. In treated tubers multiple sprouting occurs at all eyes, thus permitting a certain economy in cut seed pieces. Such treatment is also of value in the "sproutling" method of propagation, in which the separate sprouts are cut from the tuber and planted in seed-beds, subsequently being planted-out in the field.[141]

By contrast, it is often desirable to delay the sprouting of potatoes, especially of early varieties, until within a reasonable period before planting. Treatment with methyl α-naphthylacetate (100 mg. per kg.), preferably diluted with an inert carrier such as talc or fine soil, is recommended for this purpose.[142] Treated tubers contain only traces of reducing sugars, accumulation of which normally precedes sprouting.

Potato Manuring.

Normal manuring practice for potatoes has been examined exhaustively over a number of years. Current investigations are concerned more with the influence of manurial treatment on quality or on the incidence of disease, and with the occurrence of specific nutritional deficiencies, notably of the secondary nutrients. Thus L. J. H. Teakle and E. T. Morgan[143] in a general investigation of copper deficiency in crops observe the beneficial influence of this element on potato yields and recommend dressings of the order of 2·5 lb. (as Cu) per acre. Roasted, oxidised copper ones (10—20% Cu) proved effective for this purpose except on calcareous soils. Copper, iron, manganese, and zinc salts applied individually or in various combinations produced notably increased yields, largely due to greater tuber size, on soils examined by J. G. McLean, W. C. Sparks, and A. M. Binkley[144]; in many cases skin thickness was increased by use of these minor elements. A. A. Richter and T. A. Krasnoselkaja[145] also report beneficial effects following applications of zinc salts. Stem-end browning due to boron deficiency is described by F. B. Chandler[146]; in Montana soils applications of boron alone to deficient soils had little effect unless phosphate fertilisers, alone or with nitrogenous

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[140] *Contr, Boyce Thompson Inst.*, 1944, **13**, 361; B., 1945, III, 117.

[141] Puskarnath, *Indian Farming*, 1946, **7**, 182; B., 1946, III, 229.

[142] F. E. Denny, *Contr. Boyce Thompson Inst.*, 1945, **14**, 15; B., 1945, III, 241.

[143] *J. Dept. Agric. W. Australia*, 1943 **20**, 119; also L. J. H. Teakle, *ibid.*, 123; B 1945, III, 218.

[144] *Proc. Amer. Soc. Hort. Sci.*, 1944, **44**, 362; B., 1945, III, 35.

[145] *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 404; B., 1945, III, 35.

[146] *Soil Sci.*, 1944, **57**, 67; A., 1944, III, 379.

fertilisers, were applied simultaneously.[147] Magnesium deficiency on acid soils, examined by W. C. Barnes,[148] not only affects the growth of potatoes directly, but also nullifies the action of potash fertilisers, even to the extent of causing a decrease in yield when generous proportions of potash are given.

According to T. Wallace, H. E. Croxall, and P. T. H. Pickford,[149] magnesium deficiency symptoms were less severe on soils receiving farmyard manure.

Details of the gross intake of nutrients by potatoes at various stages of growth are recorded by P. A. Lorenz[150] and by A. Hawkins,[151] the latter worker noting that an average late variety absorbs approximately 25% more nutrients than does an early variety. Potato leaf-scorch, commonly associated with potash deficiency, is shown by E. C. Large, A. Blenkinsop, and H. H. Le Riche[152] to be most severe on high-lime soils, especially when the available phosphate is also high, and generally speaking is prevented by nitrogen-, phosphate-, or calcium-bearing fertilisers. The occurrence of the disorder is apparently related to the ratio (Ca + Mg) : K in the leaves; it is often delayed by spraying with Bordeaux mixture. G. A. Cowie,[153] in a study of potato manuring, also associated the occurrence of leaf-scorch with relatively excessive nitrogen and phosphate manuring but not with that of nitrogen alone. An interesting review of factors affecting potato yields is given by G. Samuel.[154]

Potato Quality.

The manifold uses to which potatoes are put have necessitated much investigation of the influence of growth conditions on the various properties of potatoes which are of commercial interest. Attempts to correlate the ascorbic acid content of potatoes have led to varied conclusions, and K. J. Karikka, L. T. Dudgeon, and H. M. Hauck,[155] after examining numerous varieties grown in different localities, trace no consistent relationships between ascorbic acid formation and soil-pH, the composition of fertilisers applied, or the supply of secondary nutrients. A. Pollard, M. E. Kieser, A. Crang, and T. Wallace[156] conclude that potato quality is dependent more on the nature of the cropping site than on manurial treatment except where specific nutritional deficiencies exist. Of the major plant nutrients, potassium induces the most general improvement in quality.[157] Excessive nitrogen feeding has an adverse effect,

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[147] F. M. Harrington, V. E. Iverson, and W. E. Pollinger, *Montana Agric. Exp. Sta.*. 1941, *Bull.* 392; B., 1943, III, 47.

[148] *Proc. Amer. Soc. Hort. Sci.*, 1944, **44**, 379; B., 1945, III, 3.

[149] *Ann. Rept. Agric. Hort. Res. Sta., Long Ashton*, 1942, 38; B., 1944, III, 106.

[150] *Proc. Amer. Soc. Hort. Sci.*, 1944, **44**, 389; B., 1945, III, 2.

[151] *Amer. Fert.*, 1942, **96**, *No.* 6, 5; B., 1943, III, 142.

[152] *J. Min. Agric.*, 1946, **53**, 211; B., 1946, III, 214.

[153] *Ann. appl. Biol.*, 1942, **29**, 333; B., 1943, III, 142.

[154] *J. Soc. Arts*, 1944, **92**, 562; B., 1944, III, 222.

[155] *J. Agric. Res.*, 1944, **68**, 49; B., 1944, III, 122.

[156] *Ann. Rept. Agric. Hort. Res. Sta., Long Ashton*, 1944, 184; B., 1946, III, 39.

[157] H. G. Wager, *J. Agric. Sci.*, 1946, **36**, 207; B., 1946, III, 230.

deficiency of phosphate is commonly associated with deterioration in consistency and flavour, and lack of potash is said to favour blackening on cooking.[156] Reference to this matter was made in an earlier Report.[158] More recently, Wallace *et al.*[156] report that blackening is accentuated by deficiency of phosphate as well as of potash. Cowie[153] reaches similar conclusions but argues that high-nitrogen–low-potash conditions in soil contribute more potently to blackening than does a simple potash deficiency.

A somewhat different type of discoloration is shown by T. Wallace and R. L. Wain[159] to be due to a deficiency of calcium. According to O. B. Nash and O. Smith[160] the shading of potatoes during growth, which like potash deficiency may restrict carbohydrate synthesis, tends to cause blackening especially when the nitrogen content of the soil is high. The physiological phenomena associated with blackening are accumulation of a α-amino-acids, mobilisation of iron, presence of a phenolic substance which acts as a component or precursor of the dark pigment, and some form of oxidase activity. Most of these factors are shown to be conducive to blackening. H. W. Nutting[161] records the presence of two flavone-like pigments, one yellow, the other grey, in aqueous extracts of potatoes. The yellow, stable pigment is related to the grey (and unstable) one and both appear to differ from melanin present in raw potatoes. These observations may have a bearing on the discoloration of potatoes in cooking. A further suggestion introduced by W. E. Tottingham, R. Nagy, A. F. Ross, J. W. Marek, and C. O. Clagett[162] is that the tendency to darken on cooking is an hereditary characteristic and is possibly related to the presence of a virus or other disease.

DDT.

The enormous literature concerning the widespread uses of DDT, now in process of exploration, defies reviewing in a Report of this character. Even if the scope of the Report is limited to the more purely agricultural uses of this insecticial, or even still further limited (as it, in fact, is) to considerations of the employment of DDT in controlling insect pests of growing crops, a comprehensive review is scarcely possible. Merely to list the many insect pests on a wide range of crops to which DDT has been applied with varying degrees of success would be a considerable task and one which would be, probably, of only limited value and, certainly, premature. It seems preferable to comment on some of the characteristics of this substance which relate to its insecticidal efficiency together with the various methods of application in field work.

From the viewpoint of the control of insect pests on field crops, the

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[158] *Ann. Repts.*, 1942, **27**, 376.

[159] *J. Min. Agric.*, 1943, **50**, 425; B., 1944, III, 28.

[160] *Proc. Amer. Soc. Hort Sci.*, 1940, **37**, 861; B., 1943, III, 216.

[161] *Food Res.*, 1942, **7**, 227; B., 1943, III, 103.

[162] *J. Agric. Res.*, 1943, **67**, 177; B., 1944, III, 11.

primary, significant attributes of DDT are its high order of toxicity to a wide range of insect species, its relatively small action on warm-blooded verbebrates, its persistence and residual action, and its relative stability which permits the use of a considerable range of solvents or other vehicles and also the admixture with other insecticidal and fungicidal materials in multi-purpose preparations.

The mechanism of the toxic action of DDT, discussed by T. F. West and G. A. Campbell,[163] is still a debatable matter. It is held by some that the toxicity is a function of the DDT molecule as a whole, in that it contains in its structural configuration a component associated with toxicity in general and also a second structural component characteristic of lipin-solubility which ensures penetration into the tissue of the insect. Alternatively it is assumed that the toxicity is simply a function of the ability of the compound to liberate hydrochloric acid from the molecule. According to R. Domenjoz,[164] neither theory entirely fits the facts. J. R. Busvine,[165] in a comparison of the properties of DDT and analogous substances, confirms this view. A number of investigations, among which those of S. J. Cristol and H. L. Haller[166] and of W. A. Gersdorff[167] are typical, serve to show the great superiority of *pp'*-DDT over its *op'*-isomer for most insecticidal purposes. From the more immediately practical point of view, DDT may be regarded both as a stomach- and as a contact-poison, affecting primarily the nervous system.

E. E. Fleck[168] examines the persistence of DDT when sprayed on to glass plates in laboratory tests. The daily loss from the exposed plates was very small and corresponded to a "life" of 1·5 years. It is reasonable therefore to expect a persistence of at least many weeks in the field. It would appear that sunlight affects the activity of DDT residues. A. W. Lindquist, H. A. Jones, and A. H. Madden[169] demonstrate this on a variety of sprayed materials by determining the residual toxicity to flies. The effect of light is influenced by the nature of the solvent used. Perhaps the commonest solvent is kerosene but high-boiling solvents are used in conjunction with this to aid dissolution. These supplementary solvents accelerate the loss of efficiency of the sprayed material. Suspensions of DDT in water or in xylene are much less affected by light. DDT sprays are commonly prepared by emulsifying a solution of the substance in oil or other solvent, the final concentration of DDT used being from 1 to 10% according to the purpose required and the kind of spraying machinery available. Dusting preparations usually contain similar proportions of the insecticide and an inert mineral carrier. Pyrophyllite is favoured in America for this purpose. In such forms DDT is reported to be of value

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[163] *Chem. and Ind.*, 1945, 154; B., 1945, III, 198.
[164] *Helv. Chim. Acta*, 1946, **29**, 1317; A., 1946, III, 1064.
[165] *Nature*, 1945, **156**, 169; B., 1946, III, 129.
[166] *Chem. Eng. News*, 1945, **23**, 2070; B., 1946, III, 32.
[167] *Soap*, 1946, **22**, *No.* 3, 126; B., 1946, III, 162.
[168] *J. Econ. Entom.*, 1944, **37**, 853; B., 1945, III, 244.
[169] *Ibid.*, 1946, **39**, 55; B., 1946, III, 245.

in the control of a very varied selection of the pests of fruit and vegetables, including numerous aphids, weevils, caterpillars, beetles (including Colorado beetle), and codling moth. According to G. F. Wilson,[170] DDT has no ovicidal properties, has little action on red spider and other acarine mites, and its toxicity to some aphids is relatively small.

Numerous investigators demonstrate that DDT has little or no injurious action on growing crops, even on tender foliage or fruits, and is compatible with most copper fungicides, with sulphur (in dusting preparations), lead arsenate, fluorine-containing insecticides, rotenone, and pyrethrum.[171] A useful collection of solubility data in over 200 organic solvents, of much service to those concerned with DDT preparations, is recorded by H. A. Jones, H. J. Fluno, and G. T. McCollough.[172]

The application of DDT in aerosol form is finding extensive use. Oil, *cyclo*hexanone, and acetone are common solvents for this purpose and methyl chloride is a serviceable carrier gas. The proportion of DDT in the aerosol is generally 5—10%.

In the control of soil pests, DDT, applied as a dust directly to the soil, is shown to afford protection to young plants against the black beetle in Australia; leather-jackets in lawns have been effectively controlled by use of 0·05% emulsions or 5% dusts. It is of agricultural interest to note that 0·1% suspensions of DDT are not toxic to earthworms but cause considerable mortality among bees. DDT seems to have no fungicidal properties. Among interesting reviews of agricultural uses of DDT may be cited those of H. Shaw,[173] G. A. H. Helson and D. F. Waterhouse,[174] and G. A. H. Helson and T. Greaves.[175]

Analytical methods for the examination of DDT are discussed in the section on Pest Control (p. 509).

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[170] *J. Roy. Hort. Soc.*, 1946, **71**, 6; B., 1946, III, 43.

[171] E. E. Fleck and H. L. Haller, *J. Amer. Chem. Soc.*, 1945, **67**, 403; B., 1945, III, 202.

[172] *Soap*, 1945, **21**, *No.* 11, 110; B., 1946, III, 32.

[173] *Nature*, 1946, **157**, 285; B., 1946, III, 169. See also *J. Roy. Agric. Soc.*, 1945, **106**, 204; B., 1946, III, 151.

[174] *J. Austral. Inst. Agric. Sci.*, 1945, **11**, 172; B., 1946, III, 227.

[175] *J. Counc. Sci. Ind. Res. Australia*, 1945, **18**, 301; B., 1946 III, 169.

PEST CONTROL.

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It is generally recognised that an "heroic age" of rapid development has set in for insecticides, but the real nature of the changes in progress is not always appreciated, so that pest control merits more than the casual mention which it customarily receives in these Reports. It will, however, be necessary to restrict this survey to the human and veterinary fields, leaving the horticultural to a later year. Even with this restriction, it will be impossible to refer to more than a small proportion of the published work; fortunately several aspects have recently been authoritatively reviewed and reference to these reviews or, in other cases, to leading papers must replace full documentation. In this survey, consideration of some general principles is followed by an account of chemical developments among specific insecticides and finally by a summary of their uses.

From the chemist's point of view, development of insecticides has been much slower than that of drugs, one reason being that insecticides must be available in exceedingly large quantities and that they had until recently to be very cheap. Of the insecticides still in use, some such as sulphur, petroleum (bitumen), and arsenic date back many centuries. During the 19th century use was also made of concoctions such as the arsenical dips for animals and Bordeaux and Burgundy mixtures for vines etc. and of cheap products and by-products of the chemical industry, such as coal-tar fractions and prussic acid; later these were more or less scientifically standardised, so that they constitute now a series of reputable and reliable products.

In 1910—1920 derris root and pyrethrum flowers, long used as insecticides by "primitive" peoples, were introduced on a large scale into Great Britain and the U.S.A. and their relative innocuousness to the host was a great advance. It will be seen that, contrary to what happened with drugs, large-scale use of exotic plant products generally came after that of chemicals.

In 1914 Riehm described the fungicidal properties of "chlorphenol-mercury," and manufacture of organic mercurials for seed dressings soon followed. This was, however, almost the only widespread use of synthetic organic chemicals until the late 1930's brought increasing use of the thiocyanates in fly-sprays and of phenothiazine as an anthelmintic. The recent war saw the introduction of DDT and "Gammexane," and there is promise of utility of sulpha drugs against coccidiosis. It is now fully realised by the chemical manufacturer that pest control is economically worthy of his consideration, and by the agriculturalist that it may be profitable to use relatively expensive chemicals.

The chemical used is, however, only one of three factors concerned. The second is the compounding and method of use : it is relevant too that popularisation of pyrethrum came only with the advent of a suitable powder blower in the U.S.A. about 1913 and the erection in 1919 of an extraction plant; other examples are described below.

The third factor is the life-histories of the host and of the parasite. The necessity of suiting the insecticide to the habits of the host needs no emphasis. As regards the parasite, differences from one to another are so great that no one insecticide can suffice for all, whilst *per contra* the similarities may be such that beneficial insects are destroyed along with or in preference to injurious ones (nevertheless, the desire sometimes expressed for an insecticide specific to one parasite is erroneous; the multiplicity of pests which afflict man, animals, and plants would then necessitate an entirely uneconomic multiplicity of manufacture); further, the value of a new development often lies not so much in its being more lethal as in its ability to attack the parasite in another and more convenient stage of its life-cycle.

Progress in pest control may thus take different forms. A new insecticide may replace an old one by virtue of greater safety or convenience in use, or a new development may provide control over parasites which resisted previous methods or chemicals. However, with the value of pest control becoming more and more realised, the final result is for new insecticides to supplement the old ones to a greater extent than they supplant them.

The stage is now being reached in which conflicting claims are made for a variety of synthetic chemicals, and it is clear that the field, large as it is, cannot find room for them all. The fierce competition already existing in curative medicine is extending to pest control and it is likely that this competition will continue with increasing vigour.

PYRETHRUM.

Material analysing as 90—100% pyrethrins is obtained from commercial kerosene solutions of pyrethrum extract by extraction with nitromethane and passage through activated charcoal.[1] This material has the freedom from insoluble matter and irritating ingredients required for aerosols (see below) and has rendered possible further investigation of the structure of the pyrethrins. The accepted structure of chrysanthemumcarboxylic acid, one of the acid components of the pyrethrins, has been confirmed by synthesis.[2] However, the parent keto-alcohol, "pyrethrolone," the structure of which was disputed, has been shown[3,4] to be a complex mixture, resolvable by fractional distillation and crystallisation of derivatives into *d*- and *dl*-forms of cinerolone, $C_{10}H_{14}O_2$, the *d*- and *dl*-forms

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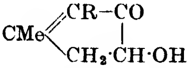
[1] W. F. Barthel, H. L. Haller, and F. B. LaForge, *Soap*, 1944, **20**, *No.* 7, 121.

[2] I. G. M. Campbell and S. H. Harper, *J.C.S.*, 1946, 283.

[3] F. B. LaForge and W. F. Barthel, *J. Org. Chem.*, 1944, **9**, 242; 1945, **10**, 106.

[4] T. F. West, *J.C.S.*, 1946, 463.

of a keto-alcohol, $C_{11}H_{14}O_2$, for which the name pyrethrolone is retained, and the *d*- and *dl*-forms of a substance believed to be a stereoisomer of pyrethrolone. Cinerolone is a 5-hydroxy-3-methyl-2-butenyl*cyclo*pent-2-en-1-one [(**I**) R = C_4H_7], and pyrethrolone is the analogous 2-penta-



$$\mathrm{CMe}\begin{array}{l}\nearrow\!\!\!\!\nearrow \mathrm{CR{-}CO} \\ \qquad\quad | \\ \searrow \mathrm{CH_2{\cdot}CH{\cdot}OH}\end{array}$$

(I)

dienyl compound [(I) R = C_5H_7], but the positions of the ethylenic linkings are still in dispute.[4,5,6] Commercially, analysis for "pyrethrins-I and -II" continues, but the empirical factor hitherto used in the Wilcoxon-Holaday method for pyrethrin-I is erroneous[7]—the results are affected by temperature[8] or bright light.[9] Attention continues to be paid to synergists and antioxidants for pyrethrum; special mention may be made of methylenedioxy-compounds (by analogy with sesamin)[10] and *iso*butyl-undecenoamide[11] as synergists, and of quinol[12,13] and "phenol S" (*iso*propylcresols)[11,12] as antoxidants.

DERRIS AND *LONCHOCARPUS*.

The classical studies of Worsley,[14] showing that the rotenone-containing resin of *Derris* root occurs in isolated specialised cells, have been confirmed and extended by other workers[15]; the resin is said to be partly in solution *in situ* in an ethereal oil (the amount of which is, however, very small), but it is definitely dissociated from the large amount of starch and smaller amounts of saponins, sucrose, and water-soluble tannins which are also present; extraction of the resin from the ground root in water is due to emulsification by the saponins. There have been few important advances since publication of the review[16] by the Imperial Institute. Insecticidal uses have been surveyed in a series of official American publications.[17]

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[5] F. B. LaForge and W. F. Barthel, *J. Org. Chem.*, 1945, **10**, 114, 222.

[6] S. H. Harper, *J.C.S.*, 1946, 892.

[7] J. J. T. Graham and F. B. LaForge, *Soap*, 1943, **19**, *No.* 11, 111.

[8] J. J. T. Graham (quotes also results of S. H. Harper), *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 571.

[9] N. Green and R. H. Carter, *Soap*, 1946, **22**, *No.* 7, 148A.

[10] *E.g.*, S. J. Gertler, J. H. Fales, and H. L. Haller, *Soap*, 1943, **19**, *No.* 4, 105. W. A. Gersdorff and S. J. Gertler, *Soap*, 1944, **20**, *No.* 2, 123. E. A. Prill, A. Hartzell, and J. M. Arthur, *Contr. Boyce Thompson Inst.*, 1946, **14**, 127. E. A. Prill and M. E. Synerholm, *ibid.*, 221.

[11] *U.S. Dept. Agric.*, 1946, *Misc. Publ.* 606, p. 53.

[12] R. C. Bushland, M. S. Schechter, H. A. Jones, and E. F. Knipling, *Soap*, 1945, **21**, *No.* 11, 119.

[13] W. A. Gersdorff and W. F. Barthel, *Soap*, 1946, **22**, *No.* 10, 155.

[14] R. R. Le G. Worsley, *Ann. Appl. Biol.*, 1939, **26**, 649. R. R. Le G. Worsley and F. J. Nutman, *ibid.*, 1937, **24**, 696; *Nature*, 1937, **139**, 883.

[15] F. A. Gunther and F. M. Turrell, *J. Econ. Entomol.*, 1942, **35**, 941; *J. Agric. Res.*, 1945, **71**, 61. Anon., *Puerto Rico Exp. Sta. Rept. for* 1939 (1940) (see *Bull. Imp. Inst.*, 1941, **39**, 248).

[16] H. J. Holman, "Survey of Insecticide Materials of Vegetable Origin" (Imp. Inst., London, 1940).

[17] R. C. Roark, *U.S. Dept. Agric., Bur. Entomol. & Plant Quar.*, 1942, *E*-579 *E*-581; 1943, *E*-593, *E*-594, *E*-598, *E*-603; 1944, *E*-625, *E*-630; 1945, *E*-652, *E*-654 *E*-655.

Methods of analysis have been reviewed by H. A. Jones[18]; modifications of the quantitative methods of the U.S. Government[19] are suggested in a collaborative investigation[20] by three British laboratories. Improved colorimetric tests, originally due to C. R. Gross and C. M. Smith[21] and to T. M. Meijer,[22] are extremely useful for investigation of small quantities[23] and of stability[24] but must be applied with caution to material other than *Derris* or *Lonchocarpus*.[25]

Marked synergism was found[26] to occur between *Derris* and high-boiling tar acids, but this combination—and indeed any combination of *Derris* and a non-volatile liquid—is unstable.[24] The degree of instability depends on the natures of the liquid and of the diluent powder, as well as markedly on temperature, being greater for liquids which are good solvents for the resin and for powders of open structure; it is suggested that the resin is distributed in solution in the liquid over the surface of the powder, thus exposing a larger amount to aërial oxidation, and further that the phenomenon may be general for oxidisable substances. A considerable stabilisation was effected by a small amount of a fairly strong acid (*e.g.*, phosphoric), a result which is in line with the general instability of rotenone etc. in alkali; the usual type of antioxidant has no stabilising effect on these powders, but on the other hand addition of acid does not always stabilise bulk solutions of rotenone in neutral organic liquids. Stabilisation of these powders was an essential step in the development of the British louse powder, A.L.63; later, owing to Japanese conquests, it became necessary to use *Lonchocarpus* from South America in place of *Derris*; *Lonchocarpus* is less stable than *Derris* and in combination with tar acids gave a powder which degraded too rapidly to be practicable; the pre-isolated resin, however, oxidises more slowly than does root, and a *Lonchocarpus* preparation based on resin had the required length of life.

SUBSTITUTES FOR PYRETHRUM AND ROTENONE.

Demands for pyrethrum for control of mosquitoes and flies and for *Derris* and *Lonchocarpus* for louse control and agricultural use created acute shortages which were not fully met until DDT and Gammexane had been developed. The quick knock-down of pyrethrum was, however, provided to an increasing extent by the thiocyanates, notably 2-dodecoyloxyethyl, 2-2′-butoxyethoxyethyl, and dodecyl thiocyanates, and

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[18] *U.S. Dept. Agric., Bur. Entomol. & Plant Qnar.*, 1942, *E*-563.

[19] "Official and Tentative Methods of Analysis of the A.O.A.C.," 1945, pp. 74–76.

[20] H. E. Coomber, J. T. Martin, and S. H. Harper, *J.S.C.I.*, 1942, **51**, 110; 1943, **52**, 73. K. B. Edwards, *ibid.*, 1942, **51**, 192.

[21] *J. Assoc. Off. Agric. Chem.*, 1934, **17**, 336. *See also* L. D. Goodhue, *ibid.*, 1936, **19**, 118. H. A. Jones, *ibid.*, 1945, **28**, 352; 1946, **29**, 127.

[22] *Rec. trav. chim.*, 1936, **55**, 954.

[23] *E.g.*, R. S. Cahn, R. F. Phipers, and J. J. Boam, *J.C.S.I.*, 1938, **57**, 200. R. S. Cahn and J. J. Boam, *ibid.*, 1939, **58**, 194.

[24] R. S. Cahn, R. F. Phipers, and E. Brodaty, *ibid.*, 1945, **64**, 33.

[25] H. L. Haller, *Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 277.

[26] H. J. Craufurd-Benson and J. Macleod, *J. Hygiene*, 1946, **44**, 294.

*iso*bornyl thiocyanoacetate. Many plant materials have been investigated[27] with little practical result, although increasing importance may attach to the long-known sabadilla seeds (*Schoenocaulon* spp.)[28]; these seeds are almost inactive when freshly ground, but are rendered highly toxic by heat and/or treatment with lime; their toxicity is due to five alkaloids, of which veratridine and cevadine are the most potent.[29] A favourable report[30] on yam bean (*Pachyrrhizus erosus*), from which rotenone was isolated,[31] has not been fully borne out since the content of insecticidal material is very low.[32]

DDT.

It is impossible fully to review here the subject of DDT (1 : 1 : 1-trichloro-2 : 2-di-*p*-chlorophenylethane), particularly in view of the immense amount of published entomological data; further, the Abstracts Bulletins, issued by the Insect Control Committee, Co-ordination Center, contain reports of the very numerous researches and trials carried out for U.S. war projects but unfortunately did not reach the present reporter in time for comparison with published work. It must suffice to refer to some of the best reviews[33–38] and to pass on to a few specific aspects. Official figures of American production have risen to over 4 million pounds a month during April and May, 1946.

DDT is prepared by condensing chlorobenzene with chloral or its hydrate or alcoholate in presence of acid. The effect of varying conditions has been reported for sulphuric acid and oleum[39] and for chlorosulphonic acid[40]; hydrogen fluoride is less satisfactory owing to the large excess needed.[41] Three grades of DDT, suitable for various purposes, are recognised in U.S.A.[42] Purification of the *pp'*-isomer has been described

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[27] For a compilation, see N. E. McIndoo, *U.S. Dept. Agric., Bur. Entomol. & Plant Quar.*, 1945, *E*-661.

[28] Reviews: *Bull. Imp. Inst.*, 1946, **44**, 102. C. H. Krieger, *Agric. Chemicals*, 1946, **1**, *No.* 4, 19.

[29] T. C. Allen, K. P. Link, M. Ikawa, and L. K. Brunn, *J. Econ. Entomol.*, 1945, **38**, 293. M. Ikawa, R. J. Dicke, T. C. Allen, and K. P. Link, *J. Biol. Chem.*, 1945, **159**, 517.

[30] R. Hansberry and C. Lee, *J. Econ. Entomol.*, 1943, **36**, 351.

[31] L. B. Norton, *J. Amer. Chem. Soc.*, 1943, **65**, 2259.

[32] L. B. Norton and R. Hansberry, *ibid.*, 1945, **67**, 1609.

[33] S. J. Cristol and H. L. Haller, *Chem. Eng. News*, 1945, **23**, 2070.

[34] Ministry of Supply, "Some Properties and Applications of D.D.T." (H.M.S.O., London, 1946).

[35] F. A. Gunther, *J. Amer. Chem. Soc.*, 1945, **67**, 189.

[36] *U.S. Dept. Agric.*, 1946, *Misc. Publ.* 606.

[37] R. C. Roark and N. E. McIndoo, *U.S. Dept. Agric., Bur. Entomol. & Plant Quar.*, 1944, *E*-631; 1946, *E*-687. R. C. Roark, *ibid.*, 1945, *E*-660.

[38] T. F. West and G. A. Campbell, "DDT, the Synthetic Insecticide" (Chapman & Hall, London, 1946).

[39] H. S. Mosher, M. R. Cannon, E. A. Conroy, R. E. Van Strien, and D. P. Spalding, *Ind. Eng. Chem.*, 1946, **38**, 916, *q.v.* for earlier references, Cf. also S. Kirkwood and J. R. Dacey, *Canad. J. Res.*, 1946, **24**, **B**, 69.

[40] W. H. C. Rueggeberg and D. J. Torrans, *Ind. Eng. Chem.*, 1946, **38**, 211.

[41] J. H. Simons, J. C. Bacon, C. W. Bradley, J. T. Cassaday, E. I. Hoeggeberg, and P. Tarrant, *J. Amer. Chem. Soc.*, 1946, **68**, 1613.

[42] *J. Econ. Entomol.*, 1945, **38**, 516.

by K. H. Cook and W. A. Cook.[43] The principal impurity is the *op'*-isomer; the numerous minor impurities[39,41,44] are such as would be expected from the methods of preparation. Crystallo-optical properties and *X*-ray diffraction data,[45–47] ultra-violet[46,47,55] and infra-red absorption spectra,[47] volatility,[48,49] and dipole moment[50] have been reported. Solubility in numerous solvents has been determined,[34,35,36,38,51] but such data require cautious interpretation in view of the varying composition of commercial supplies. It is important for the survival after application that ultra-violet light is stated to have no effect on crystalline DDT but to decompose DDT when in solution or when the crystals are moistened by benzene,[49] although an alcoholic solution is stated[52] to be stable. Pure solid DDT is stable to heat up to 200°, but loss of hydrochloric acid, with formation of the ethylene, $(p\text{-}C_6H_4Cl)_2C{:}CCl_2$, is catalysed to a remarkable extent by iron, iron chloride or oxide etc., or aluminium chloride[34,52–54]; this effect of iron is inhibited by picolinic acid or salicylideneaminoguanidine.[54] Iron-catalysed decomposition may also occur in solution[52]; the rôle of the solvent is in this case very important although not amenable to interpretation.

Of the macro-methods of determining DDT,[56,57] that most commonly used is conversion by alkali into the ethylene,[58–61] and titration of the liberated one equivalent of chloride; suitable additional manipulations are added when other insecticides etc. are present,[56,59,60] alcoholic ammonia

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[43] *J. Amer. Chem. Soc.*, 1946, **68**, 1663.

[44] H. L. Haller *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1591. J. Forrest, O. Stephenson, and W. A. Waters, *J.C.S.*, 1946, 333. O. G. Backeberg and J. L. C. Marais, *ibid.*, 1945, 803. K. Gatzi and W. Stammbach, *Helv. Chim. Acta*, 1946, **29**, 563.

[45] G. L. Clark and F. W. Cagle, jun., *Science*, 1945, **101**, 466. I. Fankuchen, M. Schneider, and J. Singer, *ibid.*, 1946, **103**, 25. E. L. Gooden, *J. Amer. Chem. Soc.*, 1945, **67**, 1616. H. Wild and E. Brandenberger, *Helv. Chim. Acta*, 1946, **29**, 1024.

[46] P. A. Neal *et al.*, *U.S. Publ. Health Repts.*, 1944, *Suppl.* 177.

[47] H. L. Andrews, W. C. White, L. R. Gamow, and D. C. Peterson, *U.S. Publ. Health Repts.*, 1946, **61**, 450.

[48] E. E. Fleck, *J. Econ. Entomol.*, 1944, **38**, 853.

[49] H. J. Wichmann, W. I. Patterson, P. A. Clifford, A. K. Klein, and H. V. Claborn, *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 218.

[50] K. Hojendahl and K. K. Møller, *Dansk Tidsskr. Farm.*, 1946, **20**, 197.

[51] H. A. Jones, H. J. Fluno, and G. T. McCollough, *Soap*, 1945, **21**, No. 11, 110. E. E. Fleck and H. L. Haller, *Ind. Eng. Chem.*, 1946, **38**, 177.

[52] E. E. Fleck and H. L. Haller, *ibid.*, 1945, **37**, 403.

[53] I. E. Balaban and F. K. Sutcliffe, *Nature*, 1945, **155**, 755. R. D. Chisholm, *U.S. Dept. Agric.*, 1945, *Bull. E*-643. E. E. Fleck and H. L. Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2095; 1946, **68**, 142. L. D. Goodhue and W. R. Ballinger, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 131.

[54] F. A. Gunther and L. R. Tow, *Science*, 1946, **104**, 203.

[55] H. Keller, M. Hochweber, and H. von Halban, *Helv. Chim. Acta*, 1946, **29**, 761.

[56,57] Partial reviews: C. G. Donavon, *Soap*, 1946, **22**, No. 6, 165. J. M. Ginsburg, *J. Econ. Entomol.*, 1946, **39**, 174.

[58] F. A. Gunther, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 149.

[59] R. H. Carter and P. E. Hubanks, *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 112.

[60] R. F. Powning, *J. Counc. Sci. Ind. Res. Australia*, 1945, **18**, 121.

[61] W. E. Baier, E. J. Edmonds, C. W. Wilson, M. I. Elliott, and F. A. Gunther, *Science*, 1946, **104**, 376.

being preferred to the more usual alcoholic potassium hydroxide when large amounts of sulphur are present[58] and use of chromatography permitting also determination of pyrethrins[60]; the results may be high if large amounts of *op'*-isomer are present, since the latter is partly converted by an independent side-reaction into di(chlorophenyl)acetic acid with liberation of three equivalents of hydrochloric acid[62]; however, by careful control of the conditions it is possible to reduce to 5—10% the decomposition of the less reactive *op'*-isomer.[63] The second macro-method depends on determination of total chlorine by combustion in coal gas[64] or by sodium in benzene containing a small amount of an alcohol.[59,65] Various colorimetric methods can be used to determine small quantities, subject to varying degrees of interference; that most commonly used is interaction with xanthhydrol and potassium hydroxide in pyridine containing a definite small amount of water[66] and can be adapted to give a very rapid qualitative field test.[67] A group of methods depends on forming the tetranitro-compound and treating this with sodium methoxide,[65,68] potassium hydroxide,[69] or ammonia and hydroxylamine in aqueous acetone.[69] Other colorimetric tests depend on Friedel–Crafts reactions[70] or formation of a carbinol ion in sulphuric–acetic acids.[71] It has also been suggested to determine DDT by its infra-red[72] or ultra-violet absorption spectrum[46] (the latter specifically for analysis of air-borne dusts), by its effect in raising the critical solution temperature of phenol and water,[73] and by its action on houseflies,[74] or qualitatively by its *X*-ray spectrum[46]; the absorption of the ethylene being very pronounced at 250 mμ., DDT may be determined by the increase in absorption at this wave-length produced by treatment with alkali[63]; and a complicated method[65] involves successively removal of hydrochloric acid, oxidation of the ethylenes to chlorobenzophenones, and colorimetric determination of the latter as 2 : 4-dinitrophenylhydrazones; separation of DDT from fat (*e.g.*, milk or meat) has been based on its insolubility in concentrated

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[62] S. J. Cristol and H. L. Haller, *J. Amer. Chem. Soc.*, 1945, **67**, 2222.

[63] R. R. Herriott, *Science*, 1946, **104**, 228. S. J. Cristol, *J. Amer. Chem. Soc.*, 1945, **67**, 1494. J. B. LaClair, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 763.

[64] S. A. Hall, M. S. Schechter, and E. E. Fleck, *U.S. Dept. Agric.*, 1944, *Bull. ET*-211. J. E. Fahey, *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 152. E. E. Fleck, *ibid.*, 585.

[65] H. J. Wichmann, W. I. Patterson, P. A. Clifford, A. K. Klein, and H. V. Claborn, *ibid.*, 1946, **29**, 188.

[66] J. C. Castillo and H. A. Stiff, jun., *Milit. Surgeon*, 1945, **97**, 500. H. A. Stiff and J. C. Castillo, *Science*, 1945, **101**, 440. F. Irrevere and N. E. Sharples, *ibid.*, 1945, **102**, 304. H. V. Claborn, *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 330.

[67] H. A. Stiff, jun., and J. C. Castillo, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 316.

[68] M. S. Schechter, S. B. Soloway, R. A. Hayes, and H. L. Haller, *ibid.*, 1945, **17**, 704.

[69] E. T. Illing and W. H. Stephenson, *Analyst*, 1946, **71**, 310.

[70] E. L. Bailes and M. G. Payne, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 438.

[71] S. W. Chaikin, *ibid.*, 272.

[72] J. R. Downing, W. V. Freed, I. F. Walker, and G. D. Patterson, *ibid.*, 1946, **18**, 461.

[73] F. G. Scholefield, S. T. Bowden, and W. J. Jones, *J.S.C.I.*, 1946, **65**, 354.

[74] E. P. Laug, *J. Pharm. Exp. Ther.*, 1946, **86**, 324.

sulphuric acid.[75] The amount of *pp'*-isomer in technical DDT is usually determined by recrystallisation from absolute or 75% alcohol[76] or from the setting point curve for *pp'*–*op'*-mixtures[77]; it may also be determined by observing microscopically the rate of growth of crystals from the melt[78] or, approximately, by the sulphuric–acetic acid colour test[71] (since the *op'*-isomer gives a much weaker colour with these reagents).

The multifarious uses for DDT may be found in the reviews cited[33–38] or various U.S. official bulletins[79]; some are considered specifically in later paragraphs. It is now generally recognised that numerous pests are unaffected by DDT, notably aphis, mites, and cotton boll-weevil, and further that care is needed during its use if beneficial insects such as bees are not to be destroyed. DDT has a small but definite toxicity—and cumulative at that—to man and higher animals, but it has been used almost without incident on an enormous scale and the risk of injury is small provided that prolonged exposure to solutions in oil or organic solvents is avoided; an excellent review of its toxicity has been issued by G. R. Cameron.[80]

"GAMMEXANE."

"Gammexane" is the trade name for the γ-isomer of benzene hexachloride (1 : 2 : 3 : 4 : 5 : 6-hexachloro*cyclo*hexane), $C_6H_6Cl_6$. The mixture of four isomers obtained by addition of chlorine to benzene has been called "666." The first published reference to the insecticidal effect of the γ-isomer appears to be that of L. Bory and R. Glasser[81] but this is antedated by I.C.I. patents[82,83] which were placed on the secret list during the war. An earlier French patent[84] is said to have been taken out but no details seem to be available. A still earlier American patent[85] refers to usefulness of benzene hexachloride as an insecticide but does not note the varying efficacy of the isomers. Benzene hexachloride was used as an insecticide during the war both in England[86] and in France,[87] but disclosure of its outstanding properties and wide applicability was first

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[75] M. S. Schechter, H. L. Haller, and M. A. Pogorelskin, *Agric. Chemicals*, 1946, **1**, *No.* 6, 27.

[76] S. J. Cristol, R. A. Hayes, and H. L. Haller, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 470; 1946, **18**, 339. I. E. Balaban and R. D. Calvert, *ibid.*, 1946, **18**, 339.

[77] E. E. Fleck and R. K. Preston, *Soap*, 1945, **21**, *No.* 5, 111.

[78] W. McCrone, A. Smedal, and J. Gilpin, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 578.

[79] *U.S. Dept. Agric.*, "Bibliography of DDT" (1944), and 1944, *Bull. E*-631; 1945, *E*-660.

[80] *Brit. Med. Bull.*, 1945, **3**, 233. Cf. G. C. Decker, *J. Econ. Entomol.*, 1946, **39**, 557.

[81] *Bull. Acad. Méd. Paris*, 1943, **39/40**, 728.

[82] With F. J. Donnithorne, B.P. 573,689.

[83] With C. R. Beveridge, B.P. 573,712.

[84] Gindraux, cited by L. B. Bourne, *Nature*, 1945, **156**, 85.

[85] H. Bender, U.S.P. 2,010,841 (B., 1936, 921; the account in *Chem. Abs.*, 1935, 6607, is inaccurate).

[86] S. Rogerson, *Nature*, 1945, **156**, 424.

[87] M. Raucourt, *La Nature, Paris*, 1945, 235 (*Rev. Appl. Entomol.*, 1945, **33**, **B**, 176).

made in England in 1945.[88] Two reviews[88,89] of some of its applications have appeared in England as well as a report[90] of preliminary American results. Where it is competitive with DDT, it appears often to be faster in action but less lasting: on the other hand, it is extremely effective against some pests, *e.g.*, locusts, cotton boll-weevil, and certain mites, which are not controlled or are less effectively controlled by DDT.

Benzene hexachloride, as usually made,[82] is a mixture of four isomers, containing about 75% of the α- and only about 12% of the γ-isomer, in which latter the insecticidal properties almost wholly reside. A brief record[91] of production of a mixture containing 42% of γ-isomer would appear to require confirmation. Separation of the isomers may be effected by crystallisation[88 92]: use of chromatography has recently led to isolation[93] also of hepta- (4%) and octa-chloro*cyclo*hexane (0·6%) from the commercial product. Dipole moments,[94] solubilitities, and vapour pressures have been recorded[88] and *X*-ray studies have elucidated the stereochemistry of the isomers.[88] The mixed isomers can be determined by analysis for total chlorine or removable hydrochloric acid ($C_6H_6Cl_6 \rightarrow C_6H_3Cl_3 + 3HCl$),[92] but determination of the γ-isomer requires infra-red spectoscopy.[88,95]

A novel effect is the death of bedbugs and mosquitoes feeding on a rabbit to which "Gammexane" had been given orally.[96] The toxicity of benzene hexachloride to man and animals has been reviewed by Cameron[80] and others[97]: it is of the same order as that of DDT.

OTHER SYNTHETIC INSECTICIDES.

There is even less theoretical foundation on which to base searches for new insecticides than in the case of drugs. Examination of almost any long set of organic compounds will disclose some compound or class of compounds toxic to one or more insects[98]; few are worth even preliminary field trial: very few survive for large-scale use. Many analogues were tested[99] before DDT was selected as the most promising; the

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[88] R. E. Slade, *Chem. and Ind.*, 1945, 314.

[89] J. S. Steward, *Nature*, 1946, **158**, 636.

[90] F. C. Bishopp, *Agric. Chemicals*, 1946, **1**, *No.* 6, 19.

[91] F. A. Gunther, *Chem. and Ind.*, 1946, 399.

[92] T. van der Linden, *Ber.*, 1912, **45**, 312.

[93] L. L. Ramsey and W. I. Patterson, *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 337.

[94] J. W. Williams and J. M. Fogelberg, *J. Amer. Chem. Soc.*, 1931, **53**, 2096. O. Hassel and E. Næshagen, *Tids. Kjemi Bergv.*, 1930, **10**, 126.

[95] H. W. Thompson, *Analyst*, 1945, **70**, 448.

[96] B. De Meillon, *Nature*, 1946, **158**, 839.

[97] See also H. Letard and G. S. de Sacy, *Compt. rend. Soc. Biol.*, 1945, **139**, 353; H. Taylor and J. Frodsham, *Nature*, 1946, **158**, 558. H. O. Calvery, *Rept.* CC-5-43, *Insect Control Commee., Co-ord. Center*, 1946, *Abs. Bull.*, *N.S.*, *No.* 8, 315.

[98] Cf. R. C. Bushland, *J. Econ. Entomol.*, 1940, **33**, 666, 669. E. F. Knipling, *ibid.*, 1941, **34**, 314. M. C. Swingle, A. M. Phillip, and J. B. Gahan, *U.S. Dept. Agric.*, 1944, *Bull. E*-621; 1945, *E*-634.

[99] P. Läuger, H. Martin and P. Müller, *Helv. Chim. Acta*, 1944, **27**, 892.

Germans are reported[100] to have considered the difluorine analogue, $(p\text{-}C_6H_4F)_2CH{\cdot}CCl_3$, and the compound $(p\text{-}C_6H_4Cl)_2CH{\cdot}CHCl_2$ to be in some respects superior to DDT; the latter compound and the dimethoxy-analogue, $(p\text{-}OMe{\cdot}C_6H_4)_2CH{\cdot}CCl_3$ (which gives a rapid knock-down of flies[101]), are on sale in America, but recent scientific tests of these and related compounds against mosquitoes,[102] lice, and bedbugs[103] still leave DDT as the best of its series. Apart from these substances, attention is being paid[90] at present mainly to substances known as "1068" ($C_{10}H_6Cl_8$, 1 : 2 : 4 : 5 : 6 . 7-hexachloro-4 . 7-dichloromethylene-3*a* : 4 : 7 : 7*a*-tetrahydroindane)[104] and "3956" (a chlorinated camphene)[105] (both these doubtless found from analogy with "Gammexane"), azobenzene (as a horticultural fumigant), hexaethyl tetraphosphate $\{[(OEt)_2PO]_3PO$; for aphis control; discovered by the Germans[100]$\}$, and 2′-hydroxy-2 : 4 : 4 : 7 : 4′-pentamethylflavan (for horticultural use), whilst the dimethoxy- and difluoro-analogues of DDT are also being further studied. The Germans had discovered insecticidal properties attaching to certain sulphones, notably di-*p*-chlorophenyl sulphone; they did not proceed far with this investigation, but from subsequent work it appears to be a potent substance.[90,103,106]

MODE OF ACTION OF INSECTICIDES.

The mode of action of insecticides has often been considered in discussions of pharmaceutical action in general, but attention has concentrated on the way in which a contact insecticide can penetrate through the lipoid layers of the epicuticle into the aqueous medium inside the cuticle. A fundamental paper by J. Ferguson[107] starts from the consideration that all equilibria involving distribution between two phases are governed by the necessity that the thermodynamic activity at equilibrium must be the same in both phases: relations connecting physiological action with partition coefficients, surface tension, vapour pressure, or adsorption are thus merely different methods of expressing the same concept. The thermodynamic activity can be measured approximately as the degree of saturation of a phase by the toxic substance and Ferguson showed that the necessary relation between thermodynamic activity and physiological action exists in a wide variety of cases: in those cases where it does not exist, chemical action rather than a physical equilibrium is

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[100] *Brit. Intelligence Objectives Sub-Commee., Item* 24, *Final Rept.* 116. *Combined Intelligence Objectives Sub-Commee. Repts., Item* 24, *File* XXIII-12, XXIII-20, XXVI-73, XXVII-4.

[101] E. A. Prill, A. Hartzell, and J. M. Arthur, *Science*, 1945, **101**, 440.

[102] C. C. Deonier, H. A. Jones, H. L. Haller, E. Hinchey, and H. H. Incho, *Soap*, 1946, **22**, *No.* 11, 118. E. P. Odum and W. T. Sumerford, *Science*, 1946, **104**, 480.

[103] J. R. Busvine, *Nature*, 1945, **156**, 169; *J.S.C.I.*, 1946, **65**, 356. R. Domenjoz, *Helv. Chim. Acta*, 1946, **29**, 1317.

[104] C. W. Kearns, L. Ingle, and R. L. Metcalf, *J. Econ. Entomol.*, 1945, **38**, 661. T. F. West, *Nature*, 1946, **158**, 951.

[105] L. A. Stearns, W. L. Parker, and J. H. Beacher, *Soap*, 1946, **22**, *No.* 12, 132.

[106] J. R. Busvine, *Nature*, 1946, **158**, 22.

[107] *Proc. Roy. Soc.*, 1939, **127**, **B**, 387.

considered to be the controlling factor. E. T. Burtt[108] noted that this relationship is disturbed when a toxic agent in one phase is brought into contact with another phase in which it is much more soluble or when the second phase is present in much larger amount and aptly describes this as the "capacity factor." J. E. Webb and R. A. Green,[109] however, point out that two phase-transferences are involved, namely into the lipoid fatty or waxy sheath of the insect and then out of this into the aqueous body-fluids; they correlated (*a*) the speed of kill (by contact action) of the sheep ked, *Melophagus ovinus*, by a dust containing 0·25% of diphenylamine and 1% of an added liquid, (*b*) the rate of passage of the "added" liquid through a beeswax membrane, and (*c*) physical properties, and concluded that speed of kill was favoured principally when (i) the liquid passed readily through beeswax, (ii) the liquid had notable solubility in both beeswax and water, and (iii) the liquid aided dissolution of the insecticide (diphenylamine) in water; they regard the liquid as transporting the insecticide through the bulk lipoid layer. H. Hurst[110] approaches the problem from a totally different angle; he connects insecticidal action with "permeability" and "functional viscosity" of the lipoid layer and postulates transference of the insecticide along the boundaries between lipoid and aqueous layers of the epicuticle, this boundary-transference being analogous to some of the thin-film phenomena observed by E. K. Rideal.[111] Meanwhile, the nature of the epicuticle is being examined anew by V. B. Wigglesworth and J. W. L. Beament,[112] whose elegant researches do not support Hurst's theories.

However, no general theory explains the specificity of insecticides, the variation in efficiency of insecticides relative to each other according to the test insect used, or the differing value of optical or steric isomers.

Certain studies have been restricted to specific insecticides. The physiological effects of DDT poisoning have been investigated in detail[113,114] without giving the chemist much lead. The Swiss discoverers[99] considered the *p*-chlorophenyl groups as the toxic portions of the molecule and the CCl_3 group as responsible for a high oil/water partition coefficient which confers on DDT superiority over its analogues; this return to the Meyer–Overton hypothesis, clearly retrograde, has been adversely criticised by others,[115] and largely modified by its original advocates,[113] whilst the fundamental relation between insecticidal activity and oil-solubility in the DDT series has been disproved.[103] H. Martin and R. L.

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[108] *Ann. Appl. Biol.*, 1945, **32**, 247.

[109] *J. Exp. Biol.*, 1945, **22**, 8.

[110] Summaries: *Nature*, 1943, **152**, 292, 400; *Trans. Faraday Soc.*, 1943, **39**, 390.

[111] Cf. *Endeavour*, 1945, **4**, *July*, 83.

[112] V. B. Wigglesworth, *J. Exp. Biol.*, 1945, **21**, 97. J. W. L. Beament, *ibid.*, 115; *Trans. Faraday Soc.*, 1945, **61**, 45; *Nature*, 1946, **157**, 370.

[113] P. Läuger, R. Pulver, C. Montiegel, R. Wiesman, and H. Wild, "Mechanism of Intoxication of DDT Insecticides in Insects and Warm-blooded Animals" (Geigy Co., Inc., New York, 1945).

[114] *E.g.*, R. D. Lillie and M. I. Smith, *U.S. Publ. Health Repts.*, 1944, **59**, 979; M. I. Smith, *ibid.*, 984; R. B. Smith, *ibid.*, 1009.

[115] T. F. West and G. A. Campbell, *Chem. and Ind.*, 1945, 154.

Wain[116] reversed the Swiss hypothesis, ascribing lipoid-solubilising effect to the *p*-chlorophenyl groups and insecticidal efficiency to the ease with which hydrochloric acid is lost from the neighbouring $CH\cdot CCl_3$ grouping; this relationship between toxicity and ease of dehydrohaloganation has, however, also been disproved by examination of analogues.[103] No explanation of the superior toxicity of DDT, other than qualitative suggestions of molecular size and shape,[103,113] has withstood examination. The toxicity of the gamma isomer of benzene hexachloride was tentatively ascribed[88] to interference with an enzyme process involving *i*-inositol, to which it is very closely related sterically; such antagonism has been proved by two sets of workers[117] to occur for growth of a yeast and a mould, whilst the insecticidally much less active other isomers show little or no antagonism to *i*-inositol. By a detailed study,[118] *Derris* dust is shown to be absorbed by the ked (*Melophagus ovinus*) mainly through the spiracles and tracheal system; when these are blocked, it slowly penetrates the external cuticle at 30°, but not at all at 20°, a difference ascribed to the different hardnesses of the lipoid layer at the two temperatures.

REPELLENTS.

Oil of citronella, oleum picis, etc. have long been used, but without great satisfaction, as insect repellents. The first synthetic chemical superior to oil of citronella was butyl 2 : 2-dimethyl-2 : 3-dihydro-4-pyrone-6-carboxylate[119]; this is prepared by condensing mesityl oxide with dibutyl oxalate and exists in equilibrium with the open-chain form, butyl 5-methylhexa-1 : 4-dien-1-ol-3-one-1-carboxylate, $CMe_2{:}CH\cdot CO\cdot CH{:}C(OH)\cdot CO_2Bu$, wherefore it has also been termed "butyl-mesityl-oxide-oxalate"; it is marketed as "Indalone." The need for protecting troops against mosquitoes and flies led to examination of some 8000 compounds and discovery of new repellents which in some cases were effective also against the mites (*Trombicula deliensis*) carrying scrub typhus and against "chiggers" (*Acariscus masoni, Eutrombicula tropica*).[120] Those used extensively during the war were Indalone (see above), dimethyl and dibutyl phthalates, 2-ethylhexane-1 : 3-diol ("Rutgers 612"),[121] and, to a lesser extent, benzyl benzoate; those more recently pronounced effective are dimethyl *cis-dicyclo*[2,2,1]hept-5-ene-2 : 3-dicarboxylate ("dimethyl carbate") and mixtures containing 70% of 2-phenyl*cyclo*hexanol with 30% of either 2-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene (to give "NMRI-201") or 2-*cyclo*hexyl*cyclo*hexanol (to give "NMRI-448").[122]

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[116] *Nature*, 1944, **154**, 512.

[117] H. W. Buston, S. E. Jacobs, and A. Goldstein, *Nature*, 1946, **158**, 22. S. Kirkwood and P. H. Phillips, *J. Biol. Chem.*, 1946, **163**, 251.

[118] J. E. Webb, *Bull. Entomol. Res.*, 1945, **36**, 15; *Proc. Zool. Soc. London*, 1945, **115**, 218.

[119] L. B. Kilgore, B.P. 495,183 (2.3.37); *Soap*, 1939, **15**, *No.* 6, 103.

[120] Reviews: R. Lewthwaite, *Brit. Med. Bull.*, 1945, **3**, 227. C. A. Setterstrom, *Chem. Industries*, 1946, **59**, 47. Cf. ref. 36.

[121] B. G. Wilkes, U.S.P. 2,407,205 (1946). P. Granett and H. L. Haynes, *J. Econ. Entomol.*, 1945, **38**, 671.

[122] L. A. Jachowski, jun., and M. Pijoan, *Science*, 1946, **104**, 266.

The different compounds are not all equally efficient against different genera or species of insects, so that mixtures were generally advocated in the U.S.A., *e.g.*, 6 : 2 : 2 or 1 : 1 : 1 mixtures of dimethyl phthalate, Indalone, and Rutgers 612 (cf. also the U.S. Navy's NMRI mixtures). The compounds may be used neat or as emulsions or creams on clothing or the exposed skin, but always rather large amounts are required, so that fastness to rain and washing is important.[123] Illumination has little effect on dimethyl phthalate or 2-ethylhexane-1 : 3-diol but converts Indalone into an insecticidally ineffective dimer.[124] The Germans[100] reported trichloroacet-2′-chloroethylamide, $CCl_3\cdot CO\cdot NH\cdot [CH_2]_2\cdot Cl$, to be a mosquito repellent but had not pushed its investigation very far. No theory is available to account for the specific properties of individual substances, nor is the physiological action understood.

AEROSOLS.[125]

In the literature of pest control, the term "aerosol" means[126] an air-borne dispersion of a finely divided solid (or liquid) which remains air-borne for an appreciably longer time than does the spray produced by a Flit-gun type of sprayer. In crude forms, they may be produced thermally by igniting mixtures of the insecticide and combustible material[127] or by spraying a solution of the insecticide onto a hot-plate.[128] These methods involve loss by combustion, which is avoided in later methods. One such uses a solvent which boils somewhat below atmospheric temperature, the solution being contained in a fairly stout vessel; it is ejected as spray by its own vapour pressure, whereafter the droplet size is reduced by evaporation of the solvent. This principle was first used by G. Jander and E. Wygash[129] for potassium iodide in sulphur dioxide; its successful application to insecticides depends on use, as solvent, of dichlorodifluoromethane ("Freon 12"), b.p. −29·8° (v.p. about 82 lb. per sq. in. at room temp.),[130] but methyl chloride has also been used successfully.[131] Such solutions, usually containing pyrethrum activated by sesame oil or lubricating oil, plus DDT and an auxiliary solvent therefor (*cyclo*hexanone), in their small portable containers found extensive use for troops' billets and tents, for airplanes, and

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[123] Cf. F. M. Snyder and F. A. Morton, *Soap*, 1946, **22**, *No.* 11, 133.

[124] H. A. Jones, G. T. McCollough, and F. A. Morton, *Soap*, 1946, **22**, 151. S. A. Hall, R. K. Adams, jun., and H. L. Haller, *J. Amer. Chem. Soc.*, 1945, **67**, 1224.

[125] Review (incomplete): L. D. Goodhue, *J. Econ. Entomol.*, 1946, **39**, 506.

[126] R. C. Roark, *J. Econ. Entomol.*, 1942, **35**, 105.

[127] L. D. Goodhue and W. N. Sullivan, *ibid.*, 1940, **33**, 329 : U.S.P. 2,306,434 (1942).

[128] W. N. Sullivan, E. R. McGovran, and L. D. Goodhue, *ibid.*, 1941, **34**, 79. W. N. Sullivan, L. D. Goodhue, and J. H. Fales, *Soap*, 1940, **16**, *No.* 6, 121. W. N. Sullivan and L. D. Goodhue, U.S.P. 2,285,950 (1942).

[129] *Kolloid-Z.*, 1938, **85**, 1.

[130] W. N. Sullivan, L. D. Goodhue, and J. H. Fales, *J. Econ. Entomol.*, 1942, **35**, 48. L. D. Goodhue and W. N. Sullivan, U.S.P. 2,321,023 (1943).

[131] L. D. Goodhue, *Ind. Eng. Chem.*, 1942, **34**, 1456.

houses.[36,131,132] Complicated relationships between (i) the amounts of insecticide, solvent, and non-volatile adjuvant, (ii) droplet size, and (iii) efficiency have required attention,[125] as well as purification of the pyrethrum,[1] apparatus suitable for testing such solutions,[133] and stability.[134] Aerosols can also be generated by using a volatile solvent (*e.g.*, acetone) and carbon dioxide[135] and in this form also found military use. For large-scale use, *e.g.*, on crops or herds of animals, in large buildings, or against mosquitoes, aerosols can be generated from oil solutions by superheated steam[136] or by hot air.[137] Although these principles have so far been applied mainly to DDT and pyrethrum, they are by no means restricted to them.

USE OF AIRPLANES.

It will have been noted that the considerable advance represented by aerosols is an advance in methods of application and not a discovery of a new insecticide. This applies equally to use of airplanes. Dusts, solutions, and emulsions may all be distributed from airplanes and various types of apparatus have been described in outline.[36 138] Airplanes were used during the recent war to control mosquitoes both before and after occupation by troops; to control flies breeding on corpses, airplane dusting was used in the Pacific Islands after and, later, before landings were effected. In the jungle surprisingly good penetration of foliage was sometimes achieved. Airplanes have for some time been used for treating horticultural crops in the U.S.A. A very specialised skill is required of the pilots; slow machines are advantageous, whilst autogiros or helicopters may be preferable for enclosed or "difficult" areas.

HUMAN APPLICATIONS.

Mosquitoes represent much the most important pest control problem of human medicine. The review by G. Macdonald[139] of recent progress should be read by all interested. Correlation of entomological, chemical, and practical progress is particularly clear in this field. For instance, eradication of *Anopheles gambiæ*, the carrier of yellow fever, from 5000 square miles in Brazil depended on finding and treating every single breeding place and was thus a major feat of organisation; in this work Paris green was the insecticide. An advance of first importance was the discovery that the incidence of malaria, though not of the mosquitoes,

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[132] P. N. Annand, *Soap*, 1943, **19**, *No.* 10, 117. L. D. Goodhue, *J. Econ. Entomol.*, 1944, **37**, 338. W. W. Rhodes, *Soap*, 1944, **20**, *No.* 9, 108. D. F. Starr, E. W. Baker, and J. A. Ramirez, *J. Econ. Entomol.*, 1945, **38**, 401.

[133] L. D. Goodhue, W. R. Ballinger, and J. H. Fales, *J. Econ. Entomol.*, 1945, **38**, 709.

[134] A. C. Hazen and L. D. Goodhue, *Soap*, 1946, **22**, *No.* 8, 151. L. D. Goodhue and W. R. Ballinger, *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 131.

[135] F. P. Mackie and H. S. Crabtree, *Lancet*, 1938, ii, 447. F. W. Knipe, *Amer. J. Trop. Med.*, 1941, **21**, 671.

[136] R. Latta, *J. Econ. Entomol.*, 1945, **38**, 668.

[137] R. D. Glasgow and D. L. Collins, *ibid.*, 1946, **39**, 227.

[138] W. N. Sullivan, *J. Aviat. Med.*, 1946, **17**, 192. C. W. Krusé and R. L. Metcalf, *U.S. Publ. Health Repts.*, 1946, **61**, 1171.

[139] *Brit. Med. Bull.*, 1945, **3**, 218, *q.v.* for other references.

is greatly reduced by control of the adults only; no adequate substitute has been found for pyrethrum for rapid knock-down of mosquitoes, although synergists (see above) effect notable economies, but the long life of DDT applied (usually in oil) to walls has been utilised with great effect; improved sprayers have great significance for such application. For larval control Paris green in kerosene–water emulsion or, later, in aqueous suspension has been widely and successfully used; DDT and "Gammexane" are also very effective against mosquito larvæ; notable economies in oil are effected, particularly when substances are added to increase the spread, and prevent rupture, of the film; nevertheless, their economic superiority over Paris green as larvicides probably remains to be demonstrated. Individual protection can be readily obtained by means of repellents, although the duration of repellency so far achieved remains at a few hours; treated nets with a wide mesh[36] are a great convenience. Macdonald concludes: "with these advances there is now no problem of disease or nuisance caused by mosquitoes which cannot be overcome, and almost always at a cost commensurate with the advantages to be gained"; however, there remains much work to be done on the detail of insecticide mixtures and of apparatus, and on deciding the best methods to be used for particular cases.

Fly control[140] can be achieved similarly (i) by attack on the adults with knock-down sprays of the pyrethrum or thiocyanate type, either in mineral oil or as aerosols, and/or by residual sprays containing DDT or "Gammexane," or (ii) by attack on the larvæ. For optimum results both methods should be used. Fly larvæ are rather resistant; *o*- and *p*-dichlorobenzene are said to be effective; the position of DDT and "Gammexane" versus larvæ is in dispute, but these insecticides do kill any emerging adults. The duration of the effect of residual sprays depends on the insecticide, the amount deposited per unit area, and the nature of the surface, but it may extend to several months. Mention should also be made of incorporation of DDT into paints, varnishes, etc.[38]; although perhaps convenient in some cases, this is uneconomical of insecticide. W. A. L. David[141] has shown how the amount of mineral oil sprays picked up by adult flies depends on various factors, notably on the activity of the fly, so that any "irritant" action of the spray is beneficial.

The successful control of the body louse (*Pediculus humanus* var. *corporis*) in the 1939–45 war,[142] in such marked contrast to the failure in the 1914–18 war, has received spectacular and sometimes accurate reporting. The first efficient powder was the British A.L.63, containing naphthalene as quick-killing agent and relying for protection on *Derris*

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[140] Review: H. J. Craufurd-Benson, *British Med. Bull.*, 1945, **3**, 224.

[141] *Bull. Entomol. Res.*, 1946, **36**, 373; 1946, **37**, 1; *Ann. Appl. Biol.*, 1946, **33**, 133. David and P. Bracey, *Bull. Entomol. Res.*, 1946, **37**, 177. Cf. E. R. McGovran and J. H. Fales, *Soap*, 1946, **22**, *No.* 9, 127.

[142] Reviews: J. R. Busvine, *Brit. Med. Bull.*, 1945, **3**, 215. C. H. Stuart-Harris *et al.*, *Proc. Roy. Soc. Med.*, 1945, **38**, 511. Reference 36.

root or, later, *Lonchocarpus* extract activated by high-boiling tar acids and stabilised by phosphoric acid[24,26,143] (cf. p. 507); the naphthalene has also some ovicidal effect.[144] The American MYL powder contained pyrethrins (0·2%), activated by *iso*butylundecenoamide (decene-1-carboxyl*iso*butylamide) and stabilised by *iso*propylcresols ("Phenol S"), as killing agent with dinitroanisole (2%) as ovicide. Diethyl dixanthate $[(OEt{\cdot}CS_2)_2]$ and diphenylamine were used by the Russians. DDT was later adopted by the British and American forces, not because of its greater killing power (and it is slow in action) but (*a*) because its supply was independent of natural sources and (*b*) because its protective effect covered at least 14 days (as against 0—8 days for A.L.63 and MYL) so that one treatment killed all lice emerging from ova as well as those originally present as adults. During the civilian Naples epidemic MYL was first used; the peak of the epidemic was reached just as DDT became available there; thus the epidemic was checked by MYL and extinguished by DDT; and throughout the Italian campaign, including the Naples epidemic, the British Army was effectively protected by A.L.63 (containing *Derris* and naphthalene), the only two typhus cases in it being amongst deserters; the credit for the Naples episode belongs mainly to the introduction of the dust gun and of the most thorough block treatments—each of the three louse powders contributed to the result.[145] Perhaps even more remarkable than the Italian epidemic was the dispersal of the louse-ridden inhabitants of the typhus-riddled German concentration and labour camps; prevention of a typhus epidemic throughout Europe is to the credit of the (mainly power-driven) dust guns, 10% DDT dust, and the routine enforced.

Other novel methods for the control of body lice were the use of thiocyanate-impregnated body-belts (which, however, were rather too often irritant) and the impregnation of underclothing with various insecticides, notably DDT.[146] Laboratory work has shown that lice are susceptible to quite low concentrations of various insecticides, but the nits (ova) are very resistant. The difficulty in controlling lice has been (*a*) the need for a treatment which will remain *in situ* long enough to cover the life cycle and (*b*) the wandering of the adult from the body where it feeds to the folds of the clothing (inner or outer) where it normally lives and reproduces. This migratory habit is not shown by the head louse or pubic louse, which breeds where it feeds, so that control is relatively easier[36,142]; a thiocyanate hair oil[147] is particularly useful for the female head as being almost unnoticeable after application, but the usual powders are also effective.

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[143] R. S. Cahn, *Chem. and Ind.*, 1945, 132.

[144] J. R. Busvine, *Ann. Appl. Biol.*, 1946, **33**, 271.

[145] H. J. Craufurd-Benson, *Brit. Med. J.*, 1946, I, 579, 710. H. D. Chalke, *ibid.*, I, 700, 977; II, 5.

[146] H. A. Jones, L. C. McAlister, jun., R. C. Bushland, and E. F. Knipling, *J. Econ. Entomol.*, 1945, **38**, 217. A. J. Musgrave, *Bull. Entomol. Res.*, 1946, **37**, 43.

[147] *Min. Health Memo.* 230*A*/*Med.* (1943) (London).

Laboratory work similarly shows the bedbug (*Cimex lectularius*) to be highly susceptible to insecticides and its control has been difficult only owing to its breeding in inaccessible places and to its ability to withstand many months of starvation. The older methods of fumigation by prussic acid or coal-tar fractions etc.[148] can now be replaced by spraying the walls with a solution or suspension of DDT[149] or "Gammexane,"[88] a few applications of which remain effective for long enough to catch the bug on its next trip to feed.

Scabies (infestation by the mite, *Sarcoptes scabei* var. *hominis*) has been intensively studied,[151] and its treatment revolutionised, notably by K. Mellanby. Gone are the hospital treatment as a highly contagious disease and the messy sulphur ointment, and even the hot bath has become a hygienic desideratum rather than a medical necessity. Benzoyl benzoate emulsion is applied thoroughly over the whole body, one treatment usually sufficing ; alternatively, an ointment containing finely-divided sulphur in a "washable" base may be effectively used.

Trombicula and mites of related species, besides having great nuisance value (harvest mites, chiggers), assumed great importance in New Guinea, the S. Pacific islands, and even the jungles of Ceylon, as carriers of *Rickettsia tsutsugamushi*, the causative agent of tsutsugamushi or "scrub-typhus," which afflicted troops in those areas as a major killing or crippling disease.[152] The natural host of the mite is the rat, vole, or other rodent ; the mite feeds only once during the life-cycle and transmits the rickettsia through the ovum. No successful attack on the mite off man has been reported but a high degree of personal protection was achieved by use of insect repellents, whilst benzyl benzoate has also been rated highly effective[36,152] ; it is noteworthy that the repellents are stated to be lethal to these mites on contact ; the repellent is applied to the person, clothing, and blankets, and resistance to water and washing is important.[153]

Cockroaches can be controlled by "Gammexane"[88,89,154] or, rather slowly, by DDT,[36,155] in dusts or sprays, but are relatively resistant, so that, *e.g.*, a 10% DDT dust is generally considered the minimum strength to be used.

VETERINARY APPLICATIONS.

The potentialities associated with the long-lasting properties of DDT

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[148] *Med. Res. Council, Spec. Rept. Ser.*, 1942, *No.* 245 (London).

[149] *E.g.*, S. Barnes, *Bull. Entomol. Res.*, 1945, **36**, 273. A. H. Madden, A. W. Lindquist, and E. F. Knipling, *J. Econ. Entomol.*, 1945, **38**, 265. E. F. Knipling, *ibid.*, 1946, **39**, 360. L. S. Henderson, *U.S. Dept. Agric.*, 1946, *Bull. E*-681. Reference 36.

[150] B. De Meillon, *Nature*, 1946, **158**, 839.

[151] Review : R. M. Gordon and K. Unsworth, *Brit. Med. Bull.*, 1945, **3**, 209.

[152] Review : R. Lewthwaite, *ibid.*, 227.

[153] R. C. Bushland, *Amer. J. Hyg.*, 1946, **43**, 219, 230. R. N. McCulloch, *Med. J. Austral.*, 1946, **1**, 717. F. M. Snyder and R. A. Morton, *J. Econ. Entomol.*, 1946, **39**, 385 ; *Soap*, 1946, **22**, *No.* 11, 133.

[154] E. R. McGovran andd P. G. Piquett, *Soap*, 1946, **22**, *No.* 8, 157.

[155] L. S. Henderson, *ibid.*, *No.* 11, 121.

and "Gammexane" for control of animal parasites are still under investigation but are already known to be very great. Various formulations require testing and probably in some cases new routines of husbandry; evaluation of results is not always simple so that optimum conditions of use may not be found for some years. In this field, the odour of "Gammexane" is not necessarily disadvantageous, so that its occasional superiority over DDT can be fully exploited. As on man, so on various animals lice can be controlled by DDT[156] or "Gammexane,"[88,89] although the value of DDT relative to, *e.g.*, sodium fluoride has been disputed by some workers.[157] Both insecticides have been used with success at low concentrations against the sheep ked (*Melophagus ovinus*),[88,89,158,159] at somewhat higher concentrations against the sheep tick (*Ixodes ricinus*)[88,89,160] and dog ticks[161]; good control of the cattle tick (*Boophilus decoloratus*; *B. australis*), which in places has developed resistance to arsenic, is reported[162] from South America and South Africa, whilst R. L. Squibb[163] has used DDT in conjunction with rotenone. Experiments with DDT and "Gammexane" against sheep blowfly (*Lucilia*) are also encouraging.[159,164] DDT is proving very valuable, as spray, for control of hornflies (*Lyperosia irritans*) on cattle in U.S.A.[165] DDT is generally considered ineffective against scab mites,[166] although isolated cases of cure of animals have been reported[167]; however, there is little doubt that "Gammexane" is a valuable remedy against sarcoptic scabies.[88,89,168]

[156] *E.g.*, H. E. Parish and C. S. Rude, *J. Econ. Entomol.*, 1945, **38**, 612; 1946, **39**, 546. H. L. Sweetman, *ibid.*, 1946, **39**, 417. H. S. Telford, *ibid.*, 1945, **38**, 573, 700. H. E. Kemper and I. H. Roberts, *J. Amer. Vet. Med. Assoc.*, 1946, **108**, 252.

[157] *E.g.*, D. C. Warren, *Poultry Sci.*, 1945, **24**, 473.

[158] G. B. S. Heath, *J. Min. Agric.*, 1946, **102**, 282. N. G. Cobbett and C. E. Smith, *J. Amer. Vet. Med. Assoc.*, 1945, **107**, 147. D. S. MacLagan, *Nature*, 1946, **158**, 132. C. S. Rude and H. E. Parish, *U.S. Dept. Agric., Bur. Entomol. and Plant Quar.*, 1946, *Bull. E*-679.

[159] W. Lyle-Stewart, *J. Min. Agric.*, 1946, **53**, 178.

[160] G. B. S. Heath, *Vet. J.*, 1946, **102**, 393. G. B. S. Heath, K. L. Blaxter, and J. G. Mitchell, *ibid.*, 130.

[161] R. Roberts, *J. Econ. Entomol.*, 1946, **39**, 539. C. N. Smith and H. K. Gouck, *ibid.*, 1945, **38**, 553. R. D. Glasgow and D. L. Collins, *ibid.*, 1946, **39**, 235. S. S. Miller, *N. Amer. Vet.*, 1945, **26**, 669.

[162] C. N. Ault, *Nature*, 1946, **157**, 699. J. A. Thorburn, *Farmers' Weekly (S. Africa)*, 1946, **71**, 1565. A. B. M. Whitnall and B. Bradford, *ibid.*, 1453. P. M. Bekker and H. Graf, *Farming in S. Africa*, 1946, **21**, 361, 420. B. N. Soni, *Current Sci.*, 1945, **14**, 334.

[163] *J. Animal Sci.*, 1945, **4**, 291; 1946, **5**, 71; *Science, Suppl.*, 1945, **102**, 10.

[164] J. B. Cragg, *Nature*, 1945, **155**, 394; *Ann. Appl. Biol.*, 1946, **33**, 127. R. Du Toit, *Farming in S. Africa*, 1946, **21**, 542. H. E. Harbour and J. A. Watt, *Vet. Rec.*, 1945, **57**, 685. L. E. Hughes, J. R. W. Jenkins, and J. M. Jones, *ibid.*, 1946, **68**, 251. G. J. Shanahan, *Agric. Gaz. New South Wales*, 1946, **57**, 382.

[165] *E.g.*, E. W. Laake, *J. Econ. Entomol.*, 1946, **39**, 65. J. G. Matthyse, *ibid.*, 62. L. M. Pears, *ibid.*, 91. R. L. Cuff, *Soap*, 1946, **22**, *No.* 8, 135; *Agric. Chemicals*, 1946, **1**, *No.* 6, 23.

[166] K. Mellanby, *Trans. R. Soc. trop. Med. Hyg.*, 1945, **38**, 367. F. F. Hillier, *Brit. Med. J.*, 1945, II, 255. Anon., *ibid.*, 1945, I, 882.

[167] E. N. Moore, *J. Amer. Vet. Med. Assoc.*, 1946, **108**, 162. E. T. Krebs, *Science*, 1946, **103**, 459.

[168] E. L. Taylor, *Vet. Rec.*, 1945, **57**, 210. E. F. Lewis, *ibid.*, 1946, **58**, 159. A. H. M. Kirby, *Lancet*, 1945, ii, 722.

Since its first trial in 1938, phenothiazine has fully consolidated its position as an anthelmintic. Its efficacy against a wide variety of worms in many types of stock has been fully evaluated. A bibliography[169] up to 1942 has been followed by numerous reviews.[170] Phenothiazine is effective against many, but by no means all, helminths of economic importance. It may be given either as a massive curative dose, repeated if necessary, or in small daily prophylactic doses with 9 parts of salt. The latter method takes advantage of the inhibitory effect of small doses on the reproductive system of helminths, which prevents or reduces oviposition; there usually results a lowering of the worm egg count and an inhibition of larval development, so that pasture contamination is reduced. Toxicity of the drug is in all cases low, but varies somewhat according to the host and is definitely greater for young than for older animals.

The pioneer work of Levine, followed by that of others,[171] has demonstrated the value of sulpha drugs against coccidiosis, particularly for poultry. Sulphaguanidine has proven prophylactic qualities; curative as well as prophylactic properties are possessed by "Sulphamerazine" and "Sulphamezathine" (= "Sulphamethazine") (2-sulphanilamido-4-methyl- and -4 : 6-dimethyl-pyrimidine, respectively), when administered up to 48—72 hours after infection. These drugs have some toxic action on the chick; recently sulphapyrazine has been claimed as effective and non-toxic, but results of large-scale trials with it are not yet to hand. The drugs may be administered in the food (about 1% by weight) or in the drinking water (0·1—0·2% solution, preferably as sodium salt). Their efficacy against coccidia has been correlated with concentrations in the blood (effective minimum : 5—10 mg. per 100 c.c.) and they are antagonised by *p*-aminobenzoic acid; their action is to prevent development of the sporozoites; properly used (*i.e.*, in the minimum effective dose), they do not prevent development of natural immunity in the host.

Hexachloroethane in very large doses (*e.g.*, 10 g. per 100 lb. body weight) shows promise against liver fluke (*Fasciola hepatica*) in cattle,[172] although it is not always 100% effective.

Finally, significance attaches to two mechanical developments: high-pressure spraying of cattle against hornfly[165] and a portable apparatus for power-dusting of lambs against keds.[173]

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[169] R. T. Lieper, "Bibliography of Phenothiazine as an Anthelmintic" [Imp. Bur. Agric. Parasit. (Helminthol.), 1942].

[170] *E.g.*, D. G. Davey and J. R. M. Innes, *Vet. Bull.*, 1942, **12**, *R*-7. H. McL. Gordon, *Austral. Vet. J.*, 1945, **21**, 90.

[171] Recent papers include : M. M. Farr and E. E. Wehr, *J. Parasit.*, 1945, **31**, 353, 359. P. A. Hawkins and H. Rausch, *Poultry Sci.*, 1946, **25**, 184. C. Horton-Smith and E. Boyland, *Brit. J. Pharmacol.*, 1946, **1**, 139. K. C. Seager, *Poultry Sci.*, 1946, **25**, 411. W. E. Swales, *J. Amer. Vet. Med. Assoc.*, 1946, **108**, 393; *Canad. J. Comp. Med. and Vet. Sci.*, 1946, **10**, 3. J. E. Alicata and E. J. Willett, *Amer. J. Vet. Res.*, 1946, **7**, 94. D. C. Boughton, *ibid.*, 1943, **4**, 66, 150.

[172] *E.g.*, O. W. Olsen, *J. Amer. Vet. Med. Assoc.*, 1943, **102**, 433; *J. Parasit.*, 1944, **30**, *Suppl.*, 14; *Amer. J. Vet. Res.*, 1946, **7**, 358 (refers to sheep). J. N. Shaw, *N. Amer. Vet.*, 1946, **27**, 625. V. A. Potemkina, *Veterinariya*, 1945, **22** (4/5), 28 (*Helminth. Abs.*, 1946, **14**, 86).

[173] J. G. Matthyse, *J. Econ. Entomol.*, 1945, **38**, 285.

SUGARS.

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The consumption of sugar is still controlled in most European countries and in North America. Willett and Gray's estimates of sugar crops of the world for 1945–46 (in long tons) are given below with comparative figures for 1941–42 [1]

	1945–46	1941–42
Beet sugar	6,262,942	9,148,770
Cane sugar	17,483,048	19,262,747
Total	23,745,990	28,411,517

There appears to be a deficit of five millions long tons, but in fact as populations have increased and visible stocks are very low in comparison with 1941, the deficit in requirements is much larger. There is no danger of overproduction in 1947 and 1948, and it seems probable that two years at least must elapse before production approaches requirements. European beet production has been responsible for most of the deficit, but cane production in Java, the Philippines, Japan, and Formosa has also contributed, although this has been largely offset by the increase in Cuban production.

The Sugar Research Foundation, referred to in last year's Report, announces that total donations made for research have now reached over $400,000. The recipient Universities will study, among other subjects, new industrial uses of sugar and its value as food.

Cane Sugar Manufacture.

The work of the Imperial College, Trinidad, was discussed at the meeting of B.W.I. Sugar Technologists at Barbados in 1944 and reported in their *Proceedings*. Precipitation of lime salts in continuous clarifiers was preferred to intermittent operation, on account of the higher juice temperature favouring precipitation. Of various stannine substitutes for Demerara crystals manufacture, titanium chloride, which was less objectionable than tin salts, was regarded as most promising. The process, although studied by the College, was originally devised and contributed to the industry by the Tate & Lyle Research Laboratory.

Improvements in multi-tray classifiers are claimed in two patents by F. P. Lasseter[2] and W. E. Geissler[3] respectively, the former by separate regulation of withdrawal of the clarified liquid and the thickened mud

[1] *Int. Sugar J.*, 1946, **48**, 223.
[2] U.S.P. 2,355,875; *Int. Sugar J.*, 1946, **48**, 26.
[3] U.S.P. 2,377,875; *Int. Sugar J.*, 1946, **48**, 109.

and the latter by combining the two clarifying actions of compound clarification in one vessel instead of the customary two.

Filtration technique includes a few innovations. The particle size of the kieselguhr used with phosphate defecation is regulated in order that filtration is not impeded.[4] Short-fibred asbestos was used by T. Lui[5] to improve clarity through relatively thin cloths and 0·15—0·3% was found fairly satisfactory for sugar for local Chinese markets; the fibre could be washed and re-used several times. W. L. McCleery[6] reports laboratory tests on bentonite as a juice clarification agent, also combined with phosphates; presumably this can be used only as a defecant but it is claimed that refining quality, especially filtration rate of sugar, should be improved by the treatment. A. L. Webre[7] has summarised information on the filterability of raw sugars received by American refineries and classes Cuban raw sugars as the most difficult. The melting point of cane wax present on the thin coating on the outside of the cane stalk is 65°, and the temperature of maceration water should not exceed this figure in order to reduce amounts reaching the juice. Temperature at centrifugals should exceed 65°, in order to keep the wax liquid and facilitate its removal with the molasses.

The use of monel metal filter leaves is described by R. F. Black,[8] who has improved the original metal cloth filter leaves of Sweetland presses, by provision of a 5 × 5-mesh bronze backing screen or grid of 0·08 in. diameter wire, with a metal screen cover of 70 × 80-mesh twilled weave monel of 0·007 in. diameter wire. The increased flow rate and reduced sweet water production compared with cotton cloths justifies their use and acid cleaning at intervals does not cause the usual deterioration experienced with cotton.

H. C. Watson,[9] of Barbados, has outlined the advantages to be gained by bleeding vapour from multiple-effect evaporators. Vapour from the first effect of a quadruple may be partly diverted to a sugar juice heater preheated by exhaust steam, enabling the latter to be utilised for heat elsewhere or for supplementary steam supply to the quadruple. If the former procedure is utilised, as working data illustrate, the condenser load is decreased, higher vacuum is obtained, and 8% increase in evaporation is possible. With the latter procedure 19% increase in water evaporation is obtained without alteration of condenser load.

N. Deerr and S. G. Smart[10] discuss Deerr's boiling house expression which Rao has criticised and for which he has suggested an alternative (cf. B., 1945, III, 246); the authors show that the two expressions are almost identical.

[4] A. B. Cummins, U.S.P. 2,362,357; *Int. Sugar J.*, 1946, **48**, 80.
[5] *Ind. Eng. Chem.*, 1946, **38**, 521; B., 1946, III, 170.
[6] *Sugar*, 1946, **41**, *No.* 12, 53; cf. B., 1947, III, 57.
[7] *Int. Sugar J.*, 1946, **48**, 123; B., 1946, III, 152.
[8] *Sugar*, 1946, **41**, *No.* 5, 38; B., 1946, III, 194.
[9] *Int. Sugar J.*, 1946, **48**, 13; B., 1946, III, 101.
[10] *Ibid.*, 46; B., 1946, III, 69.

C. F. Huttlinger and E. J. Culp[11] have devised a nomograph for cane sugar producers by means of which mathematical calculations can be eliminated in determining the various efficiencies of the factory operations. To determine the theoretical yield of 96° raw sugar and the theoretical loss of sucrose in the molasses, each expressed as percentage of cane, the nomograph gives (*a*) sucrose in cane % of cane; (*b*) sucrose extracted % sucrose in cane; (*c*) sucrose loss in press cake % of cane; (*d*) % water in raw sugar produced; (*e*) polarisation of raw produced; (*f*) purity of syrup; (*g*) purity of molasses produced.

The Cuitometer,[12] an instrument for control of grain size, working on the conductivity principle, has been improved by a stabilising device to reduce fluctuations in the factory current supply.

Raw sugar shipped in bulk from Hawaii to California continues to show little loss in transit provided the sugar is low in moisture; wet weather conditions favour a drop in polarisation.[13] H. L. Grogan[14] has given a comprehensive review of the deterioration of sugar during storage, from the particular points of view of West Indian producers; he concludes that moisture content, conditions of storage, and chemical composition of the sugar are the important factors.

The variable composition of salts in blackstrap molasses is recorded by C. A. Fort[15] in a report on examination of eight samples from Louisiana factories in 1937, and a more extensive examination of samples each from Louisiana and from Cuba in 1940. It was found that: (1) the total and the individual mineral constituents vary rather widely; (2) the organic salts far exceed the inorganic salts; (3) potash is generally the principal metallic base, but on the ion equivalent basis may be equalled in some instances by the sum of lime and magnesia; (4) at least 10% of the molasses solids are unindentified in character; (5) the total organic acid exceeds the value so far reported for aconitic acid (this has been stated previously to be the principal organic acid); (6) the dry solids content is 10% below that indicated by spindle Brix; (7) lime and magnesia are generally present in ratio of 2 : 1; (8) sulphated ash approximates to total salts; (9) carbonate ash is much lower than sulphated ash minus one tenth; (10) variations in composition of products from various mills in the same belt are very great.

Needle grain sugars are attributed in Hawaii to non-sugars, and bauxite treatment is reported by W. L. McCleery[16] to be a means of elimination of the trouble. S. E. Coalstad[17] attributes the crystallisation difficulties in impure solutions more to the surface-active colloidal impurities than to the ratio if reducing sugar to ash. His experimental treatment

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[11] *Sugar*, 1946, **41**, *No.* 6, 60; B., 1946, III, 195.
[12] *Int. Sugar J.*, 1946, **48**, 77.
[13] *Ibid.*, 27.
[14] *Ibid.*, 41, 67.
[15] *Sugar*, 1946, **41**, *No.* 11, 36.
[16] *Repts. 64th Meet. Hawaii S.P.A.*, 1944, 67; *Int. Sugar J.*, 1946, **48**, 190.
[17] *J.S.C.I.*, 1946, **65**, 206; B., 1946, III, 255.

of molasses solutions with relatively large amounts of bone charcoal and carbon should result in some removal of salts as well as organic colloids, and unless ash results are reported, doubt would exist of the relative extent to which salts and colloids contribute in the prevention of crystallisation of sucrose.

BEET SUGAR MANUFACTURE.

Attention has been drawn by H. C. Cutler and R. H. Woolley[18] to the fact that beets grown in soils rich in alkali chlorides become charged with these salts, which find their way into diffusion juice; in such cases secondary products should not be returned to the juice end of the house.

A. Bäckman[19] describes Swedish practice of flocculating colloids in both diffusion waste water and pulp press waters by means of sulphuric acid, thus making them suitable for return to the factory.

Permeability, as determined by the facility of dissolution of sucrose from cossettes at low temperature, is stated by H. Belval and S. Lemoyne[20] to be dependent on the life of the protoplasm, increasing when this is killed and to the same extent whether this is due to heat, cold, or desiccation.

Deterioration of stored molasses is again reported.[21] T. M. F. Ozil describes a beet molasses in a Turkish factory, in which destruction was so far advanced as partly to carbonise the molasses. The roots used were notably deteriorated and the decomposition is attributed to micro-organic action, although it is difficult to reconcile this with degradation to carbon.

A modified baryta process of desugarising molasses, due to A. M. Thomsen,[22] obviates the use of excessive high temperature of regeneration of baryta by conversion of saccharate successively into carbonate, sulphite, and sulphide, and re-forming hydroxide by removal of sulphur.

An improved design of centrifugal for washing sugar is described by British Sugar Corporation and W. A. Witham[23] in which the principal features are a means of oscillating the spraying device and a clutch for initiating and controlling this device.

R. S. Gaddie and W. A. Olson[24] obtained thermophil-free liquor by a single filtration with kieselguhr, but mesophilic organisms were not satisfactorily removed; neither ozone nor ultra-violet radiation had any effect on these or their spores.

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[18] *Proc. Amer. Soc. Beet Tech., 3rd Meet.*, 577; *Int. Sugar J.*, 1945, **47**, 329; B., 1946, III, 69.

[19] *Socker*, 1945, **1**, 111; *Int. Sugar J.*, 1945, **47**, 329; B., 1946, III, 69.

[20] *Bull. Assoc. Chim. Sucr.*, 1945, **62**, 105; B., 1946, III, 100.

[21] *Sugar*, 1946, **41**, *No.* 12, 36.

[22] U.S.P. 2,380,087; *Int. Sugar J.*, 1946, **48**, 194.

[23] B.P. 576,771; B., 1946, III, 234.

[24] *Proc. Amer. Soc. Beet Tech., 3rd Meet.*, 475; *Int. Sugar J.*, 1945, **47**, 272; B., 1945, III, 247.

IONIC-EXCHANGE METHODS OF PURIFICATION OF SUGAR JUICES.

Further progress in these methods is reported in many directions. The direct use of cation-removal resins followed by anion-removal resins or their carbonaceous substitutes is not as practical as might at first appear. Temperature control is essential or the low-pH juice emerging from the first vessel will rapidly invert. Many other problems arise. In consequence and in order to obtain maximum benefit from the treatments many variations of procedure have been formulated. Numerous patents have been taken out since the subject was last reported. Amongst these are found that of W. W. Durant and W. A. Blann (Assrs. to American Cyanamid Co.),[25] who subject crude sugar solution to cation- and anion-exchange materials to reduce ash (on solids) from 0·2% to 0·004%.. They refer to another patent[26] on ion-exchange products obtained by interaction of an aminotriazine such as melamine and a guanadine salt with formaldehyde under alkaline conditions to form a condensation product which is gelled under acid conditions, dried, and cured.

W. A. Blann[27] has also operated a pilot plant at the Audubon Sugar Factory in Louisiana and removed not only minerals but also organic non-sugars from cane juices. The yields appear to be most favourable[28]; from a juice containing 0·9152 ton of sucrose per ton of sucrose in the cane, ion exchange gave 0·915 ton of 96° sugar and the regular process 0·859 ton.

In purifying beet juice H. W. Dahlberg[29] utilises the greater decolorisability of acid solutions by treatment first with a cation exchanger and then with activated carbon. Incoming juice is separated into two streams, one of which is given the treatment described and the other the normal treatment of carbonatation, and after second carbonatation is cooled to 15—25°, and blended with the former, producing a final juice of approximate neutrality suitable for concentration and crystallisation. F. N. Rawlings (Dorr Co.)[30] proposes to obviate the objectionable formation of calcium sulphate in regeneration of cation exchanger loaded with lime adsorbed from juice by suitable treatment before application of regenerant sulphuric acid; economy in regenerant acid is claimed by prior use of partly exhausted acid from a previous operation. A. S. Behrman[31] treats a sugar solution successively with cation exchanger, carbon, and anion exchanger, and repeats the treatment with the latter, followed by carbon, several times to remove substances precipitable by decrease in pH. R. W. Shafor[32] combines a hypochlorite bleaching agent with successively cation and anion exchangers, and proposes to utilise

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[25] B.P. 569,661; B., 1945, I, 317.

[26] B.P. 561,896; B., 1944, II, 262.

[27] *Sugar Bull.*, 1945, **23**, *No.* 9, 69; *Int. Sugar J.*, 1946, **48**, 27.

[28] *Louisiana State Univ. Eng. Expt. Sta. News*, 1945, **1**, *No.* 3, 11. *Sugar*, 1946, **41**, *No.* 1, 50; *Int. Sugar J.*, 1946, **48**, 302.

[29] U.S.P. 2,359,902; *Int. Sugar J.*, 1946, **48**, 80.

[30] U.S.P. 2,366,650–1; *Int. Sugar J.*, 1946, **48**, 136.

[31] U.S.P. 2,388,223–4; *Int. Sugar J.*, 1946, **48**, 166.

[32] U.S.P. 2,391,649; *Int. Sugar J.*, 1946, **48**, 221.

this for the refining of raw sugar. Ion exchange has been applied by E. A. Haagensen[33] to beet-juice purification at the Burley and Nampa plants in Idaho ; the process involves clarification, filtration, and cooling, followed by five pairs of ion-exchange units. Some inversion took place but was attributed to bacterial action.

SUGAR REFINING.

Some of the methods in vogue in Cuba are described by A. de Mena y Vaillant[34] ; carbon is used to treat affinated raw liquor, followed by hydrosulphite in the pans. Difficulties of filtration lead in some cases to lowering of Brix, which will necessitate later evaporation, or, alternatively, kieselguhr–phosphoric acid filtration. The author prefers the process he originated at the San Romano refinery where a combination of carbon, phosphoric acid, calcium hydroxide, air, heat, and hydrosulphite is used ; little inversion occurs and the amount of carbon needed is 50—70% less than in the other processes. A new design of crystalliser in motion described by H. H. Fielding[35] utilises hollow heat-exchanging elements projecting from a rotating axis in a cylindrical shell, and so constructed that minimum drag-resistance to the viscous massecuite is encountered. Synthetic detergents of the sulphonated aliphatic alcohol type have been utilised for the cleaning of filter cloths.[36] The use of one of these, Teepol, at the Plaistow Refinery, London, has increased the life of the filter cloths. Kieselguhr recovery is an economical practice at the Pennsylvania Sugar Refinery.[37] The mud is pumped to a Dorr classifier to remove grit and bagasse, and passed to settling tanks, the overflow of which carries away colloidal impurities. The underflow is thickened through Oliver filters and is dosed into raw greens and granulated syrups for re-use. F. M. Chapman[38] describes the steam lay-out for an ideal refinery, *i.e.*, one producing only a small number of products, and quotes the arrangement of the Plaistow Refinery. The Panoscope[39] is a microscope fitment to the pan and enables pansmen to follow crystal growth and detect irregularities continuously throughout the boiling. A. B. Babcock[40] stresses the importance of thorough washing of bone black and has derived a formula which expresses the time required for a given removal of salts, and enables a close approximation to be made of the economical point to which it should be washed.

Some further work on bone charcoal is reported from various quarters. Heat of wetting[41] has been determined by H. C. S. de Whalley and

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[33] *Sugar*, 1946, **41**, *No.* 4, 36 ; *Int. Sugar J.*, 1946, **48**, 240 ; B., 1946, III, 255 ; 1947, III, 29.

[34] *Proc.* 18*th Meet. Assoc. Tech. Azuc. Cuba*, 57 ; *Int. Sugar J.*, 1946, **48**, 148.

[35] U.S.P. 2,379,895 ; *Int. Sugar J.*, 1946, **48**, 165.

[36] *Int. Sugar J.*, 1946, **48**, 168.

[37] *Ibid.*, 179.

[38] *Ibid.*, 316 ; B., 1946, III, 217.

[39] *Ibid.*, 328.

[40] *Sugar Ind. Eng.*, 1945 ; *Sugar*, 1946, **41**, *No.* 6, 56.

[41] *Int. Sugar J.*, 1946, **48**, 73 ; B., 1946, III, 234.

D. R. Dickinson,[41] who show that the value obtained increases with preheating up to about 450° ; chars so preheated gave values which seemed related to the decolorising power, and the suggestion is made that heat of wetting may serve as a measure of this. From the same laboratory[42] comes an account of the examination of the effect of particle size on decolorising ; in the case of porous bone char, subdivision does not alter the surface area but the greater decolorisation experienced is due to the increase in speed of adsorption of colour and, if sufficient time is given to attain equilibrium, all sizes effect equal decolorisations. A. F. Blake[43] states that decarbonisation of lower-grade stock chars under carefully controlled conditions improves decolorising and ash adsorption very markedly. Admission of air to the base of retorts gives uneven decarbonisation and is not as advantageous as the use of a Weinrich decarboniser, in which air supply is properly controlled. No serious breakage of char occurs.

L. E. Weymouth and M. C. Miller[44] describe a portable photo-electric Tyndallimeter used as both colorimeter and turbidimeter which should be found useful in controlling filtration operations.

Some data on raw sugar include a discussion of storage conditions in the West Indies, which are stated by L. S. Birkett[45] to be of utmost importance if deterioration is to be prevented ; heating and dehumidifying the warehouses has been found to give satisfactory results. C. A. Browne[46] quotes average polarisation figures of imports into the U.S.A. In 1920 polarisation was 95·09 and increased to 97·23 in 1940, but during the war there was a decline to 96·86 for 1943. Keeping qualities improved up to 1940 but losses still occur and are mainly of less importance and due to inversion. *Torula* destroying fructose conceal some loss by raising polarisation. H. C. S. de Whalley and M. P. Scarr[47] draw attention to the presence of osmophilic yeasts in raw sugars (beet and cane) and in syrups and molasses. They are capable of destroying sugars rapidly in presence of small amounts of water. Special media enable these yeasts to be grown without mesophils. The main difference in the osmophils present in beet and cane raw sugars is the relative absence of invertase in the former. Old store raws and sweepings have high counts and syrups from these may contaminate those from better raw sugars.

SUCROSE.

E. J. Culp[48] states that the figures published by P. Lyle[49] for heat of solution of sucrose in water appear to be the most accurate now available. He has, however, considered it necessary to make use of units ° F., ° Brix,

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[42] H. C. S. de Whalley and N. Albon, *Int. Sugar J.*, 1946, **48**, 125; B., 1946, III, 170.

[43] *Sugar Ind. Eng.*, 1944 ; *Int. Sugar J.*, 1945, **47**, 295 ; B., 1946, III, 7.

[44] *Int. Sugar J.*, 1945, **47**, 325 ; B., 1946, III, 70.

[45] *Proc.* 1943 *Meet. Brit. W. Indies Sugar Tech.*; *Int. Sugar J.*, 1945, **47**, 297; B., 1946, III, 22.

[46] *Proc. Inst. Food Tech.*, 1944, 174 ; B., 1946, III, 246.

[47] *Int. Sugar J.*, 1946, **48**, 180 ; B., 1946, III, 196.

[48] *Sugar*, 1946, **41**, *No.* 2, 44 ; B., 1946, III, 171.

[49] *Int. Sugar J.*, 1939, **41**, 390.

and B.Th.U. more familiar to American refiners, and convert the expressions given by Lyle into terms of these units to save arduous calculation. A heat of solution nomograph is reproduced and tables are presented which give the heat required to melt 1 lb. of crystal sucrose (32—260° F.), the heat liberated on diluting 1 lb. of liquid sucrose with water (0—100° Brix), and the heat absorbed and the fall in temperature on dissolving 1 lb. of sucrose in water (0—80° Brix).

The Sugar Research Foundation have awarded a prize to Drs. W. Z. Hassid, M. Doudoroff, and H. A. Barker,[50] who have effected a synthesis of sucrose from the component sugars dextrose and lævulose. They discovered that the organism *Pseudomonas saccharophila* (Doudoroff) is capable of splitting sucrose, but the presence of some phosphate is necessary to complete the reaction which yielded lævulose and dextrose phosphate. Having found that the reaction was reversible, they then proceeded to confirm that the product was indeed sucrose by all necessary physical and chemical tests. The importance of this work lies in the possibility of synthesising the sugar containing isotopic carbon atoms in half the molecule and thus following by the tracer technique the actual metabolic course of the individual halves of the sugar molecule, and so to determine directly the actual and possible unique rôle of sugar in the diet.

MISCELLANEOUS SUGAR PRODUCTS.

Aconitic acid has been reported by R. T. Balch[51] to be present in larger quantities than usual in a special cane cut in May and July at Louma, La. ; the content was as much as 13% on refractometer solids. The acid is of interest in the plastics industry, and when (if ever) surplus cane is available, some might be diverted for the more remunerative production. E. K. Ventre, J. A. Ambler, and S. Byall[52] propose to separate aconitic acid from plant juices by using calcium hydroxide, which is soluble in the juices but reacts to form calcium aconitate, which is precipitated when the liquid is concentrated to 32° B. and heated. pH should be 6·7—7·0 in the final syrup. They further describe the extraction of the acid from sorghum[53] as a by-product of extraction of sucrose.

Citric acid manufacture from molasses by means of *Aspergillus niger* is the subject of a B.I.O.S. report.[54] The factory visited is the only producer of citric acid in Germany and had by its efforts decreased the use of tartaric acid. A. Arrhenius[55] reviews the literature on *Streptococcus mesenteroides* (the *Leuconostoc* or frog spawn of beet factories) ; large-scale

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[50] *Sugar*, 1946, **41**, *No.* 7, 29 ; *Int. Sugar J.*, 1946, **48**, 255 ; for synthesis, see A., 1944, II, 361.

[51] *Sugar Bull.*, 1945, **23**, 197 ; *Int. Sugar J.*, 1946, **48**, 130.

[52] U.S.P. 2,359,537 ; *Int. Sugar J.*, 1946, **48**, 250.

[53] With H. C. Henry and H. S. Paine, *Ind. Eng. Chem.*, 1946, **38**, 201 ; B., 1946, III, 133.

[54] *Brit. Intelligence Objectives Sub-Commee., Final Rept.* 220, *Item* 22 ; *Int. Sugar J.*, 1946, **48**, 260.

[55] *Socker*, 1945, **1**, *No.* 11, 245 ; *Int. Sugar J.*, 1946, **48**, 269.

production has been commenced in Sweden for the extraction of dextran, which is used as a substitute for blood plasma.

The unfermentable reducing substances (glutose) of molasses have been investigated by L. Sattler and F. W. Zerban.[56] Heating without alkalinity can produce them from sugars and they appear to be mixtures of anhydro-sugars. 1 : 2-Fructopyranose anhydride reduces Fehling's solution, but the corresponding difructose anhydride does not. Glucose under similar treatment gives little unfermentable matter but can combine with amino-acids, especially asparagine, to yield large quantities of condensation products of amino-acids and their amides with glucose ; prolonged heating at higher temperatures gives similar but dark-coloured melanoidins. Hydrolysis reconstitutes the sugars and might be utilised by the distilleries. In Clerget sucrose analysis of molasses, inversion with hydrochloric acid, owing to partial inversion of these compounds, gives an unreal figure for sucrose content.

A study of the processes used in Germany for making wood sugar[57] has not revealed any new outstanding advances ; the chief use was for growth of food yeast.

P. E. Verkade, C. P. van Dijk, and W. Meerburg[58] have described the preparation of some 4-nitro-2-aminophenyl alkyl ethers, which have an intensely sweet taste. One of these, the *n*-propyl ether, is probably the sweetest substance known, being 4100 times as sweet as sucrose. All of these sweet compounds, however, possess more or less anæsthetic activity and the sweetest is about thirty times as potent as cocaine.

ANALYSIS.

The sixth edition (1945) of "Methods of Analysis of the Association of Official Agricultural Chemists" has appeared[59] and, like its predecessors, takes its place as a valuable reference book of analytical methods, amongst which "Sugars and Sugar Products" includes the most precise information on well approved methods of analysing sugars, syrups, and molasses, confectionery, honey, commercial glucose, and the like. The stability of the Lane and Eynon standard invert sugar solution[60] has been critically examined by the A.O.A.C., and no deterioration could be detected ; the method of preparing this solution has been declared official. The International Society of Sugar Cane Technologists[61] recommend that "as soon as a reliable preparation of analytical invertase is placed on the market at the right price, the invertase method should be universally adopted as has already been done by the A.O.A.C." This wise decision might well be followed by other bodies as it is universally recognised that determination

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[56] *Ind. Eng. Chem.*, 1945, **37**, 1133 ; B., 1946, III, 97.

[57] *Brit. Intelligence Objectives Sub-Commee.*, *Final Rept.* 176, *Item* 22, and *Rept.* 7, *Item* 22 ; B., 1946, III, 47.

[58] *Rec. trav. chim.*, 1946, **65**, 346 ; A., 1946, II, 586 ; III, 909.

[59] *Int. Sugar J.*, 1946, **48**, 163.

[60] *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 531 ; *Int. Sugar J.*, 1946, **48**, 214.

[61] *Int. Sugar J.*, 1946, **48**, 160.

of sucrose by the Clerget process using invertase inversion is the only method which gives a correct result for sucrose content of cane molasses and syrups.

Advances in invert sugar determinations are recorded by F.W. Zerban, W. J. Hughes, and C. A. Nygren[62] and S. E. Coalstad.[63] The former have shown that in the Eynon and Lane titration, if the titres y are plotted against concentration x, the equation of the resulting curve of $y = bx^{-m}$ or $\log y = \log b - m \log x$ is a straight line, in which b and m are constants. The agreement between the titres calculated from the equations and Lane and Eynon tables is very close. Coalstad has adapted the dead-stop end-point of titration evolved by Foulk and Bawden to the volumetric estimation of reducing sugars by Fehling's solution. The end-point is detected by the polarisation effect of two plain copper electrodes dipping into the solution, to which an e.m.f. of 10 mv. is applied. The author claims to have overcome the polarising effect of non-sugars by addition of 0·3 g. of purified animal charcoal. The methylene-blue method for determining the invert sugar in refined white sugars has been further examined in the light of the doubtful purity of the methylene-blue. H. C. S. de Whalley and P. E. Gray[64] report that recrystallisation of the methylene-blue gave results almost identical with those obtained with the original material. Some samples contain zinc salts and it is therefore advisable to recrystallise and dry the dye before using it for the test involving comparison with standard ammoniacal copper solutions.

The Karl Fischer reagent for the determination of water has been applied by F. W. Zerban and L. Sattler[65] to concentrated sugar solutions and syrups, notably impure syrups which give erroneous results by the refractometer. They have devised a rugged equipment which overcomes all manipulative difficulties. The costly reagents make the method expensive for routine work but as a standard reference method it should be of great value.

V. Olivier[66] recommends a modified procedure in Kalshoven's method for the determination of fine grain in molasses. 100 g. are weighed into each of two tightly closed cylindrical flasks, and to one 10 ml. of distilled water are also added ; both flasks contain 5 or 6 glass balls of about 12 mm. diameter. The flasks are rotated slowly in a shaker for 12—15 hours and refractive indices are then read ; fine grain is calculated from $c = 100(b - b_1)/(100 - b_1)$, where c = fine grain, b = ° Brix of diluted molasses after dissolving the grain and correcting for dilution, b_1 = ° Brix of undiluted molasses.

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[62] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 64 ; C., 1946, 190.

[63] *J.S.C.I.*, 1946, **65**, 230 ; C., 1946, 279.

[64] *Int. Sugar J.*, 1946, **48**, 212 ; C., 1946, 279.

[65] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 138 ; C., 1946, 190.

[66] *Rev. Agric.* (*Mauritius*), **23**, 95 ; *Int. Sugar J.*, 1946, **48**, 75 ; C., 1946, 279.

STARCHES.

By J. A. Radley, M.Sc., F.R.I.C.

Constitution and Properties.

G. E. **Hilbert** and M. M. MacMasters[1] find that wrinkled seeded garden peas contain a starch of a new class containing 60—70% of amylose. The granules do not gelatinise completely after prolonged heating in a water-bath ; pea starch heated with water to 97° resembles a suspension rather than a paste, which is not formed even after heating at 120° for 1 hour. C. W. Bice,[2] with the above workers, has studied the properties of wheat starch in relation to grain maturity. Starch prepared from typical hard and soft winter and hard spring wheats at various stages of maturity was fairly constant as regards nitrogen, phosphorus, and ash content, viscosity, birefringence, and reaction to iodine solution. Starch content of the grain increased linearly with time from pollination and starch granule size increased up to 12—15 days from pollination. Subsequently, the granules became less transparent and more lamellated. The amylose content of the starch, as shown by its sorptive capacity for iodine, appeared to increase from about 19% at 8—12 days from pollination to about 25% at 24 days. Immature wheat appears to be suitable for industrial use as far as the starch characteristics are concerned. S. Mukherjee and S. Bhattacharyya[3] find that the granules of Shoti starch resemble those of arrowroot, being elongated in shape ; Shoti starch is more readily hydrolysed than maize or rice starch, but similarly to potato starch, and contains more amylose than the other starches examined. They suggest various industrial uses for this starch. A. M. Briant, C. J. Personius, and E. G. Cassel[4] observed a negative correlation between the degree of mealiness of potatoes and both the number of starch granules smaller than 0·02 mm. in diameter and the temperature of first and complete anisotropy of the starch grains. Breaks in the heating curves coincident with sudden thickening of the suspensions indicate that gelatinisation of the starch is accompanied by an endothermic reaction taking place at a temperature characteristic of the sample; this, and the temperature of complete translucence, are lower with starches from mealy potatoes. More rigid gels are obtained from starch of less mealy potatoes, but penetration values could not be correlated.

Since granule size is a desirable quality in starch manufacture, G. Cours[5] has studied the variations in granule size in a number of varieties of

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[1] *J. Biol. Chem.*, 1946, **162**, 229 ; B., 1946, III, 101.

[2] *Cereal Chem.*, 1945, **22**, 463 ; B., 1946, III, 105.

[3] *J. Indian Chem. Soc., Ind. Ed.*, 1945, **8**, 4 ; B., 1946, III, 133.

[4] *Food Res.*, 1945, **10**, 437 ; B., 1946, III, 47.

[5] *Agron. Trop.*, 1946, **1**, 138 ; B., 1946, III, 152.

manioc, a wide range being found from each source. The best-developed plants give the largest grains, but their diameter falls from the base to the tip of the root. Granule diameter is independent of the density of the root; it increases up to the middle of winter, falls with bud formation, and increases again with the appearance of leaves. The characters of a number of new varieties are described and the influence of mosaic and rot is noted; a general reduction is occurring in the density of roots delivered to factories. J. A. Radley[6] has reviewed the properties and occurrence of the so-called waxy starches. J. Terrier[7] finds that the crust and crumb of white bread made with yeast contains, respectively: starch 69·95%, 72·05%; dextrin 6·9%, 4·45%: glucose 1·15%, 1·0%; he concludes, therefore, that there is no appreciable conversion of starch into dextrin during bread making.

MANUFACTURE.

G. P. Graham[8] describes the manufacture and uses of maize starch· A method of drying maize starch is claimed by L. P. Tiers[9] in which the solids collected on the cloth of a rotating drum filter are first cut circumferentially by blades or needles to produce a number of ribbons of similar narrow width, and these in turn are cut by a blade parallel with the axis of the drum, giving square or rectangular prisms of approximately uniform area and thickness; the prisms are fed on to a conveyor for passage through a drying chamber. A. L. Shewfelt and G. A. Adams[10] describe a rapid method of separating starch and gluten from wheat flour, which is applicable to large-scale operation. 3 kg. of patent flour were made into a dough with 80—85% of water by mixing for 15—25 minutes at 25—30°; the dough was agitated with twice its weight of water by a reversing paddle stirrer for 3 minutes or until the curds were 1 cm. in diameter. Primary separation of the starch from gluten was effected on an inclined (4°) gyrating screen (150-mesh) and the starch recovered by centrifuging. The crude gluten was refined by shredding, washing, and rescreening. Optimum recoveries were: 90% of the starch containing less than 0·5% of protein; 100% of the protein containing 20% of starch before repurifying and 10—12% afterwards. The method is based on the results of many experiments in which temperature, volume of mixing water, and times for mixing, conditioning, and agitation were varied. The starch and gluten recovery, protein content of starch, and starch content of the gluten in these experiments are given in full. In a further paper[11] the authors claim that the method has been applied successfully to flours from various types and grades of wheat; flours of low protein content can be successfully treated and the gluten characters of different samples have

[6] *Manufg. Chem.*, 1946, **17**, 180; B., 1946, III, 152.
[7] *Mitt. Lebensm. Hyg.*, 1941, **32**, 166; B., 1946, III, 106.
[8] *Canad. Chem.*, 1945, **29**, 415, 447; B., 1945, III, 250.
[9] U.S.P. 2,327,943; B., 1945, III, 247.
[10] *Canad. J. Res.*, 1945, **23**, **F**, 373; B., 1946, III, 105.
[11] *Ibid.*, 1946, **24**, **F**, 136; B., 1946, III, 173.

little influence on the separation. It is stated[12] that, to produce the highest quality potato starch and to minimise losses, the pH of the starch milk should be controlled to give a value of about 4, since at this point, albuminoid material does not flocculate.

The manufacture of starch from rye or maize, glucose and maize syrup from starch, and by-products is outlined by P. L. Pavcek.[13] The by-products include a composition which is sold, alone or after admixture with beet molasses, as animal fodder.

R. F. Gould[14] has discussed the dependence of the manufacture of sweet potato starch on an economic source of raw material and outlines the method of cultivation. Storage difficulties have not so far been overcome by dehydration; the working season is accordingly limited, and the small granule size of the starch as compared with that of potato involves modification of procedure to ensure a uniform product. Development of this manufacture is reviewed, and the future prospects of a recently completed large-scale plant are discussed. To sterilise maize starch without causing thinning, R. W. Kerr[15] treats the aqueous suspension for 50—180 minutes at 35—40° with 0·165—0·55% (on dry starch) of chlorine and then adds an antichlor, such as sodium bisulphite, to stop the reaction with the starch; the product is adjusted to pH 5·2, washed, and dried, and then contains less than 125 bacterial spores per 10 g., satisfying the requirements for canners' starch. Some thickening of the strarch takes place as a result of the treatment; *e.g.*, the Scott index is raised from 80—90 to 85—200, and to prevent undue thinning during subsequent pressure-cooking, as in soup manufacture, it is blended with 2% of disodium hydrogen phosphate or other edible buffer to maintain a pH of 5·0—5·2. Under acid conditions, sodium hypochorite may be used instead of chlorine.

MODIFIED STARCHES.

W. A. Nivling[16] passes finely-divided starch through a chamber with agitation while applying an atomised solution of an oxidising agent such as hypochlorite, perborate, peroxide, or permanganate. To ensure an even reaction an oxidation-retarding agent such as caustic soda, potassium carbonate, or, better, sodium stearate, resinate, or silicate is used additionally, and the rates of supply and of flow of starch and reagents are suitably controlled. M. D. Rozenbroek[17] obtains a soluble starch by mixing 100 parts of potato flour containing 8—20 parts of water with 4—15 parts of sodium carbonate and treating the mass with about 6 parts of chlorine at a temperature not above 60°.

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[12] Anon., *Bull. Assoc. Chim. Sucr.*, 1945, **62**, 146; B., 1946, III, 101.

[13] *Combined Intelligence Objectives Sub-Commee., Item* 22, *File* XXVIII-32; B., 1946, III, 217.

[14] *Chem. Eng. News*, 1946, **24**, 1518; B., 1946, III, 196.

[15] U.S.P. 2,332,320; B., 1946, III, 153.

[16] U.S.P. 2,204,615; B., 1946, III, 102.

[17] U.S.P. 2,338,457; B., 1946, III, 196.

DEXTRINS.

A. J. Rao[18] describes the torrefication process for dextrin manufacture, using hydrochloric acid as catalyst and maize starch or tapioca root flour to produce a dextrin fulfilling desired specifications to replace a tapioca product previously imported into India. Heating at 150° for 5 hours was carried out in a rotating converter with a knife-blade stirrer. W. J. Rowe and C. Hagen[19] describe a dextrin cooker of which the steam jacket has the bottom divided into a number of concentric zones in which the steam is caused to flow around 360° by a suitable arrangement of the inlet, outlet, and a radial baffle; a similar flow is ensured in the vertical jacket but it is not usually necessary to subdivide that space. The suggested arrangement is claimed to ensure uniform heating.

USES.

Starch is used as the carrier for the antioxygenic substances extracted from finely ground, unbleached, ungerminated oats or maize, or from cereal products such as germs or rice polishings, or from unbleached nuts or seeds, by S. Musher.[20] The aqueous or alcoholic extract, adjusted to pH 5—6·7, is concentrated to a solid content of 25—75% and mixed with a starch suspension containing 30—75% of starch, the mixture then being dried. The product, containing 0·02—50% of the extract (on solids), has marked antioxygenic action when added in a small proportion to essential, fatty, or hydrocarbon oils, to dairy products, or to confectionery, or it may be used for sizing paper or textiles. It is claimed that the protective efficiency is enhanced by heat-treatment of the treated starch at a temperature above 120°.

PHYSICAL TESTING.

C. C. Kesler, J. E. Killinger, and E. T. Hjermstad[21] have continued their work on film properties of resin–starch. The material under test is cooked to obtain a final concentration such that approximately 0·9 g. of dry film is produced eventually on an inflated Orsat gas bag (diameter 9 cm.) when the bag is dipped in the paste at 80° F. After shaking off excess of paste and taring the balloon on a balance, the bag is slowly rotated during drying. By means of a combination of a manometer and water reservoir, the shrinkage during drying at various humidities may be measured in terms of the volume of water expelled from the reservoir.

The sensitivity of the starch–iodide reaction has been examined by M. Bourstyn,[22] who finds it is maximum in N-sulphuric acid and corresponds with 10^{-6}N-iodine; in 6N-hydrochloric acid it diminishes tenfold owing to complex formation. Bwtween pH 0 and 7 it varies only slightly and then diminishes to zero at pH 11.

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[18] *J. Sci. Ind. Res., India*, 1945, **4**, 277; B., 1946, III, 102.

[19] U.S.P. 2,332,345; B., 1946, III, 23.

[20] U.S.P. 2,198,197; B., 1946, III, 7.

[21] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 133; B., 1946, II, 246; C., 1946, 169.

[22] *Bull. Soc. chim.*, 1941, [v], **8**, 533; C., 1945, 293.

ANALYSIS.

A number of papers have appeared dealing with the analysis and determination of starch. R. W. Kerr and O. R. Trubell[23] use a spectrometric method for analysing paper-making starches. A solution of the sample in dilute caustic soda is adjusted to pH 5·0 with hydrochloric acid and aqueous iodine–potassium iodide added; after diluting the solution to a 0·002% starch content the percentage light transmission of the solution is measured for wave-lengths 350—1000 mμ. with a Coleman model 10-S spectrophotometer. The method is standardised by the inclusion of a suitable control, which is assumed to transmit 100%. Purified amylopectins and amyloses give a maximum and minimum transmission about 610 mμ., and reddish-purple and blue with iodine, respectively. The method, therefore, measures the relative proportions of these two major constituents; although limited by the fact that the intermediate fractions of starch are not physical mixtures of these two extreme types, it is suitable for routine work. These workers consider that the efficiency of the starch as a size or adhesive depends on the relative proportions of the two major components, the linear polymer, or "amylose," and the branch polymer, or "amylopectin," giving blue and reddish-purple colours with iodine, respectively.

S. A. Watson and R. L. Whistler[24] describe a procedure for the rapid determination of the blue colours produced on mixing various small quantities of 0·01N-iodine with 0·03% dispersions of different starches and starch fractions, which can be used to determine the purity of amylopectin when contaminated with less than 6—8% of amylose.

K. A. Clendenning and D. G. Wright[25] have examined the factors affecting the specific rotatory power of wheat starch in aqueous calcium chloride solutions. The effects of solvents, pH, salt concentration, extraction temperature and time, filtration technique, starch concentration, and polarisation temperature on the $[\alpha]_D$ of wheat starch in aqueous calcium chloride solutions are described. With 15 minutes' boiling at constant temperature and constant salt concentration, the effect of pH on $[\alpha]_D$ is negligible over the range of 2·1—3·0. Above pH 4·0 the starch solutions are opalescent and revert to a gel on keeping, whilst at pH less than 2·0 the $[\alpha]_D$ is depressed. Extension of the boiling period to 1 hour at initial pH 2·5—2·2 causes only a small decrease in $[\alpha]_D$, whereas rising extraction temperature causes a depression which varies with the pH and extraction time. With increased salt concentration there is a marked increase in $[\alpha]_D$. On substituting magnesium chloride for calcium chloride $[\alpha]_D$ for wheat starch is increased by 7°. Starch concentration has negligible effect on $[\alpha]_D$, but the value decreases with rise in polarisation temperature from 20° to 35°. Absorption of water by the filter-paper when filtering starch solution causes a large increase in

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[23] *Paper Trade J.*, 1943, **117**, *TAPPI Sect.*, 161; B., 1946, III, 133; C., 1946, 90.

[24] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 75; C., 1946, 108.

[25] *Canad. J. Res.*, 1945, **23**, **B**, 113; C., 1945, 255.

$[\alpha]_D$ for the first portions of the filtrate; this effect varies with the kind and amount of filter-paper used.

K. A. Clendenning[26] has determined the $[\alpha]_D$ of nine wheat starches representing, hard, soft, and durum varieties and of 48 samples of starch representing 20 different genera or species, using the improved calcium chloride technique. All figures showed little divergence from +203°, and this figure is suitable for calculation of starch content. Potato starch has $[\alpha]_D$ slightly higher (+204·7°) and legume starch slightly lower (+200°) than this value. Storage of starch for over ten years caused a decrease of $[\alpha]_D$. Figures for the moisture, ash, fat, and protein contents of 48 starch samples are given. Clendenning has also used the method to determine the starch in cereal products such as whole wheat, granular, and patent flours.[27] In the recommended procedure 2·463-g. samples were suspended in 10 ml. of water + 60 ml. of calcium chloride solution (*d* 1·30, pH 5·5) + 2 ml. of 0·8% acetic acid, and boiled at constant salt concentration for 15 minutes, foaming being prevented by *n*-octanol. When cool, 2·5—5 ml. of stannic chloride (or 10 ml. of uranyl acetate) in calcium chloride solution were added, followed by calcium chloride to make the volume up to 100 ml., the precipitated proteins filtered off, and a portion of the filtrate was polarised in 2-dm. tubes. Assuming $[\alpha]_D = +203°$, the percentage of starch is given by the 2-dm. reading in degrees × 10. Critical experiments showed that $[\alpha]_D$ was depressed by stannic chloride solution but not by uranyl acetate. Alternatively, proteins could be removed by extraction with aqueous alcohol and dilute caustic soda. If the extraction method was used, lævorotatory hemicelluloses of the bran and endosperm dissolved by the boiling calcium chloride solution approximately compensated for the over-estimation arising from calcium chloride-insoluble solids. Using uranyl acetate precipitation, alcohol-soluble non-proteins reduced the apparent starch content by 0·5% for whole and 0·25% for patent flours. The secondary effect due to stannic chloride caused apparent reduction in starch content by not more than 1%. Starch content would be slightly over-estimated by each method if 200° is used for $[\alpha]_D$. High values obtained for wheat products in the diastase–hydrochloric acid method may partly be due to hemicelluloses.

M. P. Etheredge[28] has tabulated the collaborative results for starch in potato starch and wheat flours obtained by the tentative (A.O.A.C.) Hopkins–Mannich–Lenz and the Clendenning procedures. The latter is found to give good results and has the advantages of ease and simplicity. Moisture results are also given. Other workers have also compared various methods of estimating starch, using 17 samples of ground wheat. W. J. Eva and E. E. Rankin[29] used five methods in these determinations

[26] *Canad. J. Res.*, 1945, **23**, **B**, 131; C., 1945, 255.
[27] *Ibid.* 239; C., 1946, 188.
[28] *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 492; C., 1946, 108.
[29] *Canad. J. Res.*, 1945, **23**, **B**, 260; C., 1946, 187.

and found the following average values and standard errors: Hopkins, 63·3 ± 0·31; Clendenning, 62·8 ± 0·40; Lintner–Schwarcz, 62·9 ± 0·48; malt diastase, with acid hydrolysis, 63·6 ± 0·57; Rask, 62·2 ± 0·48. The three polarimetric methods agreed well, *inter se*, with the Hopkins method, which is the most precise and probably the most accurate method. These three methods gave largest negative correlations between starch and protein contents. Correlation between pairs of methods was highest for Hopkins and Clendenning methods, and the latter was preferred for its simplicity and rapidity.

Two papers have appeared on the determination of starch in specific materials. F. M. Garfield[30] uses a modified Whale method in which the starch is recovered from the starch–iodine complex, hydrolysed, and determined as glucose by the Munson–Walker method. Recoveries of 97·3—99·9% are reported. Fine's mayonnaise method gave recoveries of 98·0 and 99·7%.

D. G. Griffiths and N. A. Potter[31] determine starch in apple tissue by freezing the latter at −20°, grinding, and hydrolysing by takadiastase after digesting with water in a boiling water-bath. There is also another substance, possibly a dextrin, removable by 1% aqueous potassium oxalate, which is hydrolysed by takadiastase to reducing substances. Treatment with alcoholic hydrogen chloride followed by β-amylase gives results similar to those obtained with diastase after extraction with potassium oxalate.

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[30] *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 308: C., 1945, 259.

[31] *Biochem. J.*, 1945, **39**, 423; C., 1946, 118.

THE FERMENTATION INDUSTRIES.

BY E. C. BARTON-WRIGHT, D.SC., F.R.I.C., *Whitbread & Company Ltd.*,
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H. HERON[1] has reviewed some of the difficulties which confronted brewers during the late war and the methods adopted to overcome them. The introduction of food rationing led as a natural corollary to the rationing of the raw materials for brewing. A particularly severe handicap, which had a number of repercussions, was the prohibition of malting imported barleys. The normal custom of malting Californian barleys at the beginning of the malting season and continuing until November, when English barleys are fit to steep, had to be abandoned. Brewers were therefore perforce compelled to begin the malting season with English barleys. At the outbreak of hostilities the situation was by no means so critical as it became in later years. English barleys held over from a previous season will, generally speaking, malt perfectly satisfactorily. In some seasons of the war years, however, there was an insufficient quantity of such barley left, or if it were available, it was of too poor quality, to enable the malting period to be sufficiently prolonged to ensure satisfactory germination from the freshly harvested crop when steeped. As a consequence there was a deterioration in the quality of the malt.

A number of other difficulties which confronted brewers could be directly traced to poor-quality malt. The reduction in gravity of worts during the war years to low figures placed brewers in the difficult quandary of maintaining yeasts in a healthy and vigorous condition, a difficulty which was further aggravated by the poor quality of their malt supplies.

Other matters discussed in this paper are the addition of flaked barley and oats as malt adjuncts. Flaked barley was first added as a malt adjunct, but owing to a heavy increase in U-boat activity and a consequent deterioration in the shipping situation, flaked oats were substituted for flaked barley; a 10% addition was considered a safe maximum. A bad oat harvest caused its use in brewing to be abandoned. At the suggestion of the Ministry of Food dried potatoes were substituted for flaked oats. The experiment, however, proved to be a failure. The addition of potatoes was found to be unsuitable and unsatisfactory, and flaked barley was once more used in place of flaked oats.

The hop position at the beginning of the war was unfavourable for brewers owing to the policy adopted by the Hop Marketing Board of restricting production. Thus, there was little surplus in any one year and reserve supplies in the hands of brewers were small. The situation was made more critical by the Battle of Britain, which was mainly fought over the hop-growing areas at the time the hops were ready to pick.

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[1] *J. Inst. Brew.*, 1946, **52**, 117.

In the circumstances it was only natural that there was a reluctance on the part of hop pickers to go into such dangerous areas. The 1940 hop crop was large and of good quality and all the hops were sent to the Borough. Although advised to remove the crop from such a vulnerable place, brewers were slow to follow this advice, with the result that in the incendiary raid of December 29th, 1940, on the Borough, many warehouses full of hops were burnt and approximately a third of the crop was destroyed.

In spite of all difficulties, however, there was no fall in the consumption of beer. On the contrary, the beer was consumed as fast as it could be produced, and accordingly, the lowered biological stability caused no complaints.

HOPS.

J. Nott[2] was awarded the Challenge Cup offered for the best new variety of hops by Messrs. Barclay, Perkins & Co., A. Guinness, and Whitbread & Co. The new variety is known as Bullion Hop.

C. H. Lewis[3] has reviewed the quality of the 1945 hop crop. The hops were grown in particularly unseasonable weather. The early part of the season appeared promising, but later proved to be disappointing. Summer-like weather in April led to rapid growth of the bine for this time of the year, and training of the bines had to be started before the recognised time. In May, however, the weather deteriorated in many gardens and the bines were frozen; as a result, training, which is a costly process, had to be restarted. June proved to be cold, wet, and windy and the hops suffered from an attack of aphis. The increase of wilt disease (*Verticillium alboatrum*) is also a disturbing feature of the situation; the disease has now made its appearance in newly planted gardens, and cases have been reported of gardens which have been grubbed up and replanted after a lapse of time still showing the disease.

The effect of boiling time on the extraction of hop resins has been investigated by F. Rabak.[4] The hops were analysed in the usual manner for α- and β-soft resins. The hops were used at the rate of approximately $\frac{1}{2}$ lb. per barrel (31 gallons, U.S.A. measure) and the boiling time ranged from 10 minutes to 120 minutes. It was found that a boiling time of 30 minutes sufficied to remove all α-resin, but only about 57% of the β-resin was dissolved after 120 minutes' boiling. 45% of the total soft resins are dissolved after 10 minutes' boiling; thereafter, the rate increases at 3% for every 15 minutes' boiling up to 120 minutes. As a general conclusion Rabak considers that the usual prolonged boiling of hops is unnecessary and merely leads to an excessive loss of volatile constituents. Moreover, prolonged boiling tends to give beer an unfavourable and lingering bitter taste.

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[2] *J. Inst. Brew.*, 1946, **52**, 49.
[3] *Ibid.*, 33.
[4] *Wallerstein Lab. Comm.*, 1945, **8**, 194; B., 1946, III, 71.

Rabak[5] has investigated the influence of grinding and shredding hops in the extraction of their brewing constituents during boiling. Whole cones, cones shredded into pieces $\frac{1}{4}$—$\frac{1}{2}$ in. long, $\frac{1}{8}$—$\frac{1}{4}$ in. long, and coarsely ground material $\frac{1}{16}$—$\frac{1}{8}$ in. long were used in this investigation. The hops were added at the rate of 0·6 lb. per barrel. It was found that the α-resin in the treated samples was rapidly dissolved during the first 10 minutes' boiling and completely dissolved in 30 minutes. On the other hand, although the β-resin and the total soft resins dissolved rapidly in the first 10 minutes, the rate fell off in the next 10 minutes and fell still further on longer boiling. 70—80% of the total soft resins was extracted in 30 minutes from the shredded and ground samples and longer boiling did not materially increase this figure, whereas approximately only 53% of the total soft resins was dissolved from the whole hops in a similar period. Rabak considers that the odour of the aromatic constituents dissolved from the hops was retained to a greater degree in solutions submitted to a shorter boiling time. Flavour tests showed that a maximum α-resin content is needed for the production of a pleasant non-lingering bitter taste in beer, and the author makes the suggestion that the boiling of ground or shredded hops in wort for 10 or 20 minutes at a rate considerably above the normal would achieve this result and at the same time give the desirable hop aroma.

S. C. Pearce and F. H. Beard[6] have made a study of the variation in the preservative value of hops. Preservative value (P.V.) is defined as ten times the percentage of α-resins. The experiments were continued over two seasons (1944 and 1945) and the data submitted to statistical analysis. Only one variety of hops—the Fuggle—was used. The chief difference that was discovered during the course of this investigation was between the two growing seasons. Thus, for example, although the hops were picked at the same time of ripening, and dried and analysed under similar conditions, the average P.V. for all the 96 hills from which the samples were taken individually was 60 units in 1944 as against 39 in 1945—a statistically significant difference. No reason could be found for this great variation between the two growing seasons.

BARLEY AND MALT.

H. V. Garner[7] has collated information concerning the conditions for the production of malting barley from a series of conferences held at Rothamsted Experimental Station in 1934–38, as well as from the examination and grading of 1200 barley samples. Among other things discussed is the nature of the most suitable soil for the growing of barley. It is significant that 87% of the soils concerned were classified as light or medium. It is only in exceptional seasonal conditions that high-quality barley can be grown on heavy clay or coarse sandy soils. Many other

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[5] *Wallerstein Lab. Comm.*, 1945, **8**, 129; B., 1947, III, 7.

[6] *J. Inst. Brew.*, 1946, **52**, 250; B., 1947, III, 7.

[7] *J. Min. Agric.*, 1946, **52**, 483.

factors affecting quality of the barley crop are also discussed, such as soil acidity and soil nitrogen. Soils which are rich in available nitrogen, such as occur in the Fens, are not suitable for growing barley. Weather conditions also play a part. A dry spring to allow an early sowing, followed by a showery mid-season and good harvesting weather, are essential for a good-quality crop.

The advantages and disadvantages of combine harvesters still gives rise to controversy. A. F. Smith[8] deals comprehensively and critically with the whole problem. It would appear that ideal conditions for the use of combine harvesters are large level fields having a soil which will carry a heavy machine without its becoming bogged. Other conditions are an early harvest of good standing crops, bright sunshine, and moderate rainfall. In spite of the fact that such an ideal combination of conditions is rarely found, a considerable amount of success has been achieved with combine harvesters in some districts. One great advantage of combine harvesting is the elimination of waste involved in carting and stacking and from attacks of vermin. The moisture content of a crop harvested by a combine harvester fluctuates very considerably and may vary from 15 to 30%. A crop with a moisture content of 30% must be dried quickly if deterioration is to be prevented. On the other hand, the maltster is naturally suspicious of a barley which has been subjected to any form of rapid drying at relatively high temperatures, because the germ in such pre-dried material may become damaged. One particular disadvantage of combine harvesting is the presence of pulped weeds. These are macerated during threshing and may increase the moisture content of relatively dry barley. Smith holds the definite opinion that the combine havester is most effective under bad weather conditions, at least so far as Scotland is concerned.

J. H. Parker[9] has given a general description of some of the qualities to be looked for in malting barley. He recommends that farmers cultivate barley varieties suitable for malting in preference to feed varieties, as all malting varieties can be used for feed, whereas the converse is not true.

J. L. Baker and T. J. Ward[10] have examined a series of brewings from three different types of English barleys in order to determine, under ordinary brewery conditions, the effect of these malts on fermentation, yeast crop, and character and stability of the beer. The barley varieties used were Early Ripening Spratt–Archer, Spratt–Archer (as a control), and Archer–Spratt (a new variety bred from the same parents as Spratt–Archer). Although generally speaking environmental conditions were the same in most respects, Early Ripening Spratt–Archer was grown in the best part of the field and the Archer–Spratt in the worst part. Variations were shown in the malts from the three barleys and all were only of medium quality, but the five beers brewed from each behaved normally

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[8] *J. Inc. Brew. Guild*, 1946, **32**, 132.
[9] *North Dakota Agric. Coll.*, 1945; *Brewers J.*, 1946, **94**, 28.
[10] *J. Inst. Brew.*, 1946, **52**, 17; B., 1946, III, 102.

throughout the brewing process. The yeast crops were satisfactory and all the beers were sound and bright.

H. Thunaeus[11] has determined whether mutations produced by *X*-ray treatment of barley affect its suitability for malting. Samples were taken from a number of mutants of the strains Svalöp Gull and Abed Maja. Protein content, extract, wort nitrogen, diastatic power, and starch-liquefying power were analysed. Significant differences were found between controls and *X*-ray-treated material in soluble nitrogen, extract, and starch-hydrolysing enzymes. It would appear that from the technical point of view *X*-ray treatment had created new barley varieties.

MALT BIOCHEMISTRY.

A number of communications has appeared on the measurement of α- and β-amylase in malt and other products. S. Redfern and Q. Landis[12] have described methods for the determination of α-amylase in malt, bacteria, and fungi; liquefaction (measured by a viscometric method) and dextrinisation (measured by three different methods, viz., that of R. M. Sandstedt, E. Kneen, and M. G. Blish,[13] a modification of this method, and a colorimetric method devised by the authors themselves, were employed. F. R. Graesser and P. J. Dax[14] consider that previous methods that have been used for this purpose have several disadvantages and have elaborated a method based on the inactivation of β-amylase by the addition of calcium ions; α-amylase activity was determined by a modification of the technique of Sandstedt, Kneen, and Blish,[13] but precise experimental details are not given.

P. J. Dax and F. R. Graesser[15] have made a comparison of the units of weight and number for tracing the history of β-amylase in barley. It is customary to express the diastatic value of a barley or malt on a unit of weight, but according to these authors to obtain a line relation between amylase activity of barley and the malt made from it, more consistent and satisfactory data are obtained if the results be expressed on a fixed number of corns. The authors have examined the amylase content (see above) of whole corns as well as of the basal and distal ends of germinating barley. The steeping and germination of the barley was carried out with 300-g. lots placed in a metal cage. After germination the grains were dried in a laboratory kiln. The total amylase content was determined by extracting both barley and malt with a solution of papain and the Lintner value was determined on the clear filtrate. The authors conclude from their results that there is a migration of β-amylase from the distal to the basal end of the barley corn during germination and suggest that the partial loss of this enzyme after the 11th day may be due to its absorption by the embryos. On the other hand, no similar loss of α-amylase could

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[11] *Svensk Bryggeritidskr.*, 1946, **61**, 73; *Wallerstein Lab. Comm.*, 1946, **9**, 147.
[12] *Cereal Chem.*, 1946, **23**, 1; C., 1946, 188.
[13] *Ibid.*, 1939, **16**, 712.
[14] *Wallerstein Lab. Comm.*, 1946, **9**, 43; C., 1946, 280.
[15] *Ibid.*, 49; B., 1946, III, 171.

be detected. The loss of the free and bound β-amylase which are still present after 17 days' germination indicates that in the commercial production of malt it is improbable that the total potential β-amylase of barley will be available in the free form in the resulting malt.

W. D. Claus[16] has made a comparison of three methods of measuring α- and β-amylase activity of malt, viz., that of Sandstedt, Kneen, and Blish,[13] Olson, Evans, and Dickson,[17] and one devised by himself; in this method the author defines both amylases in terms of their dextrinising power in starch solution. Claus claims the advantage for his method that the units are homologously expressed and determined by a single kind of experimental procedure.

It is a well established fact that the amylase of resting barley consists almost entirely of β-amylase. It has, however, been realised in recent years that the ungerminated corn contains a very small amount of α-amylase. According to R. H. Hopkins and T. F. S. Cooper[18] the limit of hydrolysis of starch paste by purified β-amylase of barley corresponds to a malt production of 56—57% of the theoretical value. When, however, crude preparations of the enzyme made from aqueous extracts of barley are used, which may be contaminated with a small proportion of α-amylase, starch conversion proceeds much further. Moreover, in the preparation of β-amylase from barley there is always the danger of contamination with α-amylase obtained from the microflora present on the outer coat of the grain, which will influence the rate of hydrolysis beyond the 56—57% limit in the same way as a crude preparation of barley diastase.

Biochemistry and Nutrition of Yeast.

R. S. W. Thorne[19] has continued his observations on the nitrogen requirements of yeast. It has already been shown[20] that when yeast is grown on a medium containing two nitrogen nutrients there is usually an increase of growth compared with a medium containing only a single source of nitrogen. Not only, however, is there an enhancement of growth, but also a curiously exaggerated preferential assimilation of nitrogen from the more assimilable component.[21] Arguing from this result Thorne considered that mixtures of three components should show still higher growth characteristics than binary mixtures, while mixtures containing four nitrogen nutrients should give still higher values than a ternary mixture, and so on. The general conclusion reached was that while binary mixtures gave a 20% increase in growth over a single-component medium, the presence of a third nitrogen source increased growth only by a further 8%; an 8% increment of growth and fermentation brought about by the addition of a third nutrient is considerably

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[16] *Brewers' Digest*, 1946, **21**, 60.
[17] *Cereal Chem.*, 1944, **21**, 533.
[18] *J. Inst. Brew.*, 1946, **52**, 188; B., 1946, III, 218.
[19] *Ibid.*, 5; A., 1946, III, 404.
[20] *Ibid.*, 1944, **50**, 186; A., 1944, III, 841.
[21] *Ibid.*, 1945, **51**, 6; A., 1945, III, 401.

smaller than the 20% enhancement of growth found on the addition of a second. According to Thorne, the addition of a fourth nitrogen component to a ternary mixture would scarcely give more than a 5% extra increment of growth and there is probably a limiting value to this augmentation process by increasing the number of nitrogenous nutrients; Thorne places this limiting value at about 50%—a value beyond which there will be no further increment of growth however many nutrients may be added. This view is based on the average results of experiments with a limited number of amino-acid mixtures, and it is therefore possible, although unlikely, that mixtures may exist with more marked interactions than those already encountered in these investigations. In wort, the number of individual nitrogen sources is not known, but presumably is large, and in such circumstances the full benefit of enhancement comes into operation.

An important point that emerges from this investigation is that the superiority of yeast growth in wort over that of the best synthetic media (using single nitrogen nutrients) is also of the order of 50%. It is tempting, therefore, to suggest that the superiority of wort as a medium for yeast growth is largely due to its multifold mixture of nitrogen nutrients. If this suggestion be correct, the possibility of designing a synthetic medium for research purposes which will give as good growth of yeast as wort becomes a practical possibility.

Thorne[22] has also examined the growth-inhibitive effect on yeast exhibited by a mixture of the amino-acids tyrosine and glycine. A chance observation led to the discovery that mixtures of glycine and tyrosine provide an example of inhibition rather than enhancement of growth and fermentation in yeast. A comparison was made at the same time of the effect of mixtures of glycine and phenylalanine (which is, chemically speaking, closely related to tyrosine) on yeast growth. When used alone tyrosine proved to be as good a source of nitrogen for yeast as phenylalanine, yet when mixed with glycine there was a marked inhibition of growth, which extended over the range 0—40%. No such inhibition was shown by mixtures of glycine and phenylalanine.

A very complete review of his own as well as other investigations into the nitrogen metabolism of yeasts has been published by Thorne.[23]

W. B. Emery, N. McLeod, and F. A. Robinson[24] have continued the investigations initiated by P. R. Burkholder[25] on the vitamin requirements of different strains and species of yeast. In all some 20 strains and species of yeast were examined from this point of view. The yeasts were grown on a purely synthetic medium composed of mineral salts, glucose, and ammonium sulphate and asparagine to supply nitrogen. The following seven vitamins of the vitamin-*B* complex were added to the medium:

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[22] *J. Inst. Brew.*, 1946, **52**, 15; A., 1946, III, 404.
[23] *Wallerstein Lab. Comm.*, 1946, **9**, 97.
[24] *Biochem. J.*, 1946, **40**, 426; C., 1946, 274.
[25] *Amer. J. Bot.*, 1943, **30**, 206.

aneurin (vitamin-B_1, thiamin), riboflavin, calcium *d*-pantothenate, nicotinic acid, inositol (bios I), biotin (bios II), and pyridoxine (vitamin-B_6). Contrary to the findings of Burkholder, in no case was the growth response to the addition of a liver extract added to the seven vitamins enumerated above markedly greater than with the seven vitamins alone. Thus, none of the yeasts that were examined indicated the presence of any new growth factor in the liver preparation necessary for yeast growth. Several of the yeasts failed to grow satisfactorily in the absence of one or more of these seven vitamins. Calcium *d*-pantothenate and biotin were found to be of special importance in this connexion, while for one species of yeast, *Kloeckera brevis*, five factors, aneurin, calcium *d*-pantothenate, inositol, pyridoxine, and biotin, were essential for normal growth. In no case was riboflavin found to be an essential factor for any of the yeasts that were examined.

NUTRITIVE VALUE OF BEER.

F. W. Norris[26] has described the carbohydrate content, nitrogenous substances, and mineral salts found in beer. Although there is at the present time a fairly clear picture of the nutritive value of beer, there is, nevertheless, a considerable lack of detailed knowledge on the subject and Norris pleads for a more exhaustive and systematic investigation to be made.

W. J. Stringer[27] has given a useful survey of the vitamin content of beer. It is only within the last few years that there has been a revival of interest in the subject. As long ago as 1918, A. Harden and S. S. Zilva[28] concluded that beer was free from both vitamins-*B* and -*C*. It was considered at that time that vitamin-*B* was a single entity and it was only realised in later years that it was a complex mixture of different factors which were not even chemically related to one another. It remained for A. Scheunert and H. Schieblich[29] to find traces of vitamin-*B* in bottom-fermented beer, while top-fermented beer contained considerable amounts of other members of the vitamin-*B* complex. The isolation and synthesis of the different numbers of the vitamin-*B* complex has gradually led to a more exact knowledge of the vitamin content of beer. Up to the present time most attention has been focussed on the riboflavin content of beer. E. C. Barton-Wright, T. Moran, and H. S. Sarson[30] and R. H. Hopkins[31] have given quantitative figures for the amounts of this vitamin in different beers. Few figures are available for the riboflavin content of British barleys. R. H. Hopkins and S. Wiener[32] give the values 2—3·7 μg. per g. of riboflavin for barley and 4—5·5 μg. per g. for malt and E. C. Barton-

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[26] *J. Inst. Brew.*, 1946, **52**, 74.
[27] *Ibid.*, 81.
[28] *Ibid.*, 1918, **24**, 197.
[29] *Woch. Brau.*, 1927, **44**, 363.
[30] *Nature*, 1943, **152**, 273.
[31] *Ibid.*, 274.
[32] *J. Inst. Brew.*, 1944, **50**, 124.

Wright and R. G. Booth[33] 2·3 μg. per g. for barley. It is almost certain that these figures are too high. At the time these results were published, it was not sufficiently realised that extraction procedure is of the highest importance in the microbiological assay of riboflavin; this is especially the case with cereals. Moreover, the microbiological assay of riboflavin in malt presents special difficulties of its own. It is probable that the values obtained by Stringer[27] for the riboflavin content of barley (Spratt–Archer) grown in different parts of Ireland, and the malt made therefrom, are the most accurate that have been obtained so far. The average value obtained by Stringer for barley and malt was 1·37 and 2·13 μg. per g. respectively; thus, there is an average increase of 59% in riboflavin during the malting process.

C. Klatzkin, F. W. Norris, and F. Wokes[34] have examined the riboflavin content of malt extracts by fluorimetric and microbiological methods of assay. With one exception, the agreement between these two totally different methods was excellent, the fluorimetric methods averaging 103% of the microbiological assays. Wide variations in riboflavin content were found in samples of malt extract and malt preparations from different manufacturers. Changes in riboflavin content during malting and brewing were also studied. There was apparently no appreciable production of riboflavin during the first two days of steeping and the first day on the germinating floor. After this, riboflavin was produced at a steady rate which resulted in a gain of 71% after 12 days on the floor.

The nicotinic acid content of English barleys and malts has been given by E. C. Barton-Wright[35] and F. W. Norris.[36] The values show a considerable range in both barley (85—147 μg. per g.) and malt (91—127 μg. per g.). The nicotinic acid content of beer also shows a wide range (4·5—19·5 μg. per ml.). E. C. Barton-Wright[37] has given some values for the pyridoxine (vitamin-B_6) content of barley, a few different beers, and dried yeast. The values for barley were 5·25—5·9 μg. per g., for dried yeast 15·4 μg. per g., and for three beers, strong ale (brewed 1796) 1·2 μg. per ml., stout (brewed 1899) 0·5 μg. per ml., and a modern beer 0·5 μg. per ml.

Information is scanty with regard to the pantothenic acid content of barley, malt, and beer. S. Laufer, C. F. Davis, and L. T. Saletan[38] have given some figures for American barleys and the malts made from them. There seems to be a slight increase of pantothenic acid during malting. No figures appear to be available for the pantothenic acid content of beer; this should be of considerable academic interest because for a large number of brewery yeasts pantothenic acid is an essential growth factor.

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[33] *Biochem. J.*, 1943, **37**, 25.
[34] *Quart. J. Pharm.*, 1946, **19**, 376.
[35] *Biochem. J.*, 1944, **38**, 314; C., 1945, 46.
[36] *J. Inst. Brew.*, 1945, **51**, 177; B., 1945, III, 224.
[37] *Biochem. J.*, 1945, **39**, *Proc.*, x; C., 1945, 262.
[38] *Proc. Amer. Soc. Brew. Chem.*, 1942, 36; *J. Inst. Brew.*, 1943, **48**, 212.

F. M. Younger and E. H. Harvey[39] have discussed the stability of beer fortified with vitamins. Six months' exposure to daylight of beer in colourless bottles led to a 29% loss of added aneurin. There was no loss when the beer was stored in amber-coloured bottles, or in colourless bottles placed in the dark at room or refrigerator temperatures. Riboflavin was found to be more susceptible to destruction by light than aneurin. There was a 50% loss of this vitamin after seven days' exposure to daylight in colourless bottles and an 85% loss in 12 weeks. When stored in amber-coloured bottles, the destruction of riboflavin in 12 weeks was 40% in daylight and 23% in darkness at room or refrigerator temperatures. Under all the above conditions nicotinic acid remained stable in all groups during the test period of six months.

Microbiological Assays.

A spate of papers continue to be poured out on the microbiological assay of vitamins and amino-acids. The Analytical Methods Committee of the Society of Public Analysts has now published the report of the Microbiological Panel of the Sub-Committee on Vitamin Estimations[40] on the microbiological assay of riboflavin and nicotinic acid. The report gives detailed instructions for carrying out these assays on a wide variety of foodstuffs.

E. C. Roberts and E. E. Snell[41] have described a new basal medium which can be used for the assay of riboflavin, nicotinic acid, pantothenic acid, biotin, and folic acid with the lactic organism *Lactobacillus helveticus*; an enzymic digest of vitamin-free casein is used in this medium in place of the photolysed peptone originally recommended.[42]

The importance of culturing technique for the lactic organisms used in assay work has been emphasised by M. C. Nymon and W. A. Gortner[43] who recommend a liver–tryptone–agar in place of the usual yeast extract–glucose–agar.

The isolation of pantothenic acid for microbiological assay has been investigated by M. Ives and F. M. Strong.[44] Since pantothenic acid is destroyed by either alkaline or acid hydrolysis, neither of these methods can be used to liberate combined pantothenic acid preparatory to microbiological assay. Ives and Strong point out that enzymic digestion suffers from the disadvantage that many enzyme preparations contain appreciable amounts of pantothenic acid, leading to high and inaccurate values. The authors suggest the use of the enzyme preparation "mylase *P*," which acts more quickly and in smaller concentration than other enzymes that were tested; its pantothenic acid content is also low and the blank correction negligible.

[39] *Food Res.*, 1945, **10**, 397; B., 1946, III, 48.
[40] *Analyst*, 1946, **71**, 397; C., 1947, 24.
[41] *J. Biol. Chem.*, 1946, **163**, 699; C., 1946, 275.
[42] E. E. Snell and F. M. Strong, *Ind. Eng. Chem.* [*Anal.*], 1939, **11**, 36.
[43] *J. Biol. Chem.*, 1946, **163**, 277; A., 1946, III, 863.
[44] *Arch. Biochem.*, 1946, **9**, 25; C., 1946, 185.

The microbiological assay of aneurin using yeasts or the mould *Phycomyces blakesleeanus* has never been very satisfactory owing to the fact that these organisms may respond to the thiazole and pyrimidine moieties of the aneurin molecule. The introduction of the lactic organism *Lactobacillus fermenti* 36 for this purpose by H. P. Sarett and V. H. Cheldelin[45] has also proved to be unsatisfactory owing to the incidence of high blanks. The isolation by E. L. Tatum and T. T. Bell[46] of the *X*-ray-induced mutant of the mould *Neurospora crassa* (mutant 9185), which is specific for aneurin and does not respond to either thiazole or pyrimidine, may supply a suitable method for the microbiological assay of this vitamin. The organism responds quantitatively to the vitamin, but the practical details of a suitable assay procedure have still to be worked out.

A number of publications have appeared on the assay of amino-acids using the lactic bacteria. As was to be expected, most attention has been focussed on the assay of the "essential" amino-acids.[47] These essential amino-acids are arginine, histidine, *iso*leucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine. In certain circumstances, the sulphur-containing amino-acid cystine can replace the other sulphur-containing acid, methionine, in the diet of the rat, and should perhaps be included in the list of "essential" acids.

M. S. Dunn, M. N. Camien, S. Shankman, and H. Block[48] claim that *Lactobacillus fermenti* 36 has proved to be in their hands the most reliable organism for the estimation of methionine. They found that it was superior in this respect to *Leuconostoc mesenteroides* P60 and *Lactobacillus arabinosus* 17/5 (see also in this connexion Dunn, Camien, and Shankman[49]). *Lactobacillus fermenti* 36 differed from *Leuconostoc mesenteroides* and *Lactobacillus arabinosus* in its behaviour towards *d*(+)-methionine. Although *d*(+)-methionine was completely inactive in promoting the growth of the two latter organisms, it stimulated the growth of *L. fermenti* to the same extent as did the *l*(–)-enantiomorph.

E. C. Barton-Wright[50] has described assay procedure for eleven amino-acids, arginine, cystine, histidine, *iso*leucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine, using the three organisms *Lactobacillus arabinosus*, *Leuconostoc mesenteroides* P60, and *Streptococcus fæcalis* (*lactis*) Rogers, whilst E. C. Barton-Wright and T. Moran[51] have applied these methods to the determination of these acids in different parts of the wheat grain; it was found that, apart from the germ, there was an increasing gradient of these acids from the centre to the periphery of the grain.

[45] *J. Biol. Chem.*, 1944, **155**, 153; C., 1945, 44.
[46] *Amer. J. Bot.*, 1946, **33**, 15.
[47] W. C. Rose, *Physiol. Rev.*, 1938, **18**, 109.
[48] *J. Biol. Chem.*, 1946, **163**, 577; C., 1946, 289
[49] *Ibid.*, 1944, **156**, 703.
[50] *Analyst*, 1946, **71**, 267; C., 1946, 289.

I. T. Greenhut, B. S. Schweigert, and C. A. Elvehjem[52] have described a modified procedure for the microbiological assay of threonine using *Streptococcus fæcalis* (*lactis*) R. In this modified medium the main change has been to substitute sodium citrate for sodium acetate as a buffer in the medium. Sodium acetate is the usual buffer that is added to media for growing lactic organisms, but *Str. fæcalis* is a poor acid producer compared with other lactic organisms used for assay work and fails to grow after the pH of the medium has fallen to 5. On this account it has been customary in the past to use nephelometric or turbidimetric methods of estimating growth rather than direct titration with alkali. The addition of sodium citrate as buffer, however, makes it possible to follow the ordinary procedure of titrating with 0·1N-sodium hydroxide solution.

M. Gunness, I. M. Dwyer, and J. L. Stokes[53] have described a method for the estimation of tyrosine using *Lactobacillus delbruckii* L.D.5. It was found that it was more satisfactory to use alkali rather than acid hydrolysis for preparing samples for assay because tyrosine is partly destroyed on prolonged hydrolysis with strong acids.

I. T. Greenhut, B. S. Schweigert, and C. A. Elvehjem[54] have discussed hydrolytic procedures for the estimation of tryptophan microbiologically in proteins and foodstuffs. The liberation of tryptophan by acid, alkali, and enzymic hydrolysis was investigated. As is well known, tryptophan is completely destroyed by prolonged hydrolysis with strong acids and it is usual, therefore, to use alkali, *e.g.*, sodium or barium hydroxide. When alkali hydrolysis is used racemisation of the tryptophan takes place and it is therefore essential that hydrolysis should be sufficiently prolonged to ensure that racemisation is complete. Greenhut *et al.* consider that the most satisfactory recoveries of tryptophan are obtained when samples are hydrolysed with a mixture of pancreatin and hog mucosa provided that the samples are well shaken during the whole of the hydrolytic period.

ALCOHOL.

N. M. Erb and F. M. Hildebrant[55] have investigated the direct use of mycelium of moulds for saccharifying starch in the production of alcohol from granular wheat mashes prepared by the infusion process. Spores of *Rhizopus boulard* or *Rhizopus delemar* were grown in three stages using pure culture technique, and a volume of mould mycelium equivalent to 6—12% of the fermenter volume was added to the final mash, which, after conversion at 145° F. for one hour, was fermented by yeast. In this way is was possible to eliminate four fifths of the malt previously used, which led to a significant increase in the yield of alcohol.

J. W. Boyer and L. A. Underkofler[56] describe the production of mould bran (a culture of *Aspergillus oryzæ*), which is available commercially

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[51] *Analyst*, 1946, **71**, 278; A., 1946, III, 784.
[52] *J. Biol. Chem.*, 1946, **162**, 69; C., 1946, 198.
[53] *Ibid.*, **163**, 159; C., 1946, 288.
[54] *Ibid.*, **165**, 325; C., 1947, 35.
[55] *Ind. Eng. Chem.*, 1946, **38**, 792; B., 1946, III, 256.
[56] *Chem. Met. Eng.*, 1945, **52**, *No.* 12, 110; B., 1946, III, 71.

under the trade name of "Eaglezyme," and give production figures which indicate that yields of alcohol from grain are greater with mould bran than with barley malt.

L. A. Underkofler, G. M. Severson, and K. J. Goering[57] tested the suitability of mould bran for saccharifying maize mashes. When mould bran replaced malt in the yeast culture mashes the time required for the subsequent lactic souring operation was decreased to half that needed with all-malt mashes; more rapid growth of yeast and higher yeast cell counts were obtained, and fermenters inoculated with yeast cultures grown on mash containing mould bran showed better yields of alcohol. When mould bran was used to saccharify the mash for the main plant fermenters the yield of alcohol was higher than when malt was employed. The authors conclude that the economics of using mould bran in the saccharification of starchy mashes for the production of industrial alcohol are definitely favourable.

The utilisation of wood sugar for the production of alcohol played a small but significant part in the German war economy.[58] Plants producing alcohol by the Scholler process and from sulphite liquor had capacities totalling 10 million litres and 25 million litres of alcohol per annum respectively. The fermentation of wood sugar is carried out by a rapid continuous process in a series of fermenters, fitted with stirrers; feed solution containing 6% of sugars is added and wash withdrawn at a rate which gives an average holding time of 4—6 hours. The yeast is separated by centrifuges and re-cycled to a fermenter so as to maintain a cell concentration equivalent to 20—40 g. of dried yeast per litre in the fermenting liquid. About once a month it is necessary to lower the pH of the separated yeast cream to a value of 2—2·5 to kill acid-forming bacteria. The duration of the fermentation is much shorter in this German process than in the other continuous fermentation processes.

E. E. Harris and E. Beglinger[59] describe the Madison wood sugar process for the hydrolysis of Douglas fir wood-waste, which is claimed to give higher yields of sugar than the Scholler process. Details of the technique used for the subsequent fermentation of this wood sugar solution are described by E. E. Harris, G. J. Hajny, M. Hannan, and S. C. Rogers.[60]

W. L. Owen[61] discusses the influence of contaminating bacteria on the efficiency of the alcoholic fermentation of blackstrap molasses by yeast. The use of contaminated water for mashing does not necessarily reduce efficiency but sterilisation increases it. The addition of ammonium fluoride gives higher yields of alcohol with both sterilised and unsterilised mashes, indicating a beneficial influence apart from bactericidal action; the increase seems to be due to restricted yeast development. Decreased efficiency in plant practice at high temperature is believed to be caused

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[57] *Ind. Eng. Chem.*, 1946, **38**, 980; B., 1947, III, 8.

[58] *Field Information Agency, Technical, Final Rept.* 499; cf. B., 1946, III, 194.

[59] *Ind. Eng. Chem.*, 1946, **38**, 890; B., 1947, III, 6.

[60] *Ibid.*, 896; B., 1947, III, 8.

[61] *Sugar*, 1946, **41**, *No.* 6, 46; *No.* 8, 47; B., 1946, III, 256.

by bacteria with an optimum temperature about 40°, and in tropical climates where it is not possible to keep the temperature below 37° contamination of the seed yeast with lactobacilli is the most potent factor in reducing the efficiency of the fermentation.

OTHER FERMENTATION PROCESSES.

Our knowledge of the series of reactions which lead to the production of mixed solvents in the industrially important butyl fermentations is still inadequate. Most of the information available hitherto has been obtained by adding proposed intermediates and assuming that the reactions which these undergo can be determined by studying quantitative changes in the end products. This method is based on assumptions which are not necessarily valid, but by the use of ^{13}C as a tracer element a technique is available which largely eliminates these assumptions. H. G. Wood, R. W. Brown, and C. H. Werkman[62] have ascertained the fate of labelled acetate, butyrate, and acetone in corn mash fermentations by *Cl. acetobutylicum* and *Cl. butylicum*. The major portion of the added ^{13}C acetate was recovered as butyl alcohol, showing that acetic acid is not quantitatively converted into acetone or *iso*propyl alcohol as had been previously reported. 85% of the ^{13}C added as butyric acid was recovered as butyl alcohol; the authors consider that their results indicate a small conversion of butyric acid into compounds other than butyl alcohol but are not sufficient to decide whether this conversion is the result of a reversal of the reactions which lead to butyrate synthesis or the result of other reactions. The experiments with labelled acetone, which are of principal interest with respect to the fermentation by *Cl. butylicum*, indicated a quantitative conversion of acetone into *iso*propyl alcohol.

G. A. Adams and co-workers have continued the study of the production of butane-2 : 3-diol by *A. polymyxa* from wheat mashes. Aëration[63] by mechanical agitation inhibited the formation of the diol and of ethyl alcohol, but the passage of finely dispersed air increased the yield of the diol. Anaërobic conditions produced by the passage of nitrogen or hydrogen through the mash shortened the fermentation time to about 48 hours. Fermentation under reduced pressure[64] increased the rate of formation of ethyl alcohol. Fermentation at different pH levels[65] from 5·8 to 7·0 did not affect the diol : alcohol ratio. The riboflavin and nicotinic acid contents per 100 g. of the fermented mash averaged 19 and 1270 μg. respectively; the riboflavin showed an 80% increase over that present in the original wheat, whereas nicotinic acid showed a 40% increase. When fermenting wheat starch it was found necessary[66] to add additional nutrients; of various materials tested, 1% of malt sprouts proved to be the most effective.

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[62] *Arch. Biochem.*, 1945, **6**, 243; A., 1945, III, 573.
[63] G. A. Adams, *Canad. J. Res.*, 1946, **24**, **F**, 1; B., 1946, III, 172.
[64] G. A. Adams and J. D. Leslie, *ibid.*, 107; B., 1946, III, 172.
[65] *Idem*, *ibid.*, 13; B., 1946, III, 172.
[66] S. B. Fratkin and G. A. Adams, *ibid.*, 29; B., 1946, III, 172.

H. W. von Loesecke[67] reviews the information available on the production of citric acid by moulds. D. Perlman, D. A. Kita, and W. H. Peterson[68] point out that beet molasses is usually employed for this fermentation, and from a laboratory study of the production of citric acid by *A. niger* in surface culture they conclude that the low yields of citric acid which result when cane molasses is used are due to the presence of inorganic inhibitors which can be removed by pretreatment of the molasses.

L. D. Beckford, G. L. Peltier, and E. Kneen[69] have examined the possibility of using the spent wash (thin stillage) from fermentations yielding alcohol from grain as a medium for the growth of *Bacillus subtilis* with the production of an amylase. The amylase produced by the pellicle is secreted into the medium and the total production of enzyme is greatest when the organism is grown in shallow layers of the medium.

Although riboflavin was synthesised about twelve years ago, considerable interest is still maintained in the possibility of the commercial production of this vitamin by fermentation processes. It is well known that substantial amounts of riboflavin are synthesised during the butyl fermentation by *Clostridium acetobutylicum* and related organisms, particularly when cereal mashes containing rice are being fermented; U.S.P. 2,368,074[70] is an example from a number of patents which deal with the production of riboflavin by this type of fermentation. The synthesis is inhibited by the presence of traces of certain metals and special precautions[71] are essential to obtain high yields of the vitamin.

P. R. Burkholder[72] investigated the synthesis of riboflavin by the yeast *Candida guilliermondia*; the use of this organism for the production of riboflavin is described by Research Corporation, New York.[73]

In 1936, A. Guilliermond[74] showed that the mould *Eremothecium ashbyii* synthesises large quantities of a flavin which may crystallise in the vacuole. More recently W. H. Schopfer[75] investigated the production of riboflavin by this organism. According to the Commercial Solvents Corporation[76] riboflavin is produced by subjecting a substantially carbohydrate-free nutrient mash containing as its principal nutrients 10—90% of a proteinaceous material and a metabolisable lipin to the action of *Eremothecium ashbyii*; the mash is aërated and may be mechanically agitated to maintain uniform dispersion of the mould; fermentation is complete in 50—90 hours and a dried material containing 200—6000 μg. of

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[67] *Chem. Eng. News*, 1945, **23**, 1952; A., 1946, III, 136.
[68] *Arch. Biochem.*, 1946, **11**, 123; A., 1947, III, 75.
[69] *Ind. Eng. Chem.*, 1946, **38**. 232; B., 1946, III, 103.
[70] Commercial Solvents Corporation.
[71] See U.S.P. 2,326,425, Commercial Solvents Corporation.
[72] *Arch. Biochem.*, 1943, **3**, 121.
[73] U.S.P. 2,363,227.
[74] *Rev. Mycol.*, 1936, **1**, 115.
[75] *Helv. Chim Acta*, 1944, **27**, 1017; A., 1945, III, 198.
[76] U.S.P. 2,374,503.

riboflavin per g. is eventually obtained. Merck & Co. Inc.[77] describe a process for the production of riboflavin which comprises propagating *Eremothecium ashbyii* with agitation and aëration under conditions of submerged growth in a medium containing up to 10% of an assimilable carbon compound such as a sugar, molasses, or glycerol and about 0·5% of yeast or its equivalent in organic nitrogen; yields of 400—500 μg. of riboflavin per ml. of culture liquid are claimed.

R. L. Mayer and M. Rodbart[78] investigated the production of riboflavin by *Mycobacterium smegmatis* and found that the vitamin was synthesised in maximal amounts when only inorganic nitrogen was present; for *Eremothecium ashbyii*, on the other hand, the presence of organic nitrogen is of paramount importance for the synthesis of riboflavin.

FOOD YEAST.

The production of food yeast in Germany from sulphite liquor and from wood sugar obtained by the Scholler process or the Bergius process is described in B.I.O.S. Final Report No. 499.[79] The total capacity of plants for the production of dried yeast from wood sugar of all sources was greater than 25,000 metric tons per annum, and additional plants for the production of yeast from sulphite liquor were under construction at the end of hostilities. Most of the factories employ the Waldhof process of yeast production, which is continuous and makes use of mechanical aëration and foam-breaking equipment. The time of fermentation is dependent on the sugar content of the liquor used, the average time being about 4½ hours. The standard Waldhof yeast plant designed to produce about 1000 tons of dried yeast per annum yields 126 kg. of dried yeast per hour from a fermenter of 200 cu.m. capacity. The overall yield is about 40% of dried yeast based on the reducing sugar content of the sulphite liquor. *Torulopsis utilis* is the organism usually employed but *Monilia candida* and *Candida arborea* are preferred in some factories, while *Oidium lactis* is used for the fodder yeast known as "Biosyn." In some distilleries producing alcohol from sulphite liquor and from wood sugar the spent wash from the still is used as a medium for the production of food yeast; by this process the biological oxygen demand of the spent wash is reduced considerably. E. F. Kurth[80] and E. F. Kurth and V. H. Cheldelin[81] investigated the growth of three strains of yeast on still waste liquors and obtained about 0·3% of dried yeast and a 40% reduction in the B.O.D. of the effluent.

In a report dealing with some aspects of microbiological research in Germany, reference is made[82] to the production of fat by yeasts and moulds and it is claimed that strains of *Nectaromyces reukaufii* are more suitable for this purpose than strains of *Endomyces vernalis*.

[77] B.P. Appl. 10,404/1944.

[78] *Arch. Biochem.*, 1946, **11**, 49; A., 1947, III, 79.

[79] H.M. Stationery Office; cf. B., 1946, III, 194, 217, 218.

[80] *Ind. Eng. Chem.*, 1946, **38**, 204; B., 1946, III, 133.

[81] *Ibid.*, 617; B., 1946, III, 196.

[82] *B.I.O.S., Final Rept.* 691, *Item* 24; H.M. Stationery Office.

FOODS.

By E. B. Hughes, D.Sc., F.R.I.C.

With the collaboration of: L. C. Baker, M.Sc., F.R.I.C. (Meat, Fish, Poultry, and Eggs), C. A. Bassett, B.Sc., F.R.I.C. (Cocoa, Chocolate, and Confectionery), A. E. Bradfield, D.Sc. (Tea), J. H. Bushill, D.Sc., F.R.I.C. (Milk and Milk Products), D. H. F. Clayson, M.Sc., F.R.I.C. (Feeding Stuffs), G. E. Forstner, M.Sc., F.R.I.C. (General Food Analysis), C. H. F. Fuller, B.Sc., F.R.I.C. (Cereals and Cereal Foods), R. W. Money, M.Sc., F.R.I.C. (Fruit and Vegetables), and N. D. Sylvester, M.Sc., F.R.I.C. (Edible Fats).

Feeding Stuffs.

The years 1945 and 1946 saw the establishment and early activities of the Food and Agriculture Organisation of the United Nations, the objective of which is to achieve an "economy of abundance." It was realised at the Hot Springs Conference in 1943[1] that a step towards this was "to promote the uninterrupted development and most advantageous use of agricultural and other material resources for the establishment of an equitable balance between agriculture and industry in the interest of all." This is precisely the task of food chemists and agriculturists the world over, and any catalytic influence from the Organisation will be welcome.

A number of observers have been taking retrospective views over the wartime period, and information has also been received regarding wartime practice in parts of Europe that were more or less isolated. British observers have calculated that the crude weight of the average daily winter ration for cows in eastern England increased during the war from 44 to 61 lb., but that the dry matter increased only from 21·0 to 22·6 lb. and the indigestible residue from 7·2 to 8·4 lb., but, in respect of young cattle, growth is considered to have been appreciably retarded by wartime rations.[2] In Switzerland, cows were almost exclusively on a grass diet, and this appears to have caused a slight increase in the fat content of the milk.[3] This effect, coupled with reduced yield, was more marked in Denmark, and it was found to be given also by a winter ration containing fodder cellulose and fish meal; here, lowered standards of feeding applied to calves did not reduce weight increase to the extent expected, but

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[1] "Final Act of the United Nations Conference on Food and Agriculture," H.M.S.O. *Cmd.* 6451, 1943.

[2] G. H. N. Pettit, *J. Agric. Sci.*, 1946, **36**, 222; B., 1946, III, 238. K. L. Blaxter and H. A. Price, *ibid.*, 301.

[3] E. Crasemann, *Mitt. Lebensm. Hyg.*, 1942, **33**, 117; B., 1946, III, 27. P. Balavoine, *Arch. Sci. phys. nat.*, 1944, [v], **26**, *Suppl.*, 243; A., 1946, III, 48.

variable results were obtained with pigs.[4] In Norway, an experiment in which two thirds of the starch value of a standard ration was replaced by fodder cellulose showed live weight gains of steers equal to those of the controls, although flesh gains were somewhat less; the cellulose must be low in lignin content and thoroughly comminuted. With cows at pasture, fodder cellulose *ad lib* did not improve milk yield.[5]

General Nutritional Studies.

E. W. Crampton[6] has challenged food chemists to devise better methods of determining the digestibility, available energy, and nutritive value of food materials, but it is difficult to decide whether the main problem is this or the fundamental study of the causes of the variation between animals due to age, health, breed, and other factors recognised by various authors,[7] and examined mathematically by others.[8] O. Heintzel[9] and K. Breirem[10] have attempted to improve on the conventional methods of evaluation, but it must be recognised that, apart from experiments with synthetic diets, the food may be as variable as the animals. The many combined studies of the changes in digestibility and chemical composition of forage crops at different stages of maturity are therefore particularly useful.[11] C. L. Shrewsbury, C. Harper, and F. N. Andrews[12] have developed this type of research by adding proteins and crystalline vitamins to low-grade oat straw plus dehydrated lucerne rations in an attempt to bring them up to the nutritional level of dehydrated oat and rye grasses for breeding ewes. A group of workers in Pennsylvania[13] have evaluated pasture fertilisation procedures by measuring the weight gain and milk

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[4] K. Breirem, *Meieriposten*, 1944, **33**, 464, 489; B., 1946, III, 136. O. Ulvesli and K. Breirem [with G. Dahlsrud], *Norsk Landbruk*, 1944, **10**, 68, 79; B., 1946, III, 27. K. Breirem, M. Husby, and K. Presthegge, *Norg. Landbrukshøgsk. Inst. Foringsfors.*, 1943, 55 *Ber.*; B., 1946, III, 52.

[5] H. Hvidsten, *Norsk Landbruk*, 1941, *No.* **3**, 28; *No.* 7, 86; B., 1946, III, 141. *Ibid.*, 1942, **8**, 396; B., 1946, III, 158.

[6] *Trans. Amer. Assoc. Cereal Chem.*, 1945, **3**, 147; A., 1946, III, 1040.

[7] L. E. Johnson, *J. Animal Sci.*, 1944, **3**, 224; A., 1946, III, 465. B. Knapp, jun., and A. L. Baker, *ibid.*, 219; A., 1946, III, 465. C. M. Kincaid, G. W. Litton, and R. E. Hunt, *ibid.*, 1945, **4**, 164; B., 1946, III, 157.

[8] S. Brodie and H. H. Kibler, *Univ. Missouri Agric. Exp. Sta.*, 1945, *Res. Bull.* 380, 394; A., 1946, III, 288. G. S. Fraps, *Arch. Biochem.*, 1945, **8**, 21; A., 1946, III, 283. H. G. Barott and E. M. Pringle, *J. Nutrition*, 1946, **31**, 35; A., 1946, III, 383.

[9] *Mitt. Lebensm. Hyg.*, 1943, **34**, 308; A., 1946, III, 663.

[10] *K. Lantbr. Akad. Tidsskr.*, 1944, **83**; B., 1946, III, 142.

[11] K. Breirem [with O. Ulvesli, T. Homb, and H. Frank], *Norsk Landbruk*, 1944, **10**, 271, 288; B., 1946, III, 52. E. W. Crampton and I. R. C. Jackson, *J. Animal Sci.*, 1944, **3**, 333; B., 1946, III, 179. C. S. Hobbs, W. D. Gallup, and B. R. Taylor, *ibid.*, 1945, **4**, 395; B., 1946, III, 141. C. E. Fleming, M. A. Shipley, and M. R. Miller, *Nevada Agric. Exp. Sta.*, 1942, *Bull.* 159; B., 1946, III, 141. L. L. Rusoff, D. M. Seath, and G. D. Miller, *J. Dairy Sci.*, 1945, **28**, 869; B., 1946, III, 142. J. Sotola, *J. Agric. Res.*, 1946, **72**, 365; B., 1946, III, 238. T. W. Daniel, F. B. Wolberg, V. L. Miller, J. H. Alswager, M. E. Ensminger, and A. A. Spielman, *J. Animal Sci.*, 1946, **5**, 80; B., 1946, III, 238. W. E. Watkins and J. H. Knox, *ibid.*, 1945, **4**, 297; B., 1946, III, 141.

[12] *J. Animal Sci.*, 1946, **5**, 47; B., 1946, III, 238.

[13] C. F. Noll, S. I. Bechdel, P. S. Williams, S. R. Skaggs, and M. A. Hein, *Pennsylvania Agric. Exp. Sta.*, 1944, *Bull.* 460; B., 1946, III, 85.

yield of cattle fed thereon. F. L. Wynd and G. R. Noggle[14] have specified minimum values for exchangeable bases in soils for satisfactory production of dry matter and protein in immature oats. H. D. Kay,[15] in discussing the value of wheat offals for milk production, has emphasised that a good dairy cow, producing at least 750 gallons of milk a year, must be given concentrated food of good quality owing to the limited amount of dry matter it can consume.

Analytical methods for identifying feeds and measuring their rate of passage through the rumen of cattle have been described,[16] and silica has been suggested as a reference substance in digestibility trials.[17]

The physical state of food has an important bearing on its utilisation; thus the finer is the grinding of oats, the more rapid is the gain in weight of pigs fed on them.[18] Calves fed on skim milk containing a foreign fat (*e.g.*, soya) develop alopecia unless the mixture is homogenised,[19] and the addition of sulphonated wetting agents to poultry food is claimed to have beneficial effects on growth and health.[20] A well-documented review on the subject of "bloat" in cattle has appeared, and attention has been drawn to some of the dangers of rapid transition from winter feeding to early summer grass.[21]

Ten poisonous flowering plants found in North Carolina have been described, with symptoms and treatment of affected livestock. Poisoning by the water dropwort (*Oenanthe crocata*) and a spurge (*Phyllanthus abnormis*) and by hydrocyanic acid from jowar has also been reported.[22] Toxicity trials with benzene hexachloride (used against locusts) showed that cattle and sheep can tolerate 1—4 g. per kg. body weight.[23]

Nitrogen Requirements.

The development of methods for the determination of amino-acid composition of proteins by microbiological assay and specific decarboxylase techniques opens up the way for more exact correlation between protein requirements and food supplied. W. Baumgarten, A. N. Mather, and L. Stone[24] have applied microbiological assay to

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[14] *Food Res.*, 1945, **10**, 408, 415; B., 1946, III, 37.

[15] *Proc. Nutrition Soc.*, 1946, **4**, 31; A., 1946, III, 566.

[16] W. Burroughs, P. Gerlaugh, E. A. Silver, and A. F. Schalk, *J. Animal Sci.*, 1946, **5**, 272; A., 1946, III, 1041.

[17] W. D. Gallup, C. S. Hobbs, and H. M. Briggs, *ibid.*, 1945, **4**, 68; A., 1946, III, 658.

[18] E. W. Crampton and J. M. Bell, *ibid.*, 1946, **5**, 200; A., 1946, III, 749.

[19] W. Bate, D. Espe, and C. Y. Cannon, *J. Dairy Sci.*, 1946, **29**, 41; A., 1946, III, 568.

[20] B. V. Lamb, U.S.P. 2,340,063; B., 1946, III, 260.

[21] H. H. Cole, C. F. Huffman, M. Kleiber, T. M. Olson, and A. F. Schalk, *J. Animal Sci.*, 1945, **4**, 183; A., 1946, III, 473. J. Stewart, *Proc. Nutrition Soc.*, 1946, **4**, 64; A., 1946, III, 569.

[22] A. O. Shaw, H. H. Biswell, J. E. Foster, and R. W. Collins, *North Carolina Agric. Exp. Sta.*, 1943, *Bull.* 342; B., 1946, III, 99. J. Milne, *Vet. Rec.*, 1945, **57**, 30; A., 1946, III, 299. F. P. Mathews, *Cornell Vet.*, 1945, **35**, 336; A., 1946, III, 1067. G. K. Sharma, *Indian Farming*, 1945, **6**, 72; B., 1946, III, 12.

[23] H. S. Purchase, *Vet. Rec.*, 1945, **57**, 211; A., 1946, III, 300.

[24] *Cereal Chem.*, 1945, **22**, 514; B., 1946, III, 117. *Ibid.*, 1946, **23**, 135; A., 1946, III, 932.

numerous feed materials, including grains and grain by-products, distillers' and animal by-products, vegetable protein concentrates, and feed supplements. The amino-acid requirements of chicks have been more closely defined,[25] and empirical studies on feeding poultry with mixtures of animal and vegetable proteins have been continued.[26]

H. E. Woodman and R. E. Evans[27] have found that two lots of pigs on the same basal ration of cereal, weatings, and grass meal reached 200 lb. live weight at the same age although one lot received a supplement of 10% of fish meal up to 150 lb. live weight and a 5% supplement subsequently, whereas the other lot received only a 7% supplement up to 90 lb. live weight. Lucerne and grass proteins are of considerable value to pigs, although they cannot completely replace meat proteins.[28] Sardine meal contains some substance particularly valuable to pigs during growth, gestation, and lactation.[29]

Norwegian experiments have shown that urea-nitrogen can replace satisfactorily one quarter of the protein-nitrogen of the diet of dairy cattle.[30] More details of British and American work on non-protein-nitrogen utilisation by ruminants are available.[31] It has been shown that breeding cows can be wintered economically on forest range when given a daily ration of 6 lb. of cottonseed meal or soya-bean oil meal.[32]

Raw soya beans contain a substance which inhibits trypsin and reduces the availability of cystine and methionine to chicks; this substance is inactivated by autoclaving and has been isolated in crystalline form.[33] Peanut protein in excess also appears to have deleterious effects.[34]

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[25] H. J. Almquist, *Trans. Amer. Assoc. Cereal Chem.*, 1945, **3**, 158; A., 1946, III, 1041. C. R. Grau and D. W. Peterson, *J. Nutrition*, 1946, **32**, 181; A., 1946, III, 1042.

[26] A. W. Brant, C. I. Draper, and R. J. Evans, *Washington Agric. Exp. Sta.*, 1944, *Bull.* 441; B., 1946, III, 118. C. R. Grau and H. J. Almquist, *Proc. Soc. Exp. Biol. Med.*, 1945, **60**, 373; A., 1946, III, 568. A. R. Patton, J. P. Marvel, H. G. Petering, and J. Waddell, *J. Nutrition*, 1946, **31**, 485; A., 1946, III, 658.

[27] *J. Agric. Sci.*, 1945, **35**, 133; B., 1946, III, 27.

[28] C. E. Ballinger, *New Zealand J. Agric.*, 1944, **69**, 101; B., 1946, III, 118. F. B. Headley, *Nevada Agric. Exp. Sta.*, 1945, *Bull.* 175; B., 1946, III, 117. *J. Animal Sci.*, 1946, **5**, 251; B., 1946, III, 259.

[29] E. F. Ferrin, *ibid.*, 1946, **5**, 42; B., 1946, III, 239. J. L. Krider, B. W. Fairbanks, R. F. Van Poucke, D. E. Becker, and W. E. Carroll, *ibid.*, 256; B., 1946, III, 259.

[30] O. Ulvesli, *Norsk Landbruk*, 1942, **8**, 352; B., 1946, III, 179.

[31] R. C. Johnson, T. S. Hamilton, W. B. Robinson, and J. C. Garey, *J. Animal Sci.*, 1944, **3**, 287; A., 1946, III, 467. J. A. B. Smith, *Proc. Nutrition Soc.*, 1945, **3**, 203; A., 1946, III, 284. J. K. Loosli and L. E. Harris, *J. Animal Sci.*, 1945, **4**, 435; A., 1946, III, 467.

[32] J. E. Foster, H. H. Biswell, and E. H. Hostetler, *J. Animal Sci.*, 1945, **4**, 387; B., 1946, III, 142.

[33] W. E. Ham, R. M. Sandstedt, and F. E. Mussehl, *J. Biol. Chem.*, 1945, **161**, 635; A., 1946, III, 283. A. A. Klose, B. Hill, and H. L. Fevold, *Proc. Soc. Exp. Biol. Med.*, 1946, **62**, 10; A., 1946, III, 1048. R. J. Evans and J. McGinnis, *J. Nutrition*, 1946, **31**, 449; A., 1946, III, 750. M. Kunitz, *J. Gen. Physiol.*, 1946, **29**, 149; A., 1946, III, 402.

[34] E. Aubertin, A. Dangoumau, and R. Castagnou, *J. Physiol. Path. gén.*, 1941–45, **38**, 282; A., 1946, III, 566.

Hormones and Vitamins.

K. L. Blaxter[35] has reported extensive trials on the effect of iodinated protein on milk production; these trials, involving over 1000 cows of 7 breeds on 97 farms throughout England and Wales, showed that a daily dose of 20 g. of iodinated protein for 6 weeks with additional concentrated foods increased the average daily milk yield by 5·44 lb. or 22·2%, mature cows responding best. The effect is to stimulate the metabolic rate. Careful control is needed, but it is estimated that this treatment could increase the milk supply of many herds by 10% during February and March. D. M. Seath, C. Branton, and A. H. Groth[36] have reported similar results.

Experiments on the use of hormones as fattening agents for poultry are continuing.[37]

There have been several studies of the effects of deficiency of vitamin-*A* and carotene in cattle, sheep, and pigs.[38] During gestation, vitamin-*A* is passed more readily from parent to embryo than is carotene; after birth, calves depend on vitamin-*A* from colostrum for 3—7 days.[39] The chemically-determined carotene in green fodders is 85—98% pure, as shown by chromatographic adsorption, whereas that from hay is about 36·5% pure and from silage, 32·5%.[40] Two investigations of seasonal variations during 2 years of carotene and vitamin-*A* values of butter fat and serum have shown abrupt rises on turning out to pasture.[41] In butter, vitamin-*A* appears to be in solution in the fat, whereas the carotenoids and cholestrol are associated with the fat globule membrane.[42] The carotene contents of various Palestinian crops have been determined.[43] Nitrous acid has been found to have a destructive effect on carotenoids and on ascorbic acid, and it has been suggested that it may be produced from nitrate-containing plants during ensilage.[44] S. D. Rao and B. N. Banerjee[45] have reported losses of about 50% in the vitamin-*A* content of shark-liver oil stored for 18—23 months; the destruction does

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[35] *J. Agric. Sci.*, 1946, **36**, 117; A., 1946, III, 659.

[36] *J. Dairy Sci.*, 1945, **28**, 509; A., 1946, III, 378.

[37] H. S. Gutteridge, *U.S. Egg and Poultry Mag.*, 1945, **51**, 398; B., 1946, III, 53. E. E. Schnetzler, F. N. Andrews, and S. M. Hauge, *ibid.*, 554; B., 1946, III, 118.

[38] S. Norfeldt, *Landbr. Hogsk. Ann.*, 1944–45, **12**, 204; A., 1946, III, 1044. J. M. Lewis and L. T. Wilson, *J. Nutrition*, 1945, **30**, 467; A., 1946, III, 285. A. W. Pierce, *Austral. J. Exp. Biol.*, 1945, **23**, 295; A., 1946, III, 569. L. A. Moore, *J. Nutrition*, 1946, **31**, 229; A., 1946, III, 569. P. R. Frey and R. Jensen, *ibid.*, 1946, **32**, 133; A., 1946, III, 1044.

[39] G. H. Wise, M. J. Caldwell, and J. S. Hughes, *Science*, 1946, **103**, 616; A., 1946, III, 1044. T. S. Sutton and H. E. Kaeser, *J. Dairy Sci.*, 1946, **29**, 13; A., 1946, III, 569.

[40] B. C. R. Sarkar and K. C. Sen, *J. Agric. Sci.*, 1946, **36**, 95; A., 1946, III, 660.

[41] J. W. Lord, *Biochem. J.*, 1945, **39**, 372; A., 1946, III, 49. T. S. Sutton and P. A. Soldner, *J. Dairy Sci.*, 1945, **28**, 859; A., 1946, III, 531.

[42] S. K. Kon, E. H. Mawson, and S. Y. Thompson, *Nature*, 1944, **154**, 82; A., 1946, III, 49.

[43] A. Bondi and H. Meyer, *J. Agric. Sci.*, 1946, **36**, 1; B., 1946, III, 141.

[44] J. K. Wilson, *Cornell Agric. Exp. Sta.*, 1945, *Mem.* 271; B., 1946, III, 141.

[45] *Indian J. Med. Res.*, 1944, **32**, 155, 161; A., 1946, III, 935. *Ibid.*, 1946, **34**, 91; A., 1946, III, 1045.

not appear to be affected by the water content or rancidity of the oil, but is catalysed by the free fatty acids produced.

It has been again confirmed that cattle do not usually require *B*-vitamins other than those produced in the alimentary tract.[46] P. B. Pearson and A. L. Darnell (with J. Weir)[47] have determined the aneurin, riboflavin, nicotinic acid, and pantothenic acid contents of the colostrum and milk of cows and ewes ; high aneurin values persist in colostrum ten days after parturition. A considerable amount of work has been done on the storage and retention of *B*-vitamins in the muscles of pigs and poultry, and there is probably a correlation between muscle colour, vitamin content, and function.[48] Nicotinic acid appears to rectify the effects of a low or unsuitable protein diet, and deficiency in this vitamin is considered to be one of the causes of perosis in poultry.[49] Bees are susceptible to deficiency of riboflavin, normally derived from pollen.[50] Two compilations of riboflavin contents of various feeding stuffs have appeared.[51] Biotin deficiency has been induced experimentally in pigs by feeding 30% of desiccated egg white in the diet, and its effects have been studied.[52]

The vitamin-*D* requirements of cows and sheep have been reviewed.[53] Discrepancies have been observed in the vitamin-*D* requirements of turkey poults ; these have been traced to the fact that phytin-phosphorus is more readily available in the presence of vitamin-D_3 than in the presence of cod-liver oil.[54]

The incidence of a condition described as "stiff lamb disease" has been reduced by the addition of wheat-germ oil or of synthetic *dl*-α-tocopherol to the diet of pregnant ewes or of newly-born lambs.[55] A cerebellar disorder of nutritional origin in chicks was found not to be due to *E*-avitaminosis.[56] Certain congenital malformations in pigs have been

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[46] S. K. Kon, *Proc. Nutrition Soc.*, 1945, **3**, 217 ; A., 1946, III, 284. C. L. Norton, *J. Dairy Sci.*, 1945, **28**, 927 ; B., 1946, III, 157.

[47] *J. Nutrition*, 1946, **31**, 51 ; A., 1946, III, 380.

[48] M. E. Ensminger, W. W. Heinemann, T. J. Cunha, and E. C. McCulloch, *Washington Agric. Exp. Sta.*, 1945, *Bull.* 468 ; A., 1946, III, 570. J. W. Pence, R. C. Miller, R. A. Dutcher, and P. T. Ziegler, *J. Animal Sci.*, 1945, **4**, 141 ; A., 1946, III, 469. E. E. Rice, E. J. Strandine, E. M. Squires, and B. Lyddon, *Arch. Biochem.*, 1946, **10**, 251 ; A., 1946, III, 936. W. W. Heinemann, M. E. Ensminger, T. J. Cunha, and E. C. McCulloch, *J. Nutrition*, 1946, **31**, 107 ; A., 1946, III, 380.

[49] M. M. Wintrobe, H. J. Stein, R. H. Follis, jun., and S. Humphreys, *J. Nutrition*, 1945, **30**, 395 ; A., 1946, III, 286. G. M. Briggs, *J. Biol. Chem.*, 1945, **161**, 749 ; A., 1946, III, 381. G. M. Briggs, *J. Nutrition*, 1946, **31**, 79 ; A., 1946, III, 381.

[50] M. H. Haydak, *J. Econ. Entom.*, 1945, **38**, 484 ; A., 1946, III, 378.

[51] E. V. Evans, D. M. Young, and H. D. Branion, *Sci. Agric.*, 1945, **25**, 542 ; B., 1946, III, 117. A. Bondi and H. Meyer, *J. Agric. Sci.*, 1946, **36**, 6 ; B., 1946, III, 158.

[52] T. J. Cunha, D. C. Lindley, and M. E. Ensminger, *J. Animal Sci.*, 1946, **5**, 219 ; A., 1946, III, 753.

[53] G. C. Wallis, *S. Dakota Agric. Exp. Sta.*, 1944, *Bull.* 372 ; A., 1946, III, 382. E. D. Andrews and I. J. Cunningham, *New Zealand J. Sci. Tech.*, 1945, **27**, **A**, 223 ; A., 1946, III, 471.

[54] L. D. Matterson, H. M. Scott, and E. P. Singsen, *J. Nutrition*, 1946, **31**, 599 ; A., 1946, III, 755.

[55] J. P. Willman, J. K. Loosli, S. A. Asdell, F. B. Morrison, and P. Olafson, *J. Animal Sci.*, 1945, **4**, 128 ; A., 1946, III, 471.

[56] F. H. Bird, *J. Biol. Chem.*, 1945, **161**, 747 ; A., 1946, III, 383.

traced to combined deficiencies of lecithin, pyridoxine, choline, and inositol in the sow's diet.[57]

Our knowledge of the chemistry and functions of folic acid and of its variants (vitamin-*M*, -B_c, -B_{10}, -B_{11}, eluate factor and *L. casei* factor) is becoming clarified, and it appears that the known synthetic vitamins of this group are adequate for normal feathering and pigmentation in chicks.[58] Experiments with folic acid in the presence and absence of sulphonamides indicate that folic acid stimulates intestinal synthesis of an antiperosis factor.[59] A chick growth factor in cow manure has not yet been identified with any of the folic acid group.[60]

Mineral Requirements.

The mineral requirements of farm animals are supplied partly from natural and partly from artificial sources; it may be of advantage in some cases to apply supplementary mineral substances as fertilisers. The calcium, magnesium, and phosphorus contents of kale can thus be increased, but in so doing the iron content may be reduced.[61] Defluorinated rock phosphate is not such a good source of calcium and phosphorus for chicks, pigs, or rats as bone phosphate or superphosphate; the heat-treatment to remove fluorine may produce calcium metaphosphate, which causes low ash content in bones when fed to chicks.[62] It appears to be immaterial whether limestone is fed to poultry in powder or grit form, provided the amount of calcium consumed is within the optimum range for the particular stage of development.[63] The relationship between the level of dietary calcium and egg-shell thickness and porosity is complex; low-calcium diets do not necessarily produce soft-shelled eggs and high-calcium diets do not prevent their production. Manganese deficiency has an adverse effect on egg-shell quality.[64]

Diseases resulting from deficiency or excess of trace elements are now

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[57] T. J. Cunha, O. B. Ross, P. H. Phillips, and G. Bohstedt, *J. Animal Sci.*, 1944, **3**, 415; A., 1946, III, 657. O. B. Ross, P. H. Phillips, G. Bohstedt, and T. J. Cunha, *ibid.*, 406; A., 1946, III, 657.

[58] Anon., *Lancet*, 1946, **251**, 680. B. L. Hutchings, J. J. Oleson, and E. L. R. Stokstad, *J. Biol. Chem.*, 1946, **163**, 447; A., 1946, III, 1048. D. V. Frost, F. P. Dann, and F. C. McIntire, *Proc. Soc. Exp. Biol. Med.*, 1946, **61**, 65; A., 1946, III, 660. T. D. Luckey, P. R. Moore, C. A. Elvehjem, and E. B. Hart, *Science*, 1946, **103**, 682; A., 1946, III, 937.

[59] L. J. Daniel, F. A. Farmer, and L. C. Norris, *J. Biol. Chem.*, 1946, **163**, 349; A., 1946, III, 838.

[60] M. Rubin and H. R. Bird, *ibid.*, 387, 393; A., 1946, III, 663.

[61] A. D. Holmes, L. V. Crowley, and J. W. Kuzmeski, *Food Res.*, 1945, **10**, 401; B., 1946, III, 39.

[62] C. L. Shrewsbury and C. M. Vestal, *J. Animal Sci.*, 1945, **4**, 403; A., 1946, III, 468. E. S. McConnell, W. M. Insko, jun., and G. D. Buckner, *Kentucky Agric. Exp. Sta.*, 1944, *Bull.* 455; B., 1946, III, 118.

[63] L. R. Berg, G. E. Bearse, and V. L. Miller, *Washington Agric. Exp. Sta.*, 1944, *Bull.* 458; B., 1946, III, 158. D. J. G. Black, *J. Agric. Sci.*, 1946, **36**, 199; B., 1946, III, 239.

[64] C. Tyler, *J. Agric. Sci.*, 1945, **35**, 168; A., 1946, III, 48. *Ibid.*, 1946, **36**, 111; A., 1946, III, 659. M. Lyons, *Arkansas Agric. Exp. Sta.*, 1939, *Bull.* 374; A., 1946, III, 379.

receiving considerable attention. Copper and cobalt deficiencies are prevalent in various parts of the world.[65] Experiments with radioactive cobalt show that, in cattle, retention occurs in the abomasum and, to a limited extent, in the liver.[66] Applications of molybdenum (about 1 oz. per acre) have a beneficial effect on herbage legumes in South Australia,[67] but amounts in excess of 30 p.p.m., reckoned on the dry matter of the herbage, may be deleterious to livestock.[68] Symptoms of selenium poisoning occurring in steers grown on seleniferous ranges may be reduced by the inclusion of 25 p.p.m. of arsenic in the salt supplied.[69] W. O. Robinson and G. Edgington[70] have made an extensive study of the tendencies of various economic plants and weeds to accumulate trace elements, and there have been many reviews of the effects of specific elements in plant nutrition with incidental references to the subsequent use of the plants as food.[71]

Pasture Management.

Means of maintaining the productivity of hill pastures and of arid regions have been studied.[72] The problems are botanical rather than chemical, although some progress has been made in the study of chemical changes associated with drought-resistance.

Crop Preservatives.

S. J. Watson[73] has reviewed the subject of nutrient loss in the conservation of farm crops and of animal feeding stuffs. Common salt applied to hay at the rate of 25—45 lb. per ton reduced thermogenesis and mouldiness, and 10 lb. of salt per ton of grass–clover silage is beneficial.[74] J. G. Archibald[75] has studied carotene and nitrogen losses in silage, and the

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[65] G. Dunlop, *Proc. Nutrition Soc.*, 1946, **4**, 69 ; A., 1946, III, 569. O. T. Engdal and O. Ulvesli, *Norg. Landbrukshøgsk. Inst. Husdyr.*, 1942, *Circ.* 7 ; A., 1946, III, 197 *Fôringsforsøk. Norges Landbrukshøgsk.*, 1942, *No.* 52 ; B., 1946, III, 79. I. J. Cunningham, *New Zealand J. Agric.*, 1944, **69**, 559 ; B., 1946, III., 68. *New Zealand J. Sci. Tech.*, 1946, **27**, **A**, 381 ; A., 1946, III, 1043. R. Brandl, *J. Agric. Sci.*, 1945, **35**, 163 ; A., 1946, III, 49. R. P. Geyer, I. W. Rupel, and E. B. Hart, *J. Dairy Sci.*, 1945, **28**, 291 ; A., 1946, III, 197.

[66] C. L. Comar, G. K. Davis, and R. F. Taylor, *Arch. Biochem.*, 1946, **9**, 149 ; A., 1946, III, 573. C. L. Comar, G. K. Davis, R. F. Taylor, C. F. Huffman, and R. E. Ely, *J. Nutrition*, 1946, **32**, 61 ; A., 1946, III, 1051.

[67] A. J. Anderson, *J. Counc. Sci. Ind. Res., Australia*, 1946, **19**, 1 ; B., 1946, III, 229.

[68] *Ann. Repts.*, 1943, **28**, 381. H. L. Jensen, *Proc. Linnean Soc. N.S. Wales*, 1945, **70**, 203.

[69] A. L. Moxon, M. A. Rhian, H. D. Anderson, and O. E. Olson, *J Animal Sci.*, 1944, **3**, 299 ; A., 1946, III, 468.

[70] *Soil Sci.*, 1945, **60**, 15.

[71] J. S. McHargue, *ibid.*, 115 ; B., 1946, III, 252. D. R. Hoagland, *ibid.*, 119 ; B., 1946, III, 252. S. F. Trelease, *ibid.*, 125 ; B., 1946, III, 250. T. Walsh, *Nature*, 1945, **155**, 429 ; B., 1946, III, 39.

[72] O. Julander, *Plant Physiol.*, 1945, **20**, 573 ; B., 1946, III, 39. M. Jones, *Proc. Nutrition Soc* , 1946, **4**, 58 ; B., 1946, III, 157.

[73] *Proc. Nutrition Soc.*, 1946, **4**, 176 ; B., 1946, III, 201.

[74] H. G. Robinson and A C. Burns, *J. Min. Agric.*, 1945, **52**, 100 ; B., 1946, III, 79. R. Phillips, R. O. Davies, and W. M. Ashton, *ibid.*, 98 ; B., 1946, III, 79.

[75] *J. Agric. Res.*. 1946, **72**, 277 ; B., 1946, III, 201.

use of pure lactic cultures has been suggested as a means of avoiding undesirable by-products.[76] Mangold leaf silage has been used with some success for pigs and cattle.[77]

J. B. Firth and R. E. Stuckey[78] have continued their investigation of methods of determining whether burnt hay has been ignited spontaneously.

Processed Feeding Stuffs and Waste Products.

Methods for preparing protein feeds by growing micro-organisms (*e.g.*, *Torula utilis*, *Candida arborea*, and *Oidium lactis*) on hydrolysed wood and on sulphite waste liquor have been developed in America, Austria, and Germany.[79] Shark meal and seal meal are potential sources of protein; the production of fish flavour in pork fed on fish meal can be avoided by keeping the fish oil content of the diet below 1—2%.[80] The value and shortcomings of distillers' by-products for feeding pigs and cattle have been fully investigated.[81] More information is available concerning the feeding values, inorganic constituents, and phytic acid contents of grass seeds and seed cleanings.[82] Analyses of 80 types of feeding stuffs available in Canada have been recorded.[83] Methods for ensiling kitchen waste with acid in ordinary silos or in casks have been described.[84] In Norway, the composition and feeding value of forest waste were studied; coniferous needles, deciduous leaves, and some lichens were useful in emergency.[85] H. E. Woodman and R. E. Evans[86] have investigated the feeding value of horse-chestnuts for sheep and pigs; provided the saponins (which have some commercial value) are thoroughly extracted, they are a useful

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[76] J. A. Jessop and J. W. Morley, B.P. 575,262; B., 1946, III, 143.

[77] O. Ulvesli, *Fóringsforsøk. Norges Landbrukshøgsk.*, 1941, *No* 50; B., 1946, III, 142. K. Presthegge, *ibid.*, 1944, *No.* 56; B., 1946, III, 142.

[78] *J.S.C.I.*, 1946, **65**, 275; B., 1946, III, 252.

[79] R. D. Walker, jun., and R. A. Morgen, *Paper Trade J.*, 1946, **123**, *TAPPI Sect.*, 63; B., 1946, III, 239. P. L. Pavcek, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXVIII-42; B., 1946, III, 217. *Ibid.*, XXVIII-34; B., 1946, III, 218. H. J. Bunker, *ibid.*, XXIX-4; B., 1946, III, 217. *Ibid.*, XXIX-5; B., 1946, III, 218. D. B. Dill, *ibid.*, XXIV-11; B., 1946, III, 218. J. F. Saeman, E. G. Locke, and G. K. Dickerman, *Field Information Agency, Technical*, 1945, *Final Rept.* 450. D. H. F. Clayson, G. A. Ledingham, and A. K. Balls, *Brit. Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *Final Rept.* 236.

[80] M. M. Black, W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg, *J.S.C.I.*, 1945, **64**, 326; B., 1946, III, 51. S. P. Marshall and G. K. Davis, *J. Animal Sci.*, 1946, **5**, 211; A., 1946, III, 749. C. M. Vestal, C. L. Shrewsbury, R. Jordan, and O. Milligan, *ibid.*, 1945, **4**, 63; B., 1946, III, 178.

[81] R. E. Synold, *J. Animal Sci.*, 1945, **4**, 237; B., 1946, III, 157. B. W. Fairbanks, J. L. Krider, and W. E. Carroll, *ibid.*, 420; B., 1946, III, 157. W. H. Black, N. R. Ellis, and W. P. Garrigus, *ibid.*, 158; B., 1946, III, 157.

[82] W. A. Rutledge and R. H. Common, *J. Agric. Sci.*, 1945, **35**, 123; B., 1946, III, 27.

[83] I. Motzok, D. C. Hill, and H. D. Branion [with W. D. M. Graham and H. W. Schmaltz], *Sci. Agric.*, 1945, **25**, 525; B., 1946, III, 116.

[84] M. Husby, *Vestlandsk Landbr.*, 1943, **30**, 135; B., 1946, III, 141. *Norsk Landbruk*, 1941, **7**, 200; B., 1946, III, 158.

[85] K. Presthegge, *Fóringsforsøk. Norges Landbrukshøgsk.*, 1943, *No.* 54; B., 1946, III, 79. *Vestlandsk Landbr.*, 1943, **30**, 75; B., 1946, III, 142. *Norsk Landbruk*, 1944, **10**, 208; B., 1946, III, 53.

[86] *J Agric. Sci.*, 1946, **36**, 29, 42; B., 1946, III, 156.

source of digestible carbohydrate, but the residue after diastatic extraction of starch for glucose manufacture is of little value. The sea-weed, *Laminaria flexicaulis*, after extraction with lime and drying, is reported to be a good feed for horses, cattle, and poultry.[87]

FRUIT AND VEGETABLES.

Vitamins.

The urgency and practical purpose of work on vitamins in fruit and vegetables which have been noticeable during the past few years were not so marked for this past year, and there is, as would be expected, more attention to the fundamental viewpoint. A. Pollard, M. E. Kieser, and J. D. Bryan,[88] who in a study of the factors influencing the ascorbic acid and sugar contents and the acidity and pH of tomatoes grown under glass or in the open, found that, while variety was one factor concerned, the most important was the amount of sunlight received. The lower ascorbic acid content of glasshouse fruit was confirmed as being due to the reduction in the light intensity caused by the glass. The work has been confirmed, so far as field tomatoes are concerned, by G. F. Somers, K. C. Hamner, and W. L. Nelson,[89] who measured, with a photoelectric cell, the light received by the fruit in the 18 days prior to harvesting and found a direct correlation between the amount of light received and the ascorbic acid content. These authors also showed that there was little loss in ascorbic acid during the usual harvesting and transport.

The value of the sprouts of various leguminous seeds as sources of vitamins has received some detailed attention. W. A. Andreae, E. A. Chalmers, and W. D. McFarlane[90] showed that pea sprouts grown for 11 days contained 22·2—27·0 mg. of ascorbic acid per 100 g., and that the riboflavin content was high (about 100 mg. per 100 g.); irradiation of the sprouts with ultra-violet light during growth was without effect. The sprouts of navy, broad, and soya beans were found to be good sources of both ascorbic acid and riboflavin. The increases in the ascorbic acid, riboflavin, and nicotinic acid contents of peas and beans on sprouting have been reconfirmed by P. R. Burkholder and I. McVeigh.[91]

An interesting study has been made by Teng-Yi Lo and Shan-Ming Chen[92] of the effect of moistening beans with solutions of a number of salts during sprouting. It was found that the use of 10^{-6}N. solutions of zinc or nickel or magnesium salts with a complete fertiliser (ammonium sulphate, bone meal, and straw ash 3 : 1 : 4) resulted in an increase of the ascorbic acid content of the fruit by as much as 100%; similar effects were noted when the solutions were fed to growing tomato and lettuce plants.

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[87] L. Lapicque, *Compt. rend.*, 1941, **212**, 875; B., 1946, III, 179.
[88] *Ann. Rept. Agric. Hort. Res. Sta., Long Ashton*, 1945, 203; B., 1947, III, 25.
[89] *J. Nutrition*, 1945, **30**, 425; A., 1946, III, 381.
[90] *Sci. Agric.*, 1945, **25**, 504; B., 1946, III, 77.
[91] *Plant Physiol.*, 1945, **20**, 301; A., 1945, III, 704.
[92] *Proc. Inst. Food Tech.*, 1945, 154.

An allied study made by F. L. Wynd and G. R. Noggle[93] on the influence of the chemical characteristics of soil on growth showed that an increase in replaceable calcium and magnesium gave a higher ascorbic acid content in oats.

As a result of the examination of many varieties of English apples, A. Pollard, M. E. Kieser, and J. D. Bryan[94] have shown that these fruits may be a better source of ascorbic acid than is generally supposed; typical values (mg. per 100 g.) obtained were : dessert varieties 3·7—6·3, culinary varieties 3·7—18·1, and cider varieties 9·1—34·1.

A considerable amount of work has been published on the use of added ascorbic acid for the purpose of preventing browning of cut or frozen fruits. J. C. Bauernfeind and G. F. Siemers[95] have conducted experiments on the addition of ascorbic acid to the sugar or syrup used to cover sliced apples prior to freezing (1 oz. of ascorbic acid, 25 lb. of sugar, 125 lb. of apple). The treatment was effective if rapid penetration was achieved by fine slicing of the apple : a "Julienne" type of slicing was recommended. The stability of such added ascorbic acid has also been studied. J. C. Bauernfeind, F. W. Jahns, E. G. Smith, and G. F. Siemers[96] found that 80% or more of the added ascorbic acid was retained in thawed sliced peaches, apricots, and nectarines which had been frozen for 8—10 months.

A similar extent of retention was found by W. B. Esselen, jun., J. J. Powers, and C. R. Fellers[97] for ascorbic acid added to apple, cranberry, and grape juices (50 mg. per 100 ml. added) which were bottled and stored for 8—12 months ; the addition prevented darkening of the juice during storage. Darkening of frozen peaches due to the action of oxidase on pyrocatechol tannin, which also gives rise to "off" flavours, was found by E. H. Wiegand[98] to be prevented by the addition of ascorbic acid.

Preservation.

Dehydration.—In a study of the storage properties of dried cabbage, potato, and sweet potato in controlled conditions of temperature and moisture content over a period of one year, M. F. Mallette, C. R. Dawson, W. L. Nelson, and W. A. Gortner[99] showed that discoloration and the development of "off" flavours accompanied by loss of ascorbic acid occurred, if the moisture content was greater than 7%, at temperatures of 70—80° F. ; other vitamins were stable. A sulphur dioxide blanching treatment prior to drying resulted in an improved ascorbic acid retention. The data obtained did not support the view that deterioration was due to inadequate inactivation of oxidative enzymes. In the course of a similar

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[93] *Food Res.*, 1945, **10**, 525, 537 ; B., 1946, III, 63.

[94] *Ann. Rept. Agric. Hort. Res. Sta., Long Ashton*, 1945, 200; B., 1947, III, 35.

[95] *Fruit Prod. J.*, 1946, **26**, 4; B., 1947, III, 35.

[96] *Ibid.*, **25**, 324.

[97] *Ibid.*, **26**, 11; B., 1947, III, 35.

[98] *Quick Frozen Foods*, 1946, **8**, *No.* 9, 81, 92.

[99] *Ind. Eng. Chem.*, 1946, **38**, 437; B., 1946, III, 175.

study M. B. Patton and D. Comin[100] obtained no correlation between the effects of various methods of storage (glass jars, sealed and unsealed, and bags of Pliofilm) and the losses of carotene and aneurin from dried peas, corn, beans, peaches, and plums stored at 75—80° F.

A claim for an improved method of blanching vegetables prior to drying is made by W. G. Wager and A. J. Ede[101] by which the conventional water and steam methods are replaced by a blast of hot air (dry bulb temperature 110—130° C., wet bulb 95°); the time required to inactivate peroxidase is about 5 minutes, and improvements in the quality and in vitamin retention are claimed.

Canning.—Little work has been reported on the canning of fruit and vegetables. The work on tomatoes noted above has, however, been extended by W. B. Robinson, E. Stotz, and Z. I. Kertesz[102] to include investigation of the loss of ascorbic acid occurring during the commercial production of canned tomato juice. A total loss of 15—19% occurred, chiefly during the pulping stage; there was little or no loss during the actual canning.

M. K. Veldhuis[103] has studied the production of carbon dioxide in canned concentrated orange juice, and found that the ascorbic acid is either the source of the carbon dioxide or acts as a catalyst in promoting decomposition. Improvements in quality were obtained by removing the fatty constituents (peel, oil, etc.) by solvent extraction, and promising results were obtained by the return to the juice of the "ester trap" constituents separated during concentration.

Storage.—A comprehensive study of the changes occurring during the storage of dried fruit has been made by E. R. Stadtman, H. A. Barker, V. Haas, E. M. Mrak, and G. Mackinney.[104] The degree of darkening correlated with the oxygen consumed, which was found to be greatly increased by (*a*) increasing the moisture content in the range 10—25%, (*b*) increasing the partial pressure of oxygen, and (*c*) increasing the temperature. It was found that 30—45% of the oxygen consumed was utilised in oxidising sulphur dioxide, and that below 43° C. the deterioration was due entirely to loss of sulphur dioxide. Prolongation of the storage life is therefore obtained by decreasing the moisture content, reducing the available oxygen (*e.g.*, by tight packing), and storing in cool conditions. E. R. Stadtman, H. A. Barker, V. Haas, and E. M. Mrak[105] found that the logarithms of the rates of sulphur dioxide loss, of carbon dioxide production, and of oxygen consumption were each related to the reciprocal of the storage temperature (degrees absolute) in a linear manner in agreement with the Arrhenius equation, and they suggest that either the same reaction controls the rates at all temperatures or, at least,

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[100] *Ohio Agric. Exp. Sta. Bi-monthly Bull.*, 1945, **30**, 157.
[101] B.P. 576,307; B., 1946, III, 159.
[102] *J. Nutrition*, 1945, **30**, 435; B., 1946, III, 111.
[103] *Citrus Ind.*, 1946, **27**, *No.* 2, 3; *No.* 3, 11.
[104] *Ind. Eng. Chem.*, 1946, **38**, 324; B., 1946, III, 176.
[105] *Ibid.*, 541; B., 1946, III, 200.

the reactions have similar temperature coefficients. The work is of practical value in that the storage life at any temperature (within normal limits) may be obtained from the experimental results at one temperature only.

Miscellaneous.

Several communications have been made on the factors affecting stem-end blackening of potatoes, *i.e.*, blackening after cooking. For example, H. G. Wager[106] found that the blackening is due to a single pigment (not melanin), the intensity of the grey colour of which markedly increases as the pH value is made higher. The absorption coefficient of an aqueous extract exhibited a marked increase at pH 6·5 when the pH value was adjusted from 1·5 to 9·5. A. Pollard, M. E. Kieser, A. Crang, and T. Wallace[107] have confirmed the previous finding that variations in the quality of potatoes (including the liability to blacken) are associated with the soil on which the potatoes are grown rather than on varietal differences, although there is a general tendency for certain varieties (notably Majestic) to be more prone to blackening than others (*e.g.*, Kerr's Pink and Red King). Practical methods of reducing the blackening during cooking by the addition of acetic acid or sulphur dioxide have been reported by A. Crang, D. James, and M. Sturdy.[108]

A study of the acids present in lemons[109] and grapefruit[110] has been made by W. B. Sinclair and D. M. Eny. In both fruits citric and malic acids predominate, and methods of differentiation and estimation are discussed together with the variations likely to occur.

CEREALS AND CEREAL FOODS.

R. Guillemet, in a paper entitled "The rational milling of wheat,"[111] summarises the advances made in cereal chemistry and the modification in milling methods introduced to make use of this knowledge. He concludes that a flour of 80—85% extraction including the maximum proportion of the wheat germ and the minimum amount of bran is a practical compromise between the conflicting claims of the dietician, the baker, and the miller.

Phytic Acid.—One of the minor constituents of flour which is of considerable dietetic importance is phytic acid (inositolhexaphosphoric acid). Phytic acid is the form in which phosphorus is stored in resting seeds and from which the phosphorus is freed for the use of the growing plant by the action of the enzyme phytase. Wheat contains both phytic acid and phytase, concentrated in the outer, branny layers of the seed; the phytic acid (and phytase) of wheat flour therefore increases with the degree of extraction. Phytic acid can combine with calcium

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[106] *Biochem. J.*, 1945, **39**, 482; B., 1946, III, 76.
[107] *Ann. Rept. Agric. Hort. Res. Sta., Long Ashton,* 1945, 209; B., 1947, III, 23.
[108] *Ibid.*, 221; B., 1947, III, 34.
[109] *Bot. Gaz.*, 1945, **107**, 231.
[110] *Plant Physiol.*, 1946, **21**, 140; A., 1946, III, 982.
[111] *Chim. et Ind.*, 1945, **54**, 244; B., 1946, III, 24.

and with iron and render these elements wholly or partly inassimilable, thereby producing dietary deficiency (or even deficiency diseases) from diets having normal total calcium and iron levels. E. Mellanby[112] finds that although in the preparation of bread both flour-phytase and yeast-phytase are active in the destruction of phytic acid, their relative importance depending on the yeast content of the dough and on the length of the period of fermentation, the total extent of phytic acid destruction in breadmaking is 60—70% of that present in the flour.

There is, as yet, incomplete agreement as to the extent to which a dietary change from bread made with short-extraction flour to bread made with long-extraction flour may affect the calcium balance.[113] Addition of calcium (as $CaCO_3$) to the flour is the usually accepted method of preventing "calcium-stealing" by phytic acid.

Wheat Enzymes.—The vexed question of the rôle of proteolytic enzymes in the preparation of bread dough continues to receive attention. Supporters of the Jorgensen theory have ascribed softening that takes place in dough on standing to the action of "latent" proteolytic enzymes, activated by reducing substances present in the dough. M. Howe,[114] using a method which employs hexylresorcinol or sodium fluoride as an inhibitor of protease activity,[115] presents contrary evidence. The protease activity of aqueous extracts of wheat germ was found to be inhibited to the extent of 60% by addition of hexylresorcinol (40 mg. per 100 g.) or of sodium fluoride (30 mg. per 100 g.), the germ extract being buffered with sodium acetate to pH 5, the optimum for protease action. Applying these reagents to flour doughs and using the Farinograph as the method of depicting dough "strength," it was found that the addition of aqueous extract of wheat germ to the flour dough produced the expected breakdown in dough strength but that the addition of the protease inhibitors (and also inactivating the protease by heating at 80° c. for 35 minutes) failed to counteract the breakdown caused by the wheat-germ extract. The evidence is interpreted as showing that the breakdown caused by the addition of wheat-germ extract is not due to proteolysis.

E. Kneen and H. L. Hads,[116] in work on the effect of variety and environment on the amylases of germinated wheat and barley, have found that in the case of wheat there is a close positive correlation between the nitrogen content of the wheat and its total β-amylase. Germinated wheats having a high β-amylase activity tended also to have a high α-amylase activity.

Dough Structure.—The water-soluble substances in dough have generally been studied only in dilute solutions made by extracting flour

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[112] *Nature*, 1944, **154**, 394 ; B., 1946, III, 49.

[113] A. R. P. Walker, J. T. Irving, and F. W. Fox, *ibid.*, 1946, **157**, 769. E. Hoff-Jørgensen, O. Andersen, H. Begtrup, and G. Nielsen, *Biochem. J.*, 1946, **40**, 453, 555 ; A., 1946, III, 836, 934.

[114] *Cereal Chem.*, 1946, **23**, 84 ; B., 1946, III, 135.

[115] M. Howe and D. Glick, *ibid.*, 1945, **22**, 502 ; B., 1946, III, 105.

[116] *Ibid.*, 407 ; B., 1946, III, 72.

or by leaching dough dispersed in water. J. C. Baker, H. K. Parker, and M. D. Mize,[117] by centrifuging in a Sharples supercentrifuge at 40,000 r.p.m., separated liquid fractions from doughs of 73% water absorption prepared from 25 different flours. The properties of the liquid fractions that were examined included yield, gel value, viscosity, soluble solids, soluble protein, sugars, pentosans, salt, and thiol content. The effect of various dough operations, *e.g.*, mixing, keeping without yeast, fermentation, on the properties of the liquid fractions of the doughs was also examined. The sugar content of the liquid fractions increased during mixing and on subsequent keeping of the dough without yeast. During fermentation a large part of the total sugar was, of course, consumed. Soluble pentosans showed a tendency to increase in amount in the liquid fraction during mixing and keeping; the presence of yeast in the dough did not affect them. The thiol compounds in the liquid fraction were not altered in amount during mixing or keeping of the dough; fermentation caused a marked reduction. During keeping, a physical change takes place in dough which allows more of the liquid fraction to separate. This change is not accompanied by any measurable change in the soluble protein of the dough or in gluten strength and is ascribed to a rearrangement of the components, a relaxation of the strained condition of the gluten micelle produced by mixing allowing the dough solids (starch grains etc.) to pack more closely.

In a second paper[118] the authors study the distribution between the flour components of the water in the dough. Starch and gluten were purified, vacuum-dried, and exposed to the vapour from the liquid fractions centrifuged from doughs, the amount of water absorbed by the starch and gluten in these conditions being taken as a measure of their water-holding capacity in a dough. Dough is considered to consist of (1) a highly viscous liquid rendered slightly elastic by the bonds between the gluten micelles which are dispersed in the liquid and (2) an approximately equal volume of hydrated starch which adds "putty-like" properties.

The importance and extent of the occlusion of gas during the mixing of dough have been determined.[119] The gas content of the dough was measured by determination of its density, and it was found that good bread-making flours occluded gas much more slowly and to a smaller extent than weaker flours. In general the plotted curve of gas occlusion against time of mixing follows in shape the dough-consistence curve obtained in a recording dough-mixer (*e.g.*, Farinograph or Micromixer). It was, however, proved that occulsion of air was not the cause of the increase in dough consistence during mixing, although the phenomenon causing the dough-consistence curve to rise to a maximum also caused the dough to occlude gas. Loaves baked from doughs mixed for various

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[117] *Cereal Chem.*, 1946, **23**, 16; B., 1946, III, 136.
[118] *Ibid.*, 30; B., 1946, III, 136.
[119] J. C. Baker and M. D. Mize, *ibid.*, 39; B., 1946, III, 135.

times showed that the optimum baking value was obtained with a mixing time less than that required for the dough to attain maximum consistence. Severe under-mixing of the dough resulted in a small, coarse-grained loaf because of a lack of sufficient gas nuclei to yield a fine, cellular structure. Over-mixing also resulted in a small loaf of irregular grain caused by coalescence and loss of gas from the dough. It was concluded that, provided a sufficient minimum amount of gas was occluded in the dough, the extent of subdivision of the gas-cells was of more importance than the actual amount of gas in obtaining a fine grain in the bread.

Soya Flour.—There would appear to be a revival of interest in the addition of soya flour to wheat flour for the preparation of bread. It has been claimed that soya protein supplements wheat protein in animal nutrition, increasing its nutritive value by the addition of lysine and other amino-acids in which wheat protein is low. The major objections to the use of soya flour have been the undesirable flavour and the reduction in loaf volume that accompany its use. American workers[120] have found that bread of normal volume can be made from blends of wheat flour and fat-extracted soya flour provided the proportion of potassium bromate added to the flour is increased. The "buffering" action of soya flour on the effect of the addition of bromate is apparently similar to that experienced with milk powder.

MEAT, FISH, EGGS, AND POULTRY.

Since the end of hostilities certain journals have again become available, with the result that work published during the last few years may now be surveyed in addition to the current year's production. In this year's report a number of such papers dealing with the putrefaction of fish are reviewed.

Meat.

The important "Studies on muscle" carried out by A. Szent-Györgyi[121] must be mentioned here although their detailed review belongs properly to the realms of muscle physiology. Fundamental work on the contractile substance of muscle, hitherto considered to be the protein myosin, and the mechanism of contraction is clearly the concern of all those interested in meat technology. Szent-Györgyi and his co-workers found that they could obtain two forms of myosin by extraction of the water-insoluble fraction of muscle with alkaline salt solution, depending on the time of extraction ; short extraction yielded a solution of myosin *A*, which had a low viscosity, and lengthy extraction yielded a solution of myosin *B* of high viscosity. They showed that lengthy extraction yielded a new protein, named actin, which combined with myosin to give the viscous

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[120] K. F. Finney, *Cereal Chem.*, 1946, **23**, 96; B., 1946, III, 135. E. G. Bayfield and E. C. Swanson, *ibid.*, 104 ; B., 1946, III, 135.

[121] *Acta Physiol. Scand.*, 1945, **9**, *Suppl.*, 25 ; *J. Colloid Sci.*, 1946, **1**, 1 ; A., 1946, III, 633.

solution of myosin *B* or actomyosin. Myosin and actin were isolated, the former as a crystalline compound, and it was concluded that previous workers had invariably used myosin more or less heavily contaminated with actin. As a result of the study of the influence of pH, the ions of K, Mg, and Ca, and adenosine triphosphate on the colloidal properties of these proteins the authors have proposed a micelle model to explain muscular contraction on the basis of the shrinkage of a colloid due to the loss of hydrate water. This model, in addition, gives an explanation of the cross-striations of voluntary muscle. In this connexion it may be noted that the magnesium content of 71 samples of meat has been determined by V. Toscani.[122]

C. M. Vestal, C. L. Shrewsbury, R. Jordan, and O. Milligan[123] found that little or no fishy flavour could be detected in the pork from hogs fed on a diet containing 2·5—10·0% of fish meal (oil content 5%); when the fish oil content of the diet was increased to 1 or 2% a fishy flavour was perceived, particularly in the pork fat.

The relative tenderness of beef muscles was determined by J. M. Ramsbottom, E. J. Strandine, and C. H. Koonz,[124] using the Warner-Bratzler shear apparatus. These workers adopted the novel technique of cooking the pieces of meat to an internal temperature of 170° F. in lard at 250° F., the time required being 12—20 minutes; raw meat was found to be more tender than meat cooked in this way but the method differentiated between the different muscles. As a result of studies, using the apparatus of Wolodkevich for determining toughness, G. Steiner[125] came to the conclusion that the effect of freezing and thawing on the tenderness of meat is to accelerate considerably the normal ripening changes which occur after the death of the animal and, therefore, that the effect of freezing on the toughness depends on the stage of ripening at which freezing is carried out. During the development of rigor, freezing produces an increase in toughness but in the post-rigor period a decrease in toughness is observed. This author[126] also demonstrated that the ripening process proceeds at freezing temperatures, and changes are detectable in 1 year, the rate at −8·5° C. being faster than at −18° to −24° C. C. L. Shrewbury, R. Jordan, F. N. Andrews, R. J. McColloch, and F. G. King[127] found that well-ripened beef showed slight but definite deterioration in quality after quick-freezing and storage at 0° F. for 15 months. C. L. Shrewsbury, L. W. Horne, W. Q. Braun, R. Jordan, O. Milligan, C. M. Vestal, and N. E.Weitkamp[128] found that pork frozen at −32° and stored at −22° C. was in very good condition after 12 months and edible after 16 months, although some intra- and extra-cellular freezing damage

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[122] *Food Res.*, 1945, **10**, 461; B., 1946, III, 76.
[123] *J. Animal Sci.*, 1945, **4**, 63; B., 1946, III, 178.
[124] *Food Res.*, 1945, **10**, 497; B., 1946, III, 76.
[125] *Arch. Hygiene*, 1939, **123**, 1.
[126] *Z. ges. Kälte-Ind.*, 1941, **48**, 29.
[127] *J. Animal Sci.*, 1945, **4**, 151; B., 1946, III, 155.
[128] *Purdue Agric. Exp. Sta.*, 1942, *Bull.* 472; B., 1946, III, 115.

of the tissue was noticed. P. Paul and B. B. McLean[129] reported that the cooking losses, cooking time, and scores for colour, flavour, and tenderness of veal increased as the internal temperature was raised on cooking; the most satisfactory temperature was 82° C. Considerable variations were found between the muscles of any one carcass.

The influence of the presence of meat-curing agents on the thermal resistance of a putrefactive anaërobe during the processing of canned meat was studied by C. R. Stumbo, C. E. Gross, and C. Vinton.[130] These curing agents did not affect the heat processing necessary to sterilise meat products inoculated with spores of *Cl. sporogenes* and *Cl. botulinum*, and increase in the size of the inoculum necessitated increased heat-processing. Spoilage was inhibited by 3½ lb. of sodium chloride per 100 lb. of meat but not by 1½ lb. of sugar, 2¾ oz. of sodium nitrate, or ¼ oz. of sodium nitrite, although the last delayed germination.

The equipment used in America for dehydrating meat has been described by W. A. Noel, W. E. Gray, O. G. Hankins, and R. S. Hollingshead[131] and the results obtained with this equipment have been reviewed by O. G. Hankins, C. F. Dunker, and O. L. Bennett.[132] The advantages of the vacuum–rotary dryer process over the kettle cabinet method are that the operations are carried out in one piece of plant and the process is not affected by the fat content and particle size of the pieces of meat. The conditions recommended for the kettle cabinet method are that pieces of meat, about 2-in. cubes, containing about 15% of fat are cooked, ground through a ¼-in. plate, loaded on to trays at the rate of 1½ lb. per sq. ft., and dried at 180° F. H. B. Hetzer and O. G. Hankins[133] consider that dehydrated pork, when compressed, should have a density of 1 and that rehydration depends more on fat content than on the degree of crushing of the particles.

The factors influencing the quality of bacon have been investigated by D. A. Greenwood, J. E. Stritar, and H. R. Kraybill.[134] They found that insufficient nitrate or nitrite results in undercure and a poor colour, whereas excessive amounts of these salts produce "nitrite burn" and a typical brown colour. Bacon stored at four different temperatures after smoking turned rancid more quickly when the nitrite concentration exceeded 200 p.p.m. than at lower concentrations. An excessive amount of reducing sugar causes bacon to turn brown, and its concentration in curing formulæ should not exceed 0·5 lb. per 100 lb. of bacon. It was shown by F. H. Smith, D. E. Brady, and R. E. Comstock[135] that the storage life of bacon was approximately doubled by smoking, and that

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[129] *Food Res.*, 1946, **11**, 107, 116; B., 1946, III, 178.
[130] *Ibid.*, 1945, **10**, 260, 283, 293; B., 1945, III, 252.
[131] *Ibid.*, 379; B., 1946, III, 51.
[132] *Ibid.*, 445; B., 1946, III, 51. *Ibid.*, 1946, **11**, 1; B., 1946, III, 138.
[133] *Ibid.*, 1946, **11**, 32; B., 1946, III, 138.
[134] *Proc. Inst. Food Tech.*, 1945, 58.
[135] *Ind. Eng. Chem.*, 1945, **37**, 1206; B., 1946, III, 115.

with smoking together with antioxidants it would keep about five times as long as without any such treatment.

R. Campbell, M. C. Hiltz, and A. D. Robinson[136] found that the aneurin concentration fell in the order pork, liver, kidney, heart, fowl, lamb, veal, and beef. Cooking losses are generally below 25%, although fowl, kidney, and heart show greater losses. J. F. Feaster, J. M. Jackson, D. A. Greenwood, and H. R. Kraybill[137] kept canned pork luncheon meat for 1 year and found only slight losses of vitamin-B_2, nicotinic acid, and pantothenic acid. The loss of vitamin-B_1 after a year at 70° F. was about 35% and at 45° F. less than 12%. W. F. Hinman, R. E. Tucker, L. M. Jans, and E. G. Halliday[138] found an increase in riboflavin content when beef is braised, which they attribute to the presence of a precursor or complex not revealed by the fluorometric or microbiological method of estimation. According to H. P. Sarett and V. H. Cheldelin[139] the average retentions of aneurin, riboflavin, and nicotinic acid in hams are: after soaking and boiling 72%, 79%, and 79%; after subsequent frying 55%, 67%, and 68%, and after baking 50%, 79%, and 71%.

Jaffé's reaction is often used to detect and determine total creatinine and thereby the presence and approximate concentration of meat extract. G. Lagrange[140] points out that the colour is not specific for creatinine but is given by lævulic acid and furfuraldehyde, both of which may be present in meat extracts, and also by pyruvic acid and gelatin; he therefore recommends adsorption of the creatinine in acid medium on fuller's earth followed by elution in an alkaline medium. In the determination of total creatinine the method of converting creatine into creatinine by autoclaving an acid solution is criticised by J. R. Bendall[141] on the grounds that some destruction of creatinine occurs; he recommends refluxing at atmospheric pressure for 2½ hours. This work was carried out in the course of a study of the effect of cooking on creatine–creatinine, phosphorus, nitrogen, and pH values of raw lean beef. Trichloroacetic acid was found to be the best protein precipitant but it caused breakdown of protein to soluble material unless the precipitation was carried out at 0° C. In raw and in cooked meat 25% of the soluble phosphorus is present in the esterified form mainly as hexose monophosphate; a proportion may be present as adenylic acid, but there is no evidence of the presence of either adenyl pyrophosphate or phosphagen. After pressure-cooking the esterified phosphorus decreased to about 10% of the total soluble phosphorus, which itself increases by about 10%, as a result, it is deduced, of phosphorus bound to protein or lipin; the latter fractions make up about 20% of the total phosphorus of raw meat. M. Ingram and J. R. Hawthorne[142]

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[136] *Canad. J. Res.*, 1946, **24**, **F**, 140; B., 1946, III, 178.

[137] *Ind. Eng. Chem.*, 1946, **38**, 87; B., 1946, III, 115.

[138] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 296; C., 1946, 185.

[139] *J. Nutrition*, 1945, **30**, 25; B., 1945, III, 229.

[140] *Bull. Soc. chim. Belg.*, 1942, **51**, 113; C., 1945, 254.

[141] *J.S.C.I.*, 1946, **65**, 226; C., 1946, 278.

[142] *Ibid.*, 1945, **64**, 196; C., 1945, 258.

found that chloride could be titrated electrometrically with silver nitrate in the presence of nitric acid using a silver–silver chloride reference electrode; diluted brines could be titrated directly but the chloride in meat required to be extracted with water.

A. G. Perez[143] found that incipient putrefaction in meat was best detected either by extraction of amino-acid-nitrogen by Sörensen's method or by determination of total basic nitrogen; other reactions and properties failed to indicate spoilage before it was detected organoleptically.

It is claimed by R. Viollier and E. Iselin[144] that the percentage of pork fat in a mixture of fats may be calculated from the determination of *iso*oleic acid. Beef, mutton, and veal fat contain on the average 2·5% of *iso*oleic acid, whereas pork fat contains only 0·45%. The solid fatty acids are separated by a modified lead-salt method and the percentage of *iso*oleic acid in the mixed acids is calculated from the oleic value.

Fish.

In reviewing the subject of the application of chemical methods to the detection and determination of decomposition in foods, W. I. Patterson[145] maintained that it is most desirable that the method should determine one or more of the compounds responsible for the odour or taste that indicates that the sample is unfit for food, and cites as examples the determination of volatile fatty acids and trimethylamine in decomposing fish.

In 1936 S. A. Beatty and N. E. Gibbons[146] reviewed the literature dealing with tests for freshness in meats and fish, and tabulated five conditions which such a test must fulfil: (i) the method must be accurate and speedy, (ii) there should be a relationship between the results and the bacterial population, (iii) spoilage odours should appear in different fish at approximately the same concentration of the substance being determined, (iv) autolysis must play only a minor part in the production of the substance determined, and (v) the original values of the substance determined must be sufficiently low to make significant increases resulting from bacterial action. They developed a method for fractionating the volatile bases into two parts, using formaldehyde solution which holds back the ammonia and any monoamine while the triamine, together with any diamine, distils over. The latter fraction was believed to consist almost entirely of trimethylamine derived by bacterial action from trimethylamine oxide present in sea fish. The analytical procedure precluded the possibility that it was ammonia or monomethylamine and S. A. Beatty[147] later showed that it was at least 95% trimethylamine.

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[143] *Rev. Fac. Cienc. Quím., La Plata,* 1943, **18**, 69; C., 1946, 190.

[144] *Mitt. Lebensm. Hyg.,* 1941, **32**, 180; C., 1946, 109.

[145] *J. Assoc. Off. Agric. Chem.,* 1945, **28**, 233; C., 1945, 253.

[146] *J. Biol. Board Canada,* 1936, **3**, 77.

[147] *J. Fish. Res. Board Canada,* 1938, **4**, 63.

Subsequently, J. M. Shewan[148] demonstrated the presence of dimethylamine and S. A. Beatty and V. K. Collins[149] confirmed the development of a small amount of dimethylamine. S. A. Beatty[147] also demonstrated that, in spoiling cod's muscle press juice, the sum of trimethylamine and trimethylamine oxide, determined as trimethylamine after reduction with Devarda's alloy, was constant, the amount of trimethylamine increasing and trimethylamine oxide decreasing with time until none of the latter was left. This change required about 40 hours at 21°, 110 hours at 10°, and 250 hours at 0·5° c. The trimethylamine oxide content of the muscle press juice of a number of Nova Scotia fish was determined by S. A. Beatty,[150] who found a range of 0·26—0·89% in teleosts.

D. W. Watson[151] found that in fish muscle press juice at 2° c. it is the *Achromobacter* which proliferate and that it is the facultative anaërobic organisms of this group which are responsible for the reduction of trimethylamine oxide to trimethylamine. This author[152] then postulated that the *Achromobacter* in effecting this reduction simultaneously oxidised the lactic acid present, via pyruvic acid to acetic acid and carbon dioxide, thus suggesting a mechanism for the development of volatile fatty acids in decomposing fish. The production of acetic acid was confirmed by V. K. Collins.[153] J. M. Shewan[154] found that the exterior surfaces of trawled fish are more highly contaminated than those of lined fish owing to more intimate contact of the former with the bottom sludge and to squeezing out by pressure of the intestinal contents when the trawl is hoisted. He concluded that obligate anaërobes are comparatively unimportant in the spoilage of fish.

It was shown by S. A. Beatty and V. K. Collins[155] that in the decomposition of muscle press juice first lactic acid and sugar are oxidised, with the simultaneous reduction of trimethylamine oxide to trimethylamine; in the second stage the oxidation of amino-acids and the hydrolysis of proteins occur. This second stage represents advanced spoilage with the probable production of toxic compounds.

J. A. I. Paladino[156] tried a number of tests for detecting incipient putrefaction and came to the conclusion that determination of total volatile nitrogen by distillation *in vacuo* from lithium carbonate was most suitable. A concentration of 100 mg. of volatile basic nitrogen per 100 g. of sample was the maximum for fish considered edible.

W. J. Dyer[157] introduced a new method for the determination of trimethylamine by measuring the colour of the toluene solution of the

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[148] *D.S.I.R. Food Invest. Board Ann. Rept.*, 1937, 75; 1938, 79.

[149] *J. Fish. Res. Board Canada*, 1940, **5**, 32.

[150] *Ibid.*, 1939, **4**, 229.

[151] *Ibid.*, 252.

[152] *Ibid.*, 267.

[153] *Ibid.*, 1940, **5**, 197.

[154] *Proc. Soc. Agric. Bact.*, 1944, 56; B., 1945, III, 252.

[155] *J. Fish. Res. Board Canada*, 1939, **4**, 412.

[156] *Rev. Fac. Cienc. Quim., La Plata*, 1943, **18**, 105; B., 1946, III, 177.

[157] *J. Fish. Res. Board Canada*, 1945, **6**, 351; C., 1946, 110.

picrate, and decided that fish becomes unpalatable at concentrations of 10—15 mg. of trimethylamine nitrogen per 100 g. of tissue. Using this method and also the method of Beatty and Gibbons for determining trimethylamine by distillation from formaldehyde solution, W. J. Dyer and Y. A. Mounsey[158] obtained results for putrefying fish which agreed well for the first 26 hours and then diverged. Trimethylamine as determined by the Beatty and Gibbons method remained stationary while as determined by the picrate colorimetric method it continued to increase. Clearly the divergence indicates the production of non-volatile, odoriferous protein decomposition products such as putrescine, cadaverine, tyramine, and phenylethylamine. Cod fillets stored at 2° c. remained satisfactory for 6 days (2·7 mg. of trimethylamine-N per 100 g. of muscle) but not for 7 days (32 mg. of trimethylamine-N per 100 g. of muscle). W. J. Dyer, F. E. Dyer, and M. Snow[159] followed the spoilage of iced eviscerated cod by studying the distribution of trimethylamine, trimethylamine oxide, and bacteria. They found that spoilage originated in the belly cavity, that bacteria do not penetrate the flesh until spoilage is well advanced, but that the substrate trimethylamine oxide diffuses outwards to the surface and the trimethylamine formed diffuses inwards. Leaching by ice water lowers the concentration of trimethylamine oxide at the skin and a gradient of trimethylamine, high in the belly cavity decreasing through the muscle to the skin, develops. They conclude that under commercial conditions the quality of the nape (or belly wall) should be a guide to the quality of the fish, 6—8 days being required to reach 10 mg. of trimethylamine-nitrogen per 100 g. of muscle at 32—44° F. compared with 12 days under laboratory conditions at 32° F.

Satisfactory collaborative results for the determination of volatile acids as an index of fish spoilage have been reported by F. Hillig[160]; it was found that the quantity of formic and acetic acid increases as the decomposition progresses. W. H. King, F. F. Flynn, and J. N. Gowanloch[161] determined the indole in oysters used for canning by measuring the percentage transmission at 560 mμ. of the colour developed with *p*-dimethylaminobenzaldehyde; for fresh oysters the "apparent" indole content was less than 2·2 μg. per 100 g. and for decomposed oysters more than 6·5 μg. per 100 g. L. M. Beacham[162] found no indole in canned fresh oysters but increasing amounts of it as the amount of decomposing material used in the experimental packs was increased; volatile acids were found in both fresh and decomposed oysters, but in clams the volatile acid increased from low values as decomposition progressed. An increase in indole content as shrimps deteriorate was recorded by R. E. Duggan and L. W. Strasburger.[163] In studying the storage of herrings in

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[158] *J. Fish Res. Board Canada*, 1945, **6**, 359; B., 1946, III, 114.

[159] *Ibid.*, 1946, **6**, 403; B., 1946, III, 199.

[160] *J. Assoc. Off. Agric. Chem.*, 1945, **28**, 239; C., 1945, 258.

[161] *Ibid.*, 385; C., 1945, 258.

[162] *Ibid.*, 1946, **29**, 89; B., 1946, III, 200.

[163] *Ibid.*, 177.

refrigerated brines G. J. Sigurdsson[164] followed the development of volatile acids and of tyrosine as measures of decomposition. The herrings were kept at 1° and at −3·5° C. in both air and brine and it was found that at these temperatures the determination of volatile acids was of little use and that for herring stored in brine erratic results for volatile acidity were obtained because hydrochloric acid was distilled over. The concentration of tyrosine increased more rapidly, suggesting that a test for protein hydrolysis was more valuable. The brined fish were intended for canning (fish which have begun to deteriorate are liable to show skin rupture and bursting of the abdominal wall when cooked prior to canning). Herrings in 5% brine were not satisfactory for more than 2—3 days and, for 12 days, 15—20% brine is required.

H. L. A. Tarr[165] stored brined and unbrined fillets of herring, sole, and salmon for 40 days at 14° F. and found that while those stored in air were rancid, those stored in an atmosphere of nitrogen had a very good flavour. British Columbia herrings caught between January and May, made into kippers or stored at −24° F. to −28° F. and then turned into kippers, were compared for taste; those caught in February were found to give the best product.[166] E. P. Linton and A. L. Wood[167] described a cross-ventilated tunnel smokehouse which allows a continuous process to be operated for the smoking of fillets on wire mesh trays. The study of South African fish products has been continued with the object of ensuring their full utilisation as a source of oil and of fat-soluble vitamins. M. M. Black, W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg[168] have investigated the fat derived from the blubber, intestines, and liver of the seal (*Arctocephalus pusillus*) and also the composition of the body and liver oils of the Cape John Dory (*Zeus capensis* C. and V.) when the fish were in thin and in fat condition.[169]

P. Larose and A. C. Burton[170] have described the preparation of fish protein in a form known as "Wiking Eiweiss" for food purposes.

J. M. Shewan[171] has studied the changes in bacterial flora which occur when fish is dehydrated. A complete change in flora accompanies filleting and after this stage fish should not be stored except below 5° C. In drying, the temperature of the minced fish should be raised to 55° C. in 1 hour to avoid possible formation of toxin. In dried fish the surviving organisms are mostly micrococci and quite different from the flora of the original fish. For the rapid determination of moisture in dehydrated fish

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[164] *Proc. Inst. Food Tech.*, 1945, 91.

[165] *Progr. Rept. Fish. Res. Board Canada, Pacific Sta.*, 1946, *No.* 66, 17; B., 1946, III, 177.

[166] A. W. Lantz, *ibid.*, 9; B., 1946, III, 177.

[167] *Canad. J. Res.*, 1946, **24**, **F**, 81; B., 1946, III, 177.

[168] *J.S.C.I.*, 1945, **64**, 326; B., 1946, III, 51.

[169] *Ibid.*, 1946, **65**, 13; B., 1946, III, 76.

[170] *Brit. Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *Final Rept.* 90; B. 1946, III, 178.

[171] *J. Hygiene*, 1945, **44**, 193; B., 1946, III, 138.

R. Davies and W. E. Isaac[172] extracted with alcohol and obtained the composition of the aqueous alcohol mixture from the critical solution temperature with a mixture of kerosene and blended white oil.

W. Harvey[173] found that the fluorine content of the common types of fish paste varied from 3 to 9 p.p.m.

Eggs.

Using a laboratory model pasteuriser, A. R. Winter, G. F. Stewart, V. H. McFarlane, and M. Solowey[174] found that *Salmonella* inoculated into liquid egg were readily destroyed by pasteurisation. On the other hand, *Salmonella* were isolated from 3·18% of the 90 samples of high-quality powdered egg examined by M. D. Schneider[175]; of the 797 samples processed with the aid of both preheater and multistage drying only from 1·63% were *Salmonella* isolated, but of the 104 samples dried without the use of a preheater *Salmonella* were isolated from 18·27%.

J. Pritzker[176] studied the uptake of moisture and deterioration of dried egg powder on storage. The moisture content increased from 5% to 17·5% on storage for 8 days at 100% R.H. but no moisture was taken up if the powder was enclosed in two layers of parchment paper. An increase in the acidity of the ethereal extract of 2—3 "acid degrees" per month is normal but may reach 20° per month in an advanced stage of oxidation. J. A. Pearce, M. Reid, and W. H. Cook[177] found that no improvement in the storage life of dried egg powder resulted if liquid egg was acidulated before drying. The storage life at 27° c. of powder containing 1·7% of moisture was 36 weeks when judged by fluorescence tests, but the powder when judged by palatability remained usable for 64 weeks; increase of moisture content to 3·0% and 4·7% resulted in decrease in storage life to two thirds and one third of the "life" at the lowest moisture content. The addition of sufficient powdered sucrose to egg melange to give a powder containing 33% of sugar was found by R. L. Hay and J. A. Pearce[178] to retard greatly the deterioration of the powder stored at temperatures not above 120° F. J. A. Pearce, J. Whittaker, H. Tessier, and W. A. Bryce[179] found that a dehydrated mixture of egg and milk deteriorated more rapidly than milk powder similar in protein, fat, and carbohydrate contents; addition of lactose, or better of sucrose, gave some improvement, particularly at higher storage temperatures. R. W. Kline and S. W. Fox[180] claimed that addition of glycine and cysteine retarded the development of insolubility in dried egg white. The addition of glycine, however, resulted in the development of a darker colour than

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[172] *Nature*, 1944, **154**, 211.

[173] *Ibid.*, 1945, **155**, 175; B., 1946, III, 138.

[174] *Amer. J. Publ. Health*, 1946, **36**, 451; B., 1946, III, 198.

[175] *Food Res.*, 1946, **11**, 313.

[176] *Mitt. Lebensm. Hyg.*, 1944, **35**, 341; B., 1946, III, 199.

[177] *Canad. J. Res.*, 1946, **24**, **F**, 39; B., 1946, III, 175.

[178] *Ibid.*, 168; B., 1946, III, 199.

[179] *Ibid.*, 70; B., 1946, III, 175.

[180] *Iowa State Coll. J. Sci.*, 1946, **20**, 265; B., 1946, III, 175.

in the control, but the addition of cysteine resulted in less colour than in the control, suggesting an economical means of inactivating reducing sugars. The pressure of water vapour in equilibrium with samples of spray-dried whole egg powder of moisture contents ranging between 0·5 and 5·5% was determined at temperatures between 17·1° and 70° by B. Makower[181]; this worker also found that the ratio of the heat of absorption to the latent heat of condensation increased from 1 : 1 to 2 : 1 as the moisture content of the powder decreased.

As a result of following the changes that occur during storage in the solubility, concentration of reducing sugar, and free amino-groups of dried egg products, E. C. Bate-Smith and J. R. Hawthorne[182] concluded that loss of solubility is a two-stage process, the first stage being the condensation of reducing sugar with protein amino-groups. This reaction occurs without change in solubility and the further reactions which must therefore occur are discussed. H. S. Olcott and H. J. Dutton[183] considered that the fluorescence of a 10% sodium chloride extract of dried egg was due to a brown reaction product of glucose and the amino-groups of protein. B. G. Edwards and H. J. Dutton[184] showed that an ether-soluble brown material could be isolated from dried egg powder and also from the kephalin fraction of the powder; this brown material was fluorescent and yielded characteristic absorption curves. H. J. Dutton and B. G. Edwards[185] suggested that the fluorescent substance which develops in the lipins of spray-dried egg powder during storage is a reaction product of lipin amines and aldehydes. These authors[186] extracted the egg powder in a Soxhlet apparatus with ether specially purified to remove fluorescent substances. The optical density of the extract was determined spectrophotometrically at 3800 A. and 4450 A. (being respectively the carotenoid minimum and maximum), taking into account in the calculation the absorption of brown substances formed on storage. The brown lipin amine–aldehyde products were determined in the same extract by a photofluorometer at 3650 A. (Hg line) for excitation and with quinine sulphate as a fluorescent standard. Using this technique they[187] found that during storage of dehydrated egg powder the carotenoids are destroyed at a rate independent of moisture content and that brown aldehyde–amine substances are formed at a rate which increases with moisture content. The fluorescence of the brown aldehyde–amine substances in an aqueous sodium chloride extract of egg powder residues after ether extraction is proportional to — log reflectance of such residues. It is suggested that the fluorescent compound used as an index of palatability is a reaction product of glucose with protein residues. M. M. Boggs

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[181] *Ind. Eng. Chem.*, 1945, **37**, 1018; B., 1946, III, 50.

[182] *J.S.C.I.*, 1945, **64**, 297; B., 1946, III, 26.

[183] *Ind. Eng. Chem.*, 1945, **37**, 1119.

[184] *Ibid.*, 1121.

[185] *Ibid.*, 1123; B., 1946, III, 50.

[186] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 38; C., 1946, 110.

[187] *Ind. Eng. Chem.*, 1946, **38**, 347; B., 1946, III, 174.

and H. L. Fevold[188] maintain that loss of palatability is not necessarily related to loss of solubility and development of salt-soluble fluorescing substances. Using powders prepared on the laboratory scale by freeze-drying they noted that, when the white and the yolk (pH 5·5—6·0) were dried separately, the yolk powder did deteriorate in palatability but more slowly than whole egg powder. When the yolk was adjusted to pH 8·5 before drying its "life" was no longer than that of whole egg powders, and conversely when whole dried egg was adjusted to pH 5·5 before drying the powder had keeping properties like those of egg yolk dried alone. By freeze-drying fractions of the yolk, H. L. Fevold, B. G. Edwards, A. L. Dimick, and M. M. Boggs[189] traced the deterioration in flavour on the storage of dried egg to the phospholipin fraction of the yolk and concluded that the development of the fluorescing substance which may be extracted with aqueous sodium chloride is not necessarily connected with the deterioration in flavour. The relationship between palatability and (*a*) lipin fluorescence and (*b*) aqueous sodium chloride fluorescence was studied by M. M. Boggs, H. J. Dutton, B. G. Edwards, and H. L. Fevold,[190] who found for all types of powders better correlation between palatability and (*a*); between palatability and (*b*) good correlation was obtained for powders of high moisture content (5%) but not for powders of low moisture content (2%). R. W. Moncrieff[191] claimed that a difference in intensity of taste or odour in tasting reconstituted cooked dried egg is noted only if the change is as much as 30% or by trained tasters not less than 15%.

M. Reid and J. A. Pearce[192] measured the volume of the sponge cake given by a standard mix as an index of baking quality, and compared the results with those for (i) the foaming volume of a mixture of egg powder, sugar, and water; (ii) the potassium chloride value; (iii) the refractometric value, and (iv) the fluorescence; they recommended foaming volume as the most reliable index of baking quality. J. E. Ary and R. Jordan[193] compared the products obtained when fresh eggs and various qualities of egg powder were used in making (*a*) plain batter cakes and (*b*) baked custards. Egg powders of poor solubility produced cakes of smaller volume and poorer eating quality and custards which were less firm and less desirable in flavour; the poor flavour was more noticeable in custards than cakes. D. W. Grover and J. R. Hawthorne[194] found that baking quality for Madeira cakes correlated better with solubility than aërating power.

T. von Fellenberg[195] associates a change from negative to positive for the "acidity value" with spoilage, the "acidity value" being the acidity of an

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[188] *Ind. Eng. Chem.*, 1946, **38**, 1075; B., 1947, III, 59.
[189] *Ibid.*, 1079; B., 1947, III, 59.
[190] *Ibid.*, 1082; B., 1947, III, 59.
[191] *Food Manuf.*, 1946, **21**, 55.
[192] *Canad. J. Res.*, 1945, **23**, F, 239; C., 1945, 258.
[193] *Food Res.*, 1945, **10**, 476; B., 1946, III, 76.
[194] *Ibid.*, 1946, **11**, 41; B., 1946, III, 155.
[195] *Mitt. Lebensm. Hyg.*, 1944, **35**, 347; C., 1946, 189.

extract less the acidity of a potassium hydrogen phthalate extract at pH 4·3 of the residue from ethereal extraction.

In determining the free fatty acids in egg powder of normal pH (8—9) by the A.O.A.C. method, L. Kline and C. M. Johnson[196] maintain that the reconstituted egg must first be adjusted to pH 4·5 with 3N-hydrochloric acid ; the egg is then dried under vacuum from the frozen state and the oil extracted. The kephalin must be precipitated with acetone. C. F. M. Fryd, S. W. F. Hanson, G. E. W. Sexton, and G. W. Nicholls[197] found that sucrose in sugar–dried egg could be satisfactorily determined by saccharimeter readings after precipitation of the egg solids by (i) basic lead acetate and alumina cream ; (ii) silicotungstic acid, or (iii) acetic acid–zinc acetate and potassium ferrocyanide.

A method for the chemical determination of vitamin-*A* in dried whole egg is given by C. R. Thompson, M. A. Ewan, S. M. Hauge, B. B. Bohren, and R. W. Quackenbush.[198] A solution of the unsaponifiable material in light petroleum is passed through a column of slaked lime and the chromatogram is developed with a benzene–light petroleum mixture. Finally the combined vitamin-*A* and provitamin-*A* eluates are treated with antimony trichloride to develop the blue colour. The retention of vitamin-*A* in dried egg on storage was determined by B. B. Bohren and S. M. Hauge,[199] who found after 6 months 62% retention at 20° C. or less and 30% at 37° for powder stored loose or compressed in waxed fibre cartons compared with about 75% in sealed cans irrespective of temperature. For the determination of riboflavin in egg W. J. Peterson, R. S. Dearstyne, R. E. Comstock, and V. Weldon[200] separate the yolk and white after hard-boiling and macerate each separately with aqueous sulphuric acid and incubate with clarase ; the yolk emulsion may be cleared with acetone or chloroform ; they found average figures of 4·09 μg. per g. in yolk and 2·67 μg. per g. in white. T. B. Mann[201] extracted the white with absolute alcohol and the yolk with 55% alcohol, and then measured the fluorescence of the extracts at 3650 A.

MILK AND MILK PRODUCTS.

During the period under review numerous papers have appeared outlining investigations on the effects of variations in the feed of the cow and of other factors on the quantity and composition of the milk yielded. The factors concerned, however, are numerous, and it becomes increasingly difficult to correlate the findings of different investigators. In agreement with the results of previous workers, O. R. Overman[202] found that lowest fat and non-fatty solids contents were obtained during the summer

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[196] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 35 ; C., 1946, 110.
[197] *Analyst*, 1945, **70**, 458 ; C., 1946, 41.
[198] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 113 ; C., 1946, 183.
[199] *Food Res.*, 1946, **11**, 39 ; B., 1946, III, 155.
[200] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 370 ; C., 1945, 261.
[201] *Analyst*, 1946, **71**, 166 ; C., 1946, 185.
[202] *J. Dairy Sci.*, 1945, **28**, 305 ; B., 1946, III, 49.

months, different breeds of cow giving milk with consistent differences in composition. On the other hand, contrary to certain earlier investigators, P. Kästli[203] found no regular change in the fat content of milk during the period of lactation, nor did change from dry to green feed have any effect, although, as noted previously, green feed gave increased milk yield. Inadequate winter rations under wartime conditions were stated to be responsible for those non-fatty solids contents which were found in a large number of samples from an important English dairy area to be below 8·5%,[204] but in spite of reduced rations during the recent world war the fat content of milk in Switzerland was maintained at the normal average of 3·8% although the milk production fell.[205] Drought conditions in the autumn of 1942 were considered to be responsible for the reduced mineral content of Swiss milk in the 1942–43 winter.[206] K. Breirem[207] found that the fat content of the milk was not affected by varying the intake of calcium or by feeding hydrolysed straw to cows, but it was increased (accompanied by decreased milk yield) by feeding cellulose; contrary to the conclusions of previous authors, no correlation was found between fat content and protein intake. According to C. F. Monroe and W. E. Krauss,[208] yields of milk and butter fat are not significantly increased by increased fat content of the ration of cows, but J. K. Loosli, L. A. Maynard, and H. L. Lucas[209] obtained greater milk production by feeding a concentrate having 5·3% fat content instead of one with 2% of fat, irrespective of the amounts of starch and hay given to the cow, while reduction of the hay to less than 5 lb. per day in a ration sufficient for energy requirements caused a significant reduction in fat content and milk yield.[210] Addition of bakers' yeast to the ration of cows giving high milk yield did not affect the yield or the composition of the milk.[211] It was stated by H. Hostettler,[212] in a well documented review on silage manufacture, that concentrates in feeds may be replaced by properly prepared silage from protein-rich green crops, the quality of the silage determining the quality of the resulting milk.

A. D. Robinson and H. S. Samson[213] concluded from the high correlation existing between the values determined for the titratable acidity and the inorganic phosphate content of milk that the titratable acidity was primarily attributable to the inorganic phosphate present. In confirmation of previous work, E. Zollikofer[214] found that the casein, chloride, and

[203] *Mitt. Lebensm. Hyg.*, 1940, **31**, 46; B., 1946, III, 198.

[204] S. J. Rowland, *J. Dairy Res.*, 1944, **13**, 261; B., 1946, III, 9.

[205] W. Mosimann, *Mitt. Lebensm. Hyg.*, 1944, **35**, 14; B., 1946, III, 107.

[206] P. Balavoine, *Arch. Sci. phys. nat.*, 1943, [v], **25**, *Suppl.*, 204; B., 1946, III, 9.

[207] *Meieriposten*, 1944, **33**, 464, 489; B., 1946, III, 136.

[208] *Ohio Agric. Exp. Sta.*, 1943, *Bull.* 644; B., 1946, III, 136.

[209] *Cornell Agric. Exp. Sta.*, 1944, *Mem.* 265; B., 1945, III, 255.

[210] J. K. Loosli, H. L. Lucas, and L. A. Maynard, *J. Dairy Sci.*, 1945, **28**, 147; B., 1946, III, 25.

[211] C. L. Norton, *ibid.*, 927; B., 1946, III, 157.

[212] *Mitt. Lebensm. Hyg.*, 1945, **36**, 50; B., 1946, III, 173.

[213] *Canad. J. Res.*, 1946, **24**, **B**, 5; B., 1946, III, 173.

[214] *Mitt. Lebensm. Hyg.*, 1943, **34**, 74; B., 1946, III, 74.

lactose contents are of diagnostic value for the detection of milk derived from cows suffering from mastitis even in mild form. The alkalinity of the ash of milk powder varies from 66 to 127 ml. of 0·1N-acid per 100 g. depending on the breed of the cow, so that this determination is of no value for the detection of added neutralisers.[215] When milk is heated in sealed cans at 100° and 116°, there is, with increased time of heating, a progressive decrease in lactose content and of pH, accompanied by corresponding increase in titratable acidity and some increase in formol titration; these changes, which are accentuated in presence of phosphate and citrate, are also accompanied by some development of lactic and formic acids.[216]

According to H. Hvidsten, the vitamin-*A* and carotene contents of the fat in milk were higher during pasture- than during stall-feeding, but the vitamin-*A* content may be increased in the latter case by supplements of A.I.V. silage and of certain green foods.[217] The content of riboflavin in Holstein–Friesian milk was lower than that in Jersey milk but the daily production of the vitamin was higher in the former case because of greater milk yield. During the first 6—8 days after calving the riboflavin content falls sharply but is thereafter constant.[218] According to A. D. Holmes, H. G. Lindquist, and E. K. Greenwood,[219] the riboflavin content of goats' milk is lower, while the fat and ascorbic acid contents are higher, during pasture- than during stall-feeding. Of the riboflavin present 28—40% is destroyed when cows' milk is exposed to bright sunlight in uncoloured glass bottles but no loss occurs in brown glass or paper containers.[220] For milk powder, wave-length is significant as a factor in the destruction of riboflavin, which is maximum at 4450 A., the effect being therefore greater in sunlight than in ultra-violet light at 3200—4200 A.[221]

K. M. Henry, J. Houston, S. K. Kon, and S. Y. Thompson[222] demonstrated that during preparation of evaporated and sweetened condensed milk the biological value of the protein present is not impaired, in the latter case the true digestibility being significantly increased. In neither process was there loss of vitamin-*A*, carotene, or riboflavin but losses of vitamins-*C* and B_1 were 60 and 27% respectively from evaporated milk and less than 10% from condensed milk. On storage of condensed milk at 15° and 27° appreciable losses of vitamins-*C* and B_1 occur: the riboflavin content decreases at 37°.

The leucocyte count of milk was reduced by 41% by homogenisation

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[215] R. W. Kunkel and W. B. Combs, *J. Dairy Sci.*, 1945, **28**, 219; B., 1946, III, 74.

[216] I. A. Gould, *ibid.*, 367, 379; B., 1946, III, 74. I. A. Gould and R. S. Frantz, *ibid.*, 287; B., 1946, III, 74.

[217] *Norg. Landbrukshøgsk. Inst. Husdyr.*, 1943, *Circ.* 8; B., 1946, III, 49.

[218] D. R. Theophilus and O. E. Stamberg, *J. Dairy Sci.*, 1945, **28**, 259; B., 1945, III, 227.

[219] *Ibid.*, 853; B., 1946, III, 137.

[220] O. E. Stamberg and D. R. Theophilus, *ibid.*, 269; B., 1945, III, 227.

[221] W. A. Bryce, *Canad. J. Res.*, 1946, **24**, F, 123; B., 1946, III, 174.

[222] *J. Dairy Res.*, 1944, **13**, 329; B., 1946, III, 9.

at 2500 lb. per sq. in. and 143° F., this being due to fragmentation of the cells. Destruction was complete after continuous homogenisation for 10 minutes at 5000 lb. per sq. in. (complete details not stated) but the fragments still separated as a sediment, as do unbroken cells. Addition of 12 g. of leucocytes (washed separator slime) to a pint of milk caused an increase in cream layer from 63 c.c. to 77 c.c., but with 60 g. of leucocytes the cream layer was reduced to 15 c.c. and 100 c.c. of a "cream" layer appeared at the bottom of the container. The attraction between the leucocytes and the fat globules was maximum at pH 4·3 and minimum at pH 1·5—3·0.[223]

The incidence of tuberculosis organisms in milk and the efficacy of pasteurisation for their destruction have been emphasised by two authors. C. H. Chalmers[224] stated that the infection of milk on Scottish farms is declining and that all samples of pasteurised milk examined gave negative tests for *M. tuberculosis*; efficient destruction of the bacteria was obtained with certainty by heating the milk at 140° F. for 20 minutes but at 160° F. for 12—15 seconds there was less latitude. B. F. Thomas[225] found appreciable tuberculosis infection in Wales in undesignated, in accredited, and in (raw) school milk, but none in tuberculin-tested or pasteurised school milk. *Brucella abortus* was found in about 10% of the raw milk but was absent in the pasteurised milk samples.

The keeping quality of milk has been assessed by A. C. Dahlberg[226] by means of flavour and bacterial count. The best storage temperature was 35—40° F. (up to 7 days); at 55—60° F. keeping was only satisfactory up to 4 days. Other methods for determining keeping quality were examined by A. Rowlands and A. L. Provan,[227] who indicate that the colony count is unsatisfactory and the coliform test too severe, the best means of detecting milk with poor keeping quality being the methylene-blue test applied at 18° C.; the methylene-blue and resazurin tests at 37° were good alternatives. The resazurin test is the best for detecting milk suitable for keeping at 18° for more than 24 hours. Other workers[228] stated that for the same purpose determinations of pH, titratable acidity, and total bacterial count were much inferior to dye-reduction tests, the two dyes mentioned above giving results showing statistically insignificant differences. The rate of reduction of resazurin by organisms is proportional to their ability to produce acid in milk, with the exception of *S. agalactiæ* (which reduces slowly) and *B. subtilis* (which reduces readily but produces little acid).[229] Milk held at 55° F. for 16 hours had lower

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[223] I. I. Peters and G. M. Trout, *J. Dairy Sci.*, 1945, **28**, 251, 277, 283; B., 1945, III, 227.

[224] *Proc. Nutrition Soc.*, 1945, **3**, 186; B., 1946, III, 74.

[225] *Proc. Soc. Agric. Bact.*, 1944, 48; B., 1945, III, 251.

[226] *J. Dairy Sci.*, 1945, **28**, 779; B., 1946, III, 137.

[227] *Proc. Soc. Agric. Bact.*, 1944, 22; B., 1945, III, 251.

[228] S. B. Thomas, D. A. Bowie, A. Peregrine, and G. M. Phillips, *ibid.*, 28; B., 1945, III, 250.

[229] V. E. Jones and J. G. Davis, *ibid.*, 38; B., 1945, III, 250.

resazurin-reducing power than when held at lower temperatures, due to destruction of the leucocytes at the higher temperature.[230] As both bacteria and leucocytes in mastitis milk reduce the resazurin reagent, a specific inhibitor of the reducing action of the latter has been sought. Such inhibition is partly effected when the test is carried out at 67° C. Alternatively potassium cyanide, hydrogen peroxide, and mercuric chloride each inhibit the reducing effect of the leucocytes more than that of the bacteria, but the concentration of inhibitor found necessary depends on the number of leucocytes present.[231]

A. T. R. Mattick and his associates[232] carried out an important investigation on the relation between various methods of pretreatment of milk and the keeping properties and bacterial counts of the spray-dried powder produced from it. The storage life of the powder was increased to the greatest extent (to 2 years) when the milk prior to condensing and drying was preheated to 190° F. instead of to 165° F. At the higher temperature thiol compounds with antioxidant power develop; the vitamins in the resulting powder have increased stability during storage. Reduced bacterial counts were obtained in powder stored in an inert atmosphere (less than 3% of oxygen) for 10 months. During 2 years' commercial experience of high-temperature pretreatment, 78% of the samples of powder had less than 20,000 bacteria per g.[233] Milk, buttermilk, and whey dried at different plants showed marked differences in bacterial species and total counts, roller-dried products giving lower counts when incubated at 37° and 55° C. than did spray-dried products. Decrease in count occurs on storage at 15° but the reduction varies with the type of powder.[234] While whole milk powder loses palatibility during storage at temperatures above 15°, separated milk powder deteriorates only above 38°. The storage life of full-cream milk powder at 27° is best when the fat content is 30% rather than 26% or 28%, while the keeping properties of both whole and separated milk powders are optimum at 3% moisture content.[235]

Ascorbic acid and ethyl gallate are the best antioxidants for milk powder, 0·07% of the latter giving a three-fold increase in storage life[236]; wheat-germ oil also has some value, especially as an inhibitor of the oxidation that is catalysed by copper.[237] In roller-process powders with normal copper content, the effect of antioxidants is masked by the presence of reducing substances developed during drying.[238] Gas packing is especially

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[230] C. S. Morris, *Nature*, 1944, **153**, 436; B., 1945, III, 227.

[231] J. G. Davis and V. E. Jones, *Proc. Soc. Agric. Bact.*, 1944, 40; B., 1945, III, 251.

[232] A. T. R. Mattick, E. R. Hiscox, E. L. Crossley, C. H. Lea, J. D. Findlay, J. A. B. Smith, S. Y. Thompson, and S. K. Kon, *J. Dairy Res.*, 1945, **14**, 116; B., 1946, III, 49.

[233] E. L. Crossley, *ibid.*, 160; B., 1946, III, 9.

[234] C. Higginbottom, *ibid.*, 1944, **13**, 308, 324; B., 1945, III, 227.

[235] W. A. Bryce and J. A. Pearce, *Canad. J. Res.*, 1946, **24**, **F**, 61; B., 1946, III, 174.

[236] J. D. Findlay, J. A. B. Smith, and C. H. Lea, *J. Dairy Res.*, 1945, **14**, 165; B., 1946, III, 9.

[237] J. H. Hetrick and P. H. Tracy, *J. Dairy Sci.*, 1945, **28**, 687; B., 1946, III, 136.

[238] R. A. Chapman and W. D. McFarlane, *Canad. J. Res.*, 1946, **24**, **F**, 47; B., 1946, III, 174.

effective for enhancing the keeping quality of whole-milk powder.[239] After a small initial loss of palatibility due to uptake of residual oxygen, no further change takes place during 12 months' storage at room temperature, but under such conditions air-packed powder becomes unpalatable.[239] The rate of peroxide formation in the fat of air-packed powder is related to keeping quality at storage temperatures up to 45° c., while in gas-packed powder little peroxide develops.[240] Compression of milk powder into blocks reduced the interstitial air as effectively as gas packing, but such blocks will absorb oxygen and moisture from the atmosphere even when wrapped in waxed paper; addition of vanillin or 20% of sucrose to the powder before compression improves the keeping quality.[241] There appears to be some correlation between the palatability of milk powder and the rate of absorption of carbon dioxide, although the latter varies very much with powders produced at different factories. Full-cream milk powder absorbs carbon dioxide from 100% carbon dioxide at a greater rate than does separated milk powder but the rate was reduced in the former case and remained unchanged in the latter in presence of a 1 : 4 (vol.) mixture of carbon dioxide and nitrogen.[242]

Bacteriophage in relation to cheese starter cultures has been the subject of several investigations. Phage was isolated by A. A. Nichols and J. Z. Wolf[243] from cheese made from milk using a "slow" starter; it was shown to persist in the cheese after 12 months' ripening. H. R. Whitehead and J. D. Sargent[244] advocated the use of single-strain starters because of their constant acid production although they are more susceptible to phage infection. This infection, which is insidious and may assume serious proportions unless carefully guarded against,[245] may develop from the starter used, from water, equipment,[246] and the air.[245] The infection, although not found in every factory, is widespread in this country and there is therefore danger in the use of starters without knowing their origin and their susceptibility to infection.[247] As active phage is destroyed at 75° in 7½ minutes, the possibility that the milk used for starter cultures may be the source of phage infection is avoided if such milk is properly sterilised.[248]

P. M. F. Shattock[249] emphasised the importance of differentiating lactic streptococci used in starter cultures from toxin-forming enterococci,

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[239] C. C. Thiel and E. G. Pont, *J. Counc. Sci. Ind. Res., Australia*, 1945, **18**, 373; B., 1946, III, 174.

[240] G. R. Greenbank, P. A. Wright, E. F. Deysher, and G. E. Holm, *J. Dairy Sci.*, 1946, **29**, 55; B., 1946, III, 173.

[241] C. C. Thiel, *J. Counc. Sci. Ind. Res., Australia*, 1945, **18**, 391; B., 1946, III, 174.

[242] J. A. Pearce, *Canad. J. Res.*, 1945, **23**, **F**, 327; B., 1946, III, 108.

[243] *J. Dairy Res.*, 1944, **13**, 302; B., 1945, III, 229.

[244] *Dairy Res. Inst., Wellington*, 1946, *Publ.* 174; B., 1946, III, 198.

[245] H. R. Whitehead and G. J. E. Hunter, *J. Dairy Res.*, 1945, **14**, 64; B., 1946, III, 10.

[246] G. J. E. Hunter, *ibid.*, 1944, **13**, 294; B., 1945, III, 229.

[247] A. A. Nichols and J. Z. Wolf, *ibid.*, 1945, **14**, 81; B., 1946, III, 10.

[248] *Idem, ibid.*, 93; B., 1946, III, 10.

[249] *Proc. Soc. Agric. Bact.*, 1944, 69; B., 1945, III, 251.

which is possible by serological typing, although in this way *S. thermophilus* is not included in either group. The resistance to heating at 63° for 30 minutes of lactic bacteria used in Swiss cheese starter cultures depends on the temperature at which they have previously developed[250]; *e.g.*, the numbers of *L. bulgaricus* organisms which survive after heating are less, but the acid-producing power of the survivors is greater, when organisms are grown at 24·3° instead of 37°, but in the case of *S. thermophilus* the number of survivors and their activity are greater when the organisms have developed at the higher temperature.

H. J. Zahrndt, C. B. Lane, and B. W. Hammer[251] found wide ranges in the calcium and phosphorus contents and in the Ca/P ratio in various types of cheese, highest values for calcium and phosphorus contents being obtained in Edam and Swiss types. There was no correlation between the quality of the flavour of a cheese of a given type with the calcium and phosphorus contents or the Ca/P ratio. It has been shown[252] that during cheese making the ascorbic acid present in the milk disappears completely, while 80% of the vitamin-*A* and carotene, 15% of the aneurin, and 25% of the riboflavin remain in the cheese; Cheddar, Stilton, and Cheshire type cheeses have similar biological value and digestibility. F. J. Babel and B. W. Hammer[253] showed that to obtain Swiss type cheese with a desirable sweet flavour the presence of butyric acid bacteria is necessary, butyric and acetic acid then being produced from the lactic acid present. According to W. L. Langhus, W. V. Price, H. H. Sommer, and W. C. Frazier[254] the "smear" in Brick cheese contains yeast-like organisms which are rapidly replaced by micro-rod-shaped organisms of *Bact. linens* type, the latter taking no part in the ripening process although contributing to the flavour.

H. S. Purchase[255] obtained ready separation of cream from camel's milk (3·4—4·4% fat), which produced on churning white butter as a frothy mass. Ghee, produced from the butter or cream, when used with protein food contributed no flavour but conferred in baked goods a "camel" flavour. Cheese, which may be obtained from camel's milk by natural souring but not by rennet action, had a full cheesy but peculiar characteristic flavour.

EDIBLE FATS.

Of the work on fats and fatty foods not covered by other sections of these reports, the greater part is concerned with keeping properties and deterioration. The search for natural antioxidants has been continued and the use of many of these substances has been disclosed in the patent literature. Twenty-five patents granted to the Musher Foundation in

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[250] J. G. Voss and W. C. Frazier, *J. Dairy Sci.*, 1945, **28**, 545; B., 1946, III, 109.

[251] *Iowa Agric. Exp. Sta.*, 1944, *Res. Bull.* 325, 143; B., 1946, III, 109.

[252] D. V. Dearden, K. M. Henry, J. Houston, S. K. Kon, and S. Y. Thompson, *J. Dairy Res.*, 1945, **14**, 100; B., 1946, III, 10.

[253] *Iowa Agric. Exp. Sta.*, 1939, *Res. Bull.* 264, 203; B., 1945, III, 228.

[254] *J. Dairy Sci.*, 1945, **28**, 827; B., 1946, III, 138.

[255] *East African Agric. J.*, 1943, **9**, 39; B., 1945, III, 251.

1940 have not been reported in this country until this year and they cover the use of a number of products derived from cereals and beans. Of interest also is the claim that when cream is heated with dried milk products, such as skim milk, the butter prepared from the cream has improved keeping properties, and the same effect is claimed for edible oils when the addition of the milk products is made before completion of the deodorisation process. Fats are stabilised by the addition of 2—5% of expressed cacao butter and also by heating with a sugar and a phosphatide.[256] The incorporation in a hydrogenated shortening of less than 5% of sesame flour is said to reduce the development of the characteristic hydrogenated flavour and odour when such fats are used for baking and frying.[257] Patents have also specified the use of unripe fruits, seeds, and other parts of dicotyledonous plants, after grinding, macerating, and drying at not above 50°; the dried product or the macerated paste may be used for antioxidant purposes, apples, unripe peas, and cabbage being given as examples. Also, partly rancid glycerides may be restored to edible quality and in this case green coffee was given as an example.[258] Extracts from non-pathogenic bacteria, such as timothy grass bacilli, have been found to have antioxidant properties, the acetone-soluble fraction being used for fats while the insoluble fraction is recommended for products such as milk.[259] Tannins have been shown to be more effective as antioxidants for lard and beef fat than for vegetable oils: results were also presented on their effect in countering the pro-oxidant activities of copper and iron salts.[260] The stabilisation of lard by the addition of 1—10% of hydrogenated soya-bean oil has been claimed to be effective for the baked products in which the lard is used.[261] This question of the relationship existing between the stability of the fat used and the keeping properties of the baked product is a subject of great interest, and a review of the relevant literature has been given by H. O. Triebold.[262] The keeping properties of cereal products are not necessarily determined by the stability of the constituent fats and the suggestion was made that in some cases pro-oxidant substances in fats may be destroyed during the baking process. On the other hand, antioxidants for the fats are not necessarily effective in baked products, and D. J. Maveety[263] working on biscuits found that when the stability of the fat was increased by the use of antioxidants there was not as great an increase in the keeping properties of the biscuits. In spite of some inconsistencies

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[256] S. Musher, Assr. to Musher Foundation Inc., U.S.P. 2,198,198—2,198,220 and 2,198,222; B., 1946, III, 53.

[257] *Idem*, U.S.P. 2,201,112; B., 1946, III, 80.

[258] C. Ellis and F. Dannerth, Assrs. to Ellis Laboratories, Inc., U.S.P. 2,204,728–9; B., 1946, III, 143.

[259] S. Shappirio, U.S.P. 2,338,207; B., 1946, III, 202.

[260] H. T. Spannuth, T. H. McGuine, and G. A. Crapple, *Oil and Soap*, 1946, **23**, 110; B., 1946, III, 220.

[261] D. P. Grettie, Assr. to Industrial Patents Corp., U.S.P. 2,201,692; B., 1946, III, 80.

[262] *Oil and Soap*, 1945, **22**, 334; B., 1946, III, 155.

[263] *Ibid.*, 1946, **23**, 25; B., 1946, III, 173.

he nevertheless concluded that, in general, the stability of the biscuits, both at room temperatures and at 125° F., bears a direct relation to the stability of the shortening as determined by the Swift test. He also found that the induction period of a fat mixture was not always the same as would be expected from the stability of the ingredients. Induction periods have been determined directly on soya flour by heating in dry air at 100° and at 110° C.,[264] the end point being determined both organoleptically and by chemical means. As with oils and fats, an increase of 10° in the temperature at which the test is made roughly halves the length of the induction period. It was found also that the keeping time varied directly with the fat content of the soya flour.

The action of various antioxidant substances in the preservation of fish has been examined over a range of storage temperatures, from −18° F. to 32° F.[265]; ethyl and propyl gallates were effective in retarding peroxide rancidity even when salt was present, and the fish retained its normal appearance when stored at unfavourable temperatures. Storage of fish in an atmosphere of carbon dioxide or of nitrogen[266] has been shown to prevent oxidative rancidity, the efficacy of the method depending on the extent to which oxygen was removed; in carbon dioxide, however, the stored fish developed other "off" flavours. In the storage of bacon at 80° F.[267] nordihydroguaiaretic acid, gossypol, and a mixture of soya-lecithin, *d-iso*ascorbyl palmitate, and tocopherols were shown to be effective antioxidants, increasing the induction period by 200—400%. Smoked bacon was found to be more resistant to oxidative rancidity than unsmoked. Oxidation of whole-milk powder caused by the presence of copper has been inhibited by wheat-germ oil either alone or with citric acid or lecithin; removal of peroxide from the wheat-germ oil did not increase its antioxidant properties. When the copper content of the milk powder was normal, the effects of added antioxidants were found to be masked by the reducing substances naturally present.[268] These conclusions were based on accelerated keeping tests at 65°. It was only possible to follow the deterioration of the milk powder by chemical tests (either by peroxide development or by increase in reducing substances): organoleptic evaluation was not possible because of caramel-like flavours produced from constituents other than the fat.

The enhanced stability of butter fat produced by the "boiling-out" process has been attributed to the action of the milk proteins. It was found that a definite improvement in the stability of butter fat is caused by heating it with 1% of skim-milk powder and that a similar but smaller

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[264] L. J. Filer, jun., C. J. Martin, and B. F. Daubert, *Ind. Eng. Chem.*, 1945, **37**, 1180; B., 1946, III, 107.

[265] H. L. A. Tarr, *Progr. Rept. Fish. Res. Board Canada, Pacific Sta.*, 1945, *No.* 64, 57; B., 1946, III, 114.

[266] *Idem, ibid.*, 1946, *No.* 66, 17; B., 1946, III, 177.

[267] F. H. Smith, D. E. Brady, and R. E. Comstock, *Ind. Eng. Chem.*, 1945, **37**, 1206; B., 1946, III, 115.

[268] R. A. Chapman and W. D. McFarlane, *Canad. J. Res.*, 1946, **24**, F, 47; B., 1946, III, 174.

effect was obtained with molasses, ascorbic acid, or wheat germ. Milk phospholipins had no effect.[269] The oxidative deterioration of butter fat in contact with tin plate has been demonstrated and also the variation in protection afforded by different grades of lacquer.[270]

Attempts to convert New Zealand butter into a product resembling ghee were not successful,[271] but it is of interest to note that some of the samples prepared had good keeping properties, resisting oxidation for 9 years at 4·4°. In this connexion, it should be noted that a "hard" butter, containing 3% of hydrogenated groundnut oil, 4% of skim milk powder, and 2% of salt, has been suggested as suitable for use in tropical climates.[272]

Work on the storage of New Zealand butter at temperatures between —10° and 15·6° has shown that deterioration is directly related to the time and temperature of storage and that oxidation of the fat occurred in salted but not in unsalted butters.[273] An analysis of the causes of surface deterioration in stored butter showed that all the samples developing a fishy flavour had low pH values and it was concluded that surface defects are minimised by preventing contamination with micro-organisms, copper, or iron, and by storing butters only of optimum pH values (6·7—6·9).[274] The use of foils and plastic films for protecting butter from timber taint has been investigated by F. H. McDowall.[275] Aluminium foil between parchment sheets was good, but difficulty was experienced in maintaining the wrapping in contact with the butter, especially at the corners; air spaces between the butter and the wrapper are favourable to mould growth. Treatment of the wood with a plastic product containing rubber was satisfactory when the butter was also wrapped in this material. This wrapping is fragile and a trial shipment of butter to this country from New Zealand in non-refrigerated holds developed mould growth.

It has been suggested that 21° is the best tasting temperature for the scoring of butter, lower temperatures being relatively more favourable to the lower grades; 15·5° was found to be the best temperature for spreading.[276] The use of the mould mycelia count as an index of the quality of butter has been reported on adversely by P. R. Elliker and B. E. Horral.[277] They examined 1385 samples and concluded that there was very poor correlation with organoleptic grading. The counts varied with the seasons and with warm and cold weather.

The vitamin and carotene contents of butter continue to be the subject of recurrent investigation. The mean values for 1019 samples of butter

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[269] D. V. Josephson and C. D. Dahle, *Food Ind.*, 1945, **17**, *No.* 6, 80; B., 1946, III, 50.

[270] C. H. Lea, *J.S.C.I.*, 1946, **65**, 136; B., 1946, III, 220.

[271] C. R. Barnicoat, *New Zealand J. Sci. Tech.*, 1945, **27**, **A**, 309; B., 1946, III, 237.

[272] W. J. Wiley and G. W. Coombs, *J. Counc. Sci. Ind. Res.*, *Australia*, 1946, **19**, 140; B., 1946, III, 236.

[273] C. R. Barnicoat, *New Zealand J. Sci. Tech.*, 1945, **27**, **A**, 343; B., 1946, III, 236.

[274] A. H. White, *Sci. Agric.*, 1942, **23**, 41; B., 1946, III, 108.

[275] *New Zealand J. Sci. Tech.*, 1945, **27**, **A**, 303; B., 1946, III, 236.

[276] W. H. E. Reid and W. S. Arbuckle, *Missouri Agric. Exp. Sta.*, 1939, *Bull.* 408; B., 1946, III, 108.

[277] *J. Dairy Sci.*, 1945, **28**, 519; B., 1946, III, 75

produced in Minnesota in 1943 were: vitamin-*A* 6·21 ± 0·03 μg. per g., carotene 3·68 ± 0·04 μg. per g. In winter, carotene was 11—15% of the total potency and 21—23% in summer. There was a higher total potency when the cows were pasture-fed. Vitamin-*A* was not lost on storage of the butter at −10° for six months.[278] Figures for Norwegian butter showed that the highest values were 7 μg. of carotene per g. and 14 μg. of vitamin-*A* per g. for cows on pasture. In winter feeding the potency of the butter varies according to the nature of the feed and its carotene content; the effectiveness of different feeds from this point of view was indicated in the report. A slow decrease in vitamin content occurred through storage at −15°, but the drop was shown to be small in comparison with that caused by change from pasture- to stall-feeding.[279] It has been pointed out that the vitamin content of butter is highest at the time of the year when the Reichert value is lowest and the suggestion was made that butters with such abnormal analytical characteristics should not be considered as inferior products.[280] The distribution of carotene in butter-making products has been found to be: 10—14% in skim milk, 89—94% in butter, and 0·2—2% in buttermilk. The corresponding figures for vitamin-*A* were: 2—4%, 93—100%, and 0·4—1%.[281] T. W. Goodwin and R. A. Morton[282] deal with the application of methods of determination of vitamin-*A* and carotene to the analysis of butter and margarine. They were concerned with the retention of vitamin-*A* potency during the commercial life of "national" margarine and found this to be largely dependent on the quality of the constituent fats. In the fresh condition, the margarine contains no carotene and an average of 483 i.u. of vitamin-*A* per oz. After manufacture there is usually a small variable loss of vitamin-*A*, and then the losses are slight for a period of about three months, after which the rate of deterioration increases. The suggestion was made that margarine should be fortified with 20 i.u. of vitamin-*A* per g. and 10 i.u. of carotene. This would supply these compounds in the normal ratio for butter and the addition of other colouring matter would not then be necessary. Patents dealing with fat-soluble vitamins include the preservation of fish-liver oil concentrates with acetylmethylcarbinol,[283] the preparation of a product of controlled vitamin content containing skim milk, vegetable oil, and cod-liver oil,[284] and the molecular distillation of oils to give the naturally occurring esters of vitamin-*A*[285]; the esters are claimed to have better keeping properties

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[278] R. Jenness and L. S. Palmer, *J. Dairy Sci.*, 1945, **28**, 473; B., 1946, III, 75.

[279] H. Hvidsten, *Fôringsforsøk. Norges Landbrukshøgsk.*, 1943, *No.* 53; B., 1946, III, 75.

[280] P. Balavoine, *Mitt. Lebensm. Hyg.*, 1941, **32**, 203; B., 1946, III, 109.

[281] S. Berl and W. H. Peterson, *J. Dairy Sci.*, 1945, **28**, 103; B., 1946, III, 75.

[282] *Analyst*, 1946, **71**, 15; B., 1946, III, 75.

[283] E. J. Simons and L. O. Buxton, Assrs. to Nat. Oil Products Co., U.S.P. 2,331,432; B., 1946, III, 32.

[284] C. G. Hauser, H. J. Miller, and H. O. Bierbaum, B.P. 575,160; B., 1946, III, 119.

[285] K. C. D. Hickman, Assr. to Distillation Products, Inc., U.S.P. 2,205,925; B., 1946, III, 143.

and to be utilised physiologically to better advantage than vitamin-*A* concentrates prepared by saponification of the oils. A further publication from the University of Capetown is concerned with the mode and degree of storage of fats in the Cape John Dory. The fatty acid compositions of the body and liver oils were determined for the fish both in the fat and the lean condition. With increased fat content of the fish an increase in the amounts of the highly unsaturated acids was found but a decrease in the average unsaturation of the C_{18} and C_{20} acids. The iodine value increased for the body oil and decreased for the liver oil.[286]

Work on the digestibility of various shortenings in biscuits baked at different temperatures has shown that diets baked at 375° F. increased the growth of rats better than those baked at 425° F. Digestibility of the fats, however, was not affected by the baking temperature or by the fat content of the biscuits. Lard was found to be slightly more digestible than hydrogenated shortening, compound fats, or blended vegetable shortening.[287] The hydrolysis of various common fats by *Ricinus* lipase has been measured; coconut and sesame oils were the most readily digested. Of the animal fats examined, lard was hydrolysed more readily than beef, sheep, or goat tallows. Olive oil was found to be similar to beef tallow and to hydrogenated oils.[288] A patented shortening for products having a high sugar/flour ratio contains 1—5% of certain phospholipins and it is stipulated that the vegetable oils used in their preparation must not contain fatty acids with more than two double bonds, cottonseed and maize oils being suitable: prevention of reversion in soya-bean oil products is also claimed.[289] The hydrogenation of soft lards has been shown to improve the flavour, keeping quality, creaming ability, and smoking point, and, of course, to eliminate oiliness; the shortening power is, however, decreased.[290]

Finally, the manufacture of margarine in Germany from synthetic fat is a matter which should be mentioned.[291] The chief interest, however, lies in the manufacture of the synthetic fats rather than in the margarine itself and the product will probably cease to have any importance when normal conditions are restored.

COCOA, CHOCOLATE, AND CONFECTIONERY.

An attempt to provide an improved commercial index figure for the evaluation of raw cacao beans has been described by G. Mosimann.[292]

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[286] M. M. Black, W. S. Rapson, H. M. Schwartz, and N. J. van Rensburg, *J.S.C.I.*, 1946, **65**, 13; B., 1946, III, 76.

[287] E. W. Crampton and M. F. Mills, *Canad. J. Res.*, 1946, **24**, **F**, 157; B., 1946, III, 198.

[288] B. Ahmad and R. N. Sareen, *J. Sci. Ind. Res. India*, 1946, **4**, 710; B., 1946, III, 258.

[289] B. H. Thurman, Assr. to Refining Inc., U.S.P. 2,201,063; B., 1946, III, 80.

[290] R. Jordan, *Purdue Agric. Exp. Sta.*, 1944, *Bull.* 498; B., 1946, III, 115.

[291] M. E. Spaght, *Combined Intelligence Objectives Sub-Commee.*, 1945, *Item* 22, *File* XXXI-79; B., 1946, III, 257.

[292] *Mitt. Lebensm. Hyg.*, 1944, **35**, 321; B., 1946, III, 156.

Points are allotted according to degree of fermentation, proportions of nib and shell, dimensions, fat and moisture contents, etc. Such a numerical index would appear to be of very limited value, for it is difficult to see how such different properties as quality, size, and composition can be represented by a single index figure.

The composition of the acids present in cacao has been investigated by the same worker,[293] who reports that the only non-volatile acids present are oxalic and citric acids; the average values found for 8 types of cacao nibs were oxalic acid 0·40%, citric acid 0·56%, together with 0·39% of acetic acid.

The possibility of cocoa having an adverse effect on calcium utilisation in metabolism in consequence of its oxalate content has been reported by H. H. Mitchell and J. M. Smith.[294] The results of tests on rats showed that medium-grade cocoa depressed calcium utilisation in direct proportion to its oxalate content, though with lower-grade cocoa, of low fat content and containing some shell, the effect was double that to be accounted for by the oxalate content. Tests on human subjects, however, did not indicate that cocoa had any adverse effect on the calcium balance in human metabolism.

J. Drenker[295] describes the separation of cacao nib from cacao shell by use of a salt solution (3 parts of sodium chloride in 10 parts of water). The mixture of nib and shell is dispersed in the brine, in which the particles of nib float; these are then removed, washed free from salt, and dried.

Increased solubility and improved flavour of cocoa are claimed by L. C. Benedict[296] to result from treatment of the beans with hydrochloric acid, followed by a partial roasting; the beans are then neutralised, and the roasting treatment is completed.

The preparation of two non-hygroscopic, granular powders that are readily dispersed in cold water or milk has been described. The first[297] is obtained by spray-drying an emulsion of cacao mass in water, whereby a change of phase is effected, the dried product consisting of cacao butter globules coated with cocoa solids. The second[298] is a sweetened product made by adding sugar, part at least in the form of a hot aqueous syrup, to cocoa powder of low fat content, the mixture after cooling being crumbled and sieved.

Replacement of 25—75% of the sucrose in chocolate by the solids from a starch-conversion syrup, made from maize, potato, or wheat, is stated to result in a product that has less tendency to bloom and a greater breaking strength.[299]

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[293] *Mitt. Lebensm. Hyg.*, 1944, **35**, 241; B., 1946, III, 116.

[294] *J. Amer. Med. Assoc.*, 1945, **129**, 871; A., 1946, III, 569.

[295] U.S.P. 2,338,376; B., 1946, III, 203.

[296] Assr. to United-Rexall Drug Co., U S.P. 2,397,402.

[297] P. T. Zizinia and T. L. McKenna, U.S.P. 2,201,820; B., 1946, III, 80

[298] C. F. Jones, W. T. Clarke, and B. J. Zenlea, Assrs. to Rockwood & Co., U.S.P. 2,336,254; B., 1946, III, 159.

[299] R. C. Drury, Assr. to Amer. Maize-Products Co., U.S.P. 2,328,791; B., 1945, III, 257.

The effects of the conditions of solidification of cacao butter preparatory to determination of its melting point have been studied by D. M. Copley.[300] He confirms that rapid chilling is inadvisable, and recommends cooling the molten fat at 18—22° C., stirring until it has congealed, and then retaining it at this temperature for 2 hours. The melting point of cacao butter treated in this way is slightly lower than that of the original fully solidified material, but the depression is stated to be a uniform factor and the method gives more concordant results than are obtained by the official method of the United States Pharmacopœia.

Experiments have been made by H. H. Hall and F. J. Fahs[301] on increasing the protein content of confectionery products, many of which contain little or no protein, by addition of proteins separated from peanuts or soya beans. Peanut protein that had been prepared on an experimental scale had a residual peanut flavour which was imparted to the products, but no significant foreign flavour was apparent initially when up to 3—4% of soya-bean protein was added to various products, such as nougats, boiled sweets, and fondants. Darkening in colour and development of a stale flavour in some of the products occurred, however, after storage for about 4 months, and the authors point out that these changes will need to be corrected before a satisfactory shelf life of such products containing the added protein can be assured.

TEA.

As little has been published during the year, the report on tea is held over until the next issue.

GENERAL FOOD ANALYSIS.

The analytical methods reviewed in this section are those that have not been reported in the preceding specialised sections.

Although a number of papers have been published during 1946 on the determination of metallic traces in foods, no new method of outstanding importance has emerged; most of the work has been done on modifications of existing methods or on the amounts of metallic traces found in various natural and manufactured foods. P. Riou and J. J. Paré,[302] and D. Rogers and A. E. Heron,[303] determine arsenic colorimetrically by the molybdenum-blue method. The first two workers use the ordinary Gutzeit method for evolution of arsine but absorb in mercuric chloride solution before oxidation to arsenate and final reduction of the sodium arseno-molybdate to give molybdenum-blue; they claim that the method will determine 5—180 μg. of As_2O_3 to an accuracy of ±0·1 μg. and that the method is accurate in the presence of antimony. Rogers and Heron have adapted the method of R. Milton and W. D. Duffield[304] by using an electrolytic cell to evolve the arsine instead of granulated zinc and acid;

[300] *J. Amer. Pharm. Assoc.*, 1946, **35**, 78; C., 1946, 170.

[301] *Manufg. Conf.*, 1946, **26**, *No.* 11, 27.

[302] *Ann. l'Acfas*, 1942, **8**, 77.

[303] *Analyst*, 1946, **71**, 414; C., 1946, 237.

[304] *Ibid.*, 1942, **67**, 279.

the even rate of evolution of hydrogen is claimed to eliminate errors caused by the erratic rate of evolution that results from the variable surface area of different lots of granulated zinc. The formation of molybdenum-blue by the action of tervalent antimony on phosphomolybdic acid is the basis of a photometric method for the determination of 0·05—0·5 mg. of antimony[305]; quadrivalent tin, if not present in an amount more than twice that of the antimony, bivalent copper in an amount not exceeding 1 mg. per 50 ml., and up to 50 mg. of bismuth have no effect on the determination, but the presence of iron considerably reduces the intensity of the blue molybdenum colour.

The general limit test for lead given in the British Pharmacopœia has been shown to be unsuitable for creta præparata now added to bread-making flour[306]; by the B.P. method only 30—40% of the lead present was found. The proposed method, which involves redigestion of residues and filter-papers and careful adjustment of pH prior to formation of the lead sulphide, is accurate, within the range 10—30 p.p.m., to ±1 p.p.m. of lead. Using the method proposed, commercial creta præparata was found normally to contain 10—15 p.p.m. of lead. A modified dithizone method for the determination of copper is recommended by S. L. Morrison and H. L. Paige.[307] After wet destruction of the material, an aliquot containing about 7 μg. of copper is transferred to a Mojonnier flask with water to make 25 ml. The solution is neutralised with ammonia to cresol-red and then buffered to pH 2·3. 20 ml. of a solution containing 7·5 ml. of dithizone per litre of carbon tetrachloride are added and the whole is shaken for 10 minutes and the aqueous layer discarded. A solution of potassium iodide in very dilute hydrochloric acid is added and the light transmittance at 520 mμ. measured.

A volumetric method for the determination of tin in foods is proposed by H. A. McKenzie.[308] After wet destruction, the tin (in an aliquot containing 0·5—5·0 mg.) is reduced with aluminium and, after the addition of approximately 4 ml. of a solution containing 0·2% of potassium iodide and 3% of sodium bicarbonate, titrated with 0·005N-potassium iodate solution. Recovery tests in the presence and absence of 200 p.p.m. of iron and 20 p.p.m. of copper indicate that the accuracy of the method is ±3%.

A considerable amount of work has been recorded on the presence of metallic traces in natural and in manufactured foods. In a critical review O. Jones[309] concludes that, even with all reasonable care by manufacturers, some contamination of food with arsenic, lead, copper, and zinc will result, and suggests that maximum limits for various foods should be fixed. Russian workers have been concerned with the contamination of

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[305] A. I. Kokorin, *Zavod. Lab.*, 1946, **12**, 64.

[306] E. C. Dawson and A. Rees, *Analyst*, 1946, **71**, 417; C., 1946, 236.

[307] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 211; C., 1946, 146.

[308] *J. Counc. Sci. Ind. Res., Australia*, 1945, **18**, 181; C., 1946, 115.

[309] *Food*, 1945, **14**, 285; 1946, **15**, 9.

canned goods with lead and tin from cans with soldered seams; the general conclusion they reach[310] is that in a hermetically sealed can there is little danger from lead but that the tin content of certain foods may rise to an appreciable amount in long periods of storage, an amount of 340 p.p.m. of tin in canned salmon and in the fat of canned bouillon having been found after four years' storage. The natural arsenic content of various vegetables grown in Russia has been recorded by I. Schtenberg,[311] who has reported amounts in the dry material varying from 0·09 p.p.m. in carrots to 2·95 p.p.m. in tomatoes; the arsenic is not considered to be due to contamination by insecticides and fungicides. The arsenic content of wines made from grapes grown in soil treated with lead arsenate as a fungicide has been found to vary from 0 to 4 p.p.m. and the lead content from 0 to 0·08 p.p.m.[312] Nickel has been found to occur naturally in a variety of Argentine foodstuffs[313]; the amounts varied from 0·13 p.p.m. in watercress to 4·6 p.p.m. in the dry matter of squashes.

The question of the determination of moisture has not received the same amount of attention as in the last two or three years: two communications only have been noted. In the first of these,[314] it is recommended that, for dried vegetables, moisture should be determined at a pressure of 5 mm. or less of mercury on a sample ground to pass a 40-mesh sieve; the times and temperatures of drying recommended are: carrots at 70° for 29—35 hours, potatoes at 70° for 43—67 hours, cabbage at 60° for 22—40 hours, and onions at 60° for 15—45 hours. R. J. Carter and L. Williamson[315] give details of an apparatus and method using electrometric titration for the determination of moisture with the Karl Fischer reagent; the method is claimed to be particularly useful for the determination of water in coloured samples.

The war years, and the succeeding period of scarcity, have stimulated interest in artificial sweetening agents and also in food preservatives. A. Gandini,[316] C. Fazio,[317] and M. Peronnet[318] have published methods for the detection and determination of saccharin and G. La Parola and A. Mariani[319] a colour test for dulcin not subject to interference from saccharin and its derivatives. Gandini's test, which can be used for colorimetric determinations, is based on the violet precipitate, soluble in chloroform, which is formed when a saccharin solution reacts with naphthylamine and copper sulphate. Peronnet, who worked chiefly on

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[310] I. Kotljar and E. Berdakina, *Vopros Pitania*, 1941, **10**, *No.* 5—6, 40. I. V. Kizevetter, *ibid.*, 33.

[311] *Ibid.*, 29.

[312] L. Gentilini, *Ann. staz. sperim. viticolt. enol. Conegliano*, 1944–45, **12**, 1.

[313] A. Beristein, *Rev. Fac. Cienc. Quim., La Plata*, 1943, **18**, 139; C., 1946, 193.

[314] B. Makower, S. M. Chastain, and E. Nielsen, *Ind. Eng. Chem.*, 1946, **38**, 725; C., 1946, 280.

[315] *Analyst*, 1945, **70**, 369; C., 1946, 56.

[316] *Farmaco*, 1946, **1**, 34; C., 1946, 194.

[317] *Rev. asoc. bioquim. Argentina*, 1946, **13**, 3.

[318] *Ann. Chim. Analyt.*, 1944, **26**, 108.

[319] *Annali Chim. Appl.*, 1946, **36**, 134.

the determination of saccharin in wines and soft drinks, relies on the determination of the nitrogen content by the micro-Kjeldahl method after defecation with potassium ferrocyanide followed by partial purification with potassium permanganate; he states that as little as 5 mg. per litre can be accurately determined by this method. Fazio has adapted V. Arreguine's test[320] (the characteristic micro-crystalline precipitate given when a saccharin solution is added to a freshly prepared solution of a cobalt salt in ammonia) to alcoholic and soft drinks after removal of interfering materials by permanganate oxidation of the ether-soluble portion; after this oxidation, the residue is again extracted with acidified ether and the extracted material again subjected to oxidation. Arreguine's reaction is applied to this purified material and is stated to be quantitative if the saccharin concentration is at least 12 p.p.m. The test for dulcin mentioned consists in adding to the sample containing a trace of dulcin a drop of anisaldehyde and of concentrated hydrochloric acid; provided the anisaldehyde is fresh and colourless, an immediate brilliant red colour is formed.

P. E. Verkade[321] has described a new innocuous sweetening agent (4-nitro-2-amino-1-*n*-propoxybenzene) that is claimed to be more than 4000 times as sweet as cane sugar, to be more stable than saccharin, and to have a purely sweet taste with no significant secondary or after taste. It is stated that the product, which is easily obtained in a pure condition, is being manufactured on a commercial scale. Although its solubility is low (136 mg. per litre at 20°) the sweetening power is such that this is unimportant; the chief disadvantage is that the product has a pronounced red colour and can thus only be used where this colour is unimportant or can be masked.

The U.S. Army Subsistence Research and Development Laboratory have reduced the errors of the Monier-Williams method for the determination of sulphur dioxide in sulphited cabbage and carrots to about one eighth of the normal by eliminating the buffering action of carbon dioxide in the solution to be tested.[322] This is done either by boiling the solution to be titrated or by the use of oxygen-free nitrogen instead of carbon dioxide during the determination. Using this method, the recovery of 4—91 mg. of added sulphur dioxide in twelve experiments varied from 98·5 to 100·4%, using 25 g. of sample. The sulphur dioxide content of frozen and other fruits can be determined by a direct titration method with an accuracy claimed to be comparable in most cases with that of the Monier-Williams gravimetric method.[323] The material is extracted with 20% salt solution buffered to pH 4·5, filtered, treated with alkali to dissociate combined sulphur dioxide, acidified, and titrated with iodine both before and after treatment with formaldehyde.

[320] *Rev. univ. nacl. Cordoba*, 1941, 407.

[321] *Rec. trav. chim.*, 1946, **65**, 346; A., 1946, III, 909. *Food Manuf.*, 1946, **21**, 483.

[322] J. B. Thompson and E. Toy, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 612; C., 1946, 115.

[323] J. D. Ponting and G. Johnson, *ibid.*, 682; C., 1946, 114.

American workers continue to investigate methods of detection and determination of the chloroacetic acid preservatives. The qualitative test proposed for monochloroacetic acid[324] depends on the precipitation of a well-defined crystalline mass when the acid is heated in the water-bath at 60° with pyridine. The method, which can be made quantitative if the reaction is carried out under carefully controlled conditions, is specific for acids containing a reactive α-hydrogen atom, but the details of a procedure for determining monochloroacetic acid in the presence of other such acids have not been studied. *p*-Hydroxybenzoic acid and its esters can be determined colorimetrically by carefully controlling the conditions of formation of the red compound given with Millon's reagent and measuring the intensity of the colour in the Lovibond Tintometer.[325]

A considerable amount of work has been done in the U.S.A. on the determination of DDT, particularly in view of the possibility of contamination of food. As a result of consideration of animal experiments, H. O. Calvery[326] suggests that the safe limit of DDT in human foods should be not more than 10 p.p.m. Technical DDT is a mixture of isomers; it does not appear that a really specific method for the determination of the actual *pp'*-DDT isomer (1:1:1-trichloro-2:2-di-*p*-chlorophenylethane) has yet been found. Most of the American communications give full accounts of the isomers present in the sample of DDT worked on and of the interference the (insecticidally) inactive isomers exert on the method of determination or detection proposed. It has been shown[327] that *pp'*-DDT decomposes quickly when exposed to atmospheric conditions, *e.g.*, when used as a spray for codling moth on apples. These decomposition products (identified and unidentified) if present with *pp'*-DDT are capable of interfering strongly in the methods of analysis used, but, in the work carried out, the volatility of the decomposition products was sufficient to prevent any serious errors. The methods used in the determinations were those given by the same authors in an extensive paper on the determination of spray residue DDT on fresh fruit.[328] In this communication, three methods are used after recovery of the DDT from the fruit by washing with benzene (a detailed description of the method used is given). Method I consists of determination of (*a*) the labile chlorine by hydrolysis with 2N. alcoholic potash, and (*b*) the total chlorine by heating under a reflux condenser with freshly cut sodium in the presence of *iso*propyl alcohol. Method II is an application of the Schechter and Haller technique[329] by which the dry material is nitrated, the nitration

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[324] L. L. Ramsey and W. I. Patterson, *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 100; C., 1946, 249.

[325] H. W. Johnson, *Analyst*, 1946, **71**, 77; C., 1946, 86.

[326] *Food Packer*, 1945, **26**, *No.* 5, 61.

[327] H. J. Wichmann, W. I. Patterson, P. A. Clifford, A. K. Klein, and H. V. Claborn, *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 218; C., 1946, 252.

[328] *Ibid.*, 188; C., 1946, 285.

[329] M. S. Schechter and H. L. Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2129. M. S. Schechter, S. B. Soloway, R. A. Hayes, and H. L. Haller, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 704; C., 1946, 85.

products isolated by extraction with ether, dried, and dissolved in a measured volume of benzene. When a definite volume of anhydrous sodium methoxide solution of standardised strength is added to an aliquot of the benzene solution, intense and reasonably stable "colours" are produced for each of the two isomers of DDT; these can be measured in a photometer. The method is empirical; the specified procedure must be followed. Method III is based on three separate chemical reactions. The *pp'*- and *op'*-DDT are converted into the corresponding ethylenes by treatment with alcoholic potash in benzene solution, the ethylenes are oxidised with chromic acid in acetic acid to the dichlorobenzophenones, which are then converted into the 2 : 4-dinitrophenylhydrazones by treatment with 2 : 4-dinitrophenylhydrazine; these derivatives give intense colours with alkali which are qualitatively identical but differ quantitatively by about 10%, the *pp'*-isomer giving the higher value. In commercial DDT this error is negligible in comparison with other unavoidable experimental errors. A list of recoveries of DDT added to various types of vegetation is given by R. H. Carter and P. E. Hubanks,[330] who use the method of dehydrodehalogenation with alcoholic potash (this determines one chlorine atom) and also reduction with sodium and *iso*propyl alcohol (which accounts for five chlorine atoms in the molecule). A collaborative and critical study has been published[331] of the dehydrodehalogenation method with alcoholic potash and of the Winter method[332] by which DDT is volatilised, burnt in a flame of ordinary gas, and the combustion products, containing the chlorine, absorbed in an alkaline solution of sodium arsenite. Some account is given in this study of the errors due to the presence in technical DDT of the different isomers. Other colorimetric methods published for the determination of DDT are those of S. W. Chaikin,[333] who uses the yellow colour produced when *pp'*-DDT is heated in a mixture of concentrated sulphuric acid and glacial acetic acid, and of E. T. Illing and W. H. Stephenson,[334] who propose measurement of the orange colour produced after nitration and reduction of DDT to the coloured amino-compound, and also measurement of the purple colour produced when alcoholic potash is added to the tetranitro-compound of DDT. Chaikin considers the effect of the interference of *op'*-DDT and other technical impurities on the method proposed; Illing and Stephenson have worked with *pp'*-DDT of 99·6% purity. I. E. Balaban and R. D. Calvert[335] have published a note describing the method incorporated in the British Specification for determining the *pp'*-DDT content of technical DDT, which consists in weighing the amount of material produced by direct crystallisation under standardised conditions from 99·5% ethyl alcohol saturated with DDT. The method involves the

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[330] *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 112; C., 1946, 285.
[331] E. E. Fleck, *ibid.*, 1945, **28**, 585; C., 1946, 119.
[332] J. E. Fahey, *ibid.*, 152.
[333] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 272; C., 1946, 251.
[334] *Analyst*, 1946, **71**, 310; C., 1946, 251.
[335] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 339; C., 1946, 164.

use of 10 g. of material and is not intended for micro-determination. J. M. Ginsburg[336] has recorded, with comments, eight different methods for the determination of DDT and concludes that a chemical method specific for the determination of DDT is still needed.

Caramel in vinegar, wines, distilled spirits, etc. can be determined by precipitation with organic acids (*e.g.*, tartaric acid) together with organic solvents (*e.g.*, ethyl alcohol) in a form easily freed from other colouring matters[337]; the caramel is finally determined by means of the Lovibond Tintometer. The method is claimed to be of wide application and not to be affected by fruit and vegetable colours, wood extractives, or by certain dyes. Alkaline oxidation of a distillate, with potassium permanganate and sodium hydroxide, is proposed as a rapid sorting test to differentiate malt and wine vinegars from spirit and artificial vinegars[338]: under the specified conditions, malt and wine vinegars give values (expressed as the number of parts of oxygen required to oxidise 100,000 parts of vinegar) of 50—158, spirit vinegars of 5·5—13·5, and artificial vinegar of 0·5—6·7.

For the determination of glycerol[339] the material containing it is first dried and then subjected to the action of superheated ethyl alcohol in a special apparatus: the alcohol and entrained glycerol are condensed and the ethyl alcohol can be removed by heating without loss of glycerol, which is then determined by the usual method of oxidation with potassium dichromate. C. E. Sage[340] has published, on the basis of hundreds of analyses, a list of proposed maximum limits for the total and acid-insoluble ash of a number of spices and dried herbs. He comments that the normal limit of 1·4 p.p.m. of arsenic in herbs is too stringent; parsley grown in clean ground under ideal conditions may contain twice as much.

Following the series of papers noted in these Reports last year[341] on the subject of extraneous materials in foods and drugs, American workers have published more investigations. H. Welch[342] discusses, with numerous drawings and photomicrographs, the microscopical examination of food products for the presence of various forms of filth; a collaborative report by various workers of the U.S. Food and Drug Administration has also been published.[343] K. L. Harris and R. E. O'Brien[344] give in detail the method at present in use by the U.S. Food and Drug Administration for detection of insect particles and rodent hairs in alimentary pastes. The method consists essentially in disintegration of the pastes first with hydrochloric acid and then, after neutralising, with pancreatin: the latter step increases considerably the recovery of filth.

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[336] *J. Econ. Entomol.*, 1946, **39**, 174; C., 1947, 67.

[337] G. F. Mallory and R. F. Love, *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 631; C., 1946, 42.

[338] F. A. Lyne and T. McLachlan, *Analyst*, 1946, **71**, 203.

[339] R. Raveux, *Ann. Chim. Analyt.*, 1943, **25**, 70, 95.

[340] *Food*, 1946, **15**, 116.

[341] *Ann. Repts.*, 1945, **30**, 501.

[342] *Quart. Bull. Assoc. Food and Drug Officials U.S.*, 1945, **9**, *No.* 1, 3.

[343] J. D. Wildman, W. V. Eisenberg, W. G. Helsel, K. L. Harris, F. A. Hodges, and F. R. Smith, *J. Assoc. Off. Agric. Chem.*, 1946, **29**, 54, 56, 58, 60, 62, 65, 67.

[344] *Ibid.*, 84.

FINE CHEMICALS AND MEDICINAL SUBSTANCES.

By N. R. Campbell, B.Sc., Ph.D., A.R.I.C.

Antibiotics.

Penicillin.—Penicillin, first in the field, still holds pre-eminence. Production from the metabolic products of the growth of penicillium species remains the only practicable method; yields of penicillin from various cultures have been compared by M. J. Johnson, J. J. Stefanick, F. B. Gailey, and B. H. Olson,[1] who have demonstrated the superiority of No. X-1612, an *X*-ray mutant from *P. chrysogenum* No. 1951-B 25 (Northern Regional Research Laboratories, U.S.A.). Using this same strain, R. W. Stone and M. A. Farrell[2] have studied the nutritional requirements of the mould and have evolved a synthetic medium, which has a chief disadvantage of promoting slower growth than corn-steep media; yields are slightly less but purification of the product is rendered simpler. With this medium, the addition of phenylacetamide together with leucine or cystine improves the yield. Another synthetic medium, used by S. L. Mukherjee and B. C. Sarkhel,[3] employs glycerol as the sole source of carbon. E. Stice and R. Pratt[4] have described a simple apparatus by which a continuous-flow type of surface culture produces penicillin containing 40—45% of the *X* modification from *P. notatum* 1249-B 4.

Undoubtedly the greatest interest in this field attaches to the announcement by V. du Vigneaud, F. H. Carpenter, R. W. Holley, A. H. Livermore, and J. R. Rachele[5] of the synthesis and isolation of penicillin *G*, called by them "benzylpenicillin" in accordance with the recommendation of a monograph yet to be published. *d*-Penicillamine hydrochloride and 2-benzyl-4-methoxymethyleneoxazol-5(4)-one condensed together in pyridine with triethylamine yielded an inactive product which when heated in pyridine with pyridinium chloride produced antibiotic activity. The resulting reaction mixture, containing only about 0·1% of benzylpenicillin, was concentrated by use of countercurrent distribution between chloroform and ether with a phosphate buffer. Crystals of "triethylammonium benzylpenicillin" were obtained and purified by crystallisation from solvents. An important corollary to this work is the statement that the oxazolone has been condensed with various α-amino-β-thio-acids, such as *d*-cysteine; this foreshadows the preparation of entirely new "penicillins" with unknown therapeutic properties.

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[1] *Science*, 1946, **103**, 504.
[2] *Ibid.*, **104**, 431.
[3] *Nature*, 1946, **157**, 440.
[4] *Science*, 1946, **103**, 535.
[5] *Ibid.*, 1946, **104**, 431.

Increased interest has been shown in the separation and study of the individual natural penicillins. B. D. Coghill, A. E. Osterberg, and G. R. Hazel[6] have studied the rates of excretion of the pure penicillins in connexion with their relative therapeutic effectiveness. Penicillin *K* was found to be excreted in such small quantities that they conclude that its parenteral use is possibly of very little value. Excretions of *G* and *X* were found to be approximately equal (80%) under the conditions employed. Reference has also been made by these authors to a new penicillin (No. 128), which has an activity of 3500 units per mg. H. Fischbach, M. Merlin, and T. E. Eble[7] have described the determination of penicillin *K* by partition chromatography; particular interest in this determination depends on the comparative ineffectiveness of penicillin *K* in the treatment of early syphilis, coupled with the fact that the penicillin obtained from the newer strains of mould has tended to contain increased proportions of *K*.

Assay of penicillin *in vivo* by the use of *Borrelia*-infected mice is recommended by M. Buck, A. C. Farr, and R. J. Schnitzen[8] : they find that the activity of penicillin *G* is very constant by this method and claim to be able thereby to estimate the content of the very much less active *K* in mixtures.

A preliminary note relative to the mode of action of penicillin, from E. F. Gak and E. S. Taylor,[9] refers to the action of penicillin in preventing the assimilation of glutamic acid by *S. aureus*.

Streptomycin.—G. A. Le Page and E. Campbell[10] have replaced the older beef extract–peptone medium used in the surface culture of *Actinomyces griseus* by a yeast medium ; this is claimed to give more rapid production of streptomycin, greater ease in purification, and a product free from the undesirable histamine effect of earlier streptomycins. Their product had a potency of 350—450 *S* units per mg.

Since last year's Report, advance has been made in the study of the structure of streptomycin. Evidence has been forthcoming that streptidine is probably 1 : 3-diguanido-2 : 4 : 5 : 6-tetrahydroxy*cyclo*hexane, and accordingly may have biogenic relationship to inositol.[11] Alkaline hydrolysis of streptomycin has been found by J. R. Schenck and M. A. Spielman[12] to yield 0·3 mol. of 3-hydroxy-2-methyl-γ-pyrone, but this latter was not obtained by R. L. Peck, C. E. Hoffhine, and K. Folkers[13]

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[6] *Science*, 1946, **103**, 709.

[7] *Ibid.*, **104**, 84.

[8] *Ibid.*, 370.

[9] *Nature*, 1946, **158**, 676.

[10] *J. Biol. Chem.*, 1946, **162**, 163 ; A., 1946, III, 403.

[11] H. E. Carter, R. K. Clark, S. R. Dickman, Y. H. Loo, P. S. Skell, and W. A. Strong, *Science*, 1946, **103**, 540 ; also the same authors with J. S. Meek, J. T. Alberi, Q. R. Bartz, S. B. Binkley, H. M. Crooks, I. R. Hooper, and M. C. Rebstock, *ibid.*, 53, R. L. Peck, C. E. Hoffhine, E. W. Peel, R. P. Graber, F. W. Holly, R. Mozingo, and K. Folkers, *J. Amer. Chem. Soc.*, 1946, **68**, 776 ; A., 1946, II, 590.

[12] *J. Amer. Chem. Soc.*, 1945, **67**, 2276 ; A., 1946, II, 335.

[13] *Ibid.*, 1946, **68**, 1390 ; A., 1946, II, 708.

under similar conditions from dihydrostreptomycin. This dihydrostreptomycin was found to be active against *B. subtilis in vitro* and *S. schottmülleri in vivo* and was not inactivated by cysteine under conditions inactivating streptomycin.

A study of the toxicological and pharmacological properties of streptomycin has been made by H. Molitor, O. E. Graessle, S. Kuna, C. W. Mushett, and R. H. Silber[14]; the most unpleasant effect appears to be due to a histamine-like impurity not present in the best specimens. D. H. Heilman[15] has found that streptomycin, in tests carried out on tissue cultures of rabbit spleen cells, has a very low toxicity, whereas streptothricin showed a rather high toxicity for fibroblasts. Promising results have been obtained in the use of streptomycin for various infections including typhoid,[16] murine pertussis,[17] and type *B H. influenzæ*.[18]

Miscellaneous Antibiotics.—A great variety of higher and lower plants have been found to contain antibiotic substances. One example from the former type has been isolated from both *Arctium minus* Bernh. and *Onopordon tauricum* Willd. by E. P. Abraham, D. M. Crowfoot, A. E. Joseph, and E. M. Osborn[19]; the product may be identical or possibly isomeric with a substance extracted from *Arctium minus* by C. J. Cavallito, J. H. Bailey, and F. K. Kirchner.[20]

Streptothricin.—This substance has been isolated from culture broths of *Streptomyces lavendulæ* by R. L. Peck, A. Walti, R. P. Graber, E. Flynn, C. E. Hoffhine, V. Allfrey, and K. Folkers,[21] who have obtained the hydrochloride with activity 830 units per mg. Streptothricins of various states of purity have been examined for toxicity by G. Rake, D. Hamse, F. Kavanagh, W. L. Koerber, and R. Donovick[22]; a histamine-like impurity appears to be responsible for certain undesirable effects, but multiple lesions were found to follow intravenous injection of the purest material available. Similar results were obtained by H. J. Robinson, O. E. Graessle, M. Gundel, and R. N. Silber.[23]

G. H. Hogebloom and L. C. Craig[24] have isolated two crystalline antibiotic substances from *Aspergillus ustus* by countercurrent distribution treatment of a crude ethereal extract from the mould medium. One of these has been shown to be an acid of molecular weight about 350 and free from nitrogen, sulphur, or methoxyl; the other is similar.

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[14] *J. Pharm. Exp. Ther.*, 1946, **86**, 151; A., 1946, III, 666.

[15] *Proc. Soc. Exp. Biol. Med.*, 1945, **60**, 365; A., 1946, III, 666.

[16] H. A. Reimann, W. F. Elias, and A. H. Price, *J. Amer. Med. Assoc.*, 1945, **128**, 175; A., 1946, III, 666.

[17] W. L. Bradford and E. Day, *Proc. Soc. Exp. Biol. Med.*, 1945, **60**, 324; A., 1946, III, 666.

[18] H. E. Alexander and G. Leidy, *Science*, 1946, **104**, 101.

[19] *Nature*, 1946, **158**, 744.

[20] *J. Amer. Chem. Soc.*, 1945, **67**, 948; A., 1945, II, 339.

[21] *Ibid.*, 1946, **68**, 772; A., 1946, II, 628.

[22] *Amer. J. med. Sci.*, 1945, **210**, 61; A., 1946, III, 292.

[23] *J. Pharm. Exp. Ther.*, 1946, **86**, 22; A., 1946, III, 573.

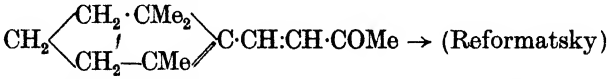
[24] *J. Biol. Chem.*, 1946, **162**, 363; A., 1946, III, 492.

Subtilin, from *B. subtilis*, has been found effective on type III pneumococcus infections in mice[25]; no toxic reactions were observed. A study of the physical and biological properties of subtilin and other antibiotics has been made by H. H. Anderson, G. G. Villela, E. L. Hansen, and R. K, Reed.[26] They find subtilin active *in vitro* against *Lactobacillus plantarum. Endamœba histolytica*, and *Trypanosoma equiperdum*; LD_{50} for subtilin and gramicidin under various conditions of administration to mice are recorded.

VITAMINS AND GROWTH FACTORS.

Vitamin-A.—Crystalline vitamin-*A* methyl ether has been prepared by A. R. Hanze, T. W. Conger, E. C. Wise, and D. I. Weisblat[27] by the action of methyl sulphate on the lithium derivative of the alcohol. W. Oroshnik[28] has described the synthesis of two substances considered probably to be stereoisomeric with this methyl ether but O. Isler, M. Kofler, W. Huber, and A. Ronco[29] claim the preparation of a vitamin-*A* methyl ether by the condensation of γ-2 : 6 : 6-trimethyl*cyclo*hex-1-enyl-α-methylbut-α-enal with α-methoxy-γ-methylpent-β-en-δ-yne, followed by hydrogenation, rearrangement, and dehydration, which, unlike Oroshnik's product, shows the characteristic absorption spectrum of vitamin-*A*. Oroshnik's claims are also criticised by J. Cymerman, (Sir) I. Heilbron, E. R. H. Jones, and R. N. Lacey,[30] whose own experience in condensing the "C_{14}-aldehyde" with hex-α-yne and with β-methoxyhex-γ-en-ε-yne suggests that under Oroshnik's conditions the expected fully conjugated system would not be obtained.

Vitamin-*A* acid [8-(2′ : 6′ : 6′-trimethyl*cyclo*hex-1′-enyl)-2 : 6-dimethylocta-1 : 3 : 5 : 7-tetraene-1-carboxylic acid] has been synthesised by D. A. van Dorp and J. F. Arens[31] from methyl ionylidenecrotonate by the following series of reactions :



$$\cdot CH{:}CH\cdot CMe{:}CH\cdot CH\cdot CO_2Me \longrightarrow \cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot CO_2H \longrightarrow$$

$$\longrightarrow (LiMe)\ \cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot COMe \longrightarrow$$

(Reformatsky) $\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CO_2Me \longrightarrow$ vitamin-*A* acid. The product has high biological potency, and the same authors[32] have shown that the activity of the sodium salt is not dependent on conversion in the organism into vitamin-*A*. Vitamin-*A* acid has also been synthesised by P. Karrer, E. Jucker, and E. Schick.[33]

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[25] A. J. Salle and G. J. Jann, *Proc. Soc. Exp. Biol. Med.*, 1946, **62**, 40; A., 1946, III, 1054.

[26] *Science*, 1946, **103**, 419.

[27] *J. Amer. Chem. Soc.*, 1946, **68**, 1389; A., 1946, II, 659.

[28] *Ibid.*, 1945, **67**, 1627; A., 1946, II, 81.

[29] *Experientia*, 1946, **2**, 31; A., 1946, II, 487.

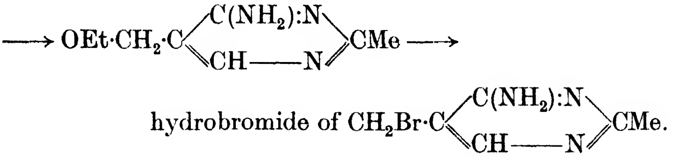
[30] *J.C.S.*, 1946, 500; A., 1946, II, 534.

[31] *Nature*, 1946, **157**, 190; *Rec. trav. chim.*, 1946, **65**, 338; A., 1946, II, 664.

[32] *Nature*, 1946, **158**, 622.

[33] *Helv. Chim. Acta*, 1946, **29**, 704; A., 1946, II, 536.

Aneurin.—G. V. Tschelintzev and Z. V. Benevolenskaja[34] have published a synthesis of aneurin which they claim to be particularly suitable for immediate industrial application. According to this, 6-amino-2-methyl-5-bromomethylpyrimidine hydrobromide is prepared by the following series of reactions: $\mathrm{OEt{\cdot}[CH_2]_2{\cdot}CN} \longrightarrow \mathrm{OEt{\cdot}CH_2{\cdot}C(CN){:}CH{\cdot}ONa} \longrightarrow \mathrm{OEt{\cdot}CH_2{\cdot}C(CN){:}CH{\cdot}OAc}$. $\mathrm{OEt{\cdot}CH_2{\cdot}C(CN){:}CH{\cdot}OAc} + \mathrm{NH_2{\cdot}CMe{:}NH}$



$$\longrightarrow \mathrm{OEt{\cdot}CH_2{\cdot}C}\left\langle\begin{array}{l}\mathrm{C(NH_2){:}N}\\ \mathrm{CH{-\!-\!-}N}\end{array}\right\rangle\mathrm{CMe} \longrightarrow$$

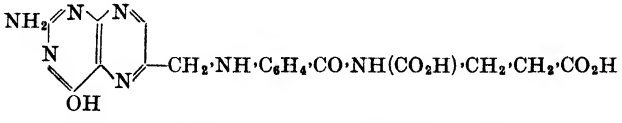
$$\text{hydrobromide of } \mathrm{CH_2Br{\cdot}C}\left\langle\begin{array}{l}\mathrm{C(NH_2){:}N}\\ \mathrm{CH{-\!-\!-}N}\end{array}\right\rangle\mathrm{CMe}.$$

W. Huber, W. Boehme, and S. C. Laskowski[35] have prepared water-insoluble derivatives of aneurin and niacin: examples include aneurin bis-(β-ethyl-*n*-hexyl sulphate), aneurin methylene-1 : 1′-bis-(2-hydroxy-3-naphthoate), aneurin bis(cholestenone-6-sulphonate), *p*-nicotinamidobenzoic acid, *N*-phenylcarbamylnicotinamide, 8-nicotinamido-6-methoxyquinoline, and butyl nicotinate methylene-1 : 1′-bis-(2-hydroxy-3-naphthoate).

Vitamin-D.—The preparation of 7-dehydrocholesterol from cholesterol has been the subject of publications during the year. The usefulness of *N*-bromosuccinimide as a brominating agent has again become apparent: H. B. Henbest, E. R. H. Jones, A. E. Bide, R. W. Peevers, and P. A. Wilkinson[36] have claimed a 30% yield of 7-dehydrocholesterol from cholesterol by bromination of cholesteryl acetate and dehydrochlorination of the product.

The use of certain quinones as dehydrogenating agents for cholesteryl acetate has been described by P. P. T. Sah.[37]

Folic Acid.—The structure of folic acid (liver *L. casei* factor) has been determined and proved by two syntheses[38] to be *N*-(*p*-2-amino-4-hydroxy-6-pteridylmethylaminobenzoyl)glutamic acid:



The first synthesis consisted of the interation of 2 : 4 : 5-triamino-6-hydroxypyrimidine, *p*-aminobenzoyl-*l*(+)-glutamic acid, and $\alpha\beta$-dibromopropaldehyde to yield a crude product containing about 15% of

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[34] *J. Gen. Chem. Russ.*, 1944, **14**, 1142; A., 1946, II, 559.

[35] *J. Amer. Chem. Soc.*, 1946, **68**, 187; A., 1946, II, 460.

[36] *Nature*, 1946, **155**, 169. Glaxo Laboratories, Ltd., E. R. H. Jones, and R. W. Peevers, B.P. 574,432; B., 1946, III, 82.

[37] *Rec. trav. chim.*, 1940, **59**, 454; A., 1946, II, 441.

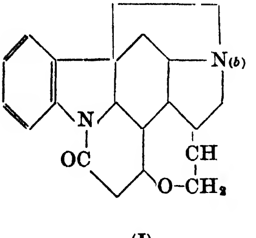
[38] R. B. Angier, J. H. Boothe, B. L. Hutchings, J. H. Mowat, J. Semb, E. L. R. Stokstad, Y. SubbaRow, C. W. Waller, D. B. Cosulich, M. J. Fahrenbach, M. E. Hultquist, E. Kuh, E. H. Northey, D. R. Seeger, J. P. Sickels, and J. M. Smith, *Science*, 1946, **103**, 667; A., 1947, II, 47.

active material, which was then purified. The second synthesis was carried out by interaction of $\alpha\beta$-dibromopropaldehyde with pyridine and condensing the product with 2 : 4 : 5-triamino-6-hydroxypyrimidine and potassium iodide; the resulting N-2-amino-4-hydroxy-6-pteridylmethylpyridinium iodide was then treated with p-aminobenzoyl-$l(+)$-glutamic acid and sodium methoxide in ethylene glycol to give a crude product also containing 15% of biologically active material (folic acid).

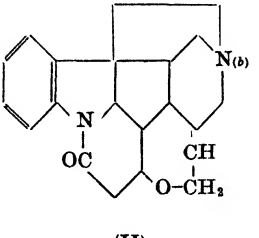
Antihæmorrhagic Compounds.—Three papers on the synthesis of compounds relating to vitamin-K were published by P. P. T. Sah[39] in Holland in 1940 but abstracted in 1946 : they refer particularly to the preparation of 2-methyl- and 2-ethyl-1 : 4-naphthaquinone. R. S. Shelton and M. G. Van Campen, jun. (Assrs. to W. S. Merrell Co.) claim the use of a water-soluble sodium bisulphite compound of 2-methylnaphthaquinone in cases of hypoprothrombinæmia.[40]

ALKALOIDS.

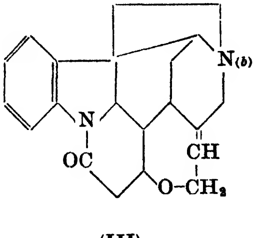
Strychnine.—The question of the structure of strychnine has been raised again, the commonly accepted structure (**I**)[41] having been modified, first by V. Prelog and S. Szpilfogel,[42] who have produced evidence in favour of ring E being six-membered, on the basis of fresh degradative experiments (**II**). (Sir) R. Robinson and H. T. Openshaw[43] have replied to Prelog and Szpilfogel, stating that this new structure does not explain the properties of ψ-strychnine (hydroxystrychnine), which undoubtedly contains the grouping $:C(OH)\cdot N_{(b)}\cdot$, and not $-CH(OH)\cdot N_{(b)}\cdot$ as required by Prelog. They further state that the new structure affords no basis for the formation of methoxymethyldihydro*chano*strychnone or of dihydrostrychnidine-*D*. Robinson and Openshaw, in the light of new data, suggest that a structure (**III**), considered by them first in 1942, is now better able to interpret the behaviour of strychnine than any other : this incorporates the six-membered E ring of Prelog and Szpilfogel and retains the G ring as six-membered by altering the point of attachment to ring E.



(I)



(II)



(III)

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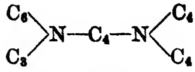
[39] *Rec. trav. chim.*, 1940, **59**, 461, 1021, 1029; A., 1946, II, 440.
[40] U.S.P. 2,331,808 ; B., 1946, III, 31.
[42] *Experientia*, 1945, **1**, 197 ; *Helv. Chim. Acta*, 1945, **28**, 1669 ; A., 1946, II, 168.
[43] *Experientia*, 1946, **2**, 28 ; *Nature*, 1946, **157**, 438 ; A., 1946, II, 512.

They point out that this latest structure shows a close relationship between cinchonine and strychnine :

$$C_6{-}N.C_5.N\langle^{C_4}_{C_4}$$

Cinchonine



$$^{C_6}_{C_3}\rangle N{-}C_4{-}N\langle^{C_4}_{C_4}$$

Strychnine

In these related groupings it is suggested that C_6 probably originated as glucose, C_3 as a triose, and that $N{\cdot}C_5{\cdot}N{\cdot}$ and $N{\cdot}C_4{\cdot}N$ were derived from *proto*lysine and *proto*ornithine respectively. The report is a preliminary one.

Curare Alkaloids.—Increased interest has been shown in curare alkaloids. T. C. Gray and J. Halton[44] have given a review of the history, pharmacology, physiology, and the use of *d*-tubocurarine chloride as an anæsthetic adjunct. A most important paper on the extraction of the alkaloids from tube curare has been published by J. D. Dutcher.[45] This paper establishes the botanical origin of *d*-tubocurarine chloride from tube curare as *Chondodendron tomentosum*, Ruiz and Pavon, N.O. Menispermaceæ. The procedure is given for isolation of crystalline *d*-tubocurarine chloride from desiccated extracts of freshly gathered plant material; the isolation of two new constituents of tube curare, *d*-*iso*-chondodendrine and its dimethyl ether, a new base *d*-chondodendrine, and *l*-curine is also described. The identification of *l*-curine is provisional, but chondodendrine is described as an alkaloid of bebeerine type, yielding quaternary salts of high potency. The subject has also brought interesting comment from H. King,[46] who states that a specimen of stems identified, with the leaves, as *Chondodendron tomentosum*, R and P., has been found to contain *l*-curine and *l*-tubocurarine chloride, the latter having a very weak curare action on rats' diaphragms. In view of Dutcher's results with Upper Amazonian material and his own results with Peruvian plants, King suggests that further botanical differentiation is required in the species of *Chondodendron tomentosum*, R and P. P. Karrer and H. Schmidt[47] have published the first paper of a projected new series on the subject of calabash curare. They describe the isolation of callebassine, *C*-curarine I, and nor-*C*-curarine I.

Cinchona Alkaloids.—N. Applezweig and S. E. Ronzone[48] have described a method suitable for extracting the alkaloids (totaquine) from low-grade South American bark. The fresh (not dried) bark is extracted with acid (81% yield from 82 hours' maceration) and the alkaloids are recovered by use of ion-exchange technique (98·6% recovery).

H. King,[49] by the use of the Bucherer reaction, has converted cupreine into cinchonidine and hydroquinidine (via hydrocupreidine) into

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[44] *Proc. Roy. Soc. Med.*, 1946, **39**, 400.

[45] *J. Amer. Chem. Soc.*, 1946, **68**, 419 ; A., 1946, II, 465.

[46] *Nature*, 1946, **158**, 515.

[47] *Helv. Chim. Acta*, 1946, **29**, 1853.

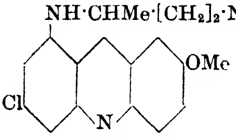
[48] *Ind. Eng. Chem.*, 1946, **38**, 576 ; B., 1946, III, 205.

[49] *J.C.S.*, 1946, 523 ; A., 1946, II, 560.

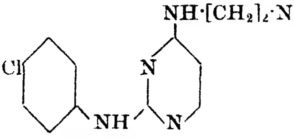
hydrocinchonidine, thereby affording support for the classification of the cinchona alkaloids proposed by King and Palmer.[50]

ANTIMALARIALS.

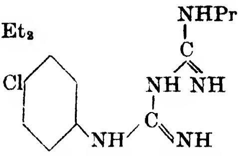
This subject has acquired new interest during the year as a result of the publication of the results of intensive war-time research in this country and in the United States. A very large number of publications on the subject have appeared and no short review could give a useful picture of the course of the researches; in this country, however, the main line of research has yielded the potent antimalarial paludrine, and an excellent account of the work leading up to its discovery has been given by F. H. S. Curd and F. L. Rose.[51] This substance is one of a series of substituted diguanides, namely N^1-*p*-chlorophenyl-N^5-*iso*propyldiguanide (No. 4888), prepared as a result of fundamental study of the structural requirements for antimalarial activity, commencing with mepacrine and pamaquine and passing through an important intermediate stage in the substance numbered 2666.



Mepacrine



No. 2666



No. 4888 (Paludrine)

The original synthesis of paludrine was as follows: *p*-$C_6H_4Cl{\cdot}N{:}NCl + NH_2{\cdot}C({:}NH){\cdot}CN \longrightarrow C_6H_4Cl{\cdot}N{:}N{\cdot}NH{\cdot}C({:}NH){\cdot}NH{\cdot}CN \rightarrow C_6H_4Cl{\cdot}NH{\cdot}C({:}NH){\cdot}NH{\cdot}CN \rightarrow C_6H_4Cl{\cdot}NH{\cdot}C({:}NH){\cdot}NH{\cdot}C({:}NH){\cdot}NHPr^{\beta}$. Very noteworthy claims have been made for the clinical importance of paludrine; the initial clinical trials showed it to be remarkably free from toxic side-effects and more active than either quinine or mepacrine.[52] The particular importance of the substance lies in its possibilities in true prophylaxis in malaria, which is not available in the use of mepacrine or quinine; it is a complete causal prophylactic in malignant tertain malaria and has a partial prophylactic effect in *Plasmodium vivax* infections.

The pharmacology of paludrine and other antimalarials has been studied by A. Spinks, M. M. Tottey, and B. G. Maegraith.[53]

American research on antimalarials has been sponsored by the Committee on Medical Research of the Office of Scientific Research and Development. A survey of antimalarial drugs has been carried out with a view to developing a compound superior to mepacrine. Very many classes of chemical compound have been studied but the most encouraging results obtained so far have been in the 4- and 8-aminoquinoline series.

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[50] *J.C.S.*, 1922, **121**, 2580.
[51] *Chem. and Ind.*, 1946, 75.
[52] Adams *et al.*, *Ann. Trop. Med. Parasitol.*, 1945, **39**, 208.
[53] *Biochem. J.*, 1946, **40**, *Proc.*, i; A., 1946, III, 478.

The substance SN (Survey Number) 7618, 7-chloro-4-(δ-diethylamino-α-methylbutylamino)quinoline, has been found to be an effective suppressive and to cause abrupt termination of clinical attacks of malaria due to *P. vivax*: *P. falciparum* malaria is also cured rapidly, while skin discoloration and gastro-intestinal symptoms such as accompany mepacrine therapy appear to be absent.[54]

The preparation and properties of SN 7618 are described by N. L. Drake, H. J. Creech, D. Draper, J. A. Garman, S. Haywood, R. M. Peck, E. Walton, and J. O'N. V. Hock.[55] Purified 4 : 7-dichloroquinoline was condensed with α-amino-δ-diethylaminopentane (by purification of commercial "Noval diamine"), followed by removal of unchanged reactants and precipitation of the diphosphate of SN 7618 from alcoholic solution. Hydrolysis of the phosphate gave the desired base. The side-chain is idential with that of pamaquin. An earlier paper by A. R. Surrey and H. F. Hammer[56] described the synthesis of this substance and a description has also appeared in the patent literature.[57] The name "chloroquine" has been used for SN 7618. Another promising antimalarial of the same general type is 8-(ε-*iso*propylaminoamylamino)-6-methoxyquinoline (SN 13276).[58,59] This is related to pamaquin in possessing the same quinoline nucleus ("toxophoric group") but differs in the side-chain ("conductophoric group"). It is prepared by alkylating 8 - amino - 6 - methoxyquinoline with α-chloro-ε-*iso*propylaminopentane hydrochloride. A statement of the biological activity of chloroquine (SN 7618) has been published by the U.S. Board for Co-ordination of Malarial Studies[60]; this gives the information that chloroquine has a toxicity comparable with that of mepacrine, does not cause skin discoloration, is sufficiently free from undesirable side reactions, and is considerably more effective as an antimalarial than mepacrine.

Steroids and Related Substances.

Bile Acids.—During the year the results of a large programme of sponsored work on the use of deoxycholic acid as a starting material for the partial synthesis of pregnane derivatives have been published in the American journals. This contributes some extremely valuable information to the general stock of knowledge of steroids and will doubtless help to pave the way to commercial applications. To do the subject justice in a short review is impossible and workers interested in this field should consult, in detail, the original papers. The collective efforts of the

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[54] *Science*, 1946, **103**, 8.

[55] *J. Amer. Chem. Soc.*, 1946, **68**, 1214; A., 1946, II, 699.

[56] *Ibid.*, 113; A., 1946, II, 401.

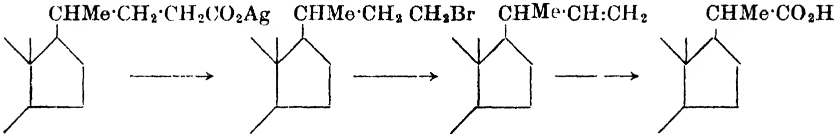
[57] U.S.P. 2,233,970.

[58] R. C. Elderfield, W. J. Gensler, J. D. Head, H. A. Hageman, C. B. Kremer, J. B. Wright, A. D. Holley, B. Williamson, J. Galbreath, L. Wiederhold, R. Frohardt, S. M. Kupchan, T. A. Williamson, and O. Birstein, *J. Amer. Chem. Soc.*, 1946, **68**, 1524; A., 1947, II, 86.

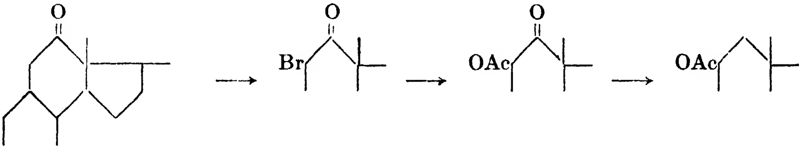
[59] N. L. Drake, J. Van Hook, J. A. Garman, R. Hayes, R. Johnson, G. W. Kelley, S. Melamed, and R. M. Peck, *ibid.*, 1529; A., 1947, II, 92.

[60] *J. Amer. Med. Assoc.*, 1946, **130**, 1069.

research teams of T. F. Gallagher, E. C. Kendall, E. S. Wallis, O. Wintersteiner, and others are to be found together in one issue of the *Journal of Biological Chemistry*.[61] The problems of major importance can be separated into three main requirements, the degradation of the bile acid side-chain, the transposition of nuclear hydroxyl or carbonyl groups, and the final conversion of a suitably hydroxylated ætio-acid into the desired pregnane derivative. The first requirement is general, but the second arises chiefly in the partial synthesis of corticosterone and related substances bearing oxygen atoms on $C_{(11)}$. N. G. Brink, D. M. Clark, and E. S. Wallis[62] have made a notable contribution to the first part of the problem by using the method, recently studied by H. Hunsdiecker and C. Hunsdiecker,[63] of degrading silver salts of carboxylic acids to alkyl bromides containing one less carbon atom, by reaction with bromine ; the bromide is then dehydrohalogenated and oxidised to the corresponding bisnor acid.



Much of the recorded work has been concerned with the second part of the problem ; the essential requirement is the replacement of the $C_{(12)}$ hydroxyl, characteristic of certain bile acids, by a $C_{(11)}$ hydroxyl or carbonyl, characteristic of corticosterone (and of digoxigenin). T. F. Gallagher and W. P. Long[64] have described an improved preparation of 3(α) : 11(α)-dihydroxycholanic acid from deoxycholic acid by bromination of methyl 3-hydroxy-12-ketocholanate, replacement of the bromine atom by acetoxy, and reduction (Wolff–Kishner) of the acetoxy-ketone.



This method is not new, having been used on several occasions previously, notably by E. Seebeck and T. Reichstein,[65] who obtained two $C_{(11)}$ epimeric 11-bromo-12-keto-esters, and by R. E. Marker and E. J. Lawson,[66] whose claim to have prepared 3(α) : 11-dihydroxy-12-ketocholanic acid has been contested by T. F. Gallagher[67] ; it appears that Marker and Lawson's acid was in reality the 11-keto-12-hydroxy-isomer.

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[61] *J. Biol. Chem.*, 1946, **162**, 491–733 ; A., 1946, II, 441–450.
[62] *Ibid.*, 695 ; A., 1946, II, 447.
[63] *Ber.*, 1942, **75**, [*B*], 291 ; cf. A., 1942, II, 444.
[64] *J. Biol. Chem.*, 1946, **162**, 521 ; A., 1946, II, 443.
[65] *Helv. Chim. Acta*, 1943, **26**, 536.
[66] *J. Amer. Chem. Soc.*, 1938, **60**, 1334.
[67] *J. Biol. Chem.*, 1946, **162**, 539 ; A., 1946, II, 444.

Other workers have shown interest in the utilisation of the unsaturated ester resulting from dehydration of esters of 12-hydroxy-3-acyloxycholanic acids. L. H. Sarett[68] has prepared methyl 12-bromo-3(α) : 11-dihydroxybisnorcholanate from methyl 3(α)-acetoxybisnorchol-11-enate via the bromohydrin, and E. M. Hicks, jun., and E. S. Wallis[69] have used a similar method for preparing methyl 11-keto-3(α)-acetoxycholanate from methyl 3(α)-acetoxychol-9(11)-enate via the bromohydrin and bromo-ketone. The preparation of 11 : 12-oxidocholanic acids has also claimed attention of E. M. Hicks, jun., C. J. Berg, and E. S. Wallis[70] and others.

J. von Euw and T. Reichstein[71] have described the dehydration of 11-hydroxy-steroids by conversion into toluenesulphonic esters and heating the esters with bases such as collidine. The same authors[72] have also published a new partial synthesis of 11-dehydrocorticosterone from methyl 3 : 11-diketoætiochol-4-enate.

C. Meystre, H. Frey, R. Neher, A. Wettstein, and K. Miescher[73] have used their degradation method for bile acid side-chains, reported last year, to prepare pregnenolone and progesterone from 3(β)-hydroxychol-5-enic acid.

ŒSTROGENS.

The work on œstrogenic carboxylic acids, the first stages of which were reported last year, has been continued by K. Miescher and his collaborators. R. Neher and K. Miescher[74] have prepared carboxylic acid analogues of "stilbœstrol" and "hexœstrol" and of the triphenylethylene group of synthetic œstrogens, with many homologues. The greatest œstrogenic activity found among these new substances so far was that of the "stilbœstrol" analogue in which one hydroxyl group is replaced by carboxyl; this replacement resulted in a dop in activity to about one fiftieth of that of the diphenol. J. Heer and K. Miescher[75] have studied relationships between the compounds of the doisynolic acid type and the œstrogenic hormones and have converted acids of the marrianolic acid type into the corresponding doisynolic acids. The resolution of *r*-*n*-bisdehydrodoisynolic acid methyl ether has been effected by R. Rometsch and K. Miescher,[76] using *l*-menthol; the synthetic (—)-acid was found to be identical with the methyl ether of the acid prepared from equilenin.

Synthetic Œstrogens.—M. Rubin and H. Wishinsky[77] have described 4-*p*-hydroxyphenyl-1-methyl-3-ethyl*cyclo*hex-3-enylethylcarbinol as an

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[68] *J. Biol. Chem.*, 1946, **162**, 591; A., 1946, II, 446.
[69] *Ibid.*, 641; A., 1946, II, 447.
[70] *Ibid.*, 633; A., 1946, II, 446.
[71] *Helv. Chim. Acta*, 1946, **29**, 654; A., 1946, II, 545.
[72] *Ibid.*, 1913; A., 1947, II, 130.
[73] *Ibid.*, 627; A., 1946, II, 546.
[74] *Ibid.*, 449; A., 1946, II, 537.
[75] *Ibid.*, 1895; A., 1947, II, 129.
[76] *Ibid.*, 1231; A., 1946, II, 667.
[77] *J. Amer. Chem. Soc.*, 1946, **68**, 338; A., 1946, II, 432.

"open model" of œstrone. Other authors have prepared and studied a variety of classes of compound with possible œstrogenic activity; the types of compound include naphthalene derivatives,[78] indene and dihydronaphthalenes,[79] indole derivatives,[80] and coumarones.[81] A. Horeau and J. Jacques[82] have commenced a study of compounds containing a phenolic group and a *cyclo*pentanone nucleus separated by varying numbers of carbon atoms; the first member of the series, 2-*p*-hydroxybenzyl*cyclo*pentanone, is described as having slight œstrogenic activity.

In the "stilbœstrol"–"hexœstrol" class, B. J. F. Hudson and E. Walton[83] have described the syntheses of 4 : 4′-dihydroxy-tetramethylstilbene and -tetramethyldibenzyl. A. E. W. Smith[84] has published an alternative route to α-ethyldeoxyanisoin, an intermediate in the standard synthesis of stilbœstrol : β-amino-αα-dianisyl-*n*-butanol was prepared by interaction of magnesium *p*-anisyl bromide with ethyl α-amino-*n*-butyrate hydrochloride in 64% yield and deaminated in 90% yield to α-ethyldeoxyanisoin.

The 3 : 3′-diallyl derivatives of "stilbœstrol" and "hexœstrol" have been prepared by E. Kaiser and J. J. Svarz[85] by Claisen rearrangement of the diallyl ethers of the parent substances; from these the dipropenyl and dipropyl derivatives have been obtained.

A. H. Stuart, A. J. Shukis, R. C. Tallman, C. McCann, and G. R. Treves[86] have prepared and studied a series of trialkyl derivatives of αγ-di-(*p*-hydroxyphenyl)propane; they find that an isomeric form of the diethylmethyl derivative, βδ-di-(*p*-hydroxyphenyl)-γ-ethylhexane, possesses the greatest activity in the series, being approximately midway between œstrone and œstradiol. This substance is now used in America in similar manner to "stilbœstrol" and "hexœstrol" under the name "Benzestol."

MISCELLANEOUS.

Rutin.—Interest has been shown during the year in the use of rutin in the treatment of capillary fragility. A useful source is the leaves and flowers of buckwheat; 2—3% have been obtained[87] by extraction of dried ground leaf with hot water, followed by precipitation of impurities with alcohol. J. F. Couch, J. Naghski, and C. F. Krewson[88] have investigated sources of rutin and have found that Japanese buckwheat can yield up to 6% but that the average yield from leaves and blossoms is 2½%.

Organic Fluorine Compounds.—Highly toxic alkyl fluorophosphonates

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[78] B. J. F. Hudson, *J.S.C.*, 1946, 76; A., 1946, II, 261.
[79] M. Silverman and M. T. Bogert, *J. Org. Chem.*, 1946, **11**, 34; A., 1946, II, 380.
[80] C. Mentzer and D. Xuong, *Compt. rend.*, 1946, **222**, 1176; A., 1946, II, 682.
[81] D. Molho and C. Mentzer, *ibid.*, **223**, 333; A., 1946, II, 681.
[82] *Bull. Soc. chim.*, 1945, [v], **12**, 1001; A., 1946, II, 498.
[83] *J.C.S.*, 1946, 85; A., 1946, II, 260.
[84] *Ibid.*, 572; A., 1946, II, 533.
[85] *J. Amer. Chem. Soc.*, 1946, **68**, 636; A., 1946, II, 484.
[86] *Ibid.*, 729; A., 1946, II, 584.
[87] *Chem. Industries*, 1946, **59**, 74; B., 1946, III, 240.
[88] *Science*, 1946, **103**, 199.

have been described by H. McCombie and B. C. Saunders[89]; they possess high toxicity as lethal inhalants, but in lower, non-fatal, concentrations produce very pronounced miosis. Production on a semi-technical scale has been accomplished in three stages without separation of intermediates. The most important member of the series, di*iso*propyl fluorophosphonate, is prepared by chlorinating, in carbon tetrachloride, the crude product from interaction of phosphorus trichloride with *iso*propyl alcohol, and heating the product with sodium fluoride; overall yields of about 60% are obtained. The esters of fluorophosphoric acid inhibit the action of the enzyme choline-esterase,[89] the di*iso*propyl ester ("D.F.P.") being active in concentrations of the order of 10^{-10}M. R. Couteaux, H. Grundfast, D. Nachmansohn, and M. A. Rothenberg[90] have studied the effect of "D.F.P." on the action potential of muscle, with the result that they consider that they have produced the first evidence that acetylcholine may play a rôle in muscle action potential. E. D. Adrian, W. Feldberg, and B. A. Kilby[91] have drawn attention to the fact that the choline-esterase-inhibiting effect of fluorophosphonates was first observed in 1941, and note the similarity of effect between the fluorophosphonates and eserine.

Antihistamine Compounds.—Three important histamine antagonists have appeared; the first, benzyl(dimethylaminoethyl)aniline ("Antergan"), has been claimed to possess a remarkable specific antihistamine effect, abolishing all of the effects of histamine and used successfully in cases of urticaria, hay fever, pruritis, and migraine.[92] Good results have also been obtained with pyridyl-*N*′-benzyl-*N*-dimethylethylenediamine ("Pyribenzamine")[93] but most attention has been paid to benzhydryl-β-dimethylaminoethyl ether hydrochloride ("Benadryl"), which is already in clinical use; Benadryl has been found most effective in the treatment of hay fever[94] whilst both Pyribenzamine and Benadryl give protection against experimental anaphylactic shock.[95] T. H. McGavack, H. Elias, and L. J. Boyd[96] have found Benadryl to have few minor untoward effects and consider it an effective agent for use in allergic diseases such as asthma; H. Elias and T. H. McGavack[97] have also stated that oral administration of Benadryl is effective in the treatment of histamine wheal and flare reactions. C. V. Winder, M. E. Kaiser, M. M. Anderson, and E. M. Glassco[98] have studied the myotropic, spasmolytic, histaminolytic, and atropine-like actions of derivatives of Benadryl.

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[89] *Nature*, 1946, **157**, 287, 776; Cf. A., 1947, II, 105.

[90] *Science*, 1946, **104**, 317.

[91] *Nature*, 1946, **158**, 625.

[92] P. Chauchard, *Rev. sci.*, 1943, 466; *Chem. Abs.*, 1946, 6167.

[93] R. L. Mayer, H. W. Hays, D. Brousseau, D. Mathieson, B. Rennick, and F. F. Yonkman, *J. Lab. clin. Med.*, 1946, **31**, 749; A., 1946, III, 1061.

[94] D. Harley, *Lancet*, 1946, **251**, 158; A., 1946, III, 950.

[95] S. Friedlaender, S. M. Feinberg, and A. R. Feinberg, *Proc. Soc. Exp. Biol. Med.*, 1946, **62**, 65; A., 1946, III, 950.

[96] *J. Lab. clin. Med.*, 1946, **31**, 560; A., 1946, III, 760.

[97] *Proc. Soc. Exp. Biol. Med.*, 1946, **61**, 133; A., 1946, III, 760.

[98] *J. Pharm. Exp. Ther.*, 1946, **87**, 121; A., 1946, III, 848

ESSENTIAL OILS, ISOLATES, AND DERIVATIVES.

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THE literature of essential oils has shown a notable increase this year, doubtless due to the fact that many scientific workers have returned to their peace-time activities and also to the renewal of contacts with continental workers. Within the Empire the cultivation of plants yielding essential oils is being pursued on sound lines. In Australia[1] extensive plantations have been established for the cultivation of small populations of *Eucalyptus australiana*, *E. amygdalina*, *E. numerosa*, *E. dives*, *E. dives* var. C., *E. polybractea*, *E. staigeriana*, *E. citriodora*, *Leptospermum citratum*, *Melaleuca alternifolia*, and *M. smithii* with a view to determining whether the species and individual trees breed true in respect to yield and type of oil, and also to ascertain whether the selected parents were superior to other trees of the same species with respect to such characteristics as vigour of growth, yield and composition of oil, etc. Some attention has been given to the natural stands of such species as *E. dives* and *E. australiana*, which are now much reduced in extent and warrant extended plantations. In some stations worthless species have been removed to allow for further development of useful Eucalypts and the planting of seedlings to fill the gaps. Samples of cinnamon-bark oil from Seychelles[2] have been examined; none of these conformed to the B.P. requirements, and it was not possible to produce an oil in conformity by fractional distillation. The main difference between these oils and that from Ceylon bark is considered to be the deficiency of eugenol in the former, which may be due to climatic and soil conditions or to the difference in age of the two types of bark when distilled. A monograph on patchouli oil[3] has been published, by the Mysore Government, in which the present position of the industry is reviewed. An account is also given of investigations carried out in India on the oil of the indigenous species *Pogostemon heyneanus* and also on that of Singapore plants of *P. patchouli* cultivated in Bangalore. A sample of patchouli oil[4] from Nyasaland was found to have constants similar to those of the Seychelles oil. S. G. Sastry[5] gives figures for the yield and constants of linaloe oil distilled from the berries and husks of trees cultivated in Mysore, whilst M. N. Subba Rao and M. Nagesa Rao[6] compare the characters of the leaf and berry oils distilled from trees grown in the same state.

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[1] A. R. Penfold and F. R. Morrison, *Perf. Ess. Oil Rec.*, 1946, **37**, 172.

[2] D. J. Cosgrove and H. T. Islip, *Bull. Imp. Inst.*, 1946, **44**, 188; B., 1947, III, 80.

[3] M. N. Subba Rao and M. Nagesa Rao, Board of Scientific and Industrial Research, Government of Mysore.

[4] H. T. Islip, *Bull. Imp. Inst.*, 1946, **44**, 12; B., 1946, III, 223.

[5] *J. Sci. Ind. Res., India*, 1945, **3**, 516; B., 1946, III, 120.

[6] *Perf. Ess. Oil Rec.*, 1946, **37**, 312.

Production.

R. S. Aries[7] points out that present practices in forestry in the north-eastern United States result in large wastes of tree constituents which might be utilised economically by the essential oil industry. Yields of oils from the leaves of various conifers are quoted. Methods of distillation are discussed and suitable types of mobile still are described.

Composition and Characters.

Some new oils have been examined and a number of familiar oils from new sources have been investigated.

Agathosma apiculata : "*Sea Buchu.*"[8]—The fresh leaves yielded 0·32% of oil with an odour suggestive of asafœtida. The chief constituents were α-β-pinene 25%, a terpene of b.p. 171—173°/730 mm. 8%, "butyl 1-pentenyl disulphide" 30%, a compound $C_{10}H_{16}O_2$ (probably a hexadienyl ester of *n*-butyric acid) 30%, resins, and a trace of free acid, probably butyric.

Anisomeles malabarica.[9]—Oils were obtained by steam-distillation, salting-out, and ether extractions of the flowers (0·07%), the leaves (0·25%), and the roots and stems (0·0045%). Citral and an unsaturated acid (possibly geranic acid) were isolated.

Artemisia balchanorum.[10]—The dried herb from wild plants of the Turkman Republic yielded 0·8—1·0%. The oil contained about 5% of citral; 40—50% of linalol, and 25—30% of geraniol.

Cinnamon-Leaf Oil.[11]—Dried leaves yielded about 2% of oil containing 70—90% of eugenol. It is suggested that in India the selection of varieties and the improvement of methods of distillation should be considered.

Quebec Conifers.[12]—An investigation of yields and characters of oils obtained by steam distillation of leaves of Eastern white cedar (*Thuja occidentalis* L.), balsam fir (*Abies balsamea* L., Mill.), white pine (*Pinus strobus* L.), black spruce (*Picea mariana* Mill.), and Eastern hemlock (*Tsuga canadensis* L.) showed that maximum yields were obtained from young trees from January to April, while the period of secondary maximum yields was from September to November. Yields to be expected on a commercial scale are: cedar 0·6—1·0%, balsam 1·0—1·4%, pine 0·6—1·0%, spruce 0·5—0·7%, and hemlock 0·4—0·6%.

Ginger scrapings[13] yielded to distillation 0·8% of an oil containing camphene, β-phellandrene and zingiberene.

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[7] *Amer. Perfumer*, 1946, **48**, *No.* 9, 45; *No.* 10, 47.

[8] J. L. B. Smith and D. E. A. Rivett, *Trans. Roy. Soc. S. Africa*, 1946, **31**, 111.

[9] S. B. Rao and D. N. Majumdar, *Indian J. Pharm.*, 1945, **7**, 123; B., 1946, III, 161.

[10] R. J. Rafanova, *Pischevaya Prom.*, 1944; *Chem. Abs.*, 1946, 430.

[11] S. Krishna, H. R. Kamath, K. T. Kudva, and K. G. Kudva, *J. Sci. Ind. Res., India*, 1946, **4**, 464; B., 1946, III, 160.

[12] J. Risi and M. Brûlé, *Lab. Produits Forestiers, Ministère Terres & Forêts Quebec, Bull.* **9**, 1945.

[13] N. S. Varier, *Current Sci.*, 1945, **14**, 322; B., 1946, III, 182.

Inula crithmoides.[14]—The flower heads yielded an oil containing about 64% of monocyclic hydrocarbons and about 21% of hydroxy-compounds. The main fraction contained *p*-cymene, *d*-α-phellandrene, and probably *l*-phellandrene. Other constituents were a phenol, a menthenediol (?), α-phellandrene glycol (?), and a compound giving a dinitrophenylhydrazone of m.p. 151°.

Juniper oils[15] distilled from *J. semiglobosa*, *J. turkestanica*, *J. polycarpus*, and *J. excelsa* have been examined and the characters recorded; the main constituent was found to be α-pinene but cedrene and cedrol were also present. Lavandin oil[16] has been investigated and found to contain *d*-camphor, *l*-α-terpineol, *d*-borneol, lavandulol, nerol, *l*-perillic alcohol, *l*- and *d*-α-pinene, *l*- and *d*-camphene, *l*-limonene, dipentene, and epoxylinalol and its acetate; methods for distinguishing this oil from lavender oil are described.

French lavender oil[17] has been found to contain *l*-*n*-amylvinylcarbinol (*l*-oct-1-en-3-ol), mainly as acetate, to the extent of about 0·5%.

Six samples of Palestinian lemon oil[18] were examined at the Imperial Institute and were found to meet the requirements of the British Pharmacopœia except that in every case the optical rotation was higher, and one sample contained more than the permissible amount of non-volatile matter; after storage in half-filled bottles in the dark for 4—5 months the specific gravity had increased while the optical rotation had decreased, as also had the citral content.

Sicilian lemon oil[19] (citral 5·35%) was fractionated to yield a terpeneless oil with a citral content of 40·5—43·2% which on further fractionation yielded 5·36% of sesquiteterpeneless oil (citral 60·5%).

Samples of oil obtained by cold compression from Persian limes[20] contained 8·01% of citral and total solids 11·4%. In an account of Mexican linaloe oil production,[21] it is stated that the oil is distilled mainly from the wood of wild trees of several species of *Bursera* which become oil-bearing when about 20 years old. After distillation for 12 hours the yield is about 2%. The berries yield about 3%, which is often blended with the wood oil.

Lophanthus anisatus Benth. ("anise-hyssop")[22] (dry plant) yields 0·079—0·76% of oil containing up to 93% of methylchavicol, some *d*-limonene, probably α-pinene, and a mono- or di-cyclic sesquiterpene.

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[14] M. Harispe-Grandperrin and J. V. Harispe, *Bull. Soc. Chim. biol.*, 1944, **26**, 192; B., 1946, III, 161.

[15] N. P. Sokolnikov, *Pischevaya Prom.*, 1944; *Chem. Abs.*, 1946, 679.

[16] Y. R. Naves, *Helv. Chim. Acta*, 1945, **28**, 1220; B., 1946, III, 81.

[17] L. Crabalona, *Bull. Soc. chim.*, 1944, [v], **11**, 67; A., 1946, II, 2.

[18] H. T. Islip and F. Major, *Bull. Imp. Inst.*, 1946, **44**, 5; B., 1946, III, 223.

[19] P. Leone, *Riv. ital. essenze profumi*, 1946, **28**, 5; *Drug & Cosmetic Ind.*, 1946, **59**, 697.

[20] *Perf. Ess. Oil Rec.*, 1946, **37**, 147.

[21] B. Du Frane, *Agriculture in the Americas*, 1946, **6**, 19; *Drug & Cosmetic Ind.*, 1946, **58**, 705.

[22] E. H. Polak and R. M. Hixon, *J. Amer. Pharm. Assoc.*, 1945, **34**, 240; B., 1946, III, 13.

Hybrid mints[23] produced by crossing Japanese *Mentha arvensis* var. *piperascens* with *M. spicata* gave good yields of oil per acre but the oil had a low menthol content, whilst hybrids of Japanese with *M. aquatica* gave low yields of oil of high menthol content. The hybrids showed good resistance to disease. Two tetraploids of spearmint, obtained by colchicine treatment, gave only traces of oil.

Ocimum gratissimum Roxb.[24] yielded 0·1% of greenish-yellow oil containing citral 66·6, geraniol 25·7, citronellol 2·8, geranyl acetate 1·5, sesquiterpenes 2·4, and residue 6·6%.

Spanish pennyroyal oil[25] distilled from *Mentha pulegium* and other species (yield about 1%) was found to contain pulegone 85—96% (assayed by neutral sulphite method, shaking on water-bath for four hours).

Coulter pine oleoresin[26] from *Pinus coulteri* D. Don yielded an oil consisting mainly of l-α-pinene, 30—35%, and l-β-phellandrene, 35—45%, with n-heptane about 5% and n-undecane about 10% ; it is suggested that the presence of paraffin hydrocarbons in turpentines may be more common than earlier investigations have indicated.

An examination of Brazilian sassafras oil[27] distilled from the wood of *Ocotea pretiosa* Benth & Hook. f. showed that it had a higher specific gravity and refractive index than the U.S.P. oil; it was also slightly lævorotatory. Taste and odour tests on 28 individuals showed that there was a marked preference for the Brazilian oil.

An oil extracted with ether and light petroleum from Spanish broom[28] (*Spartium junceum*) contained free acids including octoic, phenols with an odour of leather and pepper, fatty aldehydes, terpenes, and esters of formic, acetic, and higher fatty acids.

Sphæranthus indicus L.,[29] an annual herb distributed throughout India and Ceylon and growing in Malaya, China, Africa, and Australia, yielded to steam-distillation of the fresh flowering plants an oil having d^{30} 0·9419, n_D^{20} 1·1512, acid value 2·403, ester value 47·80, ester value (after acetylation) 74·15.

Isolates and Derivatives.

An investigation by Swiss workers[30] indicates that the odourless constituent of ambergris, ambrein, is a doubly unsaturated tertiary alcohol $C_{30}H_{52}O$; it probably belongs to a new group of tricyclic terpenes, and a structural formula is suggested.

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[23] A. J. Sievers, M. S. Lowman, and M. L. Ruttle, *J. Amer. Pharm. Assoc.*, 1945, **34**, 225; B., 1946, III, 13.

[24] S. Nigam and S. Dutt, *Indian Soap J.*, 1944, *Dec.*; *Drug & Cosmetic Ind.*, 1946, **58**, 852.

[25] *Perf. Ess. Oil Rec.*, 1946, **37**, 92.

[26] N. T. Mirov, *Ind. Eng. Chem.*, 1946, **38**, 405; A., 1946, III, 616.

[27] A. A. Dodge, *Amer. J. Pharm.*, 1946, **118**, 116; B., 1946, III, 223.

[28] S. Sabetay and G. Igolen, *Ann. Chim. analyt.*, 1946, **27**, 224.

[29] N. K. Basu and P. P. Lamsal, *J. Amer. Pharm. Assoc.*, 1946, **35**, 274.

[30] L. Ruzicka, F. Lardon, and H. Weden, *Helv. Chim. Acta*, 1946, **29**, 912; A., 1946, II, 601.

In a series of studies on the activation of camphene[31] the authors report the advantages of carrying out the procedure in emulsions. The oxidation of camphene by chromic–sulphuric acids as emulsifiers proceeds 1½—2 times as rapidly as does the reaction without emulsification, with a yield increase of 5—7% at this temperature and up to 15% at 60—70°. The yields of camphor range from 70% at 80—90° to 88% at 60—70°.

The synthesis of camphor from *p*-cymene is described by F. Schwartz,[32] the three double bonds being saturated with hydrogen and oxygen in the proportion in which they occur in water. *p*-Cymene and water are dissolved in a miscible solvent (*e.g.*, alcohol, aldehyde, ether, or ester) in presence of a catalyst such as mercury or a mercury salt, the reaction being carried out at boiling point. H. Karma and F. Grönberg[33] describe the effect of micro-sublimation on cloves. When cloves, mother cloves, or clove stalks are heated and allowed to cool, crystals of caryophyllin appear. In the micro-sublimation of cloves, the first fraction formed oily drops of eugenol. After some days, the sublimate at reduced pressure crystallised; the crystals were of vanillin. Later fractions yielded small crystals which were not identified, and finally large crystals of the last fraction were found to be caryophyllin. Y. R. Naves[34] found that epoxylinalol, free or esterified, is present in lavandin oil and free in oil of shiu; a method of detection is given. The constitution of *d*- and *l*-phellandral[35] has been verified by oxidation to *d*- and *l*-β-*iso*propyladipic acids, which showed no rotation although they yielded a series of optically active derivatives. The Essential Oil Association of U.S.A.[36] has issued a specification for hydroxycitronellal, which may be the optically active variety from Java citronella or the inactive form from *Eucalyptus citriodora* : d_{15}^{15} 0·925—0·930; α_D Java +9° to +10·5°, *E. citriodora* +0·5° to −0·5°; n_D^{20} 1·448—1·450; purity not less than 95%; solubility in alcohol: in 1½ and more volumes of 50%, soluble in all proportions of 60%. A new monoterpenic alcohol, lavandulol,[37] has been isolated from the oil of *Lavandula vera*. It is a primary, doubly unsaturated alcohol, $C_{10}H_{18}O$, showing great similarity to geraniol although it differs from the latter by its boiling point and optical activity and by the fact that it forms no crystalline additive compound with calcium chloride. Lavandulol has been shown to be 2 : 6-dimethyl-5-hydroxymethylhepta-2 : 6-diene.

M. S. Kharasch and W. B. Reynolds[38] describe a method for the production of limonene from pinene; pinene is heated to 120—200° with an organic acid and an organic acid amide and the reaction mixture steam-distilled to recover the terpene, which may contain as much as

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[31] A. A. Berlin, A. B. Davankov, and L. E. Kalliopin, *J. Appl. Chem. Russ.*, 1946, **18**, 217; *Chem. Abs.*, 1946, 3741.

[32] U.S.P. 2,389,389.

[33] *Farm. Notisblad*, 1945, **54**, 347; *Quart. J. Pharm.*, 1946, **19**, 76.

[34] *Helv. Chim. Acta*, 1945, **28**, 1231; B., 1946, III, 82.

[35] G. Burger and A. K. Macbeth, *J.C.S.*, 1946, 145; A., 1946, II, 333.

[36] Scientific Section of Essential Oil Assoc. of U.S.A., *Jan.*, 1946.

[37] H. Schinz, *Perf. Ess. Oil Rec.*, 1946, **37**, 167.

[38] Assrs. to Research Corp., U.S.P. 2,382,641.

70 or 80% of active limonene. B. Puetzer and W. J. Moran[39] describe a method for the separation of pure *l*-menthol in a yield of 61% of the theoretical from *dl*-menthol, using *l*-ephedrine as the resolving agent for the acid succinates.

Y. R. Naves[40] has shown that oil of petitgrain (*Citrus bigaradia*) contains *l*-linalyl acetate, a feebly lævorotatory mixture of linalols, and a mixture of terpineols with esters of geraniol and nerol. M. Sandoz[41] claims the extraction from the leaves and fruit of *Myrica asplenifolia* of a waxy yellow solid soluble in ethyl alcohol and fixed oils ; this substance is said to be a useful fixative, with a pleasant odour which harmonises with perfume constituents.

Analytical.

In a study of volumetric oxime and gravimetric 2 : 4-dinitrophenylhydrazine methods for the determination of benzaldehyde, cinnamaldehyde, and vanillin, M. E. Martin, K. L. Kelly, and M. W. Green[42] found that the method of the N.F. VIII gave the most satisfactory results ; the authors point out that care is necessary in titrating to the proper greenish-yellow end-point of the bromophenol-blue (pH 3·45) and in matching the samples to the blank. The Essential Oil Sub-Committee of the Analytical Methods Committee of the Society of Public Analysts and other Analytical Chemists[43] has reported that the "Schimmel's test" or "raised Schimmel's test" for the solubility of citronella oil is unsatisfactory, inasmuch as it is not sufficiently well defined to give concordant results in different hands ; a new test to be known as "The London solubility test" is described. M. Cerny[44] gives a colorimetric method for the determination of coumarin in plant material. A method claimed to be more economical and less time-consuming than that of the U.S.P. for the determination of menthol in peppermint oil is described by J. S. Jones and S. C. Fang[45] ; about 0·6 g. of oil is allowed to react with acetic anhydride in the presence of pyridine for 48 hours, and the mixture is then titrated under specified conditions with standard alkali. The allylthiocarbimide content of four samples of black mustard seed has been determined by Mme. André and M. Kogane-Charles,[46] who found close agreement by the silver nitrate and iodine volumetric methods and by Jørgensen's gravimetric method ; the same concordance was not obtained with rape seed. Essential oil of black mustard was found to contain only 92—93% of allylthiocarbimide.

Y. R. Naves[47] advocates measurements of refractive dispersion of

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[39] *J. Amer. Pharm. Assoc.*, 1946, **35**, 127 ; A., 1946, II, 451.

[40] *Helv. Chim. Acta*, 1946, **29**, 553 ; B., 1946, III, 206.

[41] Assr. to B. T. Bush, Inc., U.S.P. 2,383,517.

[42] *J. Amer. Pharm. Assoc.*, 1946, **35**, 220 ; C., 1946, 271.

[43] *Analyst*, 1945, **70**, 442 ; C., 1946, 33.

[44] *Chem. Obzor* ; *Chem. Abs.*, 1945, 3328.

[45] *Ind. Eng. Chem.* [*Anal.*], 1946, **18**, 130 ; C., 1946, 192.

[46] *Compt. rend.*, 1946, **222**, 103 ; B., 1946, III, 223.

[47] *Manufg. Chem.*, 1945, **16**, 429 ; C., 1946, 113.

essential oils as a supplement to refractive indices in the analysis of essential oils; the value of the method is demonstrated by examples of oils of pennyroyal, lovage, and jasmine.

A new method for the determination of the volatile oil content of spices is described by K. H. Landes,[48] in which the dried ground spice is mixed with anhydrous sodium sulphate and extracted with dry ether; the ether is removed at 47°, and the total extract is heated at 110° to drive off the matter volatile in steam, leaving a non-volatile residue.

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[48] *Spice Mill*, 1945, *No.* 5, 59.

PHOTOGRAPHIC MATERIALS AND PROCESSES.

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Despite difficulties to be expected in a post-war period mainly of shortages of manpower and raw materials, the quantity of published literature concerned with the photographic process has been phenomenally high. The subject of colour photography has again received the most attention, the work being largely published in the form of patents describing various types of colour-couplers, but it is interesting to note that the section on latent image and sensitivity is substantially larger, showing that the importance of pure research is recognised.

The employment of photographic methods in the most recent scientific investigations is exemplified by the preparation of special emulsions, and use of new methods for detection of fast charged particles and the studying of fission fragment tracks.[1]

Perhaps the most interesting publications from the point of view of the industry itself were the reports of the members of the various Intelligence Services, who were sent to German photographic factories, mainly those of Agfa, to investigate and report on the methods of the German manufacturers. Possibly the two most noteworthy features of these publications are in the first place a complete series of formulæ of emulsions to be coated on paper, and secondly a detailed description of the method of manufacture and processing of the Agfa colour materials. The general details of these materials were already known. Briefly the process is one of subtractive colour photography using colour development with a multi-layer material consisting of differently sensitised layers, in which are incorporated colour-couplers which are made substantive by means of groups containing long-chain carbon atoms. The detailed description should enable British manufacturers, with the facilities, to produce similar materials.

LATENT IMAGE AND THEORY OF SENSITIVITY.

Without doubt there has been a far greater contribution to our knowledge of this subject than for many years, and only a selection of the more important articles can be made.

In a number of papers A. P. H. Trivelli[2] has attempted to throw more light on the significance of sensitivity.[3] In the first, he has emphasised by

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[1] G. F. Powell, C. P. S. Occhialini, D. L. Livesey, and L. V. Chilton, *J. Sci. Instr.*, 1946, **23**, 102; C., 1946, 212. L. L. Green and D. L. Livesey, *Nature*, 1946, **158**, 272.

[2] *J. Franklin Inst.*, 1945, **239**, 269; B., 1946, II, 27; *Phot. Abs.*, 1946, 25.

examples that the sensitivity derived from the exposure to give a certain density has no general physical significance and no direct relations to the size frequency characteristics and radiation absorption of an emulsion. A density in itself does not express the effect of the probability that grains will become developable, this being given only by the relation between number of developable grains and total number of grains. Only a density having a definite relation to D_{max} is significant, the simplest being $\tilde{D}$, the density at the inflexion point of the characteristic curve. The reciprocal of the exposure (E) necessary to produce $\tilde{D}$ gives the sensitivity for a given development time and the sensitivity per grain. The intrinsic sensitivity per unit surface of the grain is obtained by dividing $1/E$ by the average grain size.

In another paper dealing with the effects on the characteristic curve, solarisation is shown to be a high-intensity effect produced by incomplete development and it disappears on prolonged development, suggesting that there are development centres of varying size in the grain, the smaller of which take a longer time to initiate development than the larger. Over a range of development times the number of developed grains is proportional to the density. The larger grains show greater developability than the smaller ones. The effect of sensitising diminishes with prolonged exposure. From this work there are indications that different kinds of sensitivity specks occur, each of which has quantitatively a different sensitising effect.

Proceeding with the work on intrinsic sensitivity, according to the Siberstein theory two factors are involved in sensitivity, one being the quantum number r, representing the minimum number of absorbed quanta required to make a grain developable and the intrinsic sensitivity ε representing the probability that a grain will absorb this number of effective quanta. ε determined experimentally was found to increase with grain size, showing that only a small part of the quanta absorbed by a grain is used for latent image formation and thus the intrinsic sensitivity is measured not by its total, but by its effective, absorption. Thus it may be concluded that the sensitivity of the grain to light is determined by the probability of the r quanta being absorbed in a restricted area εa of the grain (a being the projected area) or in other words that grain compositions and the discrete structure of the radiation are both involved in determining the sensitivity. For X-ray exposures, however, the evidence is that the sensitivity extends over the whole grain and that differences between grains are due entirely to radiation, the energy in the latter being distributed in quanta according to the probability law.

A tentative explanation that ε is related to the absorption in a limited area of the grain of only a small fraction of the total absorption can be obtained by applying the quantum exposure theory to the Gurney–Mott theory of latent image formation, and the concentration speck hypothesis.

The grain surface contains a number of sensitivity specks and the grain sensitivity is determined by the speck which during exposure first collects the *r* silver atoms necessary to produce developability. Thus the number of effective quanta is a small fraction of the total absorption depending on the number and distribution of the specks. The environment from which the speck collects silver ions is the effective surface and is not equal to the total projected area of the grain.

Investigations of the effect of double exposure on the latent image have been carried out by P. C. Burton and W. F. Berg.[4] When the first exposure was varied and the second kept constant, the second exposure rendered sub-image grains developable, having little effect on other grains. Then the second exposure was varied while the first was kept constant, thereby observing the response to variable exposure of a stock of sub-image grains. Experiments on these lines indicated that the low-intensity reciprocity failure is due only to processes occurring in the earlier stages of formation of latent image silver specks, and that the high-intensity reciprocity failure is due to processes commencing in the later stage. Both kinds of process occur at optimal intensity of the reciprocity curve; removing the high-intensity kind led to the low-intensity kind extending up to the highest intensities. Other conclusions in brief are that the average size of the latent image silver specks on the developable grain increases with intensity. Consideration of the curve of density against exposure time led to the conclusion that the occurrence of a toe region of increasing slope means that sub-image grains are left over at the end of an exposure in this region. Examination of other effects leads to the assumption that low-intensity reciprocity failure is due to recombination of photo-electrons with halogen atoms, made possible by the instability of the nascent latent image silver speck.

The latent image may be intensified before development by a second exposure to luminescent light. This may be carried out by contact with a layer of self-luminescent material or a layer of luminescent material excited by irradiation during exposure, the primary radiation being filtered out. The material may also be immersed in a bath of chemi-luminescent liquid.[5]

W. F. Berg,[6] applying a statistical investigation of the probability of aggregate formation of particles randomly scattered on a plane to the problem of developable aggregates in a photographic emulsion, has found that a developable speck contains 3 atoms and that sensitivity specks contain about 10 silver sulphide molecules.

An interesting phenomenon has been noticed by D. Raichbaum.[7]

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[3] *J. Franklin Inst.*, 1946, **241**, 1, 85, 315; B., 1946, II, 401; *Phot. Abs.*, 1946, 169, 76.

[4] *Phot. J.*, 1946, **86**, **B**, 2; *Phot. Abs.*, 1946, 180.

[5] W. F. Berg, and Kodak, Ltd., B.P. 572,633; B., 1946, II, 228; *Phot. Abs.*, 1946, 97.

[6] *Phil. Mag.*, 1945, [vii], **36**, 337; B., 1946, II, 187.

[7] *J. Tech. Phys. U.S.S.R.*, 1945, **15**, 485; *Chem. Abs.*, 1946 2749.

If a material is subjected to illumination with light of gradually increasing or gradually decreasing intensity the optical density of the image at a constant exposure is for an increasing intensity smaller than for a decreasing one, and greater than for a constant intensity and variable time. When the rate of variation of light intensity rises, density rises as well.

A theory of the mechanism of the formation of the latent photographic image expounded by S. Rischanov[8] suggested that the transfer of an electron by light from the halide ions to the semi-free state is accompanied by hole formation. Two energy bands exist, one, where the electron and the hole are bound one with another, corresponding to long-wave maximum of colour sensitive (420 mμ.), and the second one, where they are almost free, corresponding to the short-wave maximum at 320 mμ. The formation of the atomic centres of silver is the result of a catalytic reaction connected with the presence of local energy levels as well as of a thermal dissociation.

S. E. Sheppard, W. Vanselow, and R. F. Quirk,[9] surveying the hypersensitising and latensification due to certain substances, found that mercury vapour in hypersensitising was apparently adsorbed on sensitivity specks (Ag_2S) and the result is less stable than in latensification, when it is adsorbed on sublatent and latent image nuclei (Ag). This hypersensitising is antagonistic to the Herschel effect and a mercury-vaporised material shows Herschel desensitising and Becquerel colour sensitising, the latter mainly at low and the former at high exposures. Latensification by weak acids is considered most likely to arise from mobilisation of silver ions around the sublatent image speck by reason of the neutralisation of amino and imino bonds in the gelatin. Similarly with latensification by oxidants such as nitric acid and hydrogen peroxide. Ammonia may act by forming mobile $Ag(NH_3)_2$ ions, thus permitting concentration about a sub-nucleus.

Proposing a new theory of the Herschel effect, P. V. Mecklyar[10] has stated that if a definite shift of the optical density of the image is produced by raising the energy of the incident blue light from I_1 to I_2 the amount E of the energy of red light required to produce an equal and opposite shift is given by $\log (I_2/I_1) = BE(1 - r)Kd/N$, where r is the coefficient of reflexion of red light from the surface of the photosensitive layer, K is the adsorption coefficient of the layer, N is the number of halogen ions per sq. cm. of the layer, d is thickness, and B a constant depending on the wave-lengths of the blue and red lights. If the sensitivity of the layer towards red light cannot be neglected, $\log [(I_2 - I_0)/(I_1 - I_0)]$ must be substituted for $\log (I_2/I)$; I_0 is another constant depending on the relative sensitivities of the layer to blue and red. Contrary to the report of Urbach and Wolinsky, it has been found by L. Cohen-Solal[11]

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[8] *J. Exp. Theor. Phys. U.S.S.R.*, 1945, **15**, 108; *Chem. Abs.*, 1946, 283.
[9] *J. Franklin Inst.*, 1945, **240**, 439; B., 1946, II, 402.
[10] *J. Phys. Chem. Russ.*, 1945, **19**, 441; *Chem. Abs.*, 1946, 1746.
[11] *Cahiers Phys.*, 1944, No. 20, 21; *Chem. Abs.*, 1946, 3063.

that the Herschel effect by yellow rays of mercury is just as effective for simultaneous as for successive exposures to the actinic and yellow rays.

EMULSIONS.

Most of the published work on emulsions this year has been in the form of patents claiming substances which increase their speed and stability. However, certain papers of theoretical interest have been published. One, by I. I. Breido,[12] deals with the spectral properties in the ultra-violet range. He has found that for highly sensitive materials the sensitivity in sq. cm. per erg at unit optical density is near 0·8 at its maximum (450 mμ.) and near 0·15 at 250 mμ. For materials of low sensitivity it is near 0·3 at the maximum (now 400 mμ.) and still near 0·15 at 250 mμ. At optical density 0·5, a material of low sensitivity is at 250 mμ. often more sensitive than an isochromatic material. The contrast is independent of wave-lengths for highly sensitive materials and is the greater, the greater is the wave-length for materials of low sensitivity, the difference being probably due to light absorption within the emulsion. This latter conclusion is also arrived at by E. P. Davey,[13] who says that this absorption restricts the light action to a region near the emulsion surface, thus resulting in low contrast between 250 and 310 mμ. Above this the absorption decreases with a resultant higher contrast. Substances can be added to the emulsion to increase the absorption at the higher wave-length without materially affecting that at lower wave-lengths, thus giving rise to a more uniform contrast through an extended wave-length range, *e.g.*, *p*- or *m*-nitroaniline in the region 330—450 mμ. and tartrazine up to 500 mμ.[14]

In a paper dealing with the sensitivity of photographic emulsions to cystine, cysteine, and methionine, A. Steigmann[15] has stated that cystine and methionine when used in a bath for a finished but not exposed material do not desensitise, whereas cysteine does. However, if the emulsion be digested in the presence of cystine there is generally desensitising, ascribed by the author to its conversion into cysteine or a thiazolidine-4-carboxylic acid derivative. To a smaller degree under these conditions methionine also desensitises, possibly due to its conversion into homocysteine. The fact that a thiazoline-4-carboxylic acid derivative is in the penicillin molecule suggests that the latter may have an effect on photographic emulsions. The same author has also published formulæ for unwashed chlorobromide emulsions suitable for enlargements embodying two or three emulsifications and the use of cadmium chloride in the salts solutions.[16]

A study of the resolving power of emulsions by I. R. Protas and

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[12] *J. Tech. Phys. U.S.S.R.*, 1944, **14**, 199; *Phot. Abs.*, 1946, 170.

[13] *Phot. J.*, 1945, **85**, **B**, 127; *Phot. Abs.*, 1946, 178.

[14] E. P. Davey, E. W. H. Selwyn, and Kodak, Ltd., B.P. 575,991; B., 1946, II, 441; *Phot. Abs.*, 1946, 141.

[15] *Brit. J. Phot.*, 1946, **93**, 3; *Phot. Abs.*, 1946, 97.

[16] *Ibid.*, 140; B., 1946, II, 439; *Phot. Abs.*, 1946, 140.

P. M. Tschulkov[17] has shown that as the concentration of iodide increases so does the resolving power up to a maximum of 10 mol.-% AgI, after which a decline was observed; similarly an increase of concentrations of potassium bromide increases it up to 100 mol.-%. Variations of gelatin concentration at the time of emulsification are substantially ineffective. The fundamental factor is the concentration of silver nitrate and potassium halides during precipitation. Sensitising with cyanine dyes also increases the resolving power.

The adsorption of gelatin to silver bromide has been studied by S. E. Sheppard, R. H. Lambert, and D. Swinehart.[18] It is known that washing with water at 50° leaves a constant residual amount of gelatin adhering to the silver bromide crystals and this is reduced to one half by digesting with hot water. The mass of gelatin adsorbed per unit area of silver bromide surface is found by means of chemical analysis and determination of the opacity change of a silver bromide sol in the presence of varying amounts of gelatin. Results show that a monolayer of gelatin is irreversibly adsorbed to silver bromide as a result of polar forces, and that the layer is not removed by boiling water. The sol is precipitated in consequence of the hydrophobic character of the new surface. A second layer is reversibly adsorbed owing to weaker (dispersive) forces giving a new surface of hydrophilic character.

It has been found that if to a silver halide dispersed in a protein which is at low pH, or in the presence of an electrolyte, there is added an anion soap (0·3% weight of emulsion), *e.g.*, sulphated fatty alcohol, a protein–anion soap phase containing silver halide and free from soluble salts is precipitated. This phase may be separated, redispersed in colloid, precipitated with organic solvent, washed, and redispersed. This process increases the efficiency of washing. The protein–soap phase may be dried and kept as dry emulsion for future use.[19]

The speed, contrast, and stability of an emulsion can be increased according to R. K. Black and W. D. Baldsiefen[20] by adding a hydrophobic agent such as saponin and a polyoxyalkylene ether of a hexitol ring dehydration product. These include hexitans and hexides which have at least one hydroxyl group replaced by a polyoxyalkylene radical, and which may contain at least one lyophilic long-chain aliphatic hydrocarbon radical or long-chain aliphatic monocarboxylic acid ester. An example is the sorbitan monolaurate polyoxylakylene ether containing 20 oxyalkylene groups divided into 3 chains. It is claimed that these derivatives alter the induction period of development and result in increased density of silver images. Additions to emulsions of water-insoluble hydrazine derivatives, or hydrazine derivatives which are not antifoggants, or hydrazine derivative and cationic cyclammonium or

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[17] *J. Appl. Chem. Russ.*, 1944, **17**, 635; *Chem. Abs.*, 1946, 2077.

[18] *J. Chem. Physics*, 1945, **13**, 372; A., 1945, I, 334; *Phot. Abs.*, 1946, 70.

[19] C. Waller and D. P. Woosley, B.P. 580,504; B., 1946, II, 477.

[20] E. I. Du Pont de Nemours & Co., U.S.P. 2,400,532.

sulphonium compounds lead to improved speed and contrast provided the emulsion is developed at a pH above 9·5.[21]

A number of compounds giving antifoggant and stabilising properties have been put forward furing the year. They include chloroanilines free from hydroxyl groups and added in amounts of 1—15 g. per litre of emulsion before ripening,[22] and similar quantities of *o*-, *m*- or *p*-hydroxybenzamide, formanilide, or chloracetamide.[23] $\frac{1}{4000}$ — $\frac{1}{200}$ mol. of organic mono- or poly-sulphides such as morpholine disulphide, or $\frac{1}{4000}$ — $\frac{1}{2000}$ mol. of an aliphatic, aromatic, or heterocylic thiosulphonic acid or a diaryl or diheterocyclic sulphoxide, increases the stabilising properties of a sulphinate or a seleninate.[24]

Thioltetrazoles, thioltriazoles, mono- and di-thiol derivatives of diazoles and monazoles, compounds described hitherto as antibronzing agents with the hot glazing process when added to emulsion or finishing baths, if used as silver, nickel, or like metal salts in the emulsion or supercoat are without effect on its speed, as they are not decomposed with liberation of the free compound until the fixing process.[25]

Some special types of emulsions have been described. In the first place emulsions are made suitable for applying by means of a spray gun by addition of at least 2% on the weight of gelatin present of an anionic surface-active agent and 30—70% on the weight of liquid medium of water-miscible volatile organic liquid (spirit); this prevents the emulsion setting in the gun but allows it to set before running down vertical surfaces, and it also helps to produce even coatings.[26] G. B. Crouse, F. A. Holt, and J. L. Jatlow[27] have produced an emulsion the characteristic curves of which are such that the region of solarisation is reached with comparatively short exposures producing direct positives, by emulsifying and washing under acid conditions. Lastly emulsions for dry development have been the subject for investigation. E. C. Yackel, J. A. Leermakers, and C. J. Staud[28] have prepared an emulsion containing a developing agent, with or without a sulphite, which is developable with moist vapours of ammonia or an amine and fixed by hydrochloric acid vapour. In another case there is added to the emulsion containing a developing agent compounds such as guanidines, urea, or betaines which

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[21] R. E. Stauffer, W. F. Smith, and Canadian Kodak Co., Can.P. 435,333–4; A. P. H. Trivelli, W. F. Smith, and Canadian Kodak Co., Can.P. 435,335; *Chem. Abs.*, 1946, 4970.

[22] G. E. Fallesen, Assr. to Eastman Kodak Co., U.S.P. 2,384,613; *Phot. Abs.*, 1946, 8.

[23] G. E. Fallesen and J. A. Leermakers, U.S.P. 2,393,763 and 2,394,600; *Phot. Abs.*, 1946, 141, 142.

[24] F. W. H. Mueller, Assr. to General Aniline & Film Corp., U.S.P. 2,385,762; *Phot. Abs.*, 1946, 71, U.S.P. 2,394,198; *Phot. Abs.*, 1946, 141.

[25] W. H. Dimsdale and R. R. Robinson, B.P. 573,745; B., 1946, II, 146; *Phot. Abs.*, 1946, 70.

[26] J. A. Hart and E. W. Lee, B.P. 580,506; B., 1946, II, 478.

[27] Photo Positive Corp., U.S.P. 2,401,051; *Chem. Abs.*, 1946, 4612.

[28] Eastman Kodak Co., B.P. 580.497; B., 1946, II, 478.

on application of water vapour cause development due to the formation of amines.[29]

SENSITISERS.

There is a marked decline in the number of sensitisers reported, due possibly to the gradual exhaustion of the field of research, but many more supersensitisers, *i.e.*, substances which enhance the spectral sensitivity of spectrally sensitised emulsions, have been named during the year. As has been the case in recent years, publications dealing with theoretical aspects and the chemistry of sensitisers come mainly from Russian sources. Firstly S. M. Soloviev[30] has studied the chemical and photographic properties of 3 : 3′-diethylthiacyanine iodides with conjugated chains ranging in length from one to nine CH groups. As the chain lengthened the adsorption of the dyes by silver bromide grew regularly. The adsorption isotherms have a two-level form, the first level corresponding to 1 mol. of dye retained to 0·5—2 bromide ions on the surface, indicating a unimolecular layer, and the second level corresponding to 1 dye molecule to 0·2—0·6 bromide ion, indicating a dye layer thickness of 2—5 molecules. Photographically, it was found that the maximum of sensitising is displaced toward the long wave-length as the length of the chain increased, whilst the concentration of dye corresponding to optimum sensitising decreased, accompanied by an increase in fog.

Fluorogenic action has been observed by P. P. Feofilov[31] when cyanines, the structure of which admits relative rotation of two large molecular parts around the chain of conjugated double bonds, are introduced into rigid sugar or plastic solutions. The possible explanation given is that some hindrance arising to preclude relative rotation of quinoline rings around the connecting conjugated system prevents the energy of excitation being converted into kinetic energy.

After preparing and studying the absorption characteristics of numerous 6 : 6′-symmetrically substituted thiacarbocyanines, A. I. Kiprianov, I. K. Uschenko, and E. D. Sitsch[32] have found that electropositive substituents in the 6 : 6′-position form by their bathochromic activity a series which corresponds to the mobility of their electron pairs. The bathochromic action of the positive substituents can be explained by the formation of resonant structures with a negative charge on the carbon atoms of the polymethine chain.

Continuing the investigations on the effect of solvents on absorption spectra of dyes, S. E. Sheppard and A. L. Geddes,[33] after a quantitative examination of the dimerisation hypothesis for dyes in aqueous solution, using representative cyanines, have decided that the hypothesis must be

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[29] Eastman Kodak Co., S. S. Fierke, and C. J. Staud, B.P. 580,565; B., 1947, II, 36.

[30] *J. Phys. Chem. Russ.*, 1945, **19**, 451; *Chem. Abs.*, 1946, 5653.

[31] *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **45**, 367; *Phot. Abs.*, 1946, 101.

[32] *J. Gen. Chem. Russ.*, 1945, **15**, 200; *Chem. Abs.*, 1946, 2307.

[33] *J. Amer. Chem. Soc.*, 1944, **66**, 2003; A., 1946, I, 111; *Phot. Abs.*, 1945, 104.

modified to explain certain "activity" factors. The spectral aberration is said to be due to vibrational excitation of the ions of the dimer and consequent enhancement of higher-frequency satellites of the main electronic transition, rather than to the production of new polymeric bands. Some results suggest the possible incorporation of a molecule of "water of dimerisation."

The work in the series "colour and constitution" has been continued.[34] From nine heterocyclic radicals all 36 possible asymmetrical carbocyanines were made. The difference between observed and calculated absorption maxima varied from 0 to 725 A. There were exceptions to the "sensitivity rule" that the effect on deviation of a given small chemical change is the greater the higher is the asymmetry of the dye in which the change is carried out.

Of the new sensitising dyes the most interesting are certain cyanine dyes with recurring nuclei which are fast to diffusion in emulsion layers. Cyclammonium quaternary salts linked across the nitrogen atoms are prepared by treating the usual heterocyclic bases with a polyhalogeno-alkane (*e.g.*, methylene dibromide), an alkyl sulphate, or the ester of a sulphonic acid with a polyhydric alcohol. Two examples of polymeric cyanines obtained from these salts are firstly *NN*-(2-hydroxypropylene)-bis-(1″-ethylthiapseudocyanine), which is obtained by interaction of 2-methylbenzthiazole with glycerol $\alpha\gamma$-dibromohydrin and treatment of the quaternary salt with 2-methylthiolquinoline ethobromide. Secondly if the thiazole intermediate is treated with ethyl orthoacetate, polymeric *N*-(2-hydroxypropylene)-9-methylthiacarbocyanine bromide is prepared.[35]

Bases which are sensitisers have been described by L. G. S. Brooker and R. H. Sprague.[36] They may be prepared by treating heterocyclic bases having α- or γ-cyanomethyl groups with cyclammonium quaternary salts containing in a reactive position a reactive group, *i.e.*, halogen, thioether, arylaminovinyl, etc. The cyano-group need not be removed but can be removed by acid hydrolysis and elimination of carbon dioxide. The bases may be quaternised to give cyanines.

It has been found that formamide, thioformamide, or thioformanilide reacts with 2 mols. of a cyclammonium quaternary salt containing a reactive methylene (acid condensing agent) to give carbocyanines. If only 1 mol. of salt is used with 1 mol. of thioformamide, formamide, or formamidoxime, then a 2-β-acetaminovinyl substituent of the salt is obtained. This type of compound reacts with a compound having a reactive methylene group adjacent to a CO or CS in the ring (*e.g.*, 1-phenyl-3-ethyl-2-thiohydantoin) in presence of an alkali hydroxide, carbonate, or alkoxide to give a cyanine.[37]

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[34] L. G. S. Brooker, H. W. J. Cressman, and R. H. Sprague, *J. Amer. Chem. Soc.*, 1945, **67**, 1889; A., 1946, II, 237; *Phot. Abs.*, 1946, 101.

[35] E. I. Du Pont de Nemours & Co., B.P. 573,394; B., 1946, II, 82; *Phot. Abs.*, 1946, 99, 171; with C. D. Wilson, U.S.P. 2,393,351.

[36] Eastman Kodak Co., U.S.P. 2,393,743; *Phot. Abs.*, 1946, 171.

[37] E. B. Knott, and Kodak, Ltd., B.P. 577,548–9; B., 1946, II, 367.

Only one patent dealing with supersensitising by mixtures of dyes calls for comment. E. E. Nicholson and R. B. Collins[38] have discovered that an insufficient quantity of a 9-alkyl-substituted carbocyanine supersensitises an oxa-, selena-, or thia-pseudocyanine. The increase of speed to yellow light is as much as 500%. A number of compounds are described which do not sensitise in themselves, but when added to a spectrally sensitised emulsion increase or modify that spectral sensitivity. The emulsion is usually sensitised with dyes which produce two kinds of sensitising, and are normally 9-alkyl-substituted carbocyanines or pseudocyanines. Among these compounds are aromatic esters,[39] aromatic nitriles devoid of nitro- and acidic groups,[40] heterocyclic nitrogen compounds with :CXY in the α position to N, where X is H, hydrocarbon, CO_2H, ester, or aryl group, and Y is CO_2H, carboxylic ester, CN, or acrylic ester,[41] quinolines, benzthiazolones, or thiazinolones,[42] and heterocyclic compounds containing one nitrogen atom doubly bound to a carbon of the ring and containing a fused-on carbocylic ring (*e.g.*, substituted quinolines).[43] Lastly compounds NYY′·CO·CXX′·SH, where Y is H or aryl, Y′ is substituted aryl, X is alkyl or H, and X′ is alkyl, are supersensitisers for styryl dyes.[44]

DESENSITISERS.

Two types of desensitisers are mentioned. A. Steigmann[45] has found that phenazinotriazole is a powerful desensitiser whilst D. J. T. Howe[46] has discovered that 4 · 4′-dinitrophenylthiazolecarbocyanines when included in photographic emulsions decrease the sensitivity to visible light without seriously impairing the speed to *X*-rays and at the same time restrain fog.

MANUFACTURING ASPECTS.

Perhaps one of the most interesting features concerned with the manufacture of photographic materials is the work on methyl methacrylate resins carried out by J. A. H. Hart and E. W. Lee.[47] Partly hydrolysed (15—25%) methyl methacrylate polymer or the interpolymers between methyl methacrylate and maleic acid or anhydride with free carboxylic acid or anhydride groups form excellent substrata for hydrophobic surfaces, such as methyl methacrylate polymer. The latter

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[38] B.P. 574,725; B., 1946, II, 188; *Phot. Abs.*, 1946, 174.

[39] G. E. Fallesen and J. A. Leermakers, Assrs. to Eastman Kodak Co., U.S.P. 2,378,917; *Phot. Abs.*, 1945, 104.

[40] B. H. Carroll and J. S. Spence, Assrs. to Eastman Kodak Co., U.S.P. 2,380,940; *Phot. Abs.*, 1946, 28.

[41] R. B. Collins and J. Miller, B.P. 574,038; B., 1946, II, 226; *Phot. Abs.*, 1946, 173.

[42] B. H. Carroll and J. Spence, Assrs. to Eastman Kodak Co., U.S.P. 2,395,846; *Phot. Abs.*, 1946, 174.

[43] *Idem*, U.S.P. 2,398,778; *Chem. Abs.*, 1946, 3691.

[44] Gevaert Photo Producten N.V., Belg.P. 447,040; *Phot. Abs.*, 1946, 173.

[45] *Brit. J. Phot.*, 1946, **93**, 256.

[46] Elliott & Sons, Ltd., B.P. 573,544; B., 1946, II, 108; *Phot. Abs.*, 1946, 102.

[47] B.P. 573,917; B., 1946, II, 188; *Phot. Abs.*, 1946, 95. B.P. 580,511, 575,512; B., 1946, II, 227; *Phot. Abs.*, 1946, 168.

substance can be used as a dispersing medium for silver halide or as resin layers for antihalation purposes, filter layers, etc. Again the former polymers may be further hydrolysed to produce resin layers also; according to whether it is desirable for the layers to be removed in developing solutions or not, the degree of hydrolysis is adjusted from 50—70% hydrolysed to 30—35%. Hydrolysis is effected on commercial "Diakon" with 70% vol./vol. sulphuric acid. Resin layers for the above purpose and carriers in place of gelatin for silver halide can be obtained by using water-permeable water-insoluble polyamide resins which are soluble to at least 5% in aqueous alcohol at 40—70°.[48] Such polyamides have recurring intralinear oxygen atoms in ratio of 1 oxygen to 7—11 carbon atoms, *e.g.*, the resin obtained from 3 : 3′-diaminodipropyl ether and sebacic acid; these resins give flexible layers unaffected by bacteria and adhere well to polyamide resin supports.

Static electricity in photographic films is reduced if the film is coated with cellulose organic acid ester containing a metallic (aluminium) sulphate[49] or by coating as a layer or including in the base itself a dibasic acid (or anhydride)-hydroxyamine condensation product such as that from 2-amino-2-methylpropane-1 : 3-diol and phthalic anhydride.[50]

As a subcoat for polyvinyl chloride supports[51] A. E. Beguin and D. R. Swan use a layer of poly*iso*butyl methacrylate in a solvent mixture not attacking the support, followed by a gelatin-nitrocellulose subcoat.

Selected from patents dealing with stripping materials is one from C. J. Staud.[52] A dry stripping film is prepared by overcoating the emulsion with a thermoplastic adhesive layer which will allow heat-bonding of the stripping film emulsion to a rigid support, or the emulsion layer is overcoated with a white pigment layer which may or may not be thermoplastic followed by an overcoating layer of a thermoplastic material, which will permit heat-bonding of the emulsion layer to the final support. R. S. Potter and R. F. Brown[53] have described a stripping layer which when dry is water-insoluble but permeable, consisting of cellulose nitrate containing an agent conferring porosity, such as urea or a prolamine such as zein, coated on a porous temporary support. The transfer to the permanent support is made before exposure to avoid image distortion. The emulsion is applied to the wet support and squeegeed, and then plenty of water is applied to the back of the temporary support and as soon as the gelatin has adhered the temporary support and retaining layer is stripped. Proper adhesion is afforded between a dry stripping material, which has an adhesive super-coating

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[48] M. M. Brubaker, Assr. to E. I. Du Pont de Nemours & Co., U.S.P. 2,384,072; *Phot. Abs.*, 1946, 22.

[49] G. F. Nadeau and C. S. Hunter, Assrs. to Eastman Kodak Co., U.S.P. 2,386,627; *Phot. Abs.*, 1946, 168.

[50] F. J. Kaszuba, Assr. to General Aniline & Film Corp., U.S.P. 2,403,533 *Chem.*; *Abs.*, 1946, 5654.

[51] Eastman Kodak Co., U.S.P. 2,388,817; *Phot. Abs.*, 1946, 168.

[52] *Idem*, U.S.P. 2,398,056; *Chem. Abs.*, 1946, 3992.

[53] E. I. Du Pont de Nemours & Co., U.S.P. 2,392,503; *Phot. Abs.*, 1946, 95.

of an organic colloid such as a cellulose derivative, and the permanent support by applying to the latter a layer of a water-insoluble colloid composition, which when dry gels to form a tacky layer, *e.g.*, cellulose derivative or synthetic resin.[54]

To increase the wet strength of photographic paper F. W. Boughton[55] incorporates in the support 0·25—5·0% of melamine–formaldehyde resin and the aluminium salt of a monobasic acid.

To prevent the alkali-soluble resin on the face of printing paper for wet negatives becoming insoluble and to prevent sticking together on packing, the base is backed with a protein layer.[56]

The problem of halation has again received some attention. As a non-dissolving carrier for antihalation layers G. F. Nadeau[57] has suggested mixed cellulose esters of monobasic and dibasic organic acids of viscosity 50—330 centipoises in a 10% solution of ethyl alcohol and acetone (55:45). In another patent with R. F. Miller,[58] he has described how an antihalation layer containing a cellulose ester having 4—8 acyl groups per C_{24} cellulose unit, of which not more than one is a dicarboxylic acid acyl group, and the rest are monobasic acyl groups, such as cellulose acetate phthalate, may be protected with a layer of such cellulose ester dissolved in a solvent in which the dye is not soluble, such as ethyl acetate containing 13% of ethyl alcohol. The alkali salts of resins suitable for antihalation layers can be prepared by refluxing a hydrolysed acylcellulose in about 8—16 times its weight of dioxan with a polycarboxylic acid containing 3—6 carboxyl groups in the form of its anhydride or acyl halide, using a catalyst such as pyridine or its derivatives.[59] Silver salts of the hydroxy-azaindolizine dyes have been found to be suitable for antihalation and filter purposes and may be prepared by coupling diazotised aromatic amines with acetoacetic ester and interaction of the product with 3- or 4-amino-1 : 2 : 4-triazole; if the dyes are prepared from *p*-nitroaniline-sulphonic acid the nitro-group may be reduced and the resulting amine diazotised and coupled with a suitable naphthol to give a magenta dye.[60]

A material for recording cathode-ray traces consists of hardened silver halide emulsion sensitive to the trace colour, in which the colloid is dyed to absorb light of the wave-length to which the emulsion is sensitive; the material has an antihalation coating on the support.[61]

In order to detect camouflage an interesting device has been used by E. E. Jelley and L. S. Wilder,[62] which depends on the high degree of

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[54] J. A. Hart, B.P. 577,230; B., 1946, II, 442.

[55] Eastman Kodak Co., U.S.P. 2,394,289; *Phot. Abs.*, 1946, 96.

[56] S. F. W. Welford, B.P. 577,998; B., 1946, II, 442.

[57] Eastman Kodak Co., U.S.P. 2,376,175; *Phot. Abs.*, 1945, 94.

[58] *Idem*, U.S.P. 2,346,078; *Phot. Abs.*, 1946, 4.

[59] F J. Kaszuba, Assr. to General Aniline & Film Corp., U.S.P. 2,380,896; *Phot. Abs.*, 1946, 168.

[60] N. Heimbach, Assr. to General Aniline & Film Corp., U.S.P. 2,390,707; *Phot. Abs.*, 1946, 72.

[61] R. J. Hercock and R. C. M. Smith, B.P. 575,691; B., 1946, II, 228; *Phot. Abs.*, 1946, 169.

[62] Eastman Kodak Co., U.S.P. 2,403,722; *Chem. Abs.*, 1946, 5350.

infra-red reflexion of foliage compared with that of green paint. A multilayer material is prepared containing an infra-red-sensitive layer with a colour-coupler and a light-sensitive layer with another colour-coupler producing a contrasting colour to that in the other layer; after exposure it is developed to produce the dyes.

THEORY AND TECHNIQUE OF DEVELOPMENT.

As with other sections of this Report the published material has grown considerably this year, although the greater part of it is in the form of patents describing developer compositions.

Proceeding with the investigations on the subject of the charge effect in relation to the kinetics of development, T. H. James[63] has shown that when development was carried to a gamma value of 0·40 with varying developers, higher speeds were recorded with singly-charged developers (metol) than with those with a double charge (quinol). Addition of substances which reduced the charge effect (phenosafranine, thallous salts, etc.) increased the speed obtained with doubly-charged developers. Bromide ions by strengthening the barrier decreased the speed obtained with these developers. The explanation given is that the zero- or singly-charged agents overcome the barrier more easily than the doubly-charged agents, so that development proceeds more rapidly, and this leads to an explanation of the non-additive properties of metol–quinol developers. The metol is active at the beginning of development, but as development proceeds the bromide barrier decreases and the quinol takes a more prominent part in the reaction.

A theory of chemical development has been propounded by V. S. Anastasevitsch,[64] in which it is said that the developers create in silver bromide crystals *F* centres (*i.e.*, electrons occupying "positive holes" in the crystal). The equilibrium concentration of the *F* holes is the greater the higher is the concentration of reducing ions and the smaller the concentration of the oxidation products and of bromide ions. If this equilibrium concentration exceeds that of the *F* centres in the system silver–silver bromide, the silver phase appears or, if already present, grows.

In another theoretical paper C. Bagdasarjan[65] has derived an equation for kinetics of the nucleus formation in topochemical reactions. He has noted that the rate of development is controlled by the rate of formation of development nuclei and their growth; these nuclei are formed during the induction period at the spots where latent image particles are located. The same process of electrochemical reduction of silver bromide occurs in nuclear formation as in nuclear growth, the former requiring only additional activation energy. Assuming that a latent image particle must increase by a certain number of silver atoms to become a development nucleus, and the time necessary will vary for different nuclei, the equation is derived which gives an S-shaped curve.

[63] *J. Franklin Inst.*, 1945, **240**, 327; B., 1946, II, 402; *Phot. Abs.*, 1946, 178.

[64] *J. Tech. Phys. U.S.S.R.*, 1944, **14**, 467; *Phot. Abs.*, 1946, 74.

[65] *Acta Physicochim. U.R.S.S.*, 1945, **20**, 441; B., 1946, II, 187.

By studying the course of development at various pH values E. Elvegard[66] has found that the rate of increase of gamma increases at first with pH, but passes through a maximum around pH 10 and is often smaller at pH 12 than at 8·5; the curvature of the toe of the H and D curve is not influenced by the concentration of the developing agent or the pH of the solution. A similar study of ferrous ion development by T. H. James[67] has shown that the rate of development in a dilute ferrous oxalate developer of low excess oxalate increases with pH in the range 8·0—8·5. When the excess of oxalate is high the increase is not observed, and the development characteristics are those of a doubly-charged agent. There is no induction period and very little sensitivity to bromide ions at low excess oxalate concentration and pH above 8, the characteristics being those of an uncharged or positively charged agent; the developing agent is probably ferrous hydroxide or the FeOH′ ion.

Among the various developers described as giving fine-grain images are those in which the developing agent is the product of reaction between an *o*- or *p*-hydroxybenzene, an *o*- or *p*-aminophenol, and an *o*-phenylenediamine; these developers are claimed to give an increase in the stright-line portion of the characteristic curve and to be capable of colour development.[68] R. W. Henn and J. I. Crabtree[69] have shown how a metol–sulphite developer suitable for low- to normal-contrast work with negative emulsions can be modified by the addition of sodium bisulphite to produce a fine-grain developer; they have also shown that the addition of 0·5—2 g. per litre of a quaternary nitrogen salt of a 2-aminobenzthiazole to a fine-grain developer reduces graininess without increasing fog.[70] For the same purpose A. L. Bunting, E. J. Gray, and A. M. Smith[71] have proposed the addition of α-naphthol or a naphtholsulphonic acid and a wetting agent to a metol–quinol–borate developer. Again to produce fine grain the use of easily oxidisable alkali salts of substituted phenols such as *o*-dihydroxyethylaminophenols in place of the alkali has been proposed.[72] Finally for fine-grain results J. B. Dickey and J. G. McNally[73] have described the use as developing agent of *o*- or *p*-phenylenediamines in which one nitrogen is substituted by a furyl or tetrahydrofuryl group.

Various additions to developers have been suggested for different purposes. For instance urea (50—300 g.) and dicyanodiamide (40 g. per litre) when added to a developer increase the speed of development and allow development at very low temperatures; they also can be used

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[66] *Z. wiss. Phot.*, 1944, **42**, 65; *Chem. Abs.*, 1946, 803.

[67] *J. Amer. Chem. Soc.*, 1945, **67**, 1908; B., 1946, II, 146.

[68] E. I. Du Pont de Nemours & Co., B.P. 580,237; B., 1946, II, 479. R. C. Lyon and E. I. Du Pont de Nemours & Co., U.S.P. 2,397,676; *Phot. Abs.*, 1946, 145.

[69] *Phot. J.*, 1945, **85**, **B**, 105; *Phot. Abs.*, 1946, 6.

[70] Eastman Kodak Co., U.S.P. 2,376,141; *Phot. Abs.*, 1945, 96.

[71] U.S.P. 2,374,921; *Phot. Abs.*, 1945, 96.

[72] V. H. Reckmeyer, Assr. to General Aniline & Film Corp., U.S.P. 2,385,763; *Phot. Abs.*, 1946, 74.

[73] Eastman Kodak Co., U.S.P. 2,364,350; *Chem. Abs.*, 1946, 2080.

to revive exhausted developers.[74] A silver halide solvent such as a primary or secondary alkylamine having a straight chain of 3—7 carbon atoms in quantities of 1—10 g. per litre assists in the complete reduction of the exposed silver halide grains and in preventing the formation of silver clusters, thus improving the resolution.[75]

Blue-toned images are obtained by addition of a thiobarbituric acid or one of its substituents to a metol–quinol developer.[76] Another example of an addition to a developer is the use of an alkali amino-methane-sulphonate or -sulphinate to increase the solubility of developing agents and to prevent the formation of sludge during use.[77]

A combined fixing and developing solution described by H. Diamant-Eerde[78] consists of a developing and fixing agent, an alkaline salt, and a reducing sugar such as glucose, and another, described by R. J. King,[79] contains, besides the alkali and developing and fixing agents, a quantity of potassium iodide dependent on the material and the result required; the pH should be at 8·5 for optimal results.

Two methods of stabilising dry developer compositions packed as a single powder have been suggested by F. R. Bean.[80] In the first, acid substances such as metabisulphites, phthalic anhydride, maleic anhydride, benzoic anhydride, salicylic acid, benzoic sulphimide, or phthalimide are added to prevent reaction between organic intermediate and alkali in the solid state. In the second case the sodium hydroxide may be replaced by monosodium derivatives of hexahydric alcohols such as mannitol or sorbitol.

In conclusion two new types of developing agent introduced by J. B. Dickey and J. G. McNally[81] are those having the general formula NH·arylene·NR·alkylene·COR′ (where R is alkyl or hydroxyalkyl and R′ is alkyl, alkoxyl, or amino) and arylenediamines and aminophenols *N*-substituted by a phosphonoalkyl radical, *e.g.*, Na_2PO_3·CMe(OH)·CH_2-.

FINISHING.

Among the material published on the subject of the fixing process is a patent by J. R. Alburger,[82] describing an alkaline fixing bath containing sodium thiosulphate, sodium hydroxide, alum, and paraformaldehyde. The pH of the solution is that of the developer used, which may be used at high temperature without causing reticulation of the gelatin. The alum/sodium hydroxide ratio is arranged to give soluble aluminate which

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[74] F. Dersch and N. Heimbach, Assrs. to General Aniline & Film Corp., U.S.P. 2,404,774; *J. Phot. Soc. Amer.*, 1946, **11**, 467; *Chem. Abs.*, 1946, 21, 5654.

[75] L. R. M. Dearing and C. H. Guell, Assrs. to Eastman Kodak Co., U.S.P. 2,371,740; *Phot. Abs.*, 1946, 7.

[76] F. Dersch and N. Heimbach, Assrs. to General Aniline & Film Corp., U.S.P. 2,384,897; *Chem. Abs.*, 1946, 530.

[77] F. R. Bean, Assr. to Eastman Kodak Co., U.S.P. 2,388,816; *Phot. Abs.*, 1946, 144.

[78] U.S.P. Appl. 318,113; *Phot. Abs.*, 1946, 6.

[79] Photo. Technical Corp., U.S.P. 2,397,016; *Chem. Abs.*, 1946, 3066.

[80] Eastman Kodak Co., U.S.P. 2,384,592, 2,394,588; *Phot. Abs.*, 1946, 73, 144.

[81] Eastman Kodak Co., U.S.P. 2,374,337, 2,374,807; *Phot. Abs.*, 1946, 73.

[82] Radio Corp. of America, U.S.P. 2,387,000; *Phot. Abs.*, 1946, 76.

with the paraformaldehyde produces a degree of hardening. Developer carried over precipitates silver, which prolongs activity of the solution. By means of potentiometric measurements on thiosulphate solution containing dissolved silver in which the ion-activity coefficients are maintained approximately constant by adding 2N. solution of sodium perchlorate, A. Olander and O. Adelsohn[83] have shown the presence of $[Ag(S_2O_3)_2]'''$ and $[Ag(S_2O_3)_3]'''''$ ions at "hypo" concentrations of 0·01—0·5M. and silver concentrations of 0·001—0·05M. The constants $[Ag(S_2O_3)_2]'''/[Ag] \times [S_2O_3'']^2$ and $[Ag(S_2O_3)_3]'''''/[Ag] \times [(S_2O_3)'']^2$ are $0{\cdot}61 \times 10^{13}$ and $1{\cdot}15 \times 10^{13}$ at 25° respectively. At very low concentrations $[Ag_2(S_2O_3)]''$ is also formed with a constant of approximately 1×10^{22}.

A solution of ethylenediamine with aminotrimethylhydroxymethane, 2 : 4 : 6-triaminotoluene trihydrochloride, 2-amino-6-methybenzthiazolium *p*-toluenesulphonate, or thiourea can be used as the essential fixing constituents for emulsion containing resin carriers instead of gelatin.[84] A second solution for this purpose contains a thiocyanate or thiourea in mixtures of water and aliphatic alcohols.[85]

To prepare a solution for hardening, boric acid may be dissolved in a hydroxyamine and acetic acid added, the quantities of acid being such as to fix the pH at 4·5—6·5; aluminium chloride is added and sulphur dioxide passed in to dissolve it.[86]

A useful intensifying solution for weak negatives described by L. E. Muehler and J. I. Crabtree[87] is prepared by adding 2 parts of a 2·25% solution of "hypo" crystals to 2 parts of a solution of 38 g. of sodium bisulphite and 15 g. of quinol dissolved with a wetting agent in a litre of water followed by 1 part of a solution of 22·5 g. of potassium dichromate and 30 c.c. of sulphuric acid in a litre of water, and while stirring, a further 1 part of this solution. The presence of chloride ion inhibits intensification, which may be as much as ten-fold.

B. Maury[88] has demonstrated that negatives dried at low temperatures are less grainy than those dried at high temperatures, whilst L. E. Muehler, C. J. Kunz, and G. T. Eaton[89] have described how films or papers can be obtained free from drying spots due to water, by immersion in 0·1% alkylnaphthalenesulphonate or the condensation product of an aldehyde and a naphthalenesulphonic acid.

Two methods of toning are reported. An American method for obtaining blue tones depends on solutions of gold chloride, thiocarbamide, and

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[83] *Experientia*, 1946, **2**, 66; B., 1946, II, 403.

[84] J. I. Crabtree and G. T. Eaton, Assrs. to Eastman Kodak Co., U.S.P. 2,396,830; *Phot. Abs.*, 1946, 145.

[85] *Idem*, U.S.P. 2,397,924; *Phot. Abs.*, 1946, 145.

[86] H. D. Russell, Assr. to Eastman Kodak Co., U.S.P. 2,378,247; *Phot. Abs.*, 1945, 96.

[87] *Phot. J.*, 1946, **86**, B, 32; B., 1946, II, 403. *J. Phot. Soc. Amer.*, 1945, **11**, 81, 119; *Phot. Abs.*, 1946, 76 .

[88] *Photo Rev.*, 1946, **58**, 42; *Chem. Abs.*, 1946, 2078.

[89] Eastman Kodak Co., U.S.P. 2.367,516; *Phot. Abs.*, 1946, 146.

10% sulphuric acid.[90] A concentrated selenium toner can be prepared by adding selenium to a sodium sulphite solution to produce sodium selenite; a thiosulphate of a nitrogen compound (NH_4, guanidine, or ethanolamine) is used as stabiliser for the solution and the pH adjusted to 6·5—8·5 by addition of sodium bisulphite solution.[91]

COLOUR PHOTOGRAPHY.

The activity in research on the subject of colour photography and in particular the search for colour-couplers for the subtractive method dependent on the colour development process proceeds unabated. Again the published material consists mainly of patents concerned with this particular aspect of the subject.

Polymeric substances (resins in fact) which contain reactive groups which couple with the oxidation products of substituted phenylenediamine developers are described by E. I. Du Pont de Nemours & Co. in a number of patents.[92] In one case the couplers are polyamides into which reactive groups are introduced by means of quaternary salt formation. In other cases they consist of proteins or polyvinyl alcohol combined with reactive compounds containing suitable groups, *e.g.*, salicylaldehyde. A novelty is introduced in that the resin colour-formers in some cases may act as protective colloid in the emulsion in place of gelatin. Among the new colour-couplers producing blue-green images on developing are compounds having two sulphonamido-α-naphthol residues linked through the nitrogen by means of a bivalent group having at least 8 carbon atoms and containing at least one benzene ring, *e.g.*, 4 : 4′-di-(1″-naphthol-2″-sulphonamidophenyl) ether.[93] Cyanoacetamidophenols and *o*-hydroxyaminoacetanilide where the amino attached to the acetyl may be substituted[94] also produce cyan dyes and so do salts of phenols joined in the *ortho*-position to radicals such as benzthiazole, benzoxazole, or benziminazole,[95] and 1-susbtituted 2 : 5-diketo-7-methylpyrimidopyrazoles.[96]

New compounds used to give magenta dyes with amine type developers are the amides $Q{\cdot}NH{\cdot}CO{\cdot}R{\cdot}CO_2H$, where Q is pyrazolone or $R'{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHAr$ in which R′ is hydrocarbon, Ar is bivalent aromatic nucleus, and R is polymethylene. These compounds give yellow azo-dyes as well.[97]

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[90] C. Blay, *Amat. Phot.*, 1946, **96**, 39; *Phot. Abs.*, 1946, 76.

[91] W. V. Wadman and L. D. Butcher, Assrs. to Eastman Kodak Co., U.S.P 2,382,683; *Phot. Abs.*, 1946, 9.

[92] A. B. Jennings, O. W. Murray, C. F. A. White, and J. F. Kirby, U.S.P. 2,396,275, 2,396,864–5–7; B.P. 577,679, 578,666; *Phot. Abs.*, 1946, 207–8; B., 1946, II, 404, 443.

[93] E. I. Du Pont de Nemours & Co., B.P. 577,387; B., 1946, II, 355.

[94] J. D. Kendall and D. J. Fry, B.P. 576,891, 576,963; B., 1946, II, 355.

[95] A. Frölich and W. Schneider, Assrs. to General Aniline & Film Corp., U.S.P. 2,373,821; *Phot. Abs.*, 1946, 59.

[96] A. Bavley, Assr. to General Aniline & Film Corp., U.S.P. 2,403,329; *Chem. Abs.*, 1946, 5348.

[97] W. E. Hanford, J. E. Kirby, and D. W. Woodward, Assrs. to E. I. Du Pont de Nemours & Co., U.S.P. 2,396,917; *Chem. Abs.*, 1946, 3349.

J. D. Kendall and D. J. Fry[98] have described the cyano- and alkyl ester substituents of the thioacetanilides as producing red to yellow dyes, whilst A. Bavley[99] has prepared the methylenebiscoumarins, again compounds producing magenta dyes, in which category also are the diketopyrazolidines, and 2- and 3-substituted amino*iso*oxazalones described by J. D. Kendall and D. J. Fry.[100]

Included among other miscellaneous colour-couplers are a number of derivatives of heterocyclic nitrogen compounds described by workers of Ilford, Ltd. (J. D. Kendall, D. J. Fry, and H. D. Edwards), in a number of patents.[101] For instance there are the bases containing as substituent α or γ to nitrogen the group N:C(OR)·R′ where R and R′ are hydrocarbon, and the quaternary salts with a substituent group CR′:CH·CH:CH·SR, where R is alkyl and R′ is hydrogen, alkyl, or aralkyl. Other types include the bases containing a cyanomethyl substituent and the NAlkyl bases containing a $:CH \cdot CO \cdot CH_2 \cdot COR$ (R = hydrocarbon) substituent.

W. D. Peterson has discovered that it is advantageous to use the metal (*e.g.*, silver or cadmium) salts of colour-formers which form metal salts less soluble than the silver halide of the emulsion; the salts are fast to diffusion and if unused are dispersed in the fixing bath.[102] Such colour-couplers are those containing a heterocylic nucleus having NH next or next but one to the ring tervalent N or next to CO or CS. Apparently if the silver salt is added during the precipitation of the silver halide the concentration of colour-coupler and gelatin is limited; these concentrations may be increased by adding an aliphatic amine or amino-acid prior to formation of the silver salt.[103]

The problem of the diffusion of colour-couplers from one layer to another has been reviewed by W. Schneider, A. Frölich, and H. Schulze.[104] They find that with insoluble spherically shaped colour-formers $D = kT/6\pi\eta r$; T is the temperature and η the viscosity of the solution, and for practical purposes these are constant, so that the diffusion is really dependent on r, the radius of the molecule. However, increasing particle size of the colour-former affects the transparency and grain appearance detrimentally and reduces the surface for coupling with oxidation products of developer. The known methods of rendering colour-formers fast to diffusion by increasing the molecular size are enumerated; the substantive colour-former is solubilised by the introduction of sulphonic acid groups. Other observations are that: aqueous-alcoholic solutions partly remove non-diffusing couplers from gelatin layers; molecular association contributes to a limitation of diffusion; adsorption to gelatin molecules takes place;

[98] B.P. 576,855; B., 1946, II, 358.

[99] Assr. to General Aniline & Film Corp., U.S.P. 2,403,040; *Chem. Abs.*, 1946, 5348.

[100] B.P. 577,260, 576,890; B., 1946, II, 355.

[101] U.S.P. 2,394,067–9; *Chem. Abs.*, 1946, 2400–2; B.P. 577,259, 577,295; B., 1946, II, 353.

[102] With Eastman Kodak Co., B.P. 577,804, 577,812; B., 1946, II, 404.

[103] Eastman Kodak Co., and R. V. Young, U.S.P. 2,401,718; *Chem. Abs.*, 1946, 4612.

[104] *Chemie*, 1944, **57**, 113: *Chem. Abs.*, 1946, 3347.

the melting points of dried gelatin layers and the viscosities of solutions are raised by the presence of couplers, and bile acids remove non-diffusing dye images.

The colour development process has been investigated by A. E. Porai-Koschitz,[105] with particular attention to pyrazolone and phenol derivatives. The dyes formed are the same as those produced by atmospheric oxidation with aminodialkylanilines or condensation with nitrosodialkylanilines; lengthening the alkyl group in the pyrazolone dyes caused a shift in absorption of the dye towards the red. However, A. G. Tull[106] believes that coupling takes place at a selected intermediate stage of oxidation between diamine and holoquinone—in fact that it takes place with the semiquinone compound; by using the semiquinone compound instead of the diamine as developer the colour factor (dye/silver) was increased.

Dye staining or colour fog can be reduced by adding to the developer dihydroxy- or dinitro-tartaric acid or a salt, ester, or amide of these compounds,[107] or by adding ascorbic acid to the emulsion or developer.[108] In addition the stability of the dye image formed can be increased by treating the material after removal of silver images with an aqueous or alcoholic solution of an antioxidant such as quinol.[109]

In order to produce higher colour densities, and to reduce loss of definition and detrimental effect of some colour-formers on emulsion speed, L. S. Wilder[110] has produced a multi-layer material, prepared as follows: on to the base is coated a red-sensitive layer containing cyan coupler followed by a red-sensitive layer with no coupler; then follows a green-sensitive layer, immediately on top of which is a second green-sensitive layer, this time containing a magenta coupler; then follows a yellow filter layer and then a blue-sensitive layer containing a yellow coupler.

Again, to prevent the loss of speed in this case, particularly in the red-sensitive layer, the normal multi-layer material for reversal using colour development is prepared without the cyan coupler in the red-sensitive layer but with the magenta coupler in the green-sensitive layer and the yellow coupler in the blue-sensitive layer; on reversal the red-sensitive layer is re-exposed to red light and colour-developed in a developer containing a cyan coupler. The other two layers are exposed to white light and colour-developed.[111]

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[105] *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1946, 261; B., 1946, II, 28.

[106] B.P. 580,496; B., 1946, II, 480.

[107] A. Weissberger and P. W. Vittum, Assrs. to Eastman Kodak Co., U.S.P. 2,384,663; *Phot. Abs.*, 1946, 126.

[108] P. W. Vittum and L. S. Wilder, Assrs. to Eastman Kodak Co., U.S.P. 2,401,713; *Chem. Abs.*, 1946, 4612.

[109] P. W. Vittum, Assr. to Eastman Kodak Co., U.S.P. 2,384,658; *Phot. Abs.*, 1946, 130.

[110] Assr. to Eastman Kodak Co., U.S.P. 2,376,217; *Phot. Abs.*, 1945, 117.

[111] H. H. Duerr and H. W. Morreall, Assrs. to General Aniline & Film Corp., U.S.P. 2,393,027; *Phot. Abs.*, 1946, 126.

In another multi-layer material for reversal G. P. Harrison[112] has arranged the layers to be coated in the following order on to the support: a red-sensitive layer with cyan colour-former, a green-sensitive layer with magenta colour-former, a gelatin layer dyed with a yellow dye indestructible in the developer (auramine base), and finally a blue-sensitive layer with no colour-coupler. On reversal the material is exposed through the back and the bottom layers and colour-developed. The top layer is coloured by toning or some such process, and the yellow dye layer is removed. A magenta dye layer may also be used between green- and red-sensitive layers.

A variation from the normal process makes use of what is known as "contact" colour development.[113] In its simplest form the material consists of a silver halide emulsion layer with a colour-coupler, and superimposed on it is a layer of another coupler but no emulsion. A positive record is obtained in the silver halide layer in the normal fashion. The top layer is then soaked in colour developer and a bleached positive film which has been printed from the original negative is squeegeed in register contact until a dye image is formed.

H. Howe[114] describes a trichrome transfer process in which positives from separation negatives are squeegeed into contact with glass plates containing gelatin–silver bromide and bathed with a copper sulphate–bromide–dichromate solution. After removal of the positives, sheets of Cellophane having coatings of celluloid are squeegeed in contact with the plates and placed in warm water and the celluloid is stripped off and the relief image washed free from silver bromide. The Cellophane sheets are dried on glass to prevent shrinkage and the relief images hardened in dilute formalin and fixed in hypo. The reliefs may be dyed by aqueous dye solutions and transferred one at a time to coated paper and dried. The Cellophane sheets are stripped off.

There is little new on the dye bleach-out process to report. To overcome the diffusion of dyes into adjacent emulsion layers in this process M. W. Seymour[115] has proposed to coat light-sensitive inter-layers possessing the same sensitivity as one or other of the adjacent emulsion layers; on development, silver will be produced in these layers and any dye which may diffuse into it will be destroyed by the bleach bath.

Of the process depending on the formation of azo-dyes for the colour image, one patent only calls for comment. In it D. W. Woodward[116] claims the use as dye intermediates of 5- or 8-amino-1-naphthols having in position *ortho* to amino an atom or group which by preventing *ortho* coupling directs azo-dye coupling *para* to the amino-group in acid solution; to reduce mobility the molecular weight should be over 300. In examples the intermediates possess resin residue substituents.

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[112] B.P. 576,889; B., 1946; II, 355.

[113] O. W. Murray, U.S.P. 2,386,167; *Phot. Abs.*, 1946, 129.

[114] *Brit. J. Phot.*, 1946, **93**, 67.

[115] Assr. to Eastman Kodak Co., U.S.P. 2,391,198; *Phot. Abs.*, 1946, 129.

[116] E. I. Du Pont de Nemours & Co., U.S.P. 2,394,527; *Chem. Abs.*, 1946, 2398.

In conclusion there is a brief note on a process for recording sound track for colour films. A relief image of the sound is formed and the image is treated with an organic compound suitable for imbibition printing capable of being mordanted and capable of reducing a silver salt or oxide (*e.g.*, hæmatoxylin). Relief is transferred to a mordanted imbibition blank and treated with silver salt or oxide, which is reduced to silver in the region of the mordanted hæmatoxylin. This gives the sound track in grey while the light image is coloured.[117]

DIAZOTYPE AND PHOTOMECHANICAL PROCESSES.

Among the information regarding the diazotype and blue print processes is the description of a new material prepared by W. O. Wilson[118]; the material, which is stated to be of high speed and permanence and is developable by water, is prepared by treating a support with a filtered solution of ferrous ammonium citrate, potassium ferricyanide, and potassium dichromate. M. K. Reichel[119] has devised a method for intensifying the image colour of materials prepared from *o*- and *p*-diamines, *p*-aminophenols, and aminonaphthols by including in the layer a bromide or iodide of alkali, alkaline-earth, or metalloids of fifth and sixth periodic group (the metalloids are at least quadrivalent and are combined with at least three saturated or unsaturated alkyl or aryl radicals). A sensitised cloth may be prepared by waterproofing one side of unfilled cotton fabric of close weave with a compound such as ethylcellulose and sensitising the other side with ferroprussiate or diazotype solution.[120]

There have been a few innovations in the "dichromated or hardened gelatin" process. In one method a relief image is obtained by exposing a dichromated hydrophilic colloid layer which on exposure becomes more water-soluble and thus gives a positive image from a positive when subjected to treatment with water; the colloid consists of dichromated gelatin and a soft resin such as polymethyl acrylate or cellulose ester dispersed in water in such concentration that when the layer is dichromated and exposed, the layer is more readily soluble in water than when unexposed.[121] Fine lines can be excellently produced photographically by exposing a layer of dichromated fish glue, gelatin, or casein behind a line negative, water-developing, hardening with 40% tannic acid, drying, and carbonising by heat-treatment at about 230°.[122]

An intaglio lithographic plate, described by W. G. Mullen,[123] consists of a protein such as casein coated on to a waterproof layer overcoated

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[117] W. J. Weyerts, and Kodak, Ltd., B.P. 578,968.

[118] U.S.P. 2,398,986; *Chem. Abs.*, 1946, 3690.

[119] General Aniline & Film Corp., U.S.P. 2,381,984; *Phot. Abs.*, 1946, 31.

[120] A. J. Norman, and E. N. Mason & Sons, Ltd., B.P. 573,975; B., 1946, II, 108; *Phot. Abs.*, 1946, 94.

[121] H. C. Staehle, and Eastman Kodak Co., B.P. 573,771; B., 1946, II, 148; *Phot. Abs.*, 1946, 182.

[122] A. Schoen and L. L. Paterson, Assrs. to General Aniline & Film Corp., U.S.P. 2,393,821; *Phot. Abs.*, 1946, 105.

[123] Lithomat Corp., U.S.P. 2,367,420; *Phot. Abs.*, 1945, 107.

with a thin layer of soluble polyvinyl alcohol, and sensitised in an aqueous alcohol solution of dichromate. After exposure a layer of greasy ink is applied and the image is treated with water, in which the unexposed polyvinyl alcohol layer dissolves, removing the overlying ink, and the exposed casein layer swells until it extends above the hardened resin layer, producing an intaglio ink-receptive image. Colloid layers suitable for obtaining hardened images may contain as light-sensitive substance azidostyryl ketones or azidostyrylaryl azides.[124]

Among the patents concerned with the photographic engraving process in general, one by H. T. Neumann[125] describes a transfer process for making engraved plates. A stripping film with silver halide emulsion coating is exposed through the back, processed, dichromated, and washed out in water. The relief image is squeegeed to a gelatin-coated layer, dried, and stripped from base; it is then transferred to a metal sheet to leave a relief on the metal. The plate is dipped in resist-forming asphalt in carbon tetrachloride, then heated to crack the gelatin relief, and dipped in alkali to remove gelatin, leaving a positive asphaltum image.

Several patents dealing with lithographic materials have been granted to E. Bassist and W. C. Toland.[126] One deals with a wet-strength paper coated with a layer of polyvinyl alcohol and a filler; this is treated with dilute tannic acid to give a superficial grease-receptive surface, retaining markings from typewriter ribbon containing oleic acid. The plate is then treated with lithographic etch consisting of ferric chloride and chromic acid, converting the non-printing portion into a water-receptive ink-repellant surface. In another case a paper base is coated on both sides with a water-impermeable resin; one side is coated with polyvinyl alcohol folowed by gelatino-silver halide emulsion. This plate may be exposed and processed, and the print dichromated and treated with a developing ink which renders the image portion grease-receptive; the unexposed portion is washed away, revealing the water-receptive polyvinyl alcohol, which functions as a non-printing surface. In the third patent, a paper base is adapted to receive a light-sensitive emulsion by covering it on both sides with a urea–formaldehyde resin glue of the type which first sets to a partly dried and hardened condition having affinity for the aqueous mixture, and when fully dried and hardened is water-repellent. An aqueous suspension of colloidal coating material suitable to form water-receptive non-printing portions of a lithographic printing plate is applied while the resin is partly dry. The coatings dry together while the resin hardens to the water-repellent state.

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[124] Kalle & Co., Belg.P. 447,449; *Phot. Abs.*, 1946, 31.

[125] U.S.P. 2,371,773; *Phot. Abs.*, 1945, 107.

[126] U.S.P. 2,373,287; *Phot. Abs.*, 1946, 183. U.S.P. 2,373,357; *Phot. Abs.*, 1946, 107. B.P. 577,832; B., 1946, II, 442.

SANITATION AND WATER PURIFICATION.

By John Hurley, B.Sc., F.R.I.C.,

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During the year under review, research has been active in most of the subjects covered by this Report. Some of it has found rapid practical application; this has happened, for instance, in the preparation of insecticides, where use has been made of some of the considerable amount of research which has taken place on the potentialities and limitations of DDT. In some other branches, it has not been possible to make much use of recent discoveries. This is particularly true in regard to sewage treatment. Much experimental work has been carried out, some of it on a large scale, on such subjects as biological filtration, but little use has yet been made of this work. Sewage works construction necessitates the employment of the kinds of materials and labour needed for the housing drive, and for that reason it has been restricted to the bare minimum. Indeed, the feeling is growing that in many cases sewage works extensions and renovations are being pegged back too severely, and that the consequences in both cost and efficiency may prove serious. Whether this is true or not, the effect of restrictions due to the competition of other needs has been to prevent the widespread utilisation of much of the research which has been carried out.

There have been some useful publications on water supply, but it is doubtful whether the scientific side of the subject is yet receiving its full measure of attention in this country. More attention is being devoted to this work, but we cannot yet feel satisfied with our contribution in this sphere. However, there are signs that water undertakings are becoming increasingly aware of their shortcomings in this direction, so further improvement can be expected.

Water Supply.

The water supply service is faced with many problems concerning both the quantity and the quality of the water. Indeed, in general, the two types of problem are inter-related. Industrial development, improved standards of sanitation, and the carrying of piped supplies to rural areas are all making increasing calls on available supplies. In some districts the acquisition of new sources of supply of unpolluted water is now difficult and expensive. As a result, river waters (some of them far from drinkable in their raw state) will probably be more heavily drawn on for public water supplies. This raises many new purification problems, and intensifies some old ones, thus providing scope for much investigation. The experiences and procedure of the Metropolitan Water Board will supply valuable guidance to authorities which decide to utilise river water, but local investigations will be needed if the best results are to be obtained at the lowest cost.

At one time it seemed likely that water treatment would deteriorate, through too many people gaining the impression that chlorination was the right answer to all problems. There are now indications that the subject is being viewed in a truer perspective. There appears to be a growing realisation that a heavy dose of chlorine will not remedy all defects. A turbid, unpalatable water cannot be considered satisfactory, even though every single organism has been annihilated by chlorine. It is of little use for the medical profession to urge people to drink more water if the water has an objectionable taste, or its appearance arouses suspicion as to its quality. Children often resolutely refuse to drink water which has a "chemical" taste or smells of "disinfectant."

D. G. Davies[1] mentioned this matter when dealing with the principles of water purification, saying that although the chemical treatment of water supplies had proved expedient in war-time, he did not consider it to be the best method of producing wholesome water. He preferred treatment by storage, rapid sand filters or fine screens, slow sand filters, and then chlorination if necessary. He added that coagulation might be necessary if colloidal matter resisted the clarifying effect of storage; for this purpose he advocated the use of iron salts in preference to those of aluminium, as being less likely to harm the human body. He also said that chlorination of the raw water destroyed the biological action of slow sand filters, causing them to require frequent replacement.

Dealing with the provision of water supplies in rural areas, in the light of the Rural Water Supplies and Sewerage Act of 1944, W. Savage[2] considered the amounts of water needed for domestic and agricultural purposes. He drew attention to the fact that in some cases it would not be easy to provide by piped supplies all the water needed on farms. In this connexion he noted that not all the water used on farms need be of potable quality. Also, some of the water might be re-used; for example, water used for cooling milk could serve as drinking water for cattle or be used for washing cowsheds.

Coagulation and Flocculation.

Coagulation and flocculation have found increasing use in water purification in recent years. With the likelihood of an extension in the utilisation of relatively impure sources of raw water, this phase of treatment can be expected to assume even greater importance.

Improvements in the coagulation of surface waters with the use of activated silica have been discussed by L. L. Klinger.[3] He reports that activated silica prepared from sodium silicate was successful as a coagulant for both coloured and soft, and turbid and hard, lowland waters. After

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[1] *Surveyor*, 1945, **104**, 297.

[2] *J. Roy. San. Inst.*, 1945, **65**, 137.

[3] *Paper Trade J.*, 1946, **122**, *TAPPI Sect.*, 151; B., 1946, III, 164.

discussing the mechanism of the reaction, and outlining possible methods of applying the process, he gives his opinion of its capabilities. He says that, in general, with its use coagulation and colour removal are more effective, filter runs are longer, after-precipitation of alum is prevented, the dissolved silica content is reduced, and the filtered water is of high quality, less turbid, and sparkling.

Chlorine and Chlorine Compounds in Water Treatment.

Research on chlorination has remained fairly active, especially in America, but perhaps most interest will be aroused by information on the use of chlorine dioxide. An American article[4] has given several instances of the successful use of this chemical for the removal of tastes and odours. At Niagara Falls, N.Y., the water is first treated with sufficient chlorine (normally about 1·5 p.p.m.) to maintain residues of 0·4—0·5 p.p.m. of chlorine in the sedimentation tank and 0·2 p.p.m. in the filter effluents. Chlorine dioxide, made from sodium chlorite and chlorine, is added to the clear well in sufficient amount to maintain a concentration of 0·5—0·75 p.p.m. of available chlorine. When 0·08 p.p.m. of phenol was added to the water, chlorophenol tastes and odours were completely eliminated by the use of 1·5 p.p.m. of chlorine followed by sufficient chlorine dioxide to give 0·5 p.p.m. of available chlorine. It is added that break-point chlorination at Niagara Falls would have required 15 p.p.m. of chlorine and would at times have been impossible. The view is expressed that preliminary treatment with chlorine for disinfection is more economical than treatment with chlorine dioxide alone. Further cases are mentioned in which chlorine dioxide has been successfully employed under difficult conditions. At Greenwood, S.C., chlorine dioxide not only removed the tastes and odours caused by organic matter in the shallow pond from which the water is taken, but it also made possible the elimination of manganese, which had previously been troublesome. Success has also been attained in the treatment of a river water polluted by sulphite wastes and sewage.

Further encouraging information has been supplied by J. F. Synan, J. D. MacMahon, and G. P Vincent,[5] who say that chlorine dioxide is of special value for the destruction of tastes and odours which are either intensified or not abated by chlorine alone; they also note that in the production of chlorine dioxide from chlorine and sodium chlorite, an excess of not less than 50% of chlorine is necessary.

Filtration of Water.

One of the problems associated with the use of river waters, particularly if they have suffered some pollution, is the wide variation in the quality of the raw water. Amongst other difficulties, there is the upset to break-point chlorination occasioned by variable and excessive concentrations

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[4] *Amer. City*, 1945, **60**, *No.* 6 110.

[5] *J. Amer. Water Works Assoc*, 1945, **37**, 869; B., 1945, III, 264.

of free and saline ammonia. To overcome this difficulty, a nitrifying filter, with a gravel bed just over 6 ft. deep, has been installed at the Ryton water works of the Coventry Corporation. Mention of this type of plant was made in last year's Report (p. 541). Some details have now been published[6] of the first six weeks' working of the full-scale plant; during the period the free and saline ammonia in the raw water varied from 0·07 to 0·47 p.p.m., and in the filtered water from 0·03 to 0·09 p.p.m. It is possible that even better results will be obtained when the filter has had time to mature.

Corrosion and Incrustation.

An investigation of scale and corrosion control in potable water supplies at army posts has been made by R. T. Hanlon, A. J. Steffan, G. A. Rohlich, and L. H. Kessler.[7] Tests were carried out at a number of hot-water installations, served by the same hard, deep well water, to determine the effectiveness of various proprietary reagents. Organic materials by themselves were ineffective in preventing scale and corrosion; phosphatic compounds (both alone and in admixture with other materials) gave varying degrees of benefit. Particulars are also given of investigations carried out on 30 other waters.

Seeking the cause of the severe corrosion of a steel main carrying deep well water, D. H. Caldwell and J. B. Ackerman[8] formed the opinion that the attack was associated with the anaërobic reduction of nitrate. They attributed the reaction to cathodic reduction of the nitrate to either nitrite or ammonia, both of which increased at the expense of nitrate as the water passed through the pipe. They found that this reduction cannot take place in the presence of dissolved oxygen, and was inhibited by raising the pH to 8·0. Reduction of the nitrate was entirely prevented by chlorination in addition to pH control.

L. C. Secrest[9] has given an interesting account of the use of cathodic protection to prevent corrosion of a pipe line laid in Colorado and Wyoming in 1939. The pipe was first treated with a protective coating and was wrapped in asbestos. It was considered that if the pipe could be maintained at a negative potential of 0·3 volt with respect to the soil, there would be no corrosion. Wind-driven electric generating units were employed, and the positive electrode consisted of a number of pipes buried vertically and horizontally in the soil. The lower halves of the horizontal pipes were perforated. Salt was introduced into the pipes and seeped into the soil. During the four or five years which had elapsed between the laying of the main and the making of the report, no corrosion of the pipe line had occurred.

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[6] *Water and Water Eng.*, 1945, **48**, 550.
[7] *Ind. Eng. Chem.*, 1945, **37**, 724; B., 1945, III, 236.
[8] *J. Amer. Water Works Assoc.*, 1946, **38**, 61; B., 1946, III, 164.
[9] *Oil and Gas J.*, 1944, **43**, *No.* 3, 82.

Fluorine and Dental Health.

Considerable interest is still being taken in the influence of fluoride water supplies on dental conditions. E. M. Short[10] has made investigations in 12 communities in Illinois and Colorado to determine whether the time of eruption of the permanent teeth is affected by the fluorine content of the water supply. Where the water supplies contained less than 2·0 p.p m. of fluorine, no significant difference in the time of eruption of the permanent teeth was observed, but at Colorado Springs, where the fluorine content was 2·6 p.p.m. the eruption of the teeth appeared to be delayed. In the author's opinion, the marked difference in the incidence of dental caries, as between populations using water supplies containing up to 1·2 p.p.m. of fluorine, has no relation to the difference in the time of eruption of the permanent teeth.

M. Malherbe and T. Ockerse[11] have studied possible factors influencing dental caries in a high- and low-incidence area in South Africa. Conditions in the high-incidence district of George were compared with those in the Williston area, special attention being paid to drinking water and diet. It was found that the enamel and dentine of the teeth from people living in the George area contained less fluorine than those of teeth from persons living in the Williston area. The authors believe that the diet in the George area is deficient in proteins, fats, calcium, and vitamins.

T. Ockerse[12] has also reported on a comprehensive investigation into the influence of the nature of drinking water on the incidence of dental caries. The teeth of nearly eighty thousand school children in South Africa were examined, and the fluorine content, hardness, and pH value of samples of drinking water from the various districts were determined. Results showed that the incidence of dental caries was related to all these factors. Incidence was low in districts where the fluorine content of the water was over 1 p.p.m., and where the water was hard or had a high pH value. In places where the water fulfilled all these conditions, the incidence of caries was particularly low.

Water Analysis.

A method for the determination of free chlorine and of chloroamine in water, by means of *p*-aminodimethylaniline, has been worked out by A. T. Palin.[13] It is claimed that the method is accurate to within 0·01 p.p.m. for the lower, and within 0·02 p.p.m. for the higher, values in the range 0—0·5 p.p.m. of residual chlorine. Its operation depends on the production of a colour by the action of free chlorine on *p*-aminodimethylaniline, the masking (by controlling the pH value) of the colour produced by the interaction of chloroamine and *p*-aminodimethylaniline, and finally the development of the chloroamine colour at the same pH

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[10] *J. Dent. Res.*, 1944, **23**, 247.
[11] *S. Afr. J. Med. Sci.*, 1944, **9**, 75.
[12] *S. Afr. Med. J.*, 1944, **18**, 255.
[13] *Analyst*, 1945, **70**, 203; C., 1945, 269.

by addition of potassium iodide. The "chlorine" colour at pH 6·8 is matched by that produced by a known volume of standard iodine; the "chloroamine" colour is then developed by adding potassium iodide, and is matched by adding more iodine solution to the comparison tube. Free chlorine and chloroamines can thus be determined separately. Procedure has been evolved for countering interference from various sources. A field test has been devised, the colours being compared with the B.D.H. Lovibond Nessleriser disc for nitrites.

W. Schneebeli and M Staub[14] have given particulars of a simplified colorimetric method for the determination of chlorine in water. It is applicable to dilutions as low as ·0·4 mg. of chloride per litre, and is reported to be more accurate than the usual titrimetric methods. To the sample is added sufficient 10% aqueous potassium chromate to give a 1% concentration, then excess of N./35·5 silver nitrate; the stable red-brown colour which develops is compared after one minute with standards (range 0·4—2·0 mg. of chloride per litre). Samples having concentrations of chloride higher than 10 mg. per litre are diluted to avoid the formation of a curdy precipitate. It is claimed that the method allows 50 determinations to be made per hour.

Bacteriological Examination of Water.

W. Olszewski and I. Rathgeber[15] feel that silicic acid has proved such a good substitute for agar and gelatin that its use in culture media is likely to continue. The authors suggest that counts obtained on silicate medium should be designated as "silicate counts." They have developed a simplified method of examination for field work; this includes taking the total bacterial count at 22° and 37° C., the coliform count on Gessner silicate medium, the coliform count and that of indole-formers at 37° using inoculation into a lactose-silicate medium, and the coliform count at 45°. This is a fairly ambitious programme for a field test.

ATMOSPHERIC POLLUTION.

An interesting paper has been issued by the Department of Scientific and Industrial Research,[16] dealing with atmospheric pollution in Leicester. A careful study, extending over three years and using a variety of instruments, has shown that the distribution of each pollution constituent is in roughly elliptical zones of concentration, diminishing from the city centre. Winds cause some displacement of pollution, but they have little effect on the zone of greatest pollution. Pollution by smoke and sulphur dioxide is greater in winter than in summer. Most of the constituents of the deposited matter at the centre of the city have decreased in quantity since 1932, but tar shows no change, while ammonium compounds have increased. Pollution is significantly less on

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[14] *Mitt. Lebensm. Hyg.*, 1945, **36**, 20; C., 1946, 195.

[15] *Gesundsheitsing.*, 1944, **67**, 133.

[16] *Dept. Sci. Ind. Res.*, 1945, *Atm. Pollution Res. Tech. Paper* 1; B., 1946, III, 56.

Sundays than on weekdays, even in residential areas. Smoke from domestic grates is estimated to constitute more than half of the total found in the atmosphere. It is interesting to note that there is a marked daily cycle of pollution rising to a maximum in the evening. The natural dispersal is discussed, and the mass of results is subjected to statistical examination.

Present interest in systems of district heating is reflected in a paper by D. V. H. Smith.[17] Noting that the greater part of the smoke in the atmosphere of cities is derived from domestic grates, the author claims that besides providing more economical use of coal, district supplies of hot water and heat reduce atmospheric pollution, because the combustion is more efficient.

Sewage Disposal.

Owing to the need for giving all possible priority to the housing programme, constructional work on sewage disposal schemes is inevitably being retarded. Only schemes of obvious necessity and urgency are being allowed to go forward. This is both disappointing and dangerous, for after seven years of overloading and neglect, many plants are now strained to breaking point. However, there is at least one redeeming feature in this enforced delay; it is enabling scientists and designers to consider and digest the mass of research and experimental data which has been produced in the last ten years. This is no small task, for in spite of the many difficulties, there has been an impressive output of important research. Much of it has passed beyond the laboratory stage, and has been given thorough investigation on semi-scale and works-scale plants. As a result, the number of well tried and improved methods available to designers is now so large as to be almost embarrassing. Nor is there any sign that the spate of investigation is slackening. Additional information and new ideas are being brought forward month by month.

A very encouraging feature is the more enlightened outlook in official quarters, both national and local, on research and experimentation. The Department of Scientific and Industrial Research, through its Water Pollution Research Board, has itself carried out much very valuable investigation and at the same time collaborated closely with the Institute of Sewage Purification and with individual local authorities. Moreover, the Ministry of Health is showing increasing willingness to sanction the use of new methods on sewage works, providing the proposals are backed by sound arguments, the soundest argument being thorough experimental investigation on a reasonably large scale.

Research in this country is probably most active on biological filtration and on methods for dewatering and utilising sewage sludge. Both these topics are receiving close attention, and results of great practical significance have already been obtained. In view of the shortages of materials and labour, it is natural that most interest should be shown in processes which

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[17] *J. Roy. San. Inst.*, 1945, **65**, 28; B., 1946, III. 146.

can be applied to existing works with the minimum of expense and alterations to plant; this is particularly true in the case of new developments in biological filtration.

Although the war practically halted the construction of civil sewage disposal works, a vast amount of work was necessarily carried out on the installation of plants at military camps. In the United States, a determined effort has been made to collect useful knowledge from the performance of these, largely standardised, installations. The Committee on Sanitary Engineering of the National Research Council, Division of Medical Sciences, under the Chairmanship of A. Wolman, set up a Subcommittee on Sewage Treatment, with F. W. Mohlman as Chairman. The investigations and observations of this sub-committee have been set out in a very comprehensive report of some 240 pages.[18] Comment is invited for inclusion in a further report which is to be issued later. The report already issued contains a mass of useful information, which will be of value not only to the designers of camp sewage plants, but also to sewage technicians in general. Another detailed and valuable American publication is the critical review of the literature of 1945, contributed by a committee under the chairmanship of W. Rudolfs[19]; it very ably surveys recent research and its practical applications, and indicates topics which need further investigation.

As long ago as 1934, M. M. Cohn suggested that the best method of disposing of kitchen wastes was by way of the sewerage system and sewage disposal works. At that time the idea did not attract many supporters, but it has since been well tested in practice. In a recent communication, Cohn[20] gave the information that about 50,000 domestic grinding appliances have been installed in over 300 American towns. The electrically driven ($\frac{1}{4}$ h.p.) grinder is housed under the kitchen sink and fed by water from the kitchen supply. The apparatus has the necessary safety devices and its action is said to be similar to that employed for grating vegetables. The solids, so disintegrated that they will pass through $\frac{1}{16}$-in. spaces, are discharged to the drain through a standardised trap. The water consumption is reported to be about 1—2 gallons per head per day. The author is convinced that this method of disposing of domestic wastes is much better than that of storing them for collection. He gives figures to support his contention that the process would not give rise to trouble in the sewerage system, or to any insuperable problems at the sewage disposal works. Under present conditions in this country, there is no immediate prospect of such a system being employed. Waste foods still have to salvaged for animal feeding, while the prospect of getting delivery of large numbers of grinding plants and motors would not be good. However, this dual-purpose usage of the

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[18] *Sewage Works J.*, 1946, **18**, 791.
[19] *Ibid.*, 244.
[20] *Ibid.*, 477; B., 1946, III, 247.

sewerage system deserves serious attention, as indicating a possible revolutionary development in the disposal of solid wastes.

Ventilation of Sewers.

R. Pomeroy[21] has provided a thoughtful assessment of the pros and cons of sewer ventilation, and given useful particulars concerning the practical details of forced ventilation. The arguments for forced ventilation include the elimination of lethal and explosive atmospheres, the prevention of odour nuisance from the sewerage system and at the sewage works, and the reduction of corrosion of concrete sewers. Although he is of the opinion that oxygen deficiency is the cause of most sewer fatalities, he lists hydrogen sulphide, carbon monoxide, and hydrocyanic acid as poisons which may occur in sewers. He notes that the growing use of cyanides in industry is increasing the hazards, and opines that the maximum safe concentration of hydrocyanic acid in sewage is 10 p.p.m. He is careful to point out that while forced ventilation will appreciably diminish sewer risks, it will not completely eliminate them; for this reason, other precautions are necessary.

Flocculation of Sewage.

It has been known for many years that one of the principal limiting factors on the dosage and efficiency of sewage filters is the suspended and colloidal matters contained in the sewage. The ordinary sedimentation tank removes most of the suspended matter, but very fine particles and colloidal matter pass through the tanks. Amongst the methods which have been used for flocculation and subsequent separation of these matters are mechanical flocculation, chemical precipitation, short-period activated-sludge treatment, and the use of high-rate filters (colloiders). These processes are receiving investigation both in this country and in America. They are of particular interest at the present time, as they present possibilities of relieving the load on overburdened plants, at a time when major extensions are difficult to execute.

W. Watson[22] has carried out experiments on flocculation along new lines, or rather he has combined a very old method with a fairly new one. The sewage was septicised by admixture with septic sewage and sludge, and then gently circulated by mechanical means. Flocculation was effective, but the economics of the process, and the possibility of odour nuisance, would need careful investigation before contemplating its large-scale use.

Sedimentation in Sewage Treatment.

In the course of an investigation on the balancing of strength of sewage during sedimentation, S. H. Jenkins, C. H. Hewitt, and F. W. Roberts[23] collected a mass of useful data on various aspects of sedimentation.

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[21] *Sewage Works J.*, 1945, **17**, 203.

[22] *J. Inst. Sewage Purif.*, 1945, *Part* 2, 131.

[23] *Ibid.*, *Part* 1, 67.

They found that although variations in the strength of sewage were damped down during its passage through the successive stages of the sedimentation system on a large sewage works, the discharge from the sedimentation system still showed quite wide and rapid differences in composition. Their demonstration of the wide minute-to-minute variations in the composition of sewage, and to a smaller extent of tank effluent, shows the danger of attempting to gauge the strength of a sewage from a single chance sample.

Biological Filtration of Sewage.

Research on biological filtration is still very active, and much of it is of considerable practical importance. E. V. Mills[24] has made a further report on the large-scale experimental alternating double filtration plant of the Water Pollution Research Board. By stages the dosage of the alternating filters has been raised to four times that of the conventional filter used as a control. The effluents were of comparable quality, except that the conventional filter achieved a considerably higher degree of nitrification. E. V. Mills, J. T. Calvert, and G. H. Cooper[25] have described a plant for the treatment of camp sewage and laundry waste water by alternating double filtration. In its original form, this sewage works employed conventional single filtration, and at a dosage of 45 gallons per cubic yard per day the effluent was unsatisfactory. After conversion to alternating double filtration, a dosage of 71 gallons per cubic yard per day was satisfactorily treated.

Experimenting with recirculatory filtration, E. V. Mills[26] found that recirculation (on a one-to-one basis) permitted a four-fold increase in sewage dosage, as compared with an ordinary filter. The only marked difference between the effluents from the two processes was that the conventional filter produced the more nitrate. Frequent forking was necessary to keep open the surface of the recirculatory filter, so it is possible that the dosage had been pushed beyond the safe limit. From experimental work on full-size filters at Leicester, S. J. Roberts[27] has drawn the conclusion that the use of one-to-one recirculation will enable that authority to increase the filter dosage to 2½ times its present figure. Amongst other useful practical points, he states that variation of the dilution ratio does not upset the purification, provided the daily average works out at one-to-one. This will allow the filters to be fed at an approximately steady rate, thus making possible some economy in works practice.

P. B. B. Vosloo and T. P. O'Reilly[28] have investigated the effect of artificial ventilation on the treatment of sewage by biological filters. From their observations, made on actual works filters, they have formed the opinion that artificial ventilation has little influence on the performance

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[24] *J. Inst. Sewage Purif.*, 1945, *Part* 2, 35.
[25] *Ibid.*, *Part* 1, 7.
[26] *Ibid.*, *Part* 2, 94.
[27] *Surveyor*, 1946, **105**, 741.
[28] *Publ. Health, Johannesburg*, 1945, **9**, *No.* 5, 15.

of the filters. In their view, the additional purification (as compared with open filters) reported by previous workers is mainly due to the greater depth of the enclosed aerated filters. It will be recalled that various investigators have found enclosed aërated filters to be capable of purifying 2—3 times as much sewage per cubic yard of filtering media as open filters. Comparing the results of the authors with those of other workers, one gains the impression that the value of artificial ventilation may depend on local conditions, including climate.

When installing filtration plants on the double (non-alternating) filtration system, it is usual either to divide the filter capacity equally between the two stages, or to give the secondary stage the larger capacity. J. A. Montgomery[29] has carried out observations which suggest that it would be better policy to make the primary filter the larger unit, giving it up to 65% of the total amount of filter medium. He is also satisfied that two-stage filtration gives much improved results, as compared with the same amount of medium arranged in one stage. Of course, to justify its use, two-stage filtration would have to do this, for two-stage construction would be considerably more expensive than a single-stage plant with the same amount of filter medium.

The Activated-Sludge Process.

By his account of ten years' operation of the West Middlesex works at Mogden, C. B. Townend[30] has shown how efficient and reliable the activated-sludge process can be when properly designed and intelligently operated. A consistently good effluent has been produced at moderate cost. This plant differs from most others on the activated-sludge system, in that it produces considerable amounts of nitrate (about 1 part of nitric nitrogen per 100,000). This method of operation has been found to maintain a dense and healthy sludge, and to confer a capacity for coping with overloads.

Experiments carried out by C. N. Sawyer and L. Bradney[31] have indicated that the rising of activated sludge in final settling tanks, due to the biological reduction of nitrate, is most pronounced with sewages of low carbon/nitrogen ratio. Attempts to control nitrification by the use of inhibiting agents resulted in the production of inferior effluents. One of the remedies suggested by the authors—that of removing sludge from the final settling tanks as quickly as possible—is undoubtedly sound. Some other methods of control which they put forward may not meet with such general approval. One of them is the lengthening of the aëration period to the extent necessary to produce complete nitrification. It is doubtful whether it is necessary to go as far as this, for several activated-sludge plants in this country give trouble-free working with partial

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[29] *Water and Sewage Works*, 1946, **93**, 198; B., 1946, III, 186.

[30] *Sewage Works J.*, 1945, **17**, 1146; B., 1946, III, 123.

[31] *Ibid.*, 1191; B., 1946, III, 124.

nitrification. One of these is the Mogden plant mentioned above; experience there indicates that (for their conditions) no sludge rising troubles occur providing the nitrate-nitrogen figure is kept above 0·8 part per 100,000.

L. S. Kraus[32] has reported that at Peoria, Illinois, sludge bulking has been cured by aërating digested sludge and supernatant and passing this "activated" mixture into the ordinary activated-sludge plant.

The Kessener brush aëration plant installed at Rochdale during the war years has been described by D. H. A. Price and I. Withnell.[33] This plant has proved very satisfactory in regard to both efficiency and economy. Besides submitting figures relative to the operation and performance of the plant, the authors describe some very interesting supplementary investigations which they have carried out. It will be recalled that several years ago there were encouraging reports on a plant of the same type at Stockport.

Dewatering of Sewage Sludges.

One of the outstanding contributions on this subject was the report of J. M. Wishart, C. Jepson, and L. Klein[34] on experimental work carried out at Manchester sewage works. The authors made a careful study of many factors involved in the dewatering of various types of sludge by coagulation and vacuum filtration. Ferric chloride was one of the most promising coagulating agents tried, but the amount of this chemical needed (8—10% of the dried sludge solids, in the case of activated sludge) would make the process somewhat expensive in practice. The experiments are to be continued on a larger scale, and the results will be awaited with interest, particularly by authorities which are seeking a more compact and all-weather process than the ordinary sludge drying bed.

From time to time, reports from the United States have testified to the value of elutriation as a preliminary to the vacuum filtration of sludge. However, C. W. Hubbell[35] has stated that elutriation was not successful at Detroit, and has therefore been discontinued. In this connexion it is interesting to note that in the Manchester experiments, mentioned above, it was found that preliminary aëration of the sludge would give results as good as, if not better than, elutriation.

The disposal of the supernatant liquor withdrawn from sludge digestion tanks is often a difficult problem. C. V. Erickson[36] has summarised the methods available, and described a new process involving atomised aëration followed by settlement. In the discussion on the paper, the use of the methylene-blue stability test (suitably modified) was suggested to measure the "septifying" tendency of the supernatant. This would

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[32] *Sewage Works J*, 1945, **17**, 1177; B., 1946, III, 124.
[33] *Munic. Eng.*, 1946, **118**, 52.
[34] *Report of Maschester Corporation Rviers Committee*, 1945.
[35] *Sewage Works J.*, 1946, **18**, 212; B., 1946, III, 187.
[36] *Ibid.*, 1945, **17**, 889; B., 1946, III, 35.

give a good indication of the effect which the supernatant would have if returned to the sewage.

Utilisation of By-Products.

There is increasing interest in the utilisation of sewage sludge and its derivatives; in fact, this is one of the very few aspects of sewage disposal which was improved by the war. W. Parker[37] has given a very useful account of the propulsion of vehicles by compressed methane gas. Dealing with experiences at the West Middlesex sewage works, he discussed the subject ably and impartially. He evidently feels that, with petrol in fair supply at a reasonable price, methane is not likely to be widely used by the ordinary motorist in the near future. Anyone considering the use of methane for vehicle propulsion (for instance, for public service vehicles) would do well to study this paper, including the author's summary of the conditions which are essential for successful operation. An account of somewhat similar operations in Germany has been written by K. Imhoff,[38] who also included some interesting information on the gas obtainable by the digestion of stable manure and other organic substances.

Besides the better known uses of digester gas, it appears likely that its methane content may shortly be used on a large scale for synthesising other products. For example, H. Wilson[39] has described work which has been done in South Africa on the manufacture of formaldehyde from this base, by way of methyl alcohol. There are indications that the manufacture of cyanides and vinyl plastics may soon absorb fairly large quantities of sludge gas.

The use of sewage sludge, in various forms, for manurial purposes is now common practice. C. A. Chaplin and C. J. Regan[40] have carried out investigations on the presence and significance of plant-growth substances (auxins) in sewage products. The authors report that although crude and digested sludges may both (in the wet state) contain considerable quantities of auxins, yet most of these plant-growth substances are decomposed during the normal drying of the sludges. C. Bould[41] has supplied some interesting facts ascertained from experiments on the composting of town's refuse with sewage sludge, but the paper contains little information on the practical value of the compost to agriculture; he may possibly have something to say on this important matter at a later date.

The American Federation of Sewage Works Associations has issued a valuable publication on the utilisation of sewage sludge as a fertiliser.[42] The compilers of this book have brought together, in a readable form, a

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[37] *J. Inst. Sewage Purif.*, 1945, *Part* 2, 58.
[38] *Sewage Works J.*, 1946, **18**, 17; B., 1946, III, 148.
[39] *Surveyor*, 1946, **105**, 27.
[40] *J.S.C.I.*, 1945, **64**, 331; B., 1946, III, 59.
[41] *J. Inst. Sewage Purif.*, 1945, *Part* 2, 79.
[42] "Federation of Sewage Works Associations, Manual of Practice," *No.* 2, 1946.

mass of useful information, and have enhanced its value by appending a comprehensive bibliography.

Chlorination of Sewage Effluents.

L. A. Allen, N. Blezard, and A. B. Wheatland[43] have made a most significant communication concerning the toxicity to fish of chlorinated sewage effluents. Their brief preliminary summary of results obtained by the staff of the Water Pollution Research Board is of great importance to anyone contemplating the use of chlorine in sewage treatment. Confirming the findings of other workers that fish are highly sensitive to traces of free chlorine, they found that concentrations of free chlorine as small as 0·3 p.p.m. were appreciably toxic to fish. Their most striking discovery, however, was the fact that chlorine reacts with thiocyanate to form an exceedingly toxic product; only a trace of thiocyanate (0·15 p.p.m. as CNS′) is needed to yield lethal results when chlorinated. As the concentration of thiocyanate in effluents from works treating sewages to which gas liquor has been admitted is often appreciably greater than this, it is obvious that chlorination of effluent would in many cases endanger fish life.

Sewage Analysis.

After outlining the principal defects (including slowness) of the usual Gooch crucible method of determining suspended matters, R. S. Young and A. Liebowitz[44] have described a modification which they have found to be effective. Their method utilises a specially prepared mat of paper pulp in a Gooch crucible. The authors report that this method is much more rapid than the standard procedure, and gives clear filtrates. In a discussion on the paper, W. D. Hatfield and W. W. Diller confirmed the speediness of the new method, but noted that the preliminary work in preparing the mat took some time; they suggested a method of remedying this defect.

R. Pomeroy and H. D. Kirschman[45] have suggested a modification of the Winkler method for determining dissolved oxygen. They have found that the use of increasing amounts of iodide diminishes interference by organic matter, reduces loss of iodine vapour, and sharpens the end-point of the titration. The hydroxide–iodide should be 10N. with respect to NaOH and 6N. to NaI.

P. S. S. Dawson and S. H. Jenkins[46] have described methods of applying micro-analytical technique to the examination of sewage and sludge. The methods have been ingeniously devised, but it has been suggested that with such heterogeneous materials as sewage and sludge, there might be some difficulty in withdrawing truly representative micro-samples.

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[43] *Survyor*, 1946, **105**, 298.

[44] *Sewage Works J.*, 1946, **18**, 228; B., 1946, III, 187.

[45] *Ind. Eng. Chem.* [*Anal.*], 1945, **17**, 715; C., 1946, 116.

[46] *Sewage Works J.*, 1945, **17**, 525; C., 1945, 269.

Biology of Sewage Disposal.

The biological and bacteriological aspects of sewage disposal are receiving some much needed attention, and several important publications on this subject have recently appeared.

C. D. Parker[47] has given an account of some thorough work on the corrosion of concrete exposed to atmospheres containing hydrogen sulphide. He has reported the isolation of a new species of bacterium (provisionally named *Thiobacillus concretivorus*), and carried out investigations on the function of this organism in the disintegration of concrete. It appears that *Th. concretivorus* does not commence its attack until the pH value has been brought down to between 6 and 7 by other agencies.

L. Lloyd[48] has submitted a very valuable account of animal life in sewage purification processes, thus satisfying a long-felt want of sewage technicians. This contribution, together with T. G. Tomlinson's well illustrated booklet on the identification of animal organisms in percolating filters,[49] will be greatly appreciated by many workers in this field.

The rôle of protozoa in the aërobic purification of sewage has been studied by S. C. Pillai and V. Subrahmanyan,[50] who experimented with *Epistylis* sp., freed from associated bacteria. The authors consider that the results indicate that all the changes associated with the aërobic purification of sewage are due to the protozoa, and that the part played by the bacteria is purely secondary.

As might be expected, the possibility of using DDT and kindred substances for the control of filter flies is receiving close attention. Working on small experimental filters T. G. Tomlinson[51] has found that DDT, either in powdered form or as an emulsion, can kill over 90% of the larvæ of *Anisopus* and *Psychoda*, without affecting the *Colembolla* and enchytraeid worms. Equally important, it was found that dosages of DDT (300 lb. per acre as powder, or 50—100 lb. per acre as emulsion) were non-toxic to bacteria and fungi in the filter, and had no deleterious effect on purification. In respect of this favourable selectivity, DDT was preferable to creosote and to bleaching powder. Valuable accounts of large- and small-scale American work on this subject have been given by W. C. Brothers[52] and by J. A. Carollo[53]; both these observers confirm the great promise of DDT for control of filter flies.*

E. J. Stokes, E. E. Jones, A. F. Mohun, and A. A. Miles[54] have investigated the effect of the drying and digestion of sewage sludge on certain

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[47] *Austral. J. Exp. Biol.*, 1945, **23**, 81, 91; B., 1945, I, 360.

[48] *J. Inst. Sewage Purif.*, 1945, *Part* 1, 119; B., 1947, III, 84.

[49] *Dept. Sci. Ind. Res.*, *Water Pollution Res.*, *Tech. Paper* 9; B., 1946, III, 188.

[50] *Nature*, 1944, **154**, 179; B., 1945, III, 236.

[51] *Ibid.*, 1945, **156**, 478.

[52] *Sewage Works J.*, 1946, **18**, 181; B., 1946, III, 188.

[53] *Ibid.*, 208; B., 1946, III, 188.

[54] *J. Inst. Sewage Purif.*, 1945, *Part* 1, 36.

* For other references to the use of DDT, see the section on "Pest Control," p. 518.

pathogenic organisms. The development of a satisfactory bacteriological technique proved difficult, owing to the obstructive activities of the many non-pathogenic bacteria present in the sludge. By very heavy inoculations, it was found possible to obtain some survival of pathogenic organisms after quite long periods of bed drying. On the other hand, no living pathogenic bacteria of the typhoid, dysentery, or *Salmonella* groups were found in any of the samples of dried or partially dried sludge from 28 sewage disposal works; so the results as a whole are fairly reassuring.

TRADE EFFLUENTS.

The canning of fruit and vegetables is now an important industry in this country, and it seems unlikely that the cessation of hostilities will cause much, if any, diminution in its activities. The disposal of the waste waters from canneries presents many problems. The wastes are strong, and variable in both character and volume, while many of them are prone to somewhat objectionable decomposition. Moreover, many canneries are situated in rural areas, where sewage disposal works are either non-existent or of small size. These circumstances have led D. Dickinson to carry out some thorough work on the purification of the waste waters, at the cannery itself. In the first place[55] he investigated the properties of cannery effluents and their response to screening, sedimentation, and biological purification. In a second contribution[56] he set out the results obtained from an experimental plant, treating cannery waste by recirculatory filtration. It seems that the purification of cannery wastes by themselves, although practicable, would be expensive. It is also plain that cannery wastes would impose a considerable load on a sewage disposal works.

H. H. Goldthorpe and J. Nixon[57] have reported the results of extensive laboratory experiments on the treatment of the chemical trade wastes discharged to the Huddersfield sewage works. They found the waste to be more amenable to oxidation by biological filtration than by activated-sludge treatment. The most promising process appeared to be double filtration, with the primary bed taking a higher rate of dosage than the secondary bed; this process was more efficient than one-to-one recirculation.

F. Rosendahl[58] has made some favourable comments on the Phenosolvan process for extracting phenol from the waste waters from gas works and coke ovens. Phenosolvan, which is a mixture of various esters of higher aliphatic alcohols, has a greater absorptive capacity for phenol than have other solvents used for that purpose. The author reports that to reduce the content of phenol from 7 g. to 0·1 g. per litre

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[55] *J. Inst. Sewage Purif.*, 1945, *Part* 1, 48.
[56] *Surveyor*, 1946, **105**, 1001.
[57] *J. Inst. Sewage Purif.*, 1945, *Part* 1, 109.
[58] *Gas u. Wasserfach*, 1943, **86**, 424.

by countercurrent washing, the volumes of various solvents required (expressed as percentages of the volume of gas liquor) are : benzole 220, tricresyl phosphate 17·5, Phenosolvan 10.

J. Grindley[59] has reported on the testing of four methods for the treatment of waste waters containing chromate. Treatment with twice the amount of ferrous sulphate theoretically required to reduce the chromate in a waste water rapidly reduced the chromate under either acidic or alkaline conditions; subsequent treatment with lime yielded a harmless effluent. This is an interesting observation, for wastes containing ferrous sulphate (from steel dipping etc.) are often produced in the same area as chromate wastes. There seems to be a possibility of using one waste to treat the other.

The effects of wastes containing copper and lead on the purification of sewage have been investigated by M. M. Kalabina *et al.*[60] It was found that concentrations of either of these metals in excess of 0·5 p.p.m. retarded nitrification, while as little as 0·1 p.p.m. of lead retarded the biochemical oxidation of organic matter. The authors feel that concentrations of either copper or lead in excess of 0·1 p.p.m. are prejudicial to sewage purification.

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[59] *J.S.C.I.*, 1945, **64**, 339; B., 1946, III, 60.

[60] *Water and Sewage Works*, 1946, **93**, 30; B., 1946, III, 187.

NAME INDEX.

SUBJECT INDEX.