REPORTS

ON THE

PROGRESS OF APPLIED CHEMISTRY

VOL. XXXII: 1947

Published by the
SOCIETY OF CHEMICAL INDUSTRY
56, Victoria Street,
London, S.W.1.

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Printed [illegible] Bound in Great Britain for the Publishers at the works of
CO-OPERATIVE WHOLESALE SOCIETY LTD., SOUTH REDDISH, ST[illegible]

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REPORTS
ON THE
PROGRESS OF APPLIED CHEMISTRY

CHEMICAL ENGINEERING, PLANT AND MACHINERY

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THE period under review has shown a tendency among technical workers to examine physical separating processes very carefully in an attempt to improve what might be termed the " Separation Factor." Simple differences in volatility are being modified and enhanced by such processes as extractive distillation, and the possibilities of vacuum fractionation at all pressure ranges are being explored. The logical development of extractive distillation might be towards differential absorption on suitable solid masses, and certain indications of this are discernible.

The phenomena of " fluidization," or the formation of a stable fluid bed from solid particles and upward streaming gas, has been utilized on a large scale with singularly little fundamental investigation being reported in technical literature. Very divergent statements remain to be reconciled, and no doubt further knowledge on such points as heat transfer rates or suitable mass velocities will soon be available.

Automatic control of chemical plant is steadily becoming more widespread, and this is reflected in the number of papers published dealing with this branch of plant technology.

The important *Transactions of the American Institution of Chemical Engineers* appeared through the year in the monthly journal *Chemical Engineering Progress*. This comprised " General," " Transactions," and " News " sections with individual pagination. References are given as " Chem. Eng. Prog." to the general section, and should not be confused with the " Chem. Eng." of *Chemical Engineering*—a separate publication. The Transactions are listed under their original title. Reviews of both " Operations " (January) and " Materials " (October) appeared in *Industrial and Engineering Chemistry*, and are to be annual features in the future.

Fluid flow

The entrainment of one fluid by another, as in the various forms of jet or diffusion pumping, is a process of growing importance in the chemical industry. In jet pumping, steam has been usually the entraining fluid, but hot gas jets may come into wider use. V. Cleeves and L. M. Boelter[1] have surveyed previously published information on these, and compared the figures with results of their own, obtained with air at 650° as an entraining fluid. They measured temperature and velocity along the jet axis, but met with certain difficulties in the measurement of low velocities. Perhaps as a result of these, they were unable to recommend any general formulæ for the effect of jet velocities on the measured quantities. Methods for the design of steam jet exhausters, and typical figures for their performance in the operation of chemical plant have been given by P. Freneau, G. Kelso, and A. W. Hoge,[2] while an alternative method for the design of single stage jet pumps has been worked out by A. E. Kroll.[3]

Velocities in these pumps may become very high, and it should be noted that entry characteristics for any conduit then become more important. J. H. Keenan and E. P. Neuman[4] show that abnormal values for friction losses may occur with compressible fluids, owing to the formation of oblique shock waves, when the flow Mach number approaches or exceeds unity. These effects can be eliminated, apparently, by a " smoothing section " of 50 diameters or more. At the other extreme of fluid flow, in the seeping of liquids through narrow cracks or permeable solids, changes in flow characteristics with time have repeatedly been noted. R. Meyerott and H. Margeneau[5] have measured a diminution in rate, which they hold to be due to the formation of small gas bubbles, anchored by irregularities on the walls of the crevices.

R. C. Binder and J. E. Busher[6] show that a stable suspension behaves, in flow, as a plastic material, with a pseudo-viscosity varying with velocity. A chart can be constructed in which a friction factor is plotted against a Reynolds number in which this varying viscosity is taken into account. T. R. Lomer[7] suggests that a modified kinetic energy term is also required when dealing with the flow of plastic materials. A. T. Ippen[8] has measured the efficiency of two small centrifugal pumps in the pumping of liquids of varying viscosity. Data were correlated by means of a Reynolds number based on impellor diameter, tip velocity, and fluid viscosity. The performance of the pumps declined steadily with decrease in the value of this Reynolds function, and efficiency was very low for values below 1000. In general, satisfactory efficiencies were only obtained when the Reynolds number was over 1,000,000.

The process of " fluidization " referred to in the introduction has a certain analogy with the formation of a stable solid-in-liquid suspension, or with the temporary suspensions used in flotation processes as " heavy " liquids. J. D. Parent, N. Yagol, and C. S. Steiner[9] show that a fluidized suspension is formed by an upward current of gas through a bed of finely divided solids, but only when the gas velocity falls within certain limits, set by the nature of the solid particles and the size range chosen. Below this velocity range, the solid settles to a fixed bed of definite permeability, and above it, solids are blown out of the container. For carbon and graphite particles, the critical range is from 0·2 to 1ft. per sec. (based on total cross section of conduit), and the pressure drop across the fluidized mass can then be calculated on a hydrostatic head basis. The particle size range should be wide, as a layer of closely sized fragments is difficult to " fluidize," while the width of the conduit-container also plays some part which is not yet clearly defined. For the solids used, a size range from 50 to 300 mesh appeared to give fluidizing characteristics over a fivefold velocity variation in tubes from 2in. to 6in. in diameter. As the conduit is made smaller, the velocity range for fluidizing grows narrower.

Heat transfer

The most outstanding feature of claims on fluidized material is that much greater rates of heat removal can be obtained from a catalyst mass in this form, than from the conventional static mass packed round cooling tubes. Parent *et al.*,[9] in preliminary measurements on heat transfer, show that the difference in rate between a stream of nitrogen and a similar stream supporting a fluidized carbon mass is small—less than 5% more in the case of the solid-liquid mixture. This does not appear to agree with the claims made for fluidized catalysts controlling the Fischer-Tropsch reaction. E. V. Murphree, E. J. Gohr, and A. F. Kaulakis[10] suggest that the cooling surface required with these catalysts is only 1% of the surface required in the normal reaction with a static bed, a claim that is supported by R. C. Alden.[11] Now C. C. Hall and A. H. Taylor,[12] in a paper on the Fischer-Tropsch plants of Germany, showed that extraordinary attempts were made to introduce cooling surfaces into the catalyst mass, and suggested that the output of hydrocarbons was directly proportional to the amount of cooling surface per unit volume of catalyst. If these elaborate cooling arrangements can be replaced by much simpler and smaller devices, then, as the authors point out, the whole economy of the process may be altered. In view of the actual measured heat transfer rates, it does not appear that the claims of the oil technologists[10, 11] are based on heat transfer alone, but that some other factors must be introduced. Further details on this aspect of the process are awaited with interest.

J. C. Kaulbach,[13] in a description of the general phenomenon, agrees with authors previously quoted in giving gas velocities between 0·5 and 2ft. per sec., with solid particles of size range from 60 to 325 mesh. The tumultuous solid-gas mixture is of constant density, and steady reaction zones are formed when catalytic surfaces are involved. He bases[14] on these observations a mathematical analysis of the system, with an expression for the effective reaction time. A patent[15] specifies gas velocities of the order of 1ft. per sec., and claims that these should be related to the space above the fluid catalyst mass—" solid disengaging space." The height of this space should be 5ft. for a gas velocity of 1ft. per sec. The use of a large excess of solid catalyst particles as a shock cooling medium has also been described,[16] and a reaction vessel built[17] in a special shape to avoid recycling in the reaction zone.

The older and better established catalyst systems with a static bed of catalyst have generally been designed on empirical lines, with the general principle that as much cooling as possible be provided with exothermic reactions. K. B. Wilson and J. H. Tasker[18] have attempted to put the matter on a sounder theoretical basis, with particular reference to the reaction chambers in a phthalic anhydride plant. L. M. Grossmann[19] has made a general mathematical analysis of the temperature distribution in such a system, while a third and parallel paper by J. R. Arthur and J. W. Linnett,[20] dealing with the combustion of carbon, should also be noted.

The rate of heat transfer across a fluid in laminar flow in a channel of annular form has been expressed as a dimensional equation by C. Y. Chen, G. A. Hawkins, and H. L. Solberg.[21] Their results covered a range of Reynolds numbers from 200 to 2000 (based on a " diameter " of D_1–D_2), and were consistent for both heating and cooling. W. H. Corcoran, B. Roudebush, and B. H. Sage[22] have measured the rate of temperature change across a turbulent air stream flowing in a narrow conduit, and suggest that agreement with the earlier theoretical analyses of von Karman and Prandt. is not satisfactory. They indicate, however, that the results are not complete. A very compact form of heat exchanger may be constructed by coiling two spirals of flat plate co-centrally in between the same end walls, so that each spiral forms a continuous coiled channel of rectangular section, with turns of each spiral placed alternately. K. W. Coons, A. M. Hargis, P. Q. Hewes,[23] and F. T. Weems have measured the rates of heat transfer in such channels, and in the process have shown that turbulence appears to set in at lower values of Reynolds criterion (based on hydraulic mean depth) than for circular channels. Heat transfer rates are about 30% greater on such exchangers than would be expected from calculations on the Dittus-Boelter relation, but the rates vary with velocity of fluid in the same way—as $V^{0 \cdot 8}$.

D. A. Donahue[24] has suggested a simplified form of the Nusselt expression for condensing hydrocarbon vapours; it takes the form $H_f = 775\ (L/W)^{0 \cdot 33}$, where L is the length of the (horizontal) condensing tube, and W the total weight of condensate in pounds per hour. E. P. Breidenbach and H. E. O'Connell[25] have calculated values for the overall heat transfer coefficient in a number of commercial heat exchangers and condensers. They find that the results agree very well with theoretical results based upon dimensional equations. For heat transfer to boiling liquids in commercial plant, no definite correlation could be established, and they conclude that no suitable method of predicting this rate has so far been established. A common problem in many industries is the cooling of a mixture of permanent gas and condensable vapour. L. Silver[26] shows that this case can be simplified by assuming a constant sensible heat transfer coefficient, and a varying condensation coefficient. J. B. Tepe and A. C. Mueller[27] point out that considerations of head room sometimes suggest the installation of a horizontal or inclined tube condenser, with the vapour condensing inside instead of outside tubes. They have measured the rate of condensing the vapours of methanol and benzene in such a unit, with the tube set at varying angles to the horizontal. Film coefficients for condensation were rather greater than those calculated on the basis of Nusselt's expression, and tended to increase with vapour velocity, but were little affected by tube slope. When the condenser was used to supercool the liquid condensate, the heat transfer increased steadily with inclination to the horizontal, reaching a maximum with a vertical tube, as might be expected.

The bayonet type of heater tube, with fluid lead to the tip and return to the head, has been widely used in steam heaters where only one tube plate or header is required. If this bayonet tube is used for heat interchange between two fluids, both of which are changing in temperature, then the effect of the central lead tube is to diminish the effective temperature difference. According to N. L. Hurd,[28] the divergence from the logarithmic mean may be as much as 25%, and he derives a formula for the true effective temperature difference. Conditions in such tubes may also be affected by " end " conditions similar to those studied by M. Jakob and W. M. Dow.[29] They arranged for heating and cooling fluids to pass along a circular tube, in a direction parallel to the principal axis of the tube. For short tube lengths, the shape of the end section was all important, and the change from viscous to turbulent flow could be expressed as a range in Reynolds numbers based on tube length as the characteristic dimension. For tubes of 1·3in.

diam., the critical range was from 50,000 to 200,000. P. V. Tscherpakov[30] has made a mathematical analysis of a somewhat similar case.

J. Meisler,[31] in a study of the economic usage of water in tube and shell coolers, maintains that the outlet temperature of the water should not be less than the outlet temperature of the fluid being cooled, and that ideal working conditions are obtained when the outlet temperatures of both water and cooled fluid are the same. F. C. Otto[32] has provided a mass of data for future workers on the problem of economic lagging thickness. He has studied three main types of covering—cork for refrigeration lines, mineral wool in various forms, and magnesia shapes.

A great deal of attention has been given to the problem of heat interchange in liquid air plants. Streams of cold oxygen and nitrogen have to cool the entering air as effectively as possible; at the same time, the exchangers must not be blocked by deposited water and carbon dioxide. These impurities can be removed by chemical means, but this adds considerably to the cost of the process, so it is desirable to work with a regenerator system, in which deposited solids from the air run can be purged out by nitrogen, which is usually going to waste. The obvious arrangement is a three channel plant, in which nitrogen and air flow alternately through two of the channels, and oxygen through the third. J. H. Rushton and E. P. Stevenson[33] give a description of this plant but show that there is a tendency for permanent deposits to form at the " cold " end of the exchanger. A portion of the nitrogen is therefore by-passed to a fourth shorter channel at the " hot " end, where it is warmed by the incoming air. The two nitrogen streams are then remixed, and the mixture goes into the regenerator channels, where it is now hot enough to revaporize all the deposits. W. E. Lobo and G. T. Skaperdas[34] call this a system of " unbalance control " and show how it involves an adjustment of temperature difference in the various parts of the exchanger. P. R. Trumpler and B. F. Dodge[35] describe a typical heat exchanger for this work; it is built up from concentric gas passages packed with copper helices, which give metal to metal contact between all parts of the exchanger. The overall coefficients, gas to gas, were as high as 300 B.Th.U./sq. ft./hr./°F., based on the actual wall surfaces. It would be interesting to see how such figures compare with a patented form[36] of heat interchanger in which the gas conduits are of porous sintered metal.

The complicated forms of energy present in a compressible fluid in rapid flow make the expression of heat transfer difficult. W. H. McAdams, L. A. Nicolai, and J. H. Keenan[37] suggest three possible forms for a heat transfer coefficient in such cases. The normal form, based on mean stream temperature—mean wall temperature, varies very widely with temperature difference. Values based on a " still air " temperature, or on the difference between actual wall temperature and an " adiabatic " wall temperature of zero heat flow, are more satisfactory. D. G. Samaras,[38] in a mathematical analysis of the same problem, indicates alterations in the system as the velocity of the gas stream approaches that of sound.

Distillation

The general case for the separation of two or more components of a mixture by a multi-stage counter current flow, has been set out by M. Benedict.[39] He argues that the minimum amount of energy required for any such separation will be associated with thermodynamically reversible processes. Thus distillation, in which the energy put in at the still can be recovered almost completely at the condenser, will be more efficient than such processes as diffusion through a membrane, or mechanical separation through differences in density. When the differences in properties become very small, as with isotopes, these efficiency factors will become increasingly important. It is also a general rule, in counter current separation, that the mass flow is less at the ends of the processing plant than in the middle feed section. The author goes on to review isotope separation processes in the light of these generalizations, and shows that chemical exchange between liquid and vapour phases (*e.g.*, $DH + H_2O = H_2 + DHO$) simulates distillation very closely in the actual process, but irreversible work has to be done at top and bottom of the column. Thermal or membrane diffusion require such large amounts of irreversible work that they will only be used if the separation factor is much larger than that available in other methods, and similar considerations apply to density separations in general. The paper concludes with a tentative comparison of the amounts of energy and plant required by various processes for the separation of 100g. of " heavy " carbon (C^{13}).

This illustrates the probable importance, in the future, of very efficient fractional distillation for the separation of substances with a very small difference in volatility. Alternatively, some device for the alteration of these volatility ratios will be utilized, as in extractive or azeotropic distillation, or by working under reduced pressure. The pressure drop across a fractionating column will become very important, and it is regrettable that no very efficient column for work at low pressures has yet been devised. A number of attempts to fill this need have lately been described. S. F. Birch, V. Gripp, and W. S. Nathan[40] have described the development of a spinning band column of 3·6cm. diameter and 91cm. in length. The central element was a twisted metal strip, fitting the column closely, and rotating at speeds up to 1000 r.p.m. After dealing with various devices for successful working, the authors showed that a maximum plate equivalence of 16 theoretical plates could be obtained at a speed of 200 r.p.m., working at normal pressures with a heptane-*cyclo*hexane mixture. The efficiency rose from 2 theoretical plates with a stationary rotor up to 16 and then fell again to 12 at 1000 r.p.m. When the column was operated at 0·5 mm. Hg, sharply cut separations were obtained with two high boiling oil mixtures, with the same variation with rotor speed. It was suggested that these separations corresponded to at least as high a plate equivalence as in atmospheric working, while the total pressure drop across the column was only 0·1mm., with a boil up rate of 4g. mol. per hour. The pressure drop would thus be about 0·006mm. per theoretical plate.

Very similar figures have been given by C. B. Willingham, V. A. Sedlak, F. D. Rossini, and J. W. Westhaver.[41] They used a concentric tube system in which an inner tube, of 7·5cm. diameter, formed the rotor. The plate equivalence rose steadily with rotor speed, reaching 100 plates per metre length at 4000 r.p.m., with a boil-up rate of 15g. mol. per hour. The pressure drop at just under 1mm. corresponded to 0·01mm. per theoretical plate. J. Piazza[42] has given a description of a rotor carrying annular rings which, rotate inside the corresponding static annuli and form a series of transfer cells. This aims at the complete elimination of pressure drop across the column.

Research on the ordinary packed column continues, and H. O. McMahon[43] has suggested the use of squares of wire gauze stamped into a saddle form. These shapes have a packing density of about 25lb. per cu. ft., and when working on liquid air mixtures will give some 26 theoretical plates per metre length in a 7·5cm. diameter column. Further work on this type of packing is reported by W. L. Forsythe, T. G. Stack, J. E. Wolf, and A. L. Conn,[44] who built up a 15cm. diameter unit, and found that some 10 to 20 theoretical plates could be obtained per metre length, with a boil-up rate of 1 to 2lb. mol. per hour. The pressure drop was about 0·2mm. per theoretical plate, which was claimed to be half the value for Stedman packing under similar conditions.

Attempts have been made to utilize these packed towers in oxygen production from liquid air mixtures, as they would have the advantage of working in slightly tilted positions, or rolling from side to side, as on board a ship. It has even been suggested that plant should be designed to work on aircraft, when weight will be of great importance. J. G. Aston, W. E. Lobo and B. Williams[45] tested a Stedman packed column under tilted and rolling conditions; the tower was 12in. in diameter, and gave normally an H.E.T.P. of 4in. A five degree tilt from the vertical reduced the efficiency to an H.E.T.P. of 20in., but if the tower was rocked through a 10° arc with a 12 sec. frequency, the efficiency was fully restored. Pressure drop, with these liquid air mixtures, was about 1mm. per theoretical plate. Alternative packings studied were ordinary Berl saddles and an " expanded shale " (Haydite); the saddles and the Stedman gauzes were better than the Haydite, but it was notable that no packing gave as many theoretical plates per unit height of column as some bubble trays also tested. These trays were of several designs, one of which was the APV-West type (1945 Report), and showed efficiencies up to 80% of theory, with a plate spacing as small as 2in. The pressure drop here was 1·5 to 2mm. per theoretical plate. J. A. Weedman and B. F. Dodge[46] tested a number of packings in a search for the most compact liquid air column, and reported that Stedman packings in 60 by 40 mesh wire gauze were the best, with an H.E.T.P. of 2in. in a column of similar diameter, and a pressure drop of 0·5mm. per theoretical plate.

The use of extractive distillation in the separation of butane-butadiene mixtures was mentioned in the 1946 Report. C. K. Buell and R. G. Boatright[47] review the extractive agents available for this and show that the most selective agent would be water, but the very low solubility of the hydrocarbons would entail the circulation of enormous quantities of hot water. Furfural with a little water (4%) was chosen as the best compromise between selective action and solubility, and circulated in amounts of eleven to twelve times the amount of hydrocarbon mixture being treated. Butadiene is made from butane by a two stage dehydrogenation, and after each step the products are separated into re-cycle and forward streams. The effect of the furfural is to depress the vapour pressure of unsaturated compounds relatively to fully hydrogenated hydrocarbons, and a combination of normal and extractive distillation gave finally a nearly pure butadiene, with improved conversions at each pass in the reaction units as compared to processes not using extractive distillation. It would be interesting to know if the sulpholanes (sulphone derivatives of tetrahydrothiophene) could be used as extractive agents in this process. H. G. Staatermann, R. C. Morris, R. M. Stager, and G. J. Pierotti[48] claim that they are extremely effective in the separation of aromatic hydrocarbons from paraffins. The determination of vapour liquid equilibria in these ternary systems is often made difficult by the separation of the liquid into two layers. M. R. Fenske, C. S. Carlson, and D. Quiggle[49] have devised a special form of equilibrium still which allows for this phenomenon.

E. G. Scheibel and D. Friedland[50] have proposed a method for the determination of equilibria in ternary systems, when data from the three binary systems are available. Activity coefficients for the binary mixtures are used to construct a triangular diagram in which lines of constant activity coefficient can be drawn, and from these the composition of ternary mixtures can be calculated. J. P. Zwilling[51] shows how to set out a diagram for the system—two miscible components and one non-miscible entrainer—in which only the concentrations of the two miscible components appear. L. H. Horsley[52] has developed a graphical method for the prediction of azeotrope formation and, with H. S. Nutting,[53] an extension of this method to cover the effect of pressure variations.

A. J. V. Underwood[54] has suggested formulæ for plate to plate calculation in the distillation of ternary mixtures, and a further equation for the determination of the minimum reflux ratio. These equations hold rigidly for ternary mixtures, but may be extended to multi-component mixtures, with the assumption of constant relative volatilities and a sharp separation of key components. R. J. Hengstebeck[55] proposes the use of a composite " key " in the calculation of multi-component problems; these hypothetical " keys " are used in the construction of a normal McCabe-Thiele diagram. An extension of the method proposes a correction in the slope of the operating lines of the diagram to allow for the other components.

The use of total reflux periods, followed by short periods of product withdrawal, has now been established as an aid to sharpness of separation in batch distillations. W. E. Chadder and H. M. Spiers[56] show how this device was used to increase the output of batch benzole stills during the war, while D. M. Oldroyd and L. A. Goldblatt[57] have measured the increase in effectiveness given by the method with three small packed columns.

J. A. Storrow[58] has shown that a thermocouple probe will give spot sampling of liquid vapour conditions inside a fractionating column with a considerable degree of accuracy. He has used the method for exploring conditions inside a wetted wall column, and shows that wide variations in the H.T.U. occur with variations in the composition of the alcohol-water mixtures used. That this effect is not confined to alcohol-water mixtures, or to wetted wall columns, is shown in a further paper, with B. D. Willson.[59] Two typical hydrocarbon mixtures, distilling in a packed column, are shown to give similar variations. It is maintained that the results of previous workers, in which H.T.U. figures were shown to be independent of liquid vapour composition, were based on too narrow a range of experimental data. The largest variations in H.T.U. are to be found in the end stages of separation, with small concentrations of one component.

These results should be borne in mind when considering the data set out in two papers on the separation of benzene, toluene, and xylene mixtures. In the first, M. Nord[60] showed that plate efficiencies reached a maximum figure of 70% when dealing with liquids containing about 60% of benzene, but dropped as low as 28% when the concentration of any component was below 5%. J. Griswold and P. P. Stewart,[61] on the other hand, were unable to discern any clear trend in the variation of plate efficiencies. Both sets of data were based on work with 6in. diameter columns of the bubble cap type, and it was suggested that heat losses were large and sampling difficult. In view of the comments of Storrow (above) and Gerster *et al.* (Report 1946, p. 13) it is probable that closely comparable figures for plate efficiency are hardly to be expected when operating conditions differ.

An attempt to calculate the hydraulic gradient across a typical bubble cap plate, as made by J. A. Davies,[62] is based on flow through channels between the caps. Although it appears to give reliable results for this type of plate, the method would appear to have little application where the design of the plate has been radically altered, as in many modern designs. A continuous pipe still for the distillation of coal tar has been described by R. Scott;[63] corrosion problems were much greater than in the distillation of petroleum, but were overcome by the use of high chromium steel in the actual pipe still, and special cast irons in the fractionating column.

The latest form of " molecular " distillation unit, according to K. C. D. Hickman,[64] is a truncated inverted cone, of flower pot shape, and up to 5ft. in diameter. This cone is rotated at a speed sufficient to spread the distilland, introduced at the narrow base, evenly over the inner surface, while the outer surface is heated by radiant heaters. Inside the cone are hung a series of leaf condensers, which trap the bulk of the diffusing molecules. Traces of more volatile material pass between the leaves to a very cold central condenser, thus achieving some degree of fractionation. In order to obtain a still greater degree of separation a wire baffle is fixed between the rotating surface and the initial condensing leaves. A further fractionation may be achieved by arranging condensers in a step-wise fashion to return the condensates in counter current flow to a point lower down the rotor. As a measure of the degree of separation, the author proposes the term " Theoretical Molecular Plate," which is defined as the plant unit causing a change in composition, liquid-vapour, equal to that calculated from Langmuir's expression. The single rotor described above, with the double condensing system, is about equivalent to one " T.M.P.", but the addition of the wire baffle doubles this equivalence.

In the design of these low pressure units, a point that is often overlooked is the size of the connexions between still and pump, or, for somewhat higher pressures, between still and condenser. H. Griffiths[65] has discussed the problems involved in the design of these vapour connexions and suggested suitable means for their solution. A. E. Williams[66] in a review of the pumps available for these very low pressures, differentiates between vapour jet and diffusion pumping. Jet forms should be used down to pressures of 0·01mm., after which the diffusion type takes over for all lower ranges. Proper working can only be secured by providing ample capacity in the backing pump, and by keeping all impurities out of the pumping fluids. When testing the capacity of stills, or their separating capacities, use may be made of special mixtures described by F. E. Williams,[67] or by E. S. Perry and R. E. Fuguitt.[68]

Absorption and extraction

It has long been realized that spray towers would form a very effective plant for certain types of gas-liquid interaction if the disadvantage of entrainment could be overcome. H. F. Johnstone and H. E. Silcox[69] show how this trouble may be diminished by building the tower in the form of a cyclone, and they have correlated entrance design, gas velocity and nozzle spacing in such a way as to give a rational design basis. Such towers may be operated over a wide range of liquid-gas loadings, with very small pressure head losses. In experiments with the more usual packed tower, N. A. Spector and B. F. Dodge[70] have measured the rate of absorption of traces of carbon dioxide, using alkaline solutions as absorbents. They show that the mass transfer coefficient varies as the 0·2 power of the liquid rate and the 0·35 power of the gas rate. E. G. Ragatz and J. A. Richardson[71] tabulate the operating characteristics of some 40 commercial columns working on hydrocarbon absorption in the oil industry, and suggest an absorption factor chart for correlating tower performance.

It would be expected, from the growing popularity of extractive distillation on the one hand, and of chromatographic analysis on the other, that further attempts would be made to utilize differential absorption in the separation of gas mixtures. R. F. Barrow[72] shows experimentally how a gas mixture is distributed when passed through a column of active charcoal, and how this distribution can be calculated from the respective absorption isotherms. O. A. Hougen and W. R. Marshall[73] have presented a mathematical analysis of the case in which a stream of gas carrying one absorbable component passes through a bed of solid absorbent. They assume that the main resistance to absorption is in the stagnant gas film, and allow for thermal effects. C. Berg and W. E. Bradley[74] have described a " Hypersorption Unit," which is merely a bed of absorbent through which hydrocarbon gases pass, to be differentially absorbed and then removed by steaming.

In the associated field of solvent extraction, T. G. Hunter and T. Brown[75] have recorded equilibrium conditions in the extraction of hydrocarbon mixtures with aniline—a typical preferential solvent. R. H. C. Pratt and S. T. Glover[76] describe experiments on the washing of vinyl acetate to remove acetone and acetaldehyde. The solvent used was water and, as the concentration of the extracted material increased, so the relative solubility of the phases varied. However, when working in a packed tower, the acetate usually formed the dispersed phase, and the height of a typical " equilibrium stage " was about 5ft. F. A. Zenz[77] suggests that the counter current flow of two liquids in a packed tower is closely analogous to the flow of fluids through an orifice. In each case, velocity increases with fluid head up to a sharply defined maximum, after which no further increase of head is effective. Working on this conception, the author attempts to correlate a number of previously published figures for flooding velocities.

The development of chromatography to an industrial scale may be foreshadowed in a patent[78] which describes a disc of absorbent material, rotated to give a centrifugal pressure. Solution forced through this disc from the centre outwards will give absorption in zones, which can be washed out in turn.

Filtration and gas cleaning

The section on Filtration, included in the Unit Operations Review of *Industrial and Engineering Chemistry*,[79] covered the five years from 1941 to 1946, and suggested that the main developments in this period had been in the production of novel filter media from artificial fibres and plastics.

S. M. Walas[80] considers that the properties of most filter cakes can be expressed by a filter coefficient based on the percentage of voids in the cake, and on the allied factor of particle size in the slurry. He finds by experiment that such coefficients are independent of pressure for most filter cakes, at any rate up to 50lb. per sq. in.

The use of bag filters for gas cleaning has been falling off in the last decade, and this, according to L. J. Weischhaus,[81] is due to the bad reputation gained by faulty installations. Dust filters of this type should rely for filtering properties upon the layers of dust first deposited, and not on the fabric of the cloth, just as in ordinary liquid filtrations. It follows from this that a "precoat" will generally be an advantage, and asbestos "floats" are suggested for this purpose. R. B. Foley[82] maintains that the most characteristic property of any dust particle is its ultimate settling velocity, and that any analysis of dusts should therefore be based on elutriation tests. He gives a correlation of experimental tests with the performance of a large dust removal plant.

L. W. Briggs[83] has measured the effect of introducing dust into clean air streams entering a cyclone. The first effect is a drop in the fall of pressure, and this is attributed to some interference by the solid particles with the vortices set up in the clean gas stream. As the dust concentration increased, the efficiency of removal, with a fixed amount of air, showed a slow increase. On the other hand the efficiency was independent of the amount of air passing, over a very considerable velocity range. These conclusions are supported by the findings of J. D. Parent,[84] who worked with small "Aerotec" cyclones of 2–3in. in diameter. He thought, however, that the increase in efficiency with increased dust content was small enough to be ignored. Small cyclone tubes of 6in. in diameter are the basis of a high efficiency boiler waste gas deduster, for which removals of 90–94% of the total dust have been claimed.[85] A particular case of gas scrubbing has been described by J. C. Dittmer.[86] The air from blowing of linseed oil contains an unpleasant type of fume, which polymerizes to a rubbery mass in any normal packed tower. An improvised spray tower, 14ft. high and 6ft. in diameter, dealt effectively with 2000 cu. ft. of contaminated air per minute, using only 25 gal. of water, and washing out practically all the organic material.

A patent[87] on electrostatic gas cleaning claims that interrupted d.c. is just as effective and more economical of power than a steady discharge.

Evaporation

Water cooling towers are the largest of all evaporating units, and an enormous total transfer of heat is obtained in many very large units. It appears that the standard British practice utilizes double cone hyperboloid section concrete towers, while in the United States "atmospheric" towers are used in which the air is moved horizontally across the tower by local wind currents. In both countries, of course, various types of forced draught cooling towers are used. J. G. DeFlon[88] described the American type of tower and gives charts from which the performance can be predicted.

Three typical cases of industrial evaporation has been discussed from an economic standpoint by H. B. Caldwell and W. D. Kohlins.[89] In the first—the evaporation of black liquor from sulphite pulp—it may be desirable to work up to seven effects, even with cheap steam. By contrast, the evaporation of acid sodium sulphate causes such corrosion difficulties that two effects are the most that can be economically utilized. A more even balance is struck in the concentration of caustic soda solutions by forced circulation in nickel tubed vessels, and a triple effect is found the least costly. With steam at 12 pence per thousand pounds, the cost per 1000lb. of water evaporated was 3d., 8d., and 5d. respectively. In the very important field of sulphuric acid concentration, vacuum evaporators are growing more popular as materials of construction grow more reliable. F. S. Chambers and R. F. Peterson[90] give working details for a falling film evaporator, with tubes in silicon iron, 24ft. long and 8in. in diameter. J. F. Burke and E. Mantius[91] describe five types of evaporator which have been used for acid concentration. They are all single effect units, with heating surfaces which range from the normal external calandria (in hard lead) to an arrangement of bayonet tubes in high silicon iron.

H. E. O'Connell and E. S. Pettyjohn[92] state that splashing in an evaporator gives a negligible carryover if the volume of the vapour space is equal to the volume of the vapour formed per second. Foaming is determined by the nature of the solution being evaporated, and no general rule can be given. The authors are careful to state that their results were all obtained in a relatively small evaporator of the horizontal tube type. These units are rare in this country, and are generally supposed to give poor liquid circulation, a finding supported by C. A. Lee,[93] who removed two vertical rows of tubes from the side of a calandria of this type and found a greatly improved performance. A patent[94] on solar evaporation describes a series of inverted U tubes, with one limb discharging into a fresh water compartment and the other into salt water. An external cooling of the fresh water limb, and internal spraying of the other with salt water, give a steady stream of condensed fresh water.

Mixing

One of the unknown factors in mixing has always been the amount of material actually passing through the mixing device. In an attempt to measure this, J. H. Rushton, D. E. Mack and H. J. Everett[95] built up a mixing device in which the impellor forced liquid through an aperture at the base of a tank into an outer annulus. Overflow from this annulus was pumped back into the central tank by means of a metering pump, and by a suitable adjustment of levels it was hoped to simulate conditions in an ordinary mixing vessel while measuring the fluid circulated by the impellor. Unfortunately, the setting of the impellor relative to the outlet from the central tank turned out to be very critical, and no correlation of the results could therefore be attempted. J. D. Martin[96] has collected previously published data on power requirements for agitation, and shows that they can be correlated by a modified Reynolds number; the power required varied as the fluid density, the cube of the speed, and the fifth power of the stirrer diameter. A similar collection, by D. E. Mack and V. W. Uhl,[97] of data concerning the dispersion of gases in liquids, could not be correlated in this way.

R. E. Chaddock[98] discusses such practical points as the location of an impellor in a tank, the blade angle, and the relation between tank size and stirrer diameter. D. F. Riley[99] shows how particle size influences the design of mixers for pastes and powders, and an arrangement of jets in a Venturi throat to give both mixing and measuring has been patented.[100]

Drying

A discussion on the thermal efficiency of spray drying leads E. H. Farmer and C. G. Six[101] to the conclusion that much heat is wasted by spreading out the plant in the form of a cyclone separator, followed by a scrubbing tower. If these are replaced by bag filters built round the dryer itself, an insulating annulus is formed. The authors also stress the importance of keeping the surfaces of roller dryers very clean, by the use of sharp knives and a close setting. Steam pressures may thus be lowered and considerable economies result.

G. C. Gester[102] has described a distillation dryer for use in the purification of petroleum fractions. It is an ordinary fractionating column, with ten plates, and a reflux coming from a separating box so that only oil returns to the column. The water content of a typical C_6 cut was reduced from 200 to 12 p.p.m., and the cost compared very favourably with various processes for chemical drying.

W. B. van Arsdel[103] has made a theoretical analysis of the effect of diffusion rates in the interior of a porous solid during drying. He shows that where the surface film effect is negligible, as in the falling rate period of drying, the speed of drying is inversely proportional to the square of the thickness of the material being dried. There may be interference from another cause, however, if the material is easily deformed. W. H. Banks and W. W. Barkas[104] show that as water evaporates from the capillaries of a porous solid, the stress due to surface tension steadily increases. At some arbitrary critical humidity this may lead to the collapse of all remaining capillaries; as the larger passages have already dried out, a sharp break in drying should result. Some such changes have been noted in wood drying. E. Ledoux[105] proposes that a mass transfer coefficient, based on a moisture concentration head, shall be used as a basis for the calculation of dryer size.

A detailed[106] patent on the methods used for freeze drying describes the condensation of the water vapour as ice on a condensing surface at —40°. It is then removed from the condenser by scrapers and collected in a receiver at slightly higher temperatures than at the condenser. Meanwhile, the material being dried is stirred throughout the whole process of moisture removal.

Size reduction

In the 1946 Report (p. 21) a note was given of a confident claim that the amount of power required for grinding could be shown to be proportional to the fresh surface produced. Although the findings were criticized, they seemed to show that a close approach to experimental confirmation of Rittinger's Law had been achieved. Now W. F. Carey and E. M. Halton[107] have gathered together a number of examples on the distribution of energy expended in driving grinding plant. They show that almost the whole of this energy reappears as heat somewhere in the grinding system, and that no absorption of energy corresponding to the increase in surface involved could be detected. The authors suggest that solid materials may be compared to a coiled spring, held by a clip, and the energy required to release the clip may be smaller than the energy released by the spring in unwinding. If these findings are substantiated, it is difficult to see how rational figures can be obtained for the efficiency of any grinding process on the basis of surface produced.

There will still remain, however, the question of relative ease of grinding to the same particle size range. J. Brown, N. J. Ivison, and J. W. Birney[108] outline the various tests that have been suggested for grindability in coals, and H. Heywood[109] shows how the size of a mill will affect such tests. Some attempts[110] are being made in Russia to improve the operating characteristics of a ball mill by altering its shape, while a patent[111] on the introduction of vibration as well as rotation makes claims for increased rapidity in grinding. A further modification[112] in ball mill construction is the use of rubber rings compressed together on a cage of steel rods. It is claimed that this lining is very abrasion resistant and not subject to fatigue, but it remains to be seen whether the output of the mill is unaffected. A device[113] for increasing the " nip " of small crushing rolls consists of a vibrating plate hung vertically above the centre of the nip angle, and delivering a series of sharp taps to the " riding " charge.

J. E. Dunn[114] compares the performance of a shaking (mechanically operated) screen with that of an electro-magnetic vibrating plant in the screening and dewatering of coal, and comes to no definite conclusion.

Plant design and control

The steadily increasing use of automatic plant control has brought into being a new and complicated vocabulary, which N. Retlaw[115] suggests should be simplified and standardized. D. M. Considine[116] urges that instruments be built into the plant as it is being erected, and considered as an essential part of the whole project. He gives figures for typical costs of instrumentation, ranging from 1% of the total plant cost with heavy chemicals up to 15% in the case of complicated pharmaceutical products. Such an installation of controls calls for an instrument department, the staffing and arrangement of which has been described by C. S. Comstock and H. U. Fisher.[117] All instruments should be subject to weekly test and overhaul; nevertheless, the annual cost for a typical controlling instrument is only one-seventieth (1/70) part of the cost of a skilled operator. J. G. Ziegler and N. B. Nichols[118] show that the central problem in process control is the elimination of " hunting " around the control point. This is due to the existence of various time lags, and they propose means of arranging these to the least disadvantage. W. S. Ault,[119] after indicating the most usual types of control instruments, shows how these are applied in the distillation of petroleum. As an example he gives the details of instrumentation for a crude oil still, set to produce gas oil, lubricating oil on a sidestream, and a bitumen residue. All these controllers were of the throttling type, with an automatic reset.

When a controlling device operates a valve, this valve will have definite characteristics which will be imposed on the control. The most important of these, according to S. D. Ross,[120] is the variable fraction of the pressure drop formed by a valve in a pipe line of reasonable length. Special valves, with this factor allowed for, should be chosen for coupling up to a control. P. Foch,[121] however, maintains that ordinary gate valves are quite adequate for plant control work. A. L. Webre[122] describes a valve with variable counterweights, which forms a control on the pressure in a vacuum pan for sugar finishing. In the same vessel, an indication of the degree of crystallization can be obtained from the power required to drive the stirrer.

J. J. Cicalese[123] *et al.* review the possible methods for the automatic control of fractionating columns. The operation may be directed towards producing either a residue of constant vapour pressure, or a " pure " overhead product. The latter is the more usual, and various control systems based on this principle are discussed. A warning against the effect of pulsations in pipe lines has been given by E. J. Lindahl.[124] If a differential pressure meter or controller is connected to a line in these circumstances, the apparent pressure drop will be too high, and serious errors may arise with small total pressure heads. Some form of compensator, such as a surge tank, should be built into the line, or the single pipe should be split into several paths, so as to give interference of the pressure waves where the conduits rejoin to give a single stream.

R. MacFarland[125] claims that proportioning pumps can be made with a delivery accuracy of ±2%, even when delivering very large quantities. This accuracy is obtained by close attention to alignment, clearance, and gland design. They can be made in sizes taking up to 500 h.p. and, though more expensive than ordinary pumps, well repay the high cost in increased flexibility. C. A. Richardson[126] reviews the use of centrifugal pumps in the handling of corrosive solutions, and advocates simple design with easily replaced parts. A patent[127] on rupturing diaphragms describes a special thinned zone which gives a more definite rupturing pressure.

Boiler water treatment

It was in this field that ion exchange materials were first developed, but with development in selectivity and stability the importance of these reactants is steadily increasing. R. B. Thompson and E. J. Roberts[128] show how the capacity of a cation exchanger mass varies with the metallic ion which is removed, being much higher for calcium than for sodium (in both cases, of course, replacement was by H ion). The removal of sodium is quantitative up to about 2g. equiv. per cu. ft. of exchange mass, and is still 75% effective after 12g. equiv. have been removed. Regeneration requires about 350% of theory of sulphuric acid in the case of sodium; when calcium has been removed it is better to replace this with sodium by means of a concentrated NaCl solution, and then to follow with sulphuric acid. The capacity of anion exchangers varies widely with the acid being replaced with OH ion, but is somewhat higher than that of cation exchange masses, with a sharper break point at the limit of this capacity. J. J. Lurie and V. A. Kliatschko[129] describe a method of dealing with silica, which is becoming increasingly troublesome as boiler pressures increase. The water is treated with a cation exchange mass to give acid feed, containing the free silicic acid. A suitable amount of sodium fluoride is added, and the mixture air-blown for ten minutes to vaporize the silica as fluoride; the purified water then flows through anion exchange mass to give a final product containing less than 0·5 p.p.m. of silica. A patent[130] on the use of ion exchangers specifies that the mass shall always be immersed in water during the entire working life.

A decade or so ago, a " Scale Buoy "—an evacuated glass flask containing a droplet of mercury—was marketed with claims that it prevented the deposition of scale when suspended in the tanks of domestic hot water systems. This gave rise to some amusement, but it now appears, according to E. J. B. Willey,[131] that some of the claims may have been justified. A flask prepared in this way does cause local electrical disturbances when suspended in water and shaken by fluid currents. Such electrical fields—of a millivolt or so—are sufficient to modify the form in which calcium salts are deposited. The phenomena reported are certainly interesting, but whether they play much part in the deposition of solid matter in boilers remains to be demonstrated.

In the working of forced circulation boilers, with a feed pump forcing water through heating, evaporating, and superheating tubes in turn, with no boiler drum of any kind, the operation is checked sooner or later by solid deposition, no matter how carefully the feed water is purified. W. S. Patterson[132] recommends the replacement of the drum as a disengaging space between evaporating and superheating section, with a small residue of unevaporated water to blow down with residual solids. The small heating tubes are further cleaned from time to time by dilute hydrochloric acid containing an inhibitor. This same cleaning method has been advocated by S. T. Powell,[133] but he insists on the necessity for after inspection, especially where stress corrosion may occur, and on careful removal of the hydrogen formed in the process. Discussion on this paper revealed considerable doubt as to the desirability of what was admitted to be a very rapid method of boiler cleaning.

Some electrolytic corrosion in boilers has lately been attributed to the presence of copper dissolved from feed lines, pumps, etc. D. Parkhouse[134] disposes of the theory that this dissolution is due to the presence of ammonia in the feed water, and maintains that the removal of oxygen and adjustment of p_H to 8 will effectively prevent attack on copper in all its forms. V. Rodwell[135] shows that the removal of oxygen by direct electrolysis may be an economic proposition. Carbon electrodes are immersed in the feed water stream and kept at a potential just below that required for water decomposition. A small current, of less than 1 amp. is sufficient to reduce oxygen to an immeasurably small amount when combined with normal vacuum deæration. An unusual growth of organic slimes in a cooling water system was traced by C. B. Taylor and G. M. Hutchinson[136] to a slight leak from a methyl alcohol plant. The decomposition products formed a nutrient medium, and a heavy dosage of chlorine was required to check slime growth.

Materials

The American journal *Chemical Engineering* has been devoting a great deal of attention to the materials available for resisting chemical attack, while a Review of Materials has been published in the October issue of *Industrial and Engineering Chemistry*.[137] Though this Review is primarily an exhaustive bibliography, some outstanding points call for mention. The value of " Alclad " aluminium products, in which a layer of corrosion resisting alloy is bonded to another alloy body of better mechanical properties, is illustrated by a number of examples. The increasing use of hydrofluoric acid and its derivatives has stimulated the production of carbon " Karbate " plant, already widely used for hydrochloric acid. Another non-metallic material—glass—is becoming more important, and ways for rapid sealing and jointing are described. Chemical stoneware is still without a substitute in the handling of hydrogen peroxide, and " armoured " stoneware pumps have given very good service with all types of mixed acids other than those containing fluorine.

Typical of a number of Reviews in *Chemical Engineering* is a set of tables[138] on the resistance of constructional materials to a wide range of chemicals, while another[139] deals with the construction of acetic acid plant, a case in which laboratory tests are apt to give misleading results. A more specialized paper by W. F. Armstrong[140] deals with the manufacture of hydrochloric acid and shows the great advances made by " Karbate " in this field. Gases from the salt pans are cooled in an acid-resisting brick tower, using as cooling medium hydrochloric acid circulated by Karbate pumps. The gases are then absorbed in Karbate cooler absorbers, and re-evaporated to give a 99·5% HCl gas in a Karbate evaporator, jointed with Neoprene.

When weak acids are to be stored in large quantities, the wooden vat is still cheaper in many ways than special metal vessels, according to S. E. Chaney.[141] Such construction can also be considered for any type of acid material in conjunction with acid resisting tile linings. W. R. Collings[142] shows how the temperature-resisting qualities of silicones can be utilized in plant. A silicone grease gives good lubrication of valves between 15 and 175°, and the film is not stripped from metal by steam, acids or ether. Silicone resin varnish is heat and moisture resistant, a very important point in electrical work, and a silicone rubber standing temperatures up to 200° is now available. W. Z. Friend and F. L. LaQue[143] give examples of troublesome plant corrosion which could not be predicted from normal laboratory tests. The nickel tubes of a caustic soda evaporator were being rapidly attacked, and this was ultimately traced to a small content of sulphide in the caustic solution. When this was eliminated, a further localized attack was noted, and found to be due to suspended sodium chloride. A. Wachter and R. S. Tresider[144] review the whole question of laboratory tests for corrosion, and suggest suitable equipment for such experiments as corrosion due to rapid liquid motion.

Miscellaneous

Sir James Chadwick[145] has outlined the present position of energy supply from atomic fission, and quoted American sources to show that the total cost is only some 25% greater than that of power derived from coal. Such relative cost figures will probably be maintained, but a warning against absolute figures is found in an article[146] on process equipment costs based on the prices current at the beginning of the year. All United States figures had risen by 25% in the previous eighteen months, and were still rising quite as sharply. E. Woollatt[147] has discussed the problems arising in continuous plant processes from the thermodynamic viewpoint, and has derived various energy balance equations movement of materials in such plants. A. E. Kroll[148] has suggested a method for assessing the area under an irregular curve, reminiscent of Simpson's rule for irregular shapes. An attempt[149] has been made by the American Institution of Chemical Engineers to standardize the symbols used in technical literature to describe chemical and physical processes.

So much has been published on the methods available for the production of cheap oxygen that a review[150] of the various methods will be of general interest. The various possible cycles are set out and discussed. These may involve the use of special expansion turbines, working at very low temperatures. J. S. Swearingen[151] discusses the design problems involved, one of the most difficult of these being the supports. These must be rigid, but of very low heat conductivity; the ultimate solution was found in stainless steel construction.

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GAS, DESTRUCTIVE DISTILLATION, TAR AND TAR PRODUCTS

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THE year under review has seen the carbonizing industries in process of being nationalized. Coke ovens owned by the collieries were brought under the National Coal Board on January 1st, 1947. Regional Officers, all of whom were coke oven managers prior to the date of their appointment, were appointed to take administrative charge of the coke ovens and of the further development of the industry in each of several regions, subject to general direction from headquarters. The coke oven industry operates now as a separate branch of the National Coal Board, working in collaboration with the local colliery management, but responsible only to headquarters in London. The opportunity for technical development on a national, and certainly on a regional, basis which the technologists in the industry have long sought has now been provided. Coke ovens owned by units of the iron and steel industry and a few privately-owned plants have not come under the National Coal Board. The view has been expressed that a National Carbonization Board[1] should undertake the control of all carbonization, including gasworks and coke ovens not owned by the steel industry. During the year under review this proposal has been revived on many occasions,[2] on the ground that it would be in the best interests of technical development of coal processing. The Government announced its intention of bringing into Parliament during 1948 a Bill to nationalize the gas industry.

The British Gas Council has issued a memorandum on the future organization of the gas industry[3] in which the view was expressed that the industry should be re-organized on a regional basis. It was urged that the local units of which the industry is composed as a result of organic growth should not be divided because an industry which deals with over 11 million individual consumers would not respond to centralized regional operational control. The organization visualized would comprise a national board concerned with finance, broad policy planning and other affairs which require handling at a national level. Under this national Board would be 13 regional boards responsible for policy, planning and co-ordination at regional level. Below them in turn would be district management groups, responsible for one or more undertakings and consisting wholly of persons " well qualified and experienced in operating gas undertakings."

The gas industry has developed rapidly since the war of 1914–18 and its rate of progress has again accelerated as the result of the war of 1939–45. The demand for domestic gas and coke has increased and so also—and perhaps to an even greater degree—has the demand for gas for industry. Repair of plant has still been difficult through shortages of materials and labour and although much new plant is under construction, the amount is not sufficient to begin to overtake the leeway caused through war conditions. The economic crisis which became acute half-way through the period under review caused national capital investment to be reduced by £180 million annually and the gas industry comes under this reduction. During the war, in place of the pre-war consumption of 180,000 tons of steel a year, the gas industry received on the average 50,000 tons a year. Sufficient steel is to be provided during 1948 for the gas industry to meet its " minimum requirements ",[4] but in view of the 10% increase in the demand for gas that has occurred between 1943 and 1947, the steel available appears to be insufficient to provide for the technical developments that the industry regards as necessary.

The desirability of increasing the scope of the carbonizing industries has been emphasized during the year. The Fuel and Power Advisory Council appointed by the Minister of Fuel and Power has previously reported[5] that there should be a large expansion in the production of coke. A memorandum submitted to the Prime Minister by Col. W. M. Carr[6] called for the expansion of the gas industry to four times its present capacity and for the carbonization before use of all bituminous raw coal now burnt for heating purposes in homes and industry, boiler plant being excluded, at a cost of between £400 million and £450 million during the next 10 years, on the ground that this would save 50 million tons of coal a year and provide better heat service for industry and the domestic consumer.

A report issued by P.E.P.[7] during the year has given comprehensive details of the carbonization industries. A similar report[8] was issued in 1937 and this present report brings the story of the development of the carbonization industries up to date. This remarkable document of over 400 pages summarizes published statistical information on the British Fuel and Power industries in an unique manner. According to the information here provided, the output of gas from carbonization in the gas industry rose by 44% from 194,518 million cu. ft. to 279,454 million cu. ft. between 1921 and 1937 and again to 307,092 million cu. ft. by 1945. Over this period there has been increased use of continuous and intermittent vertical retorts. Between 1938 and 1945 the quantity of gas purchased from coke ovens by the gas industry increased from 29,621 million cu. ft. to 52,192 million cu. ft. Adding water gas, the total distributed by the gas industry increased from 349,171 million cu. ft. in 1938 to 433,106 million cu. ft. in 1945. Coke ovens were kept short of coal during the winter of 1946–47 due to a short-sighted belief that carbonization *consumed* coal, whereas there is plentiful evidence that it *conserves* the coal that is carbonized. The position in 1948 is that the iron and steel industry has been given a target of 14 million ingot tons of steel and that this target cannot be reached unless the production of furnace coke is increased materially. Towards the end of 1947 the quantity of furnace coke available was increased by one-fifth, but this only put production back to the figure ruling in 1937.[9] The need for increased production will be the key-note of the carbonization industries in 1948.

Carbonization

Low temperature carbonization

The one major company operating a low temperature carbonization process achieved a marked increase in output and further batteries of retorts are under construction.[10] W. A. Bristow[11] has described the methods in use at the works of Low Temperature Carbonization Ltd. for working-up the liquid products from low temperature carbonization. The crude tar is distilled in a pipe still of the conventional design and the oil leaving at 350° passes into a single C.I. fractionating column one-sixth of the way up from the bottom, superheated steam being simultaneously introduced at the base of the column. Fractions, comprising light oil, middle oil, heavy oil and wax oil, are taken from the column at various heights in the usual way and pitch is removed from the base. The middle oil is washed for tar acids in a continuous plant and there is in course of erection a continuous tar acid fractionation plant. The light spirit and diesel oil are also refined in continuous distillation and washing plants. Tar acids recovered are 80% phenol, 80% *o*-cresol, 49–51% *m*-cresol, xylenols free from high boiling tar acids, and high boiling tar acids free from xylenols. It is proposed to produce chlorinated tar acids of high germicidal value. When the complete plant is erected the yield of finished products is expected to be as follows:

	Crude oil, %	
Phenol	1·00	– 22
o-Cresol	0·25	
m-, *p*-Cresol	2·25	
Xylenols	4·00	
High-boiling tar acids	14·50	
Diesel oil	22·00	
Washed light oil	3·00	
Cresylic pitch	4·00	
Heavy residue (florastic)	20·00	
Paraffin wax	1·50	
Fuel oils Fluxing oils Residues Loss	27·50	
	100·00	

Detailed descriptions[12, 13] have been given of the Krupp-Lurgi process. Two commercial-sized plants have been in operation in Germany since 1936 for the production of surplus fuel from low-grade bituminous coal. The installation at Wanne-Eickel has a capacity of 700 tons of coal a day and that at Velsen (140 tons initially) was being enlarged to 280 tons a day when the war ended. This system carbonizes stationary coal in tapered narrow charges (3in. top, 4in. bottom) placed between steel walls of welded construction indirectly heated by products of combustion entering at 620° and leaving at the top of the flues at 570–580°. A " unit " consisting of six of these cells, each 12ft. 6in. long and about 7ft. high is charged simultaneously with about 3¼ tons of coal, the capacity being about 12 tons of coal per unit per day. The coke is discharged mechanically with a V.M. content of 8–10% through bottom doors into wagons where it is quenched. Some 6–8% by weight of tar is also produced. Experience suggests a life of the plant of about 10–12 years.

The principal new developments in low temperature carbonization seem to be in America. The Disco Company, which has had a plant in operation for some years, has now under construction a new plant with a capacity of 1000 tons of coal a day.[14]. This produces low temperature coke in the shape of balls containing 15–17% V.M. produced in continuous inclined rotating steel cylinders, 9ft. diam. and 126ft. long, externally heated. The heating gases circulate through an annulus surrounding each retort at 450° and then flow through the flues of a multi-deck pre-heater where they raise the incoming coal to 315°. The charge consists of a mixture of breeze and slack below ¼in. The rolling action to which the charge is subjected in the retort causes the plastic coal to form balls which are carbonized and discharged at 450°. The yields quoted are coke (commercial product) 72%, tar 15 gal., and gas 3,700 cu. ft. per short ton.

The Coal Logs process has had a plant in operation at Salt Lake City for some time and has now further plants in course of construction; a new plant at Wellington, Utah, commenced work in July, 1947, which is to be extended from its present output of 100 tons/day to 500 tons/day.[15] Plants are under erection for the Colorado Iron and Steel Corporation and for the U.S. Steel Corporation. In this process, the coal is compressed to 40lb./sq. in. while heated in the plastic range of temperature, and issues from the retort in the form of " logs ", 6in. in diam. and 12in. long, coal-like in appearance, and containing 12–15% of V.M.[16]

Coke oven practice

A few—a very few—technical papers of importance have come from the coking industry during the year. In Britain, the change to nationalization and the accumulation of post-war operating difficulties seem to have turned thoughts in other directions. The German coke oven industry is not yet in a position to contrive new technical developments. In America there have been improvements in coal-handling machinery but few changes in the basic design of coke ovens. America is facing the problem that confronted this country after the first world war of increasing the financial returns from coking, and there have been great efforts to do this. For example, many plants now recover pyridine on a large scale, and the tendency is towards the production of more highly-refined aromatic hydrocarbons.[17] Attention has been concentrated in Britain on fuel economy and a valuable account has been given by T. C. Finlayson[18] of what has been done. The movement for reduced fuel consumption started in 1928–38 through increased demand for coke oven gas. The Fuel Efficiency Committee of the coking industry issued in Bulletin No. 1 rules of operating procedure: The ovens should be charged to their full capacity with a coal charge uniform as regards fineness of crushing, moisture content (which should not exceed 8%) and bulk density; they should be operated on a regular pushing schedule, with the shortest period between discharging and charging; combustion in the flues should be completed with the minimum quantity of excess air. Finlayson and D. T. Barritt[19] have pointed out that to secure economy in fuel the heating system must be so designed that, with a uniform charge of coal, coking is simultaneously completed along the length of the charge, that the level along the top of the heating flues must be correctly located to suit the characteristics of the coal charged, and that the regenerators must be correctly designed so that the heat imparted to the ingoing air (and lean gas in the case of compound ovens) must be as near as theoretical as possible. Finlayson and A. Taylor[20] have recorded an experimental investigation upon a full-scale regenerator, in which it was concluded that surface area has so much more influence on the heat transfer than either the velocity or the efficiency of sweeping of the surface, that in a given regenerator chamber a filling giving the largest surface per cubic foot is considerably more efficient than any other arrangement. The regenerators must be designed so that they do not offer appreciable back pressure and leave sufficient heat in the waste gases to provide the chimney pull. The most promising field for further reducing fuel consumption is believed to lie in the reduction of the losses by radiation and convection, particularly in better insulation of the oven top and behind the side buck-stays; high temperature insulating materials are being used in oven construction. Greater advantage should be taken of modern technique of steam generation with use of back pressure steam for heating purposes.

The Fuel Efficiency Committee of the Coking Industry has issued Bulletin No. 2 dealing with the influence of the moisture content on coals in coke oven operation. About half the coke ovens in Britain are charged with a moisture content greater than the 9% maximum which is generally regarded as desirable from the point of view of thermal efficiency. The uniform distribution of moisture in the coal between different parts of a given oven and in different oven charges, is important, as it is stated that this results in steadier conditions of operation and longer oven life. The water of coking coals is present in three different forms: surface moisture, which accounts for most of the water present and can be removed, by drainage first, and then finally by thermal drying or some mechanical method; capillary moisture; and coarse capillary moisture held in larger pores and removable by drainage. It has been shown that after prolonged draining the thickness of the layer of surface moisture is independent of the size of coal particles, so that the lower the mean particle size of a slack, the greater will be the final moisture content. The size distribution is of great importance in preliminary draining of coals, a small percentage of very fine coal having considerable effect on the efficiency of gravitational dewatering. For a given size distribution a variation in water content produces a minimum bulk density of a coking slack between 4 and 10 % of moisture, depending on the percentage of fine particles in the coal. An increase in the percentage of fines is to reduce the bulk density for a particular water content and to increase the moisture content at which the minimum value of the bulk density occurs. The increase in fuel gas required at the ovens with increase in moisture content of the coal does not become appreciable up to 9% of moisture. High uniform moisture contents of oven charges, especially if the coal is of large particle size, result in draining in the ovens and may cause damage to the lower courses of oven bricks. If the moisture content is below 4%, charging difficulties may occur, due to the evolution of dust-laden gas, with consequent damage to buckstays and other parts of the oven structure.

Difficulties that occurred at the Pinxton coking plant, due to inability to dry-clean wet small coal led to the installation of a Buell horizontal rotary thermal coal dryer operated by the hot waste gases leaving the ovens.[21] The gases at 250° are withdrawn, by the chimney fan via a 5ft. lagged pipe, through the dryer and are returned to the chimney after removal of dust in a series of cyclone extractors. A damper allows a portion of the waste gases to go direct to the chimney. The gases leave the dryer at 110° (dewpoint 50°) and the coal is heated therein to 50°, its moisture content being reduced from 12% to 5%. The treatment has no observed effect on the coking power of the coal. The net result has been an increase in coal throughput at the ovens of 7% with a reduction in fuel gas used of 5%. It was necessary to install a chimney fan in view of the conditions; this fan takes 100 h.p., and the whole system absorbs 120 h.p.

Fluctuations in the bulk density of coke oven charges result in uneven plant operation and poor quality of coke output, due to under- or over-coking as the case may be. Excessively low bulk density may result in fluxing of the brickwork, and excessively high bulk density may cause damage to brickwork by the development of high pressures.[22] D. T. Barritt[23] has recorded an experience of damage to coke ovens in Scotland by a swelling coal which develops high pressure during carbonization. The dangerous characteristics of this coal were unsuspected because the Kilsyth coking coal was previously regarded as safe, but, after the coals had been tested, the mine workings reached a particular area which had been metamorphosed through an igneous intrusion with reduction in its volatile content. It was found that this coal became dangerously swelling in the form of compressed charges, having a density of 65lb./cu. ft. when the volatile matter fell below 26·8% on the d.a.f. basis. It was concluded that the Koppers expansion test apparatus can be used to determine whether the coal is safe or not.

A Committee set up by the Ministry of Fuel and Power is investigating the desirability of dry quenching coke. F. Pearson [24] has described the Sulzer dry-quenching plant at the Ford Motor Company's coke ovens at Dagenham, and has pointed out that since the installation of this plant the Ford blast furnaces have produced (1) the largest quantity of iron in one lining, and (2) the largest quantity of iron in one furnace in (*a*) one year, (*b*) one month, (*c*) one day, with a lower coke usage per ton of iron, and it is believed that the use of dry-quenched coke played an important part in these results. The author states that the benefits derived at his plant from the dry cooling of coke comprise the following: (*a*) 1,000lb. of steam at 170lb./sq. in. are produced per ton of hot coke from heat which would otherwise be lost. Repeated over the whole country this would amount to a saving of 600,000 tons of coal annually at coke ovens. (*b*) Whilst the life of a coke car under normal wet quenching is 1½ to 2 years the Ford cars are still in good condition after 12 years' work with renewals of the wearing plate on one car only. (*c*) The quality of dry-quenched coke is much superior to wet-quenched because it is stronger, harder, and contains no moisture which must be driven off in the furnaces. (*d*) Breeze from dry-quenched coke can be used to produced sinter from fine iron ores, whereas that from wet-quenched coke cannot be screened for this purpose with the necessary size grading of ¼in.–0. There is some evidence that the use of dry-quenched coke in blast furnaces leads to a saving of 5% of the coke consumption.[25]

The utilization of breeze has received consideration in addition to the proposal just quoted. T. W. Mills[26] has proposed that crushed breeze to the extent possibly of 30% should be blended with coal for use in certain carbonizing plant set aside for the manufacture of domestic coke. Experimental evidence obtained on a full manufacturing scale has confirmed the feasibility of this proposal on Durham coal.

Gasworks practice

It has seemed for some time as if the distinction hitherto drawn between gasification and carbonization would disappear. New processes under investigation by the Gas Research Board partook of the characteristics of both processes. Whatever hopes some may have had of an early change to total gasification methods by the gas industry are now seen to have been premature, and it is evident that difficulties encountered in the method of gasification of coal in hydrogen under pressure have caused a return to fundamental investigations, although on a large, almost semi-manufacturing scale.

The shortage of gas-making plant has caused considerable activity in building new plant during the year, though the difficulty of securing materials of construction and labour has slowed down construction. In the circumstances the emphasis has been placed on future developments in carbonizing practice rather than on any positive advances made during the year under review. One change in practice that seems likely is in the use of mechanical producers for heating retort settings. The normal built-in producer has given good service; it costs only about one-seventh of the cost of a modern installation of mechanical producers and has a very high hot gas efficiency. The hard labour required for cleaning built-in producers, the loss of carbon in ashes, the longer life of the retort settings secured by uniform temperatures, and reduction in dust content of the gas, are all reasons why the future is likely to see an increasing number of retort houses equipped with mechanical producers.[27]

The increasing interest taken in coke ovens by the gas industry in Britain is a sign of the emphasis now placed on the carbonization of coal in bulk. The Gas Light and Coke Company is doubling the size of the Koppers coke oven plant that has been operating so successfully at Beckton since 1932.[28] The South Metropolitan Gas Company has under construction a Simon-Carves plant of 44 compound ovens with a capacity of 1,000 tons of coal a day.[29] It is anticipated that when the industry is reorganized into larger units, there will be further coke oven plants installed on, or in connexion with, gasworks. J. G. King[30] has pointed out that " when the reconstruction stage has been successfully completed in the United States and Britain, it will be possible to consider more revolutionary changes involving, for example, large-scale gas-making plants in the coalfields, with high pressure gas transmission to towns. . . . With the introduction of a co-ordinated plan for the gas industry, and in the absence of a system of complete gasification, it seems probable that coke ovens may be favoured for new central plants." H. Riedl[31] has concluded that the gasification of low-grade fuels at the mines in Lurgi high-pressure machines producing gas of 420 B.Th.U./cu. ft. provides gas cheaper than normal town gas, which is produced at a high pressure, capable of being transmitted without further compression over a considerable distance. J. G. King[30] believes that no revolutionary changes can be expected in coke oven design, and that the adoption of vertical retorts in place of horizontals will continue in Britain.

Fuel efficiency has been a keynote of gas practice during the year and King[30] believes that on new works, in which every advantage is taken of improvements in heat transfer and heat recovery, the fuel requirement of the entire works may be reduced to below 10% of the coal carbonized. G. C. Pearson[27] and G. M. Rimmer[32] have described the new works at Swan Village, Birmingham, in which the whole of the steam produced in the waste heat boilers at 350lb./sq. in and 650°F. will be used to generate power which will be used to drive the whole works, the surplus being synchronized with the grid supply and delivered into the grid interchangeably with a supply from the grid as conditions demand. The steam exhausted at 25lb./sq. in. with 50°F. of superheat will be used on the works. T. C. Finlayson[18] has discussed fuel economy on British gasworks and has given the following figures as representing " best modern practice which have only been attained by the joint efforts of plant designer and plant operator."

	Non-recuperative continuous vertical retorts (slight steaming) Therms	Recuperative horizontal retorts Therms	Recuperative intermittent vertical retorts (slight steaming) Therms	Regenerative coke ovens Therms
Heat used/ton of coal—				
Sensible heat in coke	6·0	10·9	11·3	11·3
Crude coal gas	3·5	6·4	6·4	6·1
Radiation, etc., loss	4·6	7·1	5·6	3·1
Steam reaction	—	—	1·0	—
Total	14·1	24·4	23·7	20·5
Overall heating efficiency of carbonizing system %	43	60	62	64·5
Fuel to producers, therms per ton of coal	33	41	38	32
Less therms of waste heat steam recovered	10	5·5	5	—
Net fuel consumption ...	23	35·5	33	32
Less therms recovered by dry cooling coke	nil	6·0	7·2	7·5
Overall net fuel consumption allowing for waste heat steam and dry cooling of coke..........................	23	29·5	25·8	24·5

The Ministry of Fuel and Power instituted a Fuel Expenditure Index to express the heat economy of a gasworks, namely:—

$$\text{F.E.I.} = 100 - \frac{(\text{therms in gas} + \text{coke} + \text{tar} + \text{benzole}) \times 100}{\text{therms in coal}}$$

T. C. Finlayson (loc. cit.) considers that it is possible to attain under optimum conditions on an ideal works a F.E.I. of not much above 12·5—or a little more than half the F.E.I. for the gasworks of Great Britain, with a consequent saving of over 1½ million tons of coal a year.

Much attention has been devoted to peak loads, and particularly to seasonal loads. The daily peaks can be covered by adequate gasholder capacity, but the seasonal peaks are more difficult to meet. F. M. Birks[33], from an analysis of temperatures in the South of England has shown that the average temperature on the coldest day in mid-winter is not likely to be below 20°F. and the warmest day in mid-winter can be 10°F. above the coldest day in mid-summer. The frequency of exceptionally cold weather in winter (*e.g.*, 1947 with 19 days below 30°F. and a lowest daily average of 22°F.) is only about twice a century. During periods of cold weather the space heating appliances are put on in groups so that the heat load $\propto$ (degree days) $^{1.4}$. This means in practice that much gas-making capacity must be reserved for these seasonal space heating loads, and the lower the temperature falls the more expensive is it to meet them, since the gas must be made in plant that may only be used for a few days in the year. The present space-heating load factor in the gas industry is about 20%, whereas for purposes other than space heating it is about 80%. Means are therefore sought in the gas industry to produce this gas by methods which involve the minimum of capital and labour charges arising from low load factor.

J. G. King[30] has stated that carburetted water gas is still the only practical insurance in Great Britain for peak loads, though, as pointed out by S. G. Irvin,[34] other methods are (1) to maintain the settings under sufficient heat to enable them to be brought into operation at short notice, (2) temporarily to increase the coal throughput on existing plant, and (3) interconnexion of districts by gas grids. After a detailed consideration of the merits and demerits of all these methods, Irvin concludes that none of them provides a sufficiently flexible process capable of producing a gas of high calorific value and constant combustion characteristics without an accompanying reduction in the efficiency of the gasmaking process. E. Crowther[35] points out that in present conditions, peak loads are an embarrassment to many undertakings by reason of insufficiency of plant to meet them, rather than from the financial aspect of expensive plant remaining in idleness throughout the greater part of the year, but when plant extensions have made good this deficiency, the financial disability will become evident. He suggests that a way out of both difficulties is the addition, at peak load times, of producer gas, washed chimney gas, or even air, carburetted with a volatile hydrocarbon, *e.g.*, petrol, to the normal full load production of a gas works, up to a maximum of some 10% of the whole make. This process has been operated at Newcastle-on-Tyne in February, 1947, using rectified benzole and producer gas, but the cost of benzole is too high for it to be used except in emergency and it is suggested that " tax-free petrol " should be used instead to relieve the coal situation.

During the year a large number of attempts were made to produce oil-gas in normal gas retorts with a view to increasing the capacity of the retorts during seasonal peak loads.[36] A method developed by the Gas Light and Coke Company[36] was to atomize gas oil under pressure at the rate of about 15 gal./hr., the oil accompanied by a steam-air mixture being projected into a horizontal retort. The combustion chamber temperature was kept at 1100°, and the inside retort temperature was 500° in the middle and 700° at the ascension pipe end. Each gallon of oil yielded 0·95 therms of gas and 0·15 gallons of gas tar, the gas having a C.V. of 520 B.Th.U.

and containing 54% of nitrogen. The output of the plant was thereby increased roughly 2½ times over that secured by normal carbonization. A method used in vertical retorts was to fill the retorts about half-full of coke, heated to 800–900° and to spray gas oil on to the coke from the top through a pipe extending 10ft. down the retort, steam being admitted at the base of the retort to provide B.W.G. as a carrier. This yielded 1·17–1·08 therm of gas per gallon of oil, the gas having a C.V. of 1489 to 1657 B.Th.U./cu.ft.[36] Another method involved shooting a jet of atomized oil up an empty retort, the internal temperature being maintained at 900°. This yielded oil gas of 1406 B.Th.U., which was diluted by increased steaming of the coal gas retorts or by addition of producer gas. At Birmingham gas works[36] it was found that a W.D. continuous vertical retort could readily and simultaneously be used as a B.W.G. generator and an oil cracking chamber, " thus making it unnecessary to resort to the elaborate system of air, steam and oil injection found necessary for horizontal retorts." Coke was fed hourly at the rate of ¾ cwt./hr. and extracted at the same rate, the retort being about half-full. Steam was admitted at the base of the retort at 92lb./hr. and oil was fed at about 30 gal./hr. in a thin stream which flowed downwards on to the coke surface without touching the walls during descent. The yield of gaseous therms was 50 to 60% greater per retort than when carbonizing coal. The best result was a production of 919 therms/retort/day, the gas having a C.V. of 970 B.Th.U./cu. ft. All these attempts to develop a satisfactory technique of increasing the rate of production of gas came to an end in October, 1947, when suddenly and unexpectedly, the tax rebate hitherto granted on gas oil for gas manufacture was removed, thereby making the production of gas from oil too expensive.

The manufacture of gas by methods involving dilution with gases of lower C.V., except as a temporary and emergency measure, must be assessed in the light of the work of the Gas Research Board on the combustion characteristics of town gas. A final report on the first stage of this work[37] concludes that the present methods of control of gas quality involving a uniform level of calorific value should be supplemented by a method involving combustion, the quality of gas sent out being maintained uniform as shown by such apparatus as the Aeration Test Burner. Dilution with waste gas, producer gas, or water gas materially affects the A.T.B. No. of coal gas in the direction of reducing the quantity of heat available from a gas appliance. Most of the methods of dilution or increased production previously mentioned are detrimental to the maintenance of constant gas combustion characteristics, and there is now doubt whether the correct procedure is to maintain a constant A.T.B. number, which may involve higher cost of production, or to require that gas appliances shall be designed to use gas having a wider variation in A.T.B. number, with some loss in efficiency of use.

Interest has been displayed in the new " fluidized " technique now being used in the oil industry for effecting and controlling catalysed reactions, and descriptions of the method and its possible application to the gas industry have been published.[38, 39]

From the point of view of durability of brickwork, the continuous vertical retort has been divided into four zones.[40] At the top of the retort, the inner surfaces of the wall may crumble, due probably to frequent volume changes due to repeated inversion of α–β quartz at 573° caused by uneven travel of the charge. The second zone, generally between 4ft. and 15ft. from the top of the retort is prone to flaking away of chips of brickwork. This seems to be caused by the adherence of scurf having a different coefficient of expansion to that of the brick; local high surface temperatures when scurfing may cause pieces of scurf to fall away, taking flakes of brick with them. The only palliative yet known appears to be greater care during scurfing. The third zone from the bottom of zone 2 to the bottom of the silica or siliceous material (21–25ft. from the retort top) is prone to slagging attack, and this can only be circumvented to some extent by using bricks of low permeability. At the bottom there is a zone in which abrasion occurs.

In 1943 there was described by A. E. Haffner an experiment in which a working installation of continuous vertical gas retorts, owned by the Gas Light and Coke Company and about to be rebuilt, was quenched suddenly by supplying a stream of cooling water to the combustion chambers. A second experiment utilizing the experience gained in the earlier one has been described by F. R. Weston.[41] The results point to the desirability of arranging for taper on the major axis of the upper 15ft. of the retort, with taper of the minor axis over the whole height of the retort. Internal void spaces detrimental to operation and durability occur in continuous vertical charges and can be reduced by measures which promote even and continuous travel of the charge.

Purification and storage

Difficulties have been experienced in the operation of oxide purifiers and in the disposal of the spent oxide. The labour for handling oxide boxes is considerably more expensive than before the war. Many users prefer to pay higher prices for brimstone than to buy spent oxide, since acid made from spent oxide is not suitable for all purposes. The result has been during 1947 that more spent oxide has been made than buyers are prepared to take, and the problem of storing this material is becoming acute in many works.[42] The late P. Parrish[43] has proposed that gasworks and coke ovens should recover cyanogen and benzole before the purifiers and thus be enabled to produce relatively pure sulphur by extraction. Arsenical pyrites is used in Europe on contact plants and the gas industry should establish a case for the employment of spent oxide in substitution for brimstone. The Gas Research Board has announced that work is to be started on the purification of gas from hydrogen sulphide, including the extraction of the spent oxide to produce sulphur. There is an interesting development in the Saar basin, where gas is brought from a number of coke ovens at a pressure of 200lb./sq. in. to be purified under that pressure in a central tower purification plant. The gas is heated to 35° and humidified by steam. Much smaller area of oxide is required and a sulphur content of 70% is attained. CS_2 extraction plant is to be added.[44]

A new liquid purification process in full scale operation at Manchester gasworks has been described.[42] The gas leaving the Livesey washers and containing ammonia is washed by an alkaline solution, containing ferric hydrate in suspension.

$$(NH_4)_2CO_3 + H_2S = NH_4HS + NH_4HCO_3$$

This reaction takes place rapidly, and the solution is then allowed to stand for a short time to permit the next reaction to take place.

$$3NH_4HCO_3 + 3NH_4HS + Fe_2(OH)_6 = 3(NH_4)_2CO_3 + Fe_2S_3 + 6H_2O$$

The liquor is then revivified by being blown with air.

$$2Fe_2S_3 + 3O_2 + 6H_2O = 2Fe_2(OH)_6 + 6S$$

A proportion of liquor is tapped off daily, sufficient to contain sulphur equal to the day's make, and is filtered. It is intended later to extract the sulphur.

Much attention has been paid to the reduction of the organic sulphur content of town gas to some 5 grains or so per cu. ft. The Gas Research Board has presented a final report on the distribution of sulphur compounds in town gas[45] in which it is shown that these comprise thiophen, CS_2, more volatile sulphur probably COS, with traces of mercaptans. Thiophen and most of the CS_2 can be extracted by benzole washing with excess of oil, or by active carbon, but COS is unaffected by this treatment; COS and CS_2 can be removed by the oxidation catalytic process, but thiophen is unaffected; consequently a two-stage process of absorption and catalysis is necessary. Details are given in this report of the distribution of the sulphur compounds and of the effect of conditions on the quantity present. In all types of coal gas CS_2 is the largest organic sulphur constituent, but there is very little of it present in C.W.G. or B.W.G., while thiophen is absent from B.W.G. The sulphur content of the coal is the principle cause of variations in organic sulphur content. J. J. Priestley and H. Q. Marris[46] have described further progress in a catalytic plant operating at Mirfield gasworks on a metallic thiomolybdate catalyst at 360°. The sulphur content was reduced to 4·5 grains. F. H. Darlington[47] has described an organic sulphur purification process that has been in use for 17 years past at a New Jersey glass works designed to reduce the organic sulphur content of B.W.G. from 15 grains to 3 grains; as B.W.G. contains no thiophen, all the sulphur present should be susceptible to catalytic attack. The gas is first pre-heated to 800°F. by being conveyed through a 2-in. pipe in the crown of the glass-annealing lehr. At this temperature it passes downward through four layers of catalyst ($MgSO_4$ + ZnO) each 1ft. thick at a mean temperature of 700–800°. Fine dust is removed by passing the gas into a dust-trap built into a vertical air-cooled condenser pipe, which cools it to 100–150°, whence it travels to an oxide box for removal of H_2S formed in the catalyst chamber. The catalyst is revivified weekly by circulating air through the system. The total cost of purification is said to be 5·4 cents per million cu. ft. of gas.

The reduction in the selling price of ammonia, consequent upon the widespread production of synthetic ammonia, caused emphasis to be placed upon the production of concentrated liquor. By 1939 there were 65 plants producing concentrated liquor of between 12% and 25% NH_3. Considerable improvements in design have been made in about 40 modern plants, erected at the outbreak of war, embodying automatic control. The experiences gained in the operation of these plants have been described.[48] A review of the problems of effluent liquor disposal with flow sheets for phenol recovery and manufacturing plant, based on extraction with benzole and recovery of phenol from the benzole by caustic soda, has been published.[49]

A comprehensive engineering paper on the design of welded high pressure holders has been published.[50] L. Silver has discussed the purging of gas holders by inert gas, pointing out that the control of the operation, in order that it shall be conducted with safety and at minimum cost, requires consideration of the inflammable limits of gaseous mixtures.[51] Charts based on Le Chatelier's principle are given for the guidance of operating chemists.

Benzole, tar, and tar products

Considerable interest has been shown in the availability of carbon black for motor tyre manufacture. One grade of black has been manufactured for some years in this country by the Jones Gas Process at Cheltenham, Swindon, and other gasworks. Attempts were made at the Chemical Research Laboratory to produce channel black by burning tar fractions, and these have been published in detail by F. H. Burstall, F. G. Lane, and J. B. Ditcham.[52] D. D. Howat[53] has discussed German plants for the manufacture of carbon black and has expressed doubts whether use for the manufacture of this substance would be the best outlet for tar products.

An exhaustive review, too detailed for summary, has been given by K. Gordon of developments at Billingham in the hydrogenation of tar oils.[55, 56]

The production of ethylene from coke oven gas, which is already practised at certain plants is recommended by D. D. Howat.[57] The annual output of gas contains some 150,000 tons of methane and this is required to be recovered at about £20 a ton.

The dehydration of water-gas tar emulsions is discussed by A. G. Hall and A. R. Bayer.[58] The most usual method is thermal, the water content being reduced by heat and decantation to 15% and the remainder driven off by distillation. Some chemical agents can simultaneously dehydrate the tar and bring about the classification of certain heat-sensitive components. High speed centrifugal action is a relatively new and successful method, provided provision is made for keeping the centrifuge free from solid material. At Brooklyn gasworks the emulsion is delivered to the centrifuge at 200°F. after removal of particles over 0·01in. by a self-cleaning filter. Dry tar and water are recovered by action of a high-speed rotor and disc assembly, 6000 r.p.m., with a mean effective force 8000 times gravity. Similar work, with equal results on the dehydration of coke oven tar emulsions is described by E. W. Young,[59] this being undertaken in consequence of an observation that tar stored in one-million gallon tanks for months at 200°F. still retained 5% of water.

The 82nd report of the Chief Inspector of Alkali, etc. works contains an account of the work of the Inspectors in promoting benzole recovery during the war. Most benzole distillation plants, being designed for the production of motor fuel, needed additions to enable a satisfactory toluene fraction to be separated. Great difficulty was also experienced owing to the presence of paraffins. Azeotropic distillation was practised in Scotland on a large scale, but not in England. Most benzole recovery plants erected before the war at gasworks were intended to remove only a portion of the benzole. It is stated that there is a division of opinion as to the economics of benzole recovery, but a growing appreciation of its technical advantages. The Inspector believes that benzole recovery will eventually come to be regarded as an essential part of gas purification.

G. Claxton[60] has recalled the success of the inhibitor process in enabling benzole containing unsaturated compounds to be used as a motor fuel, but points out that the chief difficulty is still the removal of sulphur compounds other than CS_2; corrosion sets a maximum of 0·4% as the highest practicable limit for sulphur in motor benzole. There is no evidence of corrosion when benzole below 0·4% is used. During the war most of the 106 million gallons of benzole produced in Britain was shipped to America for conversion into *iso*propyl benzene for use in aviation fuels to improve rich-mixture performance. Later, butyl benzene was made synthetically by I.C.I. at Heysham under the name of " Victane."[55] Claxton concludes that in the foreseeable future motor benzole will remain the chief outlet for benzole. Benzene can be produced more cheaply in the U.S.A. than in Britain and synthetic fuels will probably be made in that country where propylene and butane are available. The growing tendency to refine petroleum in this country may change this position. Research is in progress by the National Benzole Association on the nature and removal of the sulphur compounds with particular reference to corrosion troubles; an interesting observation is that two non-corrosive benzoles, one containing a trace of H_2S and the other of elementary sulphur may produce a corrosive benzole when they are mixed. There have been no revolutionary changes in refining technique during the war. Hydrogenation refining shows promise, but cannot yet compete with existing methods, partly on account of cost and partly because present methods do not permit the destruction of thiophen without causing disruption of the aromatic nucleus.

In view of the anxiety shown to remove thiophen from town gas and benzole it is of interest to observe a U.S. method due to H. E. Rasmussen and F. E. Day to produce thiophene and thiophene thiol in commercial quantities at comparatively small cost. Butane is converted into butene, butadiene, and finally thiophene, using sulphur as a dehydrogenating agent, followed by cyclization with sulphur to form the thiophene ring.[61]

Tar distillation has continued to be active during the year 1946–47.[62] Considerably increased demands for road tar have been met and there was increased demand for pitch, naphthalene, phenols and creosote. A considerable tonnage of creosote was exported to U.S.A.

A. L. Curtis[63] has described the Koppers continuous pipe still, in which the tar is heated to 160° in a coil, dehydrated in a distillation column, and reheated to 360° before entering a pitch column from which the vapour passes in series through five columns. A portion of the oil leaving each column is returned to the previous column as reflux, and the temperature at the top of each column is automatically controlled by the control of the reflux.

Gasification

Town gas

Work by the Gas Research Board and the Fuel Research Station on the synthesis of methane has now reached the stage at which, as announced by H. Hollings, now Chairman of the Board in succession to E. V. Evans, it is probable that during 1948 a final report can be issued. The large-scale trials of catalysts have proceeded satisfactorily and it should be possible to suspend this work pending some industrial development of the process.[64]

Work on the gasification of coal under pressure carried out on a semi-scale plant at Bournemouth by the Gas Research Board has been continued, and in consequence of what has been learned it is proposed to construct a new pressure vessel designed to study the behaviour of bituminous coals when gasified under different pressures of steam and air.[64] No detailed report has been issued during the year on this work.

The Lurgi system of high-pressure gasification, which was the prototype of the work on this subject by the Gas Research Board, is known to be operating on a large scale on lignite,[65] one at Bohlen, Saxony, which supplies gas to Leipzig, and another in Silesia.[66] The Bohlen plant, having a 1 to 2m. deep fuel bed, is blown continuously with a steam-oxygen mixture and produces a gas under 18 atm. pressure containing 30% CO_2. After purification, the analysis of the gas was: H_2 48–49%; CO 22–24%; CH_4 25–29%; with small amounts of higher hydrocarbons, nitrogen, and CO_2. R. Riedl[67] maintains that the cheapest method of making gas in the Czechoslovakian nationalized gas industry is by pithead gasification on brown coal in a Lurgi producer. He estimates that the cost of making 420 B.Th.U. gas in his country in a 3000 million cu.ft./yr. works is 3·78 U.S.A. cents/cu.m. (107 cents./1000 cu. ft.) by the normal gasworks carbonization plant using coal, while a similar gas can be produced under 18 atm. pressure in a Lurgi works of some 20% larger capacity for only 2·06 cents/cu.m. (58·3 cents/1000 cu. ft.).

Gasification problems, in the newer processes, appear to be developing in a well-defined pattern. Many of these processes were devised initially to deal with peat, lignite and brown coal in countries where these fuels are predominant and must be utilized for reasons of national economy. Many of these processes have achieved quite a considerable degree of technical success and attempts—which seem generally to be beset with difficulties—are then made to apply these processes, or some modification of them, to bituminous coals. The observation made at the Fuel Research Station some years ago that hydrogen can react with a non-caking coal under pressure and at a temperature of 370° to give a solid product with an exceedingly high coking power, has a bearing on this problem.

D. T. A. Townend[68] has pointed out that in all gasification processes, the composition of the gaseous products is influenced by the Le Chatelier principle of equilibrium in reversible systems so that the result of a change in conditions can be predicted in advance. The use of pressure in the Lurgi process is one example. Gasification has an advantage over carbonization in that the retort is internally heated, with consequential better heat transfer. The newer German processes that are of special general interest require oxygen—or oxygen-enriched air—and include the "Lurgi-Drawe" operating under pressure at the lowest reaction temperature consistent with fuel bed reactivity (900–1000°), the "Winkler" operating at 1000° with a "boiling" bed at atmospheric pressure, and the "Thyssen-Galocsy" slagging producer operating at 1600° with removal of the ash as molten slag. The cost of oxygen is not considered to be a handicap for British conditions because of higher British fuel costs. These processes, with the "Pintsch-Hillebrand" and the "Bubiag-Didier" plants, are described.[68] Townend considers that in view of the near exhaustion of British coking coals it is essential that gas should be used extensively in place of coke and that continuous total gasification processes should be developed for this purpose.

These processes have also been discussed by L. L. Newman[69], who also describes the Koppers powdered fuel generator. This consists of several sections placed one above the other and connected by staggered openings to promote turbulence. The inclined bottom of each section directs particles of carbon and sintered ash to the opening, and each section has a port for the admission of oxygen and, if necessary, powdered coal. Primary oxygen and steam, preheated in a regenerator, are admitted at the base of the generator. The use of unpurified 95% O_2 saves power and chemicals as compared with the use of pure oxygen. For use in these processes, with power at 0·25d. per kw. hr., the cost of oxygen of 98% purity should be of the order of 6d. per 1000 cu. ft. This author concludes that, whilst critical study is required to determine how best to adapt the use of oxygen to American fuels and American economic conditions, it seems certain that the use of oxygen offers advantages in making complete gasification relatively simple, even with fuels that are quite suitable for intermittent water gas processes. The more expensive the fuel, the greater is the saving that may result from the increase in fuel efficiency, and the higher the cost of fuel, the higher the cost of the oxygen that can be afforded. On the other hand, an examination of the Koppers process for Belgian conditions[70] has led to the conclusion that, whilst this process met the special needs of Germany and was well suited to the available supplies of lignite and low-grade dust fuels, conditions are different in Belgium, where such pulverulent low-grade fuel as exists can probably be used to better advantage by collieries and power stations, though this conclusion may be modified if oxygen is available as a waste product from some other process.

Producer gas

Swiss work on the gasification of peat for the manufacture of producer gas for steel-works purposes during the war has been described by H. T. Schoedler,[71] using two revolving-hearth generators. Practical operation of a gas producer plant has been described by K. F. Bray.[72] M. W. Thring[73] has stated that the two main problems in gas producer research are segregation and ash handling. Townend[68] believes that improvements in the efficiency of gas producer practice can be effected by (i) heat recovery from the hot gases and return to the plant, thus pre-heating the blast to facilitate increased conversion of steam in the fuel bed, (ii) maintaining as low an oxygen-steam ratio as possible, and (iii) reducing other heat losses from the system. The segregation problem has been investigated by means of models by M. L. Hughes, as recorded last year, and further publications have been made by this author.[74] The path of the gas has been shown to depend mainly on size segregation and on the relative porosity of the ash bed and fuel bed. J. E. de Graaf[75] has discussed the quality of producer gas with particular reference to its tar content in the light of war experiences in a Belgian steelworks. The tar content of the gas was found to vary between 2 and 10 grains/cu. ft., the principal reason being the proportion of fines (below ⅜in.) in the coal, which altered the resistance to gas flow, and therefore the velocity of flow; a local increase in speed of flow, due to a pillar of high resistance, increased slightly the amount of tar carried away with the gas, but a local decrease in speed was followed by a large decrease in tar production. Even small percentages of fines had an appreciable effect. The influence of channelling on gas composition is thus stated from experimental data obtained on a commercial plant:

	Serious channel	Channel just visible	Good fuel bed
H_2O—grains/cu. ft.	81	47	30
Tar—grains/cu. ft.	about 1	about 2·5	6·5
Gas composition, %—			
CO_2	15·7	10·8	5·5
CO	7·3	17·6	26·0
H_2	4·3	10·3	15·0
CH_4	0·3	1·0	2·9
C_nH_m	0·4	0·6	1·3
N_2	72·0	60·2	49·3

The conclusion drawn by all these investigators is that grading of coal is highly important and that better screening of producer coal is necessary.

Water gas production

The importance of water gas as a low capital-cost plant for taking up peak and seasonal loads in the gas industry has already been indicated. Builders of plant have in consequence been very busy during the year on large new installations. It is perhaps in consequence of this that few papers appear to have been published on the technique of water gas production. Automatic sets with full waste heat recovery are now the rule.

Experiments have been started for the American Gas Association on the mechanism of the water-gas reaction, and the preliminary work has been reported by J. F. Foster and D. A. Vorum.[76] This work is fundamental in character and its object is to characterize the fuel bed of the generator as completely as possible under controlled conditions, with respect to temperatures and gas compositions occurring at fixed times, locations, and rates of material flow, with the ultimate object of understanding the various factors that influence the volume and composition of the gas produced in order to devise improvements in commercial practice.

Underground gasification

Much interest has been displayed abroad in underground gasification, but in this country it seems to have been tacitly agreed that the wastage of coal and general inefficiency of the method make it unsuitable for British coals, except for seams which are uneconomic to mine by normal methods. It is understood, however, that work will be started in this country by the N.C.B. when a suitable site has been selected, particularly with reference to the gasification of abandoned coal seams.[77] A large-scale trial of the process has been undertaken at Bois la Dame colliery, Liège, Belgium, where mining has been abandoned owing to the thinness of the seam.[78] Prof. Demart, who is in charge of this work, has pointed out[79] that the behaviour of the surrounding strata exercises considerable influence on the result, since it is necessary to control the conditions of gasification. These investigations have shown[80] that 70% of the calorific value of the coal in unmineable seams can be recovered by underground gasification, using one-tenth of the labour required for town gas production by the conventional processes. The gas recovered had the composition: CO 14–22%, H_2 16–22%.

An important American trial has been made at Gorgas mines, Alabama, by the U.S. Bureau of Mines and the Alabama Power Company. The preparations have been described by M. H. Fies[81] and G. E. Stedman,[82] and the results by R. R. Sayers.[83] The site occupied was 3½ acres. Two parallel 150ft. shafts were driven to enclose a block of approximately 1000 tons of coal with 33ft. cover in a seam 36in. thick. The shallow top above the block was pierced with 20 boreholes in which 4in. standpipes were installed to sample the gas. The two entries had reverse flow and were connected with a blower system capable of delivering 6000–7000 cu. ft./hr. with some air by-passed. Using picks, the coal was undercut 18in. by 12in. high along the connecting entry and was thrown back to start the fire. The fire was started by dropping a thermite bomb through one of the boreholes at the top. No difficulty was found in maintaining combustion but the resistance resulting from roof falls and other undetermined causes prevented an air flow sufficient to obtain the burning temperature and the gas quality sought, so a limited amount of oxygen was introduced to enrich the air. After the oxygen had been exhausted, an air blast was used through the tunnel, resulting in a steady improvement in operating conditions and gas quality. By blowing gas and air alternately through the mine synthesis gas reaching 250 B.Th.U./cu. ft. was produced. It is proposed to remove the cover by bulldozers to examine the strata after the test has been completed.

Underground gasification has been pursued most enthusiastically in Russia. M. R. Mandlekar[84] claims that underground gasification has the following proved advantages over mining:—80–90% of the coal can be won, compared with 60% by mining; 15% of labour is required underground, compared with 90% for mining; thermal output, even of lean gas (100–150 B.Th.U./cu. ft.), represents 100–120 tons of coal a man a month, compared with 30 tons by mining. The cost of production of lean gas is about 0·375–0·5d. a therm and of rich gas (250 B.Th.U./cu. ft.) 1d. a therm. The capital cost of the plant is said to be 60–70% of that for an above-ground producer. For a combined underground electric power station the capital cost is about £60 a kw. and the prime cost of power 0·4–0·6d. a kw. hr. G. O. Nusinov[85] has stated that gasification of a panel of coal between two interconnected shafts at Gorloff yielded power gas of 90–100 B.Th.U./cu. ft. when blown with air, and synthesis gas of 190 B.Th.U. when blown with oxygen, the cost of the higher C.V. gas being 2½ times that of the lower C.V. gas. Unless the roof collapses as the burnt-out space widens, blasting or back-filling becomes necessary to ensure contact of the air or oxygen with the ignited coal-face. At Podmoskov, connexion between two shafts was maintained without manual assistance by forcing air through the crevices in the seam.

Gaseous combustion

An outstanding paper has been presented by E. A. Watson and J. S. Clarke on " Combustion and combustion equipment for aero gas turbines,"[86] dealing with combustion problems on those units, such as aircraft, where space and weight are important. Reference may also be made here to an earlier paper on the same subject.[87] The Gas Research Board held a discussion on the gas turbine at its annual meeting on April 16th.[88]

Combustion research is receiving much attention, particularly in America, and it is of special interest that the Gas Research Board in Britain is planning to pursue fundamental research in this subject. It is hoped to build up a combustion research group to study such subjects as flame characteristics, gas flame spectroscopy, combustion characteristics of gas mixtures, ignition theory, high-speed combustion, corrosion problems occuring when burning gases and noise in gas appliances. It is believed that what is being done in this and other countries is opening a new era in combustion research. A debate on the subject of combustion was staged by the Gas Research Board at its annual meeting[89] at which D. T. A. Townend called attention to the work now being done in America on heats of reaction under Rossini (Amer. Bur. Standards). Work in Britain on slow combustion had demonstrated that combustion is a sequence of chain reactions which explains the fact that the energy released is not dependent upon temperature alone but is confined to specific molecules or atoms, and is passed on from one to another; the reactants are no longer considered to be energized molecules, but depend upon such species as OH, HCO, O and H atoms. While the behaviour in slow combustion of the comparatively simple bodies present in town gas provides no difficulties, with higher hydrocarbons the story is less simple because of the intermediate formation of peroxides which lead to " knocking " in internal combustion engines. Two types of flame are distinguished, explosion and diffusion, which are to be found in the bunsen flame, the inner cone being an explosion flame in which the rate of flame travel is compensated by the feed velocity, while the outer zone is diffusive. The flame speeds of the separate inflammable constituents are characteristic, depending on heat of combustion, oxygen requirement, conductivity, heat capacity, thermal losses, etc., and although it is known that "chain" processes are involved, except in the combustion of CO, there is little outward manifestation of them. The problem of securing higher rates of heat release than is possible with normal flame combustion processes requires a comprehensive study of physical disturbances; it is known that flame combustion in certain enclosures sets up compression waves, greatly accelerating completion of energy release. There also appears to be scope for subjecting the combining gases to radiation from external sources. H. Hartley[89] has pointed out that practical development in the design of gas appliances has been virtually unaffected by the fundamental work that has been done on combustion in the last half-century, and consideration should be given to the reasons why there has not been greater advance.

Reference has already been made to the work of J. W. Wood and his colleagues on the combustion characteristics of town gas.[37] G. W. Culshaw and J. E. Garside have given a critical survey of recent work on aerated burner flames.[90] J. K. Kilham[91] has confirmed experimentally his previous deduction that the transfer of energy from a flame to a solid immersed in it is by forced convection. Problems in burner design and flame behaviour have been discussed by L. T. Minchin.[92] P. W. R. Morpurgo and R. S. Silver, in an interim report,[93] have recorded experiments on the measurement of radiation from gas fires; it is desirable that a test method for this purpose should be generally agreed between various authorities, *e.g.*, the N.P.L., the Fuel Research Station, the Gas Research Board, appliance manufacturers, etc.

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INTERMEDIATES AND COLOURING MATTERS

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THE review presented on this occasion differs in some respects from that of the last few years. While there is an almost uninterrupted flow of publication on intermediate products, especially in the aliphatic division, a marked hiatus is now observed in dyes patents. This especially applies to dyes other than those of the azo class. The anthraquinone and other miscellaneous dyes are therefore omitted this year, and the next review will deal with two years' publications in those fields.

In both Intermediates and azo dyes, a full review is given of the intelligence reports published recently on German industrial methods.

INTERMEDIATES

By D. A. W. ADAMS, B.Sc., Ph.D.

Aliphatic intermediates

Halogen derivatives

The developments with regard to halogenated hydrocarbons are chiefly concerned with the vinyl halides and with fluorine derivatives.

Vinyl chloride is made by Wingfoot Corporation[1] from acetylene and hydrogen chloride at 250–300° in presence of a mercuric chloride catalyst supported on carbon, whilst E. I. Du Pont de Nemours & Co.[2] treat ethyl chloride with oxygen at 300–600° in presence of a metal oxide catalyst. Imperial Chemical Industries[3] prepare chlorinated olefines such as 1 : 1 : 5-trichloropent-1-ene by passing, *e.g.*, 1 : 1 : 1 : 5-tetrachloropentane with steam over a phosphotungstic acid-silica gel catalyst at 300–310°. Chlorovinyl acetylenes are prepared by the Society of Chemical Industry in Basle[4] by treating chloroethynyl alcohols with, for example, phosphoric acid at 90–160°.

The preparation and properties of a large number of fluorohydrocarbons, including chlorofluoroheptenes and polyfluoroheptanes as well as some aromatic derivatives, have been described in a series of papers by various American workers.[5] E. I. Du Pont de Nemours & Co.[6] treat $CH_2 : CF_2$ with aqueous sodium sulphite under pressure to give a mixture of sodium 1 : 1 : 2 : 2-tetrafluoroethane sulphonate and sodium difluoroacetate. Kinetic Chemicals Inc.[7] obtain 1-chloro-1 : 1 : 2 : 2-tetrafluoroethane by treating tetrafluoroethylene with hydrogen chloride in presence of a manganese phosphate catalyst, and the same firm[8] pyrolyse saturated chlorofluorohydrocarbons at 700° to form unsaturated fluoro-compounds; tetrafluoroethylene is thus formed from dichlorofluoromethane. E. I. Du Pont de Nemours & Co.[9] heat a mixture of $CCl_3{\cdot}CCl : CCl_2$, $CHClF_2$, and aluminium chloride at 150–200° and obtain $CF_3{\cdot}CCl : CCl_2$ and chloroform as the main products. Imperial Chemical Industries[10] obtain chlorofluoroalkanes such as $C_3HCl_4F_3$ by interaction of a chlorofluoroethylene with a halogenated methane in presence of $AlCl_3$. Stable liquids or waxy solids are obtained by E. I. Du Pont de Nemours & Co.[11] by treating aliphatic or aromatic hydrocarbons, or alcohols, ethers, &c., with tetrafluoroethylene in presence of a catalyst such as oxygen, borax, zinc chloride, phosphoric acid, &c.; thus ethanol and C_2F_4 yield ethyl 1 : 1 : 2 : 2-tetrafluoroethyl ether whilst phenol similarly gives phenyl 1 : 1 : 2 : 2-tetrafluoroethyl ether.

Nitro-compounds

Interest continues in the preparation of nitro-paraffins and their derivatives such as the nitro-alcohols, -thiols, -ethers, &c. Imperial Chemical Industries[12] prepare dinitro-paraffins, nitroalkyl nitrates, and/or nitro-alkanols by interaction of N_2O_4 with C_{3-6}-aliphatic olefines; propylene, for example, gives a mixture of 1 : 2-dinitropropane and 1-nitropropan-2-ol. The same firm obtain 1-nitro*iso*butene by heating 1 : 2-dinitro-2-methylpropane either with an aqueous solution of an alkali or alkaline earth oxide,[13] or with methanol.[14]

Purdue Research Foundation[15] condense nitromethane with aliphatic or alicyclic ketones in presence of a base such as an alkylamine to give mixtures of dinitroalkanes and nitroketones. Thus, acetone and nitromethane give mainly 1-nitro-2 : 2-dimethylpentan-4-one with some 1 : 3-dinitro-2 : 2-dimethylpropane.

Imperial Chemical Industries[16] interact primary or *sec.*-nitro-paraffins, -ethers, or -thioethers with nitro-olefines in presence of basic substances to give dinitro-alkanes, ethers or sulphides. The nitro-ethers[17] and -thioethers[18] used are made by interaction of a nitro-olefine with an alcohol or thiol. The same firm[19] obtain nitro-trimethylolmethane by treating nitromethane with excess of formaldehyde in presence of caustic potash.

Interaction of nitro-olefines with alkali cyanides yields nitro-cyanoalkanes;[20] thus, 1-nitro*iso*butene gives 1-nitro-2-cyano-2-methylpropane. Imperial Chemical Industries[21] also make nitro-sulphones by condensing nitroalkanes with unsaturated sulphones in presence of an alkali. 3-Nitro-1 : 5-di(butanesulphonyl)-3-methylpentane is obtained from nitroethane and butyl vinyl sulphone; benzene- and toluene-sulphonyl derivatives are formed similarly.

Resinous Products and Chemicals Co.[22] make esters of nitro fatty acids by interaction of a nitro-alkane with an acrylic ester in presence of a quaternary ammonium hydroxide; for example, dimethyl 3-nitropentane-1 : 5-dicarboxylate is obtained from nitromethane and methyl acrylate in presence of benzyltrimethylammonium hydroxide.

Aromatic intermediates

In the series of papers on fluorinated hydrocarbons already referred to,[5] the preparation of the bis(trichloromethyl)benzenes and their conversion into the corresponding trifluoromethyl derivatives is described; in the treatment of the trichloromethyl compounds with anhydrous hydrofluoric acid under pressure, the *meta* isomer reacts quicker than the *para*, although the overall yield from the latter is higher.

of dispersed potassium permanganate at 100–120° and the mixture (30% conversion) then saponified and given a heat treatment at 270–300° to convert hydroxy-acids into unsaturated acids.

The lower fatty acids (C_4–C_9) produced similarly were esterified[44] with the corresponding alcohols and hydrogenated at 270°/250 atm. in presence of a copper-chromium catalyst to give alcohols.

Acetic acid was made at Burghausen[48] in 96% yield by a continuous oxidation at 50° of acetaldehyde using acetic acid as medium and a mixed manganese-cerium acetate catalyst. Monochloroacetic acid was made both by the usual chlorination of acetic acid in presence of 3% of acetic anhydride and 0·7% of sulphur[40] and, since 1941 at Höchst, by a continuous sulphuric acid hydrolysis of trichloroethylene at 130–134°.[40, 49]

I. G. Höchst[50] made ethyl acetate by feeding continuously into a reactor at 0–5°, acetaldehyde (2 mol.) and a slurry of aluminium ethoxide (1 mol.) prepared by adding aluminium filings, ferric chloride, and aluminium chloride and finally absolute ethanol to ethyl acetate.

Formamide, as a source of acrylonitrile, was made by interaction of carbon monoxide and methanol in presence of 1% sodium ethoxide at 98–110°/200 atm. to give methyl formate, followed by reaction with ammonia.[51]

Chloral was made at I. G. Leverkusen[52] by chlorination of ethanol in two stages, the first, to give probably chiefly monochloroacetaldehyde, being operated continuously at 45–50° with irradiation, and the second batchwise at 50–70° (8–10 days).

Acetic acid was oxidised at Knapsack[53] in the vapour phase at 400° in presence of a catalyst containing 10% of cerium oxide deposited (as acetate) in pumice to give a 95% yield of acetone. Continuous aldol condensation of acetaldehyde at 8–10° gave crotonaldehyde which was hydrogenated to butanol at 230–240° in presence of a copper-on-pumice catalyst.[38, 48]

Formaldehyde was manufactured by the I. G. both at Leverkusen and Ludwigshafen using the standard controlled oxidation of methanol at 600–650° in presence of a silver-pumice catalyst; the successful control of the operation depends apparently on the use of a catalyst of carefully controlled particle size.[54 55]

Diethylamine was produced at Ludwigshafen[56] by passing acetaldehyde, hydrogen and ammonia over a catalyst, at 110–120° to 140–150° (depending on age), made by treating pumice with nickel carbonate, sodium silicate, and ammonium chromate, drying, and reducing in the reactor; mono- and tri-ethylamines were re-cycled giving a 90% overall yield. Butylamine was made similarly (80% yield) but the secondary and tertiary bases could not be re-cycled in this case because of the higher boiling points.

Aromatic intermediates

Benzene series.—Several reports[57, 58, 59, 60] describe the production, by the I.G. at Ludwigshafen and Schkopau, of styrene. Continuous ethylation of benzene (50% molar excess) at 90° (Schkopau) or 104° (Ludwigshafen) using an aluminium chloride catalyst gives a mixture containing 45% of benzene, 35% of ethylbenzene and 15% of diethylbenzenes, separated by distillation with re-cycling of the benzene and diethylbenzene; overall yield 92–94% on ethylene and 95–96% on benzene. Dehydrogenation is effected at 560–610° (Schkopau) or 650° (Ludwigshafen) in presence of steam to give a 40% conversion and 58% of unchanged ethylbenzene (yield 93–94% with fresh catalyst, falling to 88% after 16 months' use). The most satisfactory catalyst as developed at Ludwigshafen was one containing ZnO 77·4, Al_2O_3 7·6, CaO 4·7, MgO 4·7, K_2SO_4 2·8, and K_2CrO_4 2·8%, formed into rods, and dried.

In the manufacture of the chloro- and nitro-derivatives of benzene, toluene and xylene, the most significant feature is the use of direct methods combined with physical separation of the isomers so formed by fractionation, crystallization, sweating, &c.[61-66]. Such methods are well known in the case of the chlorobenzenes, chloronitrobenzenes, nitrotoluenes, etc., but their application to the production of *o*- and *p*-chlorotoluenes and to the various nitroxylenes does not appear to have been disclosed previously. Toluene[65] is chlorinated to give a mixture, containing approximately equal proportions of the *o*- and *p*- isomers, which is resolved by careful fractionation (difference in b.p. approximately 3°) into two main fractions containing respectively 90% of the *ortho* and 90% of the *para* isomer; on redistillation the former gives essentially pure *o*-chlorotoluene whilst pure *p*-chlorotoluene is obtained from the latter by sweating at −5°. Nitration of *p*-chlorotoluene gives a mixture containing 65% of 4-chloro-2- and 35% of 4-chloro-3-nitrotoluene, which is fractionated to give the former as a lower-boiling fraction and a residue containing mainly the 3-nitro-isomer; this is collected, redistilled, and sweated. 4-Chloro-2-nitrotoluene is also obtained as the minor constituent of the chlorination of *o*-nitrotoluene. Its main use is for the important Fast Red KB Base by reduction. The by-product 4-chloro-3-nitrotoluene is utilized, at least partly, by conversion, *via* the 4-methoxy-compound, into 3-amino-*p*-tolyl methyl ether (cresidine).[61]

In addition to preparing a mixed xylidine by nitration and reduction of crude xylene, the three isomeric xylenes are all separately nitrated, with separation of any isomeric nitroxylenes, arising from positional nitration, prior to reduction.[66] The three xylenes necessary for this series of operations are obtained by initial fractionation to give two main fractions, a lower boiling one containing mainly the *m*- and *p*-isomers and a higher boiling one rich in the *o*-isomer. The former is crystallized at −60° to give pure *p*-xylene and the liquor from this is subjected to preferential sulphonation and hydrolysis to give pure *m*-xylene; the *ortho*-rich fraction is redistilled and the crude *o*-xylene crystallized at −25 to −26°. Nitration of *p*-xylene gives only one product, but the *m*-xylene gives a mixture of 75% 4-nitro- and 25% 2-nitro-*m*-xylenes, which is distilled to remove the 2-nitro-isomer; *o*-xylene on nitration gives a mixture, containing chiefly the 3-nitro- and 4-nitro-*o*-xylenes in a ratio of 55 : 45, again separated by fractionation followed by sweating.

m-Chloronitrobenzene is obtained both by chlorination of nitrobenzene and as a recovery from the eutectic oils, after separation of *o*- and *p*-chloronitrobenzenes, from the nitration of chlorobenzene; this crude residue is reacted under pressure with aqueous caustic soda to hydrolyse the *o*- and *p*-isomers to the easily separated nitrophenols.[62]

An ingenious process was devised for the production of *m*-dichlorobenzene.[61, 67] Chlorine was passed into boiling *m*-dinitrobenzene, the reaction products, after passing up a column, being distilled off and separated to give a 79·3% yield of *m*-dichlorobenzene.

A catalytic air oxidation of an aqueous alkaline solution of 4-nitrotoluene-2-sulphonic acid in presence of manganese sulphate was used at Leverkusen for the manufacture of 4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid; the plant used, and especially the agitator, was of special design to ensure good distribution of the air.[63]

Nitroanisoles and nitrophenetoles were in general manufactured from the corresponding chloronitro-compounds by interaction with an alcoholic (methanol or ethanol respectively) solution of caustic soda. In the Griesheim processes for the *o*- and *p*-nitroanisoles,[61] the reaction was carried out by pumping a methanolic solution of caustic soda gradually into a solution of the chloronitrobenzene in methanol at 70–95° under pressure. In the case of 3-nitro-*p*-tolyl methyl ether, air was forced in to give a pressure of 13 atm. before starting the reaction, presumably to prevent reduction of the nitro group to azoxy. Air was also used at Leverkusen for the same purpose in the production of *o*- and *p*-nitrophenetoles,[63, 68, 69] but the operating technique here was different. Air was passed into a boiling ethanol solution of the chloronitrobenzene, the issuing vapours condensed, and the ethanol returned to the reactor *via* a vessel fitted with a basket containing solid caustic soda. By careful control of the temperature in this vessel and of the distillation rate, the concentration and quantity of the ethanol solution of caustic soda entering the reactor could be controlled within very narrow limits. In the reaction 10–16% of nitrophenol is formed and this is converted into nitrophenetole by an after-treatment of the crude reaction mixture with ethyl chloride under pressure. The overall yields are 96% for *p*- and 92% for *o*-nitrophenetole.

The manufacture of phthalic anhydride by the I.G. at Ludwigshafen and Uerdingen has been described in several reports.[70, 71, 72, 73] Both works operate the standard type of process with an air : naphthalene ration of 28 : 1 and a vanadium pentoxide catalyst mounted on silica and promoted with potassium sulphate. Cooling was effected with a molten mixture of sodium nitrite and nitrate, although potassium nitrate and sodium nitrite would be preferred if easily obtainable, this mixture itself being air-cooled.

Salicylic acid was manufactured at Leverkusen[63, 74] by the Kolbe reaction using a vertical reactor with a powerful slow-moving agitator fitted with blades operating between baffles fixed to the wall; in this way the mass was subjected to a strong shearing action. Sodium phenate, dried at 180° *in vacuo*, is treated with carbon dioxide at 150–160° for 36 hours at 4–4½ atm.; the pressure is released, free phenol is distilled in vacuo, and a second similar carbonation then carried out at 180°. After a second vacuum distillation the residue is dissolved out, worked up normally, and the salicylic acid finally sublimed from trays. The yield is 90–92% on phenol consumed.

2 : 5-Dichlorobenzoic acid and the corresponding acid chloride were made on the small scale at Ludwigshafen[69] by a Friedel-Crafts reaction between *p*-dichlorobenzene and phosgene in tetrachloroethane solution in presence of aluminium chloride. The double compound of the dichlorobenzoyl chloride and aluminium chloride so formed was hydrolysed with water and the product worked up either by distillation (after drying) to give the acid chloride or by alkaline hydrolysis to give the acid. The yields were 92·9% and 81·9% respectively.

The nitroanilines (*o*- and *p*-nitroanilines, 2-chloro-4-nitroaniline and 4-chloro-2-nitroaniline) had been made for a number of years by the well-known pressure (autoclave) amination of the corresponding chloronitrobenzenes[61] but the occurrence of two major explosions had led to an intensive examination at Höchst of a continuous process.[75] This work had been fully developed on the pilot-plant scale by 1939 but the erection of the planned 600 tons per year plant was prevented by the outbreak of war. In the case of *p*-nitroaniline itself, molten *p*-chloronitrobenzene and 40% ammonia (mol. ratio 1 : 17) were pumped at 200 atm. pressure through a N8 steel reaction coil at 237–240° (contact time approx. 10 min.) into an expansion chamber, the inlet pipe being set tangentially to a spray of hot water; the resulting magma was then conveyed from the bottom of the vessel by an inclined eccentric screw to the run-off pipe leading to the isolation tanks. The *p*-nitroaniline was of high quality and the yield was almost quantitative. Similar processes, with slight differences in reaction conditions, had been developed for the other products.

The important and highly toxic 5-chloro-*o*-toluidine (for Fast Red TR Base and Naphthol AS.TR) was made in a specially designed plant erected in 1933, claimed to give the minimum of hazard to the operatives.[61] Acet-*o*-toluidide was chlorinated in chlorobenzene solution below 50°, the hydrochloric acid gas stripped out by heating to 130°, and the product hydrolysed with dilute caustic soda under pressure; the crude base was then given a clean-up distillation and finally fractionated to give a yield of 67–69% theory, with an 8% recovery of *o*-toluidine and 12% of 3-chloro-*o*-toluidine. Conversion into hydrochloride for sale as Fast Red TR Base was effected by passing hydrochloric acid gas from the stripping stage into a solution of the base in chloroform, followed by removal of the solvent, finally under vacuum.

A somewhat novel method was used in the production of 4-nitro-*o*-anisidine hydrochloride (Fast Scarlet RC Base) at Griesheim.[61] *o*-Anisidine was converted into the nitrate by treatment with dilute nitric acid and the centrifuged product (containing $<$ 4% of water) was then charged into 95% sulphuric acid at 0–5° ; addition of water and then of brine precipitated high quality 4-nitro-*o*-anisidine hydrochloride in 82% overall yield. There was also a recovery of 4-nitro-*o*-anisidine at Offenbach from the 5-nitro-*o*-anisidine process;[61] the dilute sulphuric acid solution obtained from hydrolysis of the acetyl compound was treated, after filtration of the 5-nitro-*o*-anisidine, with naphthalene-1 : 5-disulphonic acid to precipitate the insoluble salt, which, after filtration, was converted into the base by treatment with dilute sodium carbonate solution.

Rather unusual methods of reduction were employed at Leverkusen for some of the Fast Bases manufactured there.[76] Thus 4-chloro-6-benzamido-*m*-toluidine (Fast Corinth LB Base) was obtained by reduction of the corresponding nitro-compound in aqueous pyridine solution by addition of sodium bisulphite. In the case of 4-benzamido-2 : 5-dimethoxy- and -diethoxy-anilines (for Fast Blue 2R and 2B Bases), a similar procedure was adopted, but the reduction was completed by addition of zinc dust.

The various substituted trifluoromethylanilines, required for certain Fast Salts, were prepared from the trichloromethyl compounds by treatment with anhydrous hydrofluoric acid under pressure with careful release of the liberated hydrochloric acid gas.[61, 62, 76] The procedure followed closely that used by American workers and referred to earlier in this report.[5] In the preparation of 2-ethanesulphonyl-5-trifluoromethylaniline (for Fast Golden Orange GR Base) an interesting method was used for introduction of the ethane sulphonyl group.[76] 4-Chloro-3-nitrotrifluoromethylbenzene was reacted in methanol with sodium ethane sulphinate obtained by zinc-acetic acid reduction of ethane sulphonyl chloride, stated to be manufactured at Leuna from ethane, chlorine, and sulphur dioxide.

The process employed for thioaniline disulphonic acid [bis-(4-amino-2-sulphophenyl)sulphide][69] does not appear to have been disclosed previously. 4-Chloronitrobenzene-3-sulphonic acid is heated under pressure at 113–115° with aqueous sodium thiosulphate and magnesium oxide to give the dinitro-compound, which is then reduced with iron (overall yield 75–77%).

Naphthalene intermediates.—In general, the published information on the naphthalene intermediates discloses very little which is novel, and only amplifies that given in the standard text-books, patent-applications, &c.

The manufacture of H acid for instance[63] follows the well-known route but involves the isolation (in 65% yield on naphthalene) of the intermediate 1-naphthylamine-3 : 6 : 8-trisulphonic acid as the acid sodium calcium salt; fusion then gives a 50% overall yield of H acid on naphthalene. It is stated that in the fusion approx. 2–3% of 1-amino-6-naphthol-3 : 8-disulphonic acid is formed.

Chromotropic acid was made[63] both by fusion of 1-naphthol-3 : 6 : 8-trisulphonic acid and by combined hydrolysis and fusion of 1-naphthylamine-3 : 6 : 8-trisulphonic acid; the quality from the latter process was inferior and the product was only used in certain non-critical dyes.

The important 2 : 3-hydroxynaphthoic acid was made at Offenbach[61] by the Kolbe reaction using equipment and procedure similar to that described previously for salicylic acid. Carbonation was carried out in three stages with vacuum distillation of β-naphthol after each; the conversion obtained was 35–36% with a yield, allowing for recovery of β-naphthol, of 72–76%.

In addition to the normal manufacture from α-naphthylamine by acid hydrolysis under pressure, a special high grade of α-naphthol (free from β-isomer) was obtained by a similar process starting from 1-naphthylamine-5-sulphonic acid, there being simultaneous desulphonation and hydrolysis of the amino-group.[77]

N-Substituted 2-amino-5-naphthol-7-sulphonic and -8-naphthol-6-sulphonic acids are finding increasing uses as dyestuff intermediates and a comparatively large range was manufactured by the I.G.[78] by the conventional Bücherer process. For *N*-alkyl and some substituted *N*-aryl (*e.g.*, carboxyphenyl) derivatives the dihydroxynaphthalene sulphonic acids were preferred, as starting materials, to the amino-naphthol sulphonic acids as they gave better yields of higher quality products.

Polynuclear and heterocyclic compounds.—With the exception of anthraquinone itself it is not proposed in this review to deal with anthraquinone intermediates as they are better considered as part of the manufacture of the derived dyes.

Anthraquinone was manufactured both by a dichromate oxidation (at Leverkusen)[63] and, until the plant was destroyed during the war, by a catalytic process at Ludwigshafen.[79] In the latter, a heated mixture of air, steam (to retard excessive oxidation), and anthracene vapour was passed over a vanadium-iron catalyst, supported on pumice, at 322–390°, the yield being 82% of theory.

In the manufacture of 1-phenyl-3-methyl-5-pyrazolone[62] a rather unusual process was employed, presumably to guarantee the high quality necessary when used as a medicinal intermediate. Phenylhydrazine hydrochloride was made by the normal reduction of diazobenzene with bisulphite and, after isolation, was converted into free base in presence of xylene, the xylene solution being separated and distilled, firstly at normal pressure to remove xylene, and then under vacuum (yield 85·7% on aniline). Conversion to pyrazolone in 93% yield was effected by condensation of the distilled hydrazine with ethyl acetoacetate in aqueous alcohol, the product being allowed to crystallize from the solution.

The manufacture of the several polynuclear and heterocyclic *o*-hydroxycarboxylic acids required for the specialized members of the Naphthol AS series has been described in detail.[76] In the synthesis of 2-hydroxyanthracene-3-carboxylic acid from 4-methylbenzoquinone-2′-carboxylic acid, the replacement of Cl by OH at the final stage is unusual in that aqueous piperidine is used under pressure in presence of copper and copper sulphate as catalysts.

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AZO-DYES

By A. H. KNIGHT

THE considerable number of patent specifications which have required consideration in preparing this review, covering the period November, 1946, to October, 1947, inclusive, bears testimony to the continuation during the period of the recent war of at least some research activity in the field of azo dyestuffs by the chief American, British and Swiss dye-making firms. The main directions of effort have been on dyestuffs for cotton, wool and acetate rayon. To meet considerations of space, a review of patents for dyes for wool, leather and acetate rayon and for lakes and pigments is postponed until next year when a two-year period will be covered on these topics.

The manufacture of azo dyestuffs in Germany

The past year has witnessed the publication of a vast amount of information on the constitutions of and manufacturing processes for members of the various ranges of azo dyestuffs, pigments and azoic components marketed or projected by I. G. Farbenindustrie A.-G. In this connexion attention is drawn particularly to B.I.O.S. Final Reports Nos. 961, 986, 988, 1149, 1548 (Item No. 22) and to B.I.O.S. Miscellaneous Report No. 20, all published by H.M. Stationery Office. The last mentioned document describes the results of an American investigation to ascertain the new dyes (of all chemical classes) and intermediates and new colour application processes developed in Germany and Italy during the war years 1939–1945. The other mentioned reports have been drawn up by members of British investigating teams and cover both old and newly developed azo products of I. G. In surveying the lists of constitutions of azo products the reader is struck by the very large number of such for which a special intermediate is required.

Of particular interest are the summaries of reports issued from the Ludwigshafen Research Laboratories on Azo Dyestuffs and Pigment Research during the years 1935–1945 given on pp. 82–96 of B.I.O.S. Final Report No. 961, and the minutes of certain conferences on azo dyestuff research referred to in the list of documents forming the appendix to B.I.O.S. Report No. 1548. The researches referred to cover intermediates and dyestuffs for both established fibres such as wool, leather, cotton and acetate rayon, and for new synthetic fibres of the superpolyamide class as well as for union materials of spun rayon and wool. In this review it is proposed to refer to certain recent trends and progress in respect of I. G. investigations on azo colouring matters only in so far as they are directed to the colouring of cotton and the artificial rayons.

The chief advances, as far as proposed new ranges or extensions of old ranges for specific purposes are concerned, may be summarized as follows:—

(*a*) A series of water-soluble monoazo dyes for acetate rayon covering shades from yellow to red, violet and brown, built up, apart from the yellow, on the chemical pattern:—A diazotized *p*-nitroaniline → a tertiary amine of the benzene series, being a mixture of an arylamino-propionic acid and its glycol ester.

An example is:—Acetate Silk Scarlet 5892, *p*-nitroaniline → N-methylphenylaminopropionic acid (0·6 mol.) + its glycol ester (0·4 mol.).[1]

For the yellow member of this range there was selected a product first discovered by Imperial Chemical Industries Ltd., the monoazo dye *p*-aminophenyl β-hydroxyethyl ether sulphuric ester → *p*-cresol.[1A] The blue member was to be an anthraquinone dye (1-methylamino-4-β-hydroxyethoxyethylaminoanthraquinone, Cellition Fast Blue FW). Presumably it was intended that these dyestuffs should compete against the Solacet range of water-soluble dyestuffs for acetate rayon and nylon marketed by Imperial Chemical Industries Ltd.

(*b*) A range of about a dozen metal-containing monoazo dyes devoid of sulphonic acid groups for dyeing the synthetic superpolyamide fibre " Perlon ", the latter being made by polymerizing and orienting caprolactam. " Perlon " may be regarded as the I. G. synthetic fibre corresponding to the American " Nylon 66 ", made from hexamethylene diamine and adipic acid.[2]

A number of these " Perlon Fast " dyes are solubilized by means of sulphonamido groups, the others to be applied by dispersion techniques.[3] The metals involved are chromium and cobalt. According to one report the solubility of the pre-metallized " Perlon Fast " dyes is due to sodium salt formation made possible by metallizing with a proportion of metal salt to dye such that a free valence of the metallic portion of the dye complex remains available for this purpose.[4] Examples are:—Perlon Fast Yellow R, the cobalt complex of 4-nitro-2-aminophenol → acetoacetanilide, and Perlon Fast Red BS, the chromium complex of 2-aminophenol-4-sulphonamide → β-naphthol.

Certain of the " Perlon Fast " dyes and the short chain alkyl esters of water-soluble dyes from N-alkyl-N-arylamino-propionic and butyric acids as coupling components were selected for dyeing " Pe Ce " Fiber, a synthetic fibre developed by I. G. from chlorinated vinyl chloride.[3, 4]

(*c*) A short range of five new Benzo Fast Chrome dyes intended for use in union dyeing (mixtures of wool and vegetable fibres). These represent known types of direct cotton colours into which one or more salicylic acid residues have been introduced. Examples are:—a condensation product 4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid and aminosulphosalicylic acid (A) (1-OH, 2-COOH, 4-NH_2, 6-SO_3H) for an orange, and A → 1 : 6-Clèves acid → α-naphthylamine → phenyl-J-acid for a blue.

For use in conjunction with the above direct cotton colours five new neutral-dyeing wool dyes of the premetallized " Palatine Fast " type of product were developed, one of these being a chromium complex of an azomethine dye. The four azo members are solubilized by means of the sulphonamido group in place of the more usual sulphonic acid group. This alteration resulted in the metallized dyes being suitable for application from a neutral or weakly acid dyebath.[5]

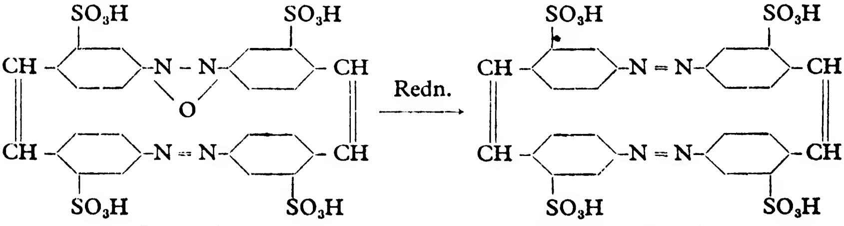
(*d*) A short series of dyes for producing fast black and blue shades on union materials of spun rayon and wool (*e.g.*, the " ersatz " fibre Woolstra). These dyes, known as " Autazol Chrome " colours, contain diazotizable amino groups and, in some cases, an *o* : *o*′-dihydroxyazo configuration as well which permits of metallizing. The dyeing process appears to be carried out from substantially a neutral bath after which the dyeing is submitted to treatment with nitrous acid whereby the primary amino group (or groups) is (are) diazotized, the material then being given a treatment with ammonia, and finally a treatment with a chromium salt. From the information so far published on these dyestuffs the precise chemical mechanism whereby the dyeings are rendered fast to washing is not clear, but presumably, in those cases where the constitution of the parent dyestuffs permits, the alkaline treatment given after diazotization causes self coupling and, therefore, substantially a doubling of the molecule, whilst the chroming process will convert any *o* : *o*′-dihydroxyazo- or *o*-hydroxy-*o*′-aminoazo-structure into a chromium complex which should also result in increased fastness to washing as well as to light. However, in some cases, other reactions occurring during the alkaline treatment of the diazo compound and/or during the subsequent chroming process are likely to be involved since one or two of the selected parent dyestuffs do not contain the customary configurations leading to the formation of stable metallic complexes. Moreover, the fact that the use of a special chroming agent, " Autazol Chrome Salt R ", is recommended for use with certain of the Autazol dyestuffs, suggests that the ingredients of this composition may play a special part in bringing about such reactions during the chroming process.

Examples of Autazol Chrome dyestuffs are:—

Autazol Chrome Black R: 5-nitro-2-aminophenol $\xrightarrow{\text{alk}}$ J acid;

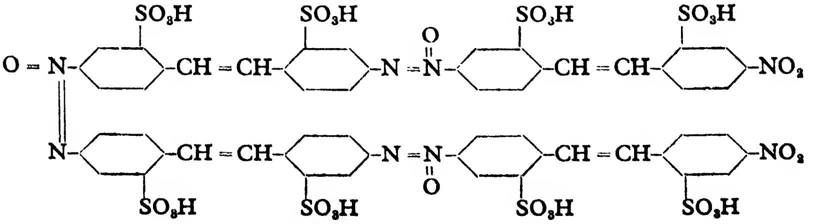
Autazol Chrome Black BA: 1-amino-5-hydroxynaphthalene-7-sulphonic acid → 1 : 7-Cleves acid → Gamma acid.[6]

In the field of stilbene chemistry I. G. have advanced new constitutional formulæ for the product obtained by the action of caustic soda on 4-nitrotoluene-2-sulphonic acid and known as Curcumine S (= Diamine Fast Yellow A) (Colour Index No. 620) as well as for its alkaline reduction product Diamine Orange D (= Chloramine Orange G) (Colour Index No. 621). The formulæ for these products proposed by Green and Crossland,[7] viz:—

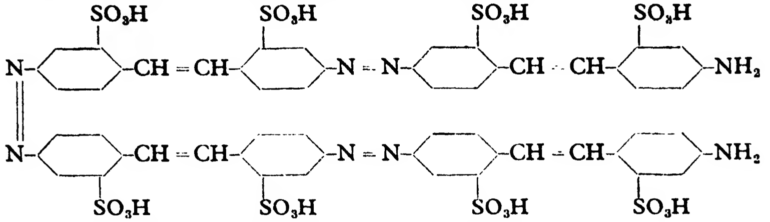


Curcumine S *Diamine Orange D*

were considered not to agree with the properties of these dyestuffs. The new formula proposed for Curcumine S is



whilst Diamine Orange D is considered to be a mixture of Curcumine S of the above formula and its completely reduced product:—

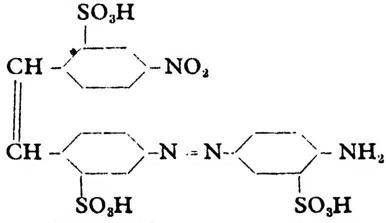


in which the unreduced Curcumine S is in excess.[8]

An important bright dye was obtained by acetylating a brand of Diamine Orange D in which the proportion of reduced dye predominated: incidentally, the fact that a different product was obtained by this process lends strong support to the new formulation for Diamine Orange D with its terminal amino groups.

Stilbene-azo dyes said to be homogeneous and to have very good discharge properties as well as good light fastness have been obtained by I. G. by stepwise condensation in caustic alkaline medium of 4:4′-dinitrostilbene-2 : 2′-disulphonic acid with *p*-phenylene diamines (1 mol. thereof or 2 mol. of the same one or one mol. of each of two different ones) to give mono-amino or diamino compounds.[9] These can be diazotized or tetrazotized as the case may be and coupled with a *para*-coupling phenol, the resulting product being alkylated to inhibit alkali sensitivity.[10] The primary condensation is carried out below 50° and the secondary condensation at 80–85°.

Only by the new process can the condensation products of 4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid and sulphonic acids and carboxylic acids of *p*-phenylenediamine and their substitution products be prepared, as for example, the compound



as the corresponding aniline-sulphonic or carboxylic acids (in this example, orthanilic acid) couple only very feebly if at all. Thus the new process renders accessible symmetrical and unsymmetrical dis- and tetrakis-azo compounds which could not be obtained, or not readily, through the medium of weakly coupling or non-coupling aniline-sulphonic or carboxylic acids.

Review of recent literature and patent publications relating to azo dyes

The following section of the review, concerning a selection of publications, patent and otherwise, on azo compounds which have appeared during the twelve months under consideration, takes the form adopted in previous years.

General

Bamberger[11] has described results of a spectroscopic examination of the effect of introducing into the benzene nucleus of *o*-hydroxyazo dyes of the type Aniline → R-acid groupings such as Me, OMe, NH_2, NHAc, Cl, NO_2, CO_2H, and SO_3H on the tendency of OH in these dyes to dissociate in aqueous solution. He found that a bathochromic effect is parallel to an increased fastness to alkali, i.e., a decreased tendency to dissociation of OH. *Ortho*-substitution with respect to the azo group considerably increases fastness to alkali and this effect would appear to originate at a distance from the azo group since there is no parallel optical effect. The effect of a second *ortho*-substituent on fastness to alkali is small and changeable.

A similar series of dyes, with analogues in which the substituents in the benzene nucleus are in turn in *o*-, *m*- and *p*- position with respect to the azo group, has been used by R. H. Kienle, E. I. Stearns and P. A. van der Meulen[12] to investigate relationships between constitution and light fastness, in aqueous solution, on wool and in gelatine. Fading on wool and in gelatine is reproducible, fading in solution is not. Fastness to light is decreased by substituent groups which are *m*- directing in secondary substitution in the benzene nucleus and increased by *o*- and *p*- directing substituents. The *o*- position relative to the azo group is the most sensitive to the effect of a substituent. Of the dyes examined, those with an *o*- COOH had the best and those with *o*- NO_2 or *o*- Cl the poorest light fastness.

H. E. Fierz-David, L. Blangey and H. Streiff[13] have investigated the chemical and dyeing properties of the N-methyl-*p*-hydroxyazo dyes obtained by condensing *as*.-N-methyl-phenylhydrazine-*p*-sulphonic acid with *α*-naphthaquinone and its 2-methyl derivative. They resemble the corresponding O-methyl ethers and the non-alkylated dyes in both respects. Salt formation at the sulphonic group has no influence on the *p*-hydroxyazo dyes. Substitution of the labile hydrogen atom in these dyes by an alkyl group increases the sensitivity to alkali, but the change in colour of the non-alkylated dye cannot be explained on the basis of the formation of an abnormal hydrate because the quinonoid N-alkyl-derivative should then exhibit an even greater change in colour. The free hydrogen atom, alone, is considered to be responsible for the alkali-sensitivity of the non-alkylated dye. The change in colour produced with mineral acids is independent of the constitution of the dye since such change occurs in the non-alkylated as well as in the O-alkyl- and N-alkyl-derivatives. The alkyl group, also, is not connected with the change in colour. Comparisons of dyeings indicate that the non-alkylated dyes exist either completely in the hydroxyazo form or completely in the quinonehydrazone form. The general mechanism of the splitting of *p*-hydroxyazo dyes and some of their aminoazo derivatives by the action of hot mineral acids is discussed from the results of a systematic and quantitative investigation.

An interesting investigation on the monoazo coupling of 1-amino-5-naphthol with benzene- and *p*-nitrobenzene-diazonium chlorides at various p_H values has been described by A. E. and B. A. Poraï-Koshits and V. V. Perekalin.[14] Only *o*- and *p*-hydroxyazo and *o*-aminoazo compounds were obtained. The latter diazonium compound gave almost exclusively hydroxyazo compound at all p_H values, but the former gave the *o*-amino-derivative at $p_H < 6$. In alkaline solutions the *p*-hydroxyazo compound always predominated, the yield of *o*-hydroxy-compound increasing with decreasing p_H. All the dyes made were weakly acidic and yielded bordeaux-brown or grey-violet shades on wool.

The free radical hypothesis is employed by K. H. Saunders and W. A. Waters[15] to explain the appearance of azo compounds and polyaryls among the products of decomposition of diazo compounds in aqueous solution near the neutral point in presence of a mild reducing agent, and also the conversion of tetrazotized 2 : 2′-diamino-diphenyl into diphenylazone. It is also suggested that diazo-sulphides undergo homolysis in aqueous media to produce radicals.

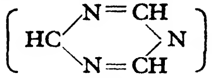
A general method for the preparation of solid, dry, crystalline aryldiazonium sulphates has been described by H. H. Hodgson and A. P. Mahadevan.[16] The sulphates, prepared by diazotization methods previously described by Hodgson and his co-workers,[17] are precipitated from their solutions by addition of ether or other suitable solvent. The diazonium sulphates from 2-nitro-, 2 : 4-dinitro-, and 2 : 4-dibromo-1-naphthylamine and of 1-nitro-2-naphthylamine, usually prone to pass into diazo-oxides, have been prepared by this method, as have those from *α*- and *β*-naphthylamines, *m*-toluidine and *m*-anisidine, previously reported as not diazotized but nitrosated by nitrosyl sulphuric acid.[18]

Substantivity indexes and spectroscopic observations on 0·005% solutions of azo combinations from a number of homocyclic[19] and heterocyclic[20] arylides of 2-hydroxy-3-naphthoic acid (methods of preparation and m.p.s. are given) have been described and discussed by A. Mangini and R. Andrisano.

Dyes for cotton

The trend of development, noted in last year's review, in the direction of after-coppering dyes, continues, particularly on the part of Swiss manufacturers. From the patenting activity of the latter it must be concluded that they regard this as an important class of dye of which they intend to establish themselves as leading manufacturers.

In addition to the Benzo Fast Copper dyestuffs of I. G. there are now such commercial ranges as " Coprantine " of Society of Chemical Industry in Basle and " Cuprophenyl " of J. R. Geigy A.-G. Simultaneous dyeing and coppering (a one-bath process) can be carried out by means of a process patented some years ago by the Society of Chemical Industry in Basle[21] involving the use of copper sulphate and sodium tartrate in the dyebath.

Another feature of the activity of dye manufacturers in investigations on direct cotton dyestuffs during the last few years is the renewed interest in " stilbene " and " stilbene-azo " dyes. For many years some of the fastest-to-light dyes in manufacturers' ranges have been drawn from this type of dye but the shades covered were, in general, only yellow, orange and scarlet. In recent years, by using in the " stilbene " reaction aminoazo compounds containing a metallizable system in *o* : *o*′-positions with respect to the azo group, either alone or in conjunction with non-metallizable amino compounds (including aminoazo compounds), dyes have been obtained which, in the form of their copper complexes, still have good light fastness but extend the shade range to browns, greys and olives. It is worth noting that the triazine residue  continues to be widely used in patent specifications for linking two similar or dissimilar aminoazo residues by means of a " chromophoric block ", or, in some cases, an aminoazo residue and an aminostilbene derivative. Here, again, much of the attention seems to have been paid to the after-coppering types of dyes.

In considering the patents on azo direct cotton dyes coming into consideration for review this year it is difficult to pick out any which represent striking advances in the art. Instead, one has to record steady progress in extending and intermixing still further the known main " chemical types " of substantive dyes. For these reasons it is proposed to indicate as briefly as possible the scope of the inventions in question and to group them according to the patentee. The majority of the specifications are in the names of Swiss manufacturers but there is still a steady flow from American sources.

Dyes patented by the Society of Chemical Industry in Basle

Greenish-yellow to reddish-yellow dyes for after-coppering containing triazine or urea linkages and made by more than one route are exemplified by (5-nitroanthranilic acid → 3-methyl-5-pyrazolone) reduced and 2 mol. condensed with 1 mol. of the diprimary condensation product of 4 : 4'-diaminostilbene-2 : 2'-disulphonic acid and 2 mol. of cyanuric chloride, the remaining chlorine atoms of the latter being replaced by aniline.[22] Reddish-yellow dyes rendered fast to light and washing by after-coppering are also obtained by coupling 2 mol. of an acidylaminoaniline-2-carboxylic acid with twice-coupling components obtained by converting 4-nitro-4'-aminostilbene-2 : 2'-disulphonic acid (I) to the corresponding pyrazolone, reducing the nitro group, and either condensing 2 mol. of the resulting amino compound with a linking agent, *e.g.*, phosgene or cyanuric chloride, or converting the amino group to a pyrazolone. An example is:—5-benzoylamino-2-aminobenzoic acid (2 mol.) ⇉ the urea obtained by converting I to the pyrazolone, reducing and phosgenating.[23]

Grey-shade trisazo and polyazo dyes yielding various shades of grey to blue when coppered by one- or two- bath processes are of the type:—Aminosalicylic acid → M^1 → M^2 → (J-acid linked to an aminosalicylic acid derivative either by -CO- or by the C atom of a -$\overset{|}{\mathrm{C}}$=N- grouping forming part of a six membered heterocyclic ring such as a triazine.[24] Dyestuffs which dye cotton in fast green shades from a weakly alkaline bath in the presence of copper sulphate and sodium tartrate are obtained by coupling a diazotized aminoazo compound of type aminosalicylic acid → *m*-toluidine or cresidine with a cyanuric condensation product of the type $\triangle \equiv ARX$ where $\triangle$ is a triazine residue, A is an aminonaphthol sulphonic acid, R is an aminoazo compound such as *p*-aminobenzene-azo-salicylic acid, and X is a primary or secondary amine. Thus, the coppered combination 4-aminosalicylic acid → cresidine → (the ternary condensation product from cyanuric chloride, H-acid, *p*-aminobenzene-azo-salicylic acid and aniline) yields blue-green shades, fast to washing.[25] Non-sulphonated dyes particularly suitable for dying wool/viscose union materials from a neutral bath and specifically for after-coppering are exemplified by the ternary condensation product of cyanuric chloride (1 mol.), *p*-aminobenzene-azo-salicylic acid (2 mol.) and anthranilic acid → J-acid (orange brown shades).[26]

Yellow polyazo dyes fast to light and washing as copper complexes are obtained by condensing cyanuric chloride with in turn (*a*) 4″-aminostilbene-4′-(3-methyl-5-pyrazolone)-2′ : 2″-disulphonic acid, (*b*) a metallizable aminoazo compound A → E where E is a keto-enol type of coupling component (*i.e.*, a yellow component), and (*c*) one of the usual inert components such as aniline, and finally coupling to this condensation product a diazotized arylamine carrying a metal complex forming group *ortho* to the diazo group.[27] Asymmetrical urea dyes yielding yellow after-coppered shades are obtained by phosgenating a mixture of (*a*) $R\text{-}X\text{-}R^1\text{-}Y\text{-}R^2NH_2$, where X and Y represent azo and amido groups respectively or *vice versa*, R is a sulphosalicylic acid residue and R^1 and R^2=arylene residues, and (*b*) $R^4N : NR^3NH_2$ in which R^4 and R^3 are a salicylic acid residue and a *p*-arylene residue respectively.[28]

Metallizable dyes particularly suitable for application by the one-bath coppering process of B.P. 455,274 and giving brown shades are of the type *o*-hydroxycarboxylic acid (*e.g.*, salicylic acid) ← benzidine → 1 : 3-dihydroxynaphthalene ← *o*-metallizing amino compound.[29] Such dyes are, therefore, of the type of Sirius Supra Brown BRL (I. G.)[30] but having 1 : 3-dihydroxynaphthalene in place of resorcinol. Dis- and poly-azo dyestuffs yielding *inter alia* valuable red shade after-coppered dyeings on cotton and viscose are obtained from tetrazotized 3-hydroxy-4 : 4′-diamino-diphenyl (3-hydroxybenzidine) (D) by first coupling with any desired coupling component (which may contain azo groups) and then with a 3-alkylpyrazolone. Thus:—salicylic acid ← D → 1-(4′-hydroxy-3′-carboxyphenyl)-3-methyl-5-pyrazolone gives red after-coppered shades and 1-(4′-hydroxy-3′-carboxyphenyl)-3-methyl-5-pyrazolone ← D → resorcinol → 2-aminophenol-4-sulphonamide gives violet-brown shades by the one-bath coppering process.[31]. In a very similar way 3-hydroxy-3′-alkoxybenzidines are used as tetrazo components.[32]

Grey shade dyes having good fastness to light and boiling, particularly alkaline boiling which mades them suitable for materials which are difficult to dye throughout, are of the type:—2 : 6-dichloro-4-nitro-aniline (specifically) $\rightarrow M^1 \rightarrow M^2 \rightarrow$ J-acid or a derivative thereof (including A $\xrightarrow{\text{acid}}$ J-acid). M^1 and M^2 are α-naphthylamine or a Clèves acid.[33]

Polyazo-stilbene dyes, yielding red after-coppered dyeings, in which anthranilic acid (M) is used at least once as a middle component are of the general pattern:—4 : 4′-diaminostilbene-2 : 2′-disulphonic acid $\rightrightarrows (M)_2 \rightrightarrows$ (1-phenyl-3-methyl-5-pyrazolone)$_2$. Various alternative methods of making these dyestuffs are described.[34] 8-Hydroxyquinoline is used as end component (E) of disazo dyes containing not more than two $-SO_3H$ groups and of the type A → aminoaroyl derivative of J-acid → E.[35]

Dyestuffs patented by J. R. Geigy A.-G.

4-Nitro-4′-aminostilbene-2 : 2′-disulphonic acid (A) has been widely used in the past by I. G. Farbenindustrie A.-G. as the starting point for some of the members of their " Sirius " and " Sirius Supra " ranges of direct cotton colours (*e.g.*, Sirius Orange I, Sirius Green GT, Sirius Supra

Olive GL).[36] Messrs. Geigy have condensed monoazo compounds of the type of Sirius Orange I (A → phenol followed by O-alkylation) or A → salicylic acid in caustic alkaline medium with metallizable aminoazo compounds of the benzene series and coppered the condensation products to give a variety of fast-to-light shades. Thus, the coppered condensation product of A → phenol (ethylated) and 2-aminophenol-4-sulphonic acid → *m*-anisidine gives yellow brown shades and the coppered product of condensing A → salicylic acid with 2-aminophenol-4-sulphonic acid → 2 : 5-dimethoxyaniline gives bronze shades on cotton.[37] In another specification ternary condensation products are made from cyanuric chloride, A (1 mol.), and aminoaryl residues X and Y (1 mol. of each) and these ternary products are then submitted to alkaline reduction (glucose or sodium sulphide) whereby the molecule is doubled by conversion of the nitro of A to an azoxy or azo group. Yellow to red shade dyes are obtained. Thus, when glucose reduction is applied to the case where X = Y = 5-aminosalicylic acid, a fast-to-light orange dye is obtained, the washing fastness of which is considerably improved by after-treatment with chromium salts.[38]

Cotton and viscose are dyed in blue, violet-brown to black shades, made fast to water and washing by aftertreatment with copper salts, by tris- and tetrakis-azo dyes obtained by coupling tetrazotized dianisidine (or an analogue thereof) firstly with a monoazo compound, anthranilic acid (or substituted derivative) $\xrightarrow{\text{acid}}$ J-acid and then, in the presence of pyridine if necessary, with a naphthol which may also contain an azo substituent. Thus, dianisidine $\rightrightarrows$ (J-acid $\xleftarrow{\text{acid}}$ anthranilic acid)$_2$ gives a navy blue shade, somewhat deepened by coppering, and salicylic acid ← dianisidine → J-acid $\xleftarrow{\text{acid}}$ anthranilic acid gives a violet brown.[39] Acid-coupled monoazo compounds of the type of anthranilic acid → J-acid are used as coupling components (E) in another specification for polyazo dyes of the general pattern:—$\overbrace{\text{aminosalicylic acid} \rightarrow M^1}^{A} \rightarrow M^2 \xrightarrow{\text{alk}}$ E, where M^2 may contain *o*-OCH_3, -OC_2H_5, or -O.CH_2COOH and A may be salicylic acid ← diamine → M^2, &c. For example, the tetrakisazo combination 5-aminosalicylic acid → Clèves acid → cresidine $\xrightarrow{\text{alk}}$ J-acid $\xleftarrow{\text{acid}}$ 5-chloro-anthranilic acid gives bluish-grey shades on cotton becoming grey on after-coppering.[40]

Dyestuffs patented by Sandoz Ltd.

An interesting specification describes the preparation of stilbene condensation products obtained by reacting in caustic alkaline medium 4 : 4′-dinitrostilbene- or -dibenzyl-2 : 2′-disulphonic acid with N-monoalkylated amino compounds (including aminoazo compounds). It is said that deeper shades are obtained than with corresponding products from primary amines. No indication is given of the mechanism of the reaction(s) involved.[41]

Metallizable brown dyes are of the type:—salicylic acid ← diaminodiaryl → resorcinol ← *o*-aminophenol ← A. The portion A → *o*-aminophenol is obtained via the N-acetyl derivative of the latter followed by hydrolysis. Fastness to both washing and light is increased by after-coppering.[42] Improvements in the same properties are obtained by after-coppering the red-shade disazo dyestuffs of the pattern:—salicylic acid (or substituted derivative) ← 4 : 4′-diaminobenzanilide → benzoyl-J-acid.[43] Bright blue shade dyes having outstanding exhaustion properties and which can be coppered are obtained by coupling a diazotized *p*-aminoazo compound $NH_2R.N : N.R^1$, where R is phenyl and has an alkyl or alkoxy groups *o*- to the azo group and an alkyl group *o*- to the NH_2 group and R^1 is the residue of salicylic acid, on to one side of di-J-acid, and a diazotized 5-nitro-2-aminophenol, which may carry alkyl or halogen in the 4-position, on to the other side.[44]

Dyes patented by du Pont de Nemours & Co.

This firm has continued their investigations leading to dyes for aftertreatment with formaldehyde, whereby washing fastness is increased, and to dyes for diazotization and development on the fibre. Two patents come into consideration in the former connexion. The first provides for the making of dyes containing a dihydroxybenzoylamino-grouping from parent amino-dyes by treating the latter with 3:5-diacetoxybenzoyl chloride or with 3 : 5-bis(carbomethoxyoxy)-benzoyl chloride followed by hydrolysis. The derived dyes yield dyeings of greater brightness and light fastness than those from the parent dyes or with corresponding dyes obtained by diazotizing the parent dyes and coupling with resorcinol.[45] The second relates to dyes of the patterns:—naphthol or N- substituted naphthylamine sulphonic acid ← a benzidine → a 1-aminonaphthalene → resorcinol and that in which a further 1-aminonaphthalene component is inserted before the resorcinol. Both light and washing fastness is said to be improved by formaldehyde aftertreatment.[46]

In the field of dyes for diazotizing and development on the fibre this firm employs as final coupling component for disazo dyes a di-(aminobenzoylamino)-benzoylamino-J-acid which on the fibre tetrazotizes and couples with two mol. of coupling component developer for greater fastness to washing.[47] Scarlet shades giving excellent white discharges are obtained when the dye 3-toluidine-6-sulphonic acid → *o*-anisidine → 1-(3′-aminophenyl)-5-pyrazolone-3-carboxylic acid → *m*- aminobenzoyl-J-acid is diazotized on the fibre and developed with *β*-naphthol.[48] The use of N-(3′-amino-4′-methoxybenzoyl)-J-acid (E) as final coupling component for secondary disazo dyes results in brighter dyeings on cotton than those obtained from corresponding known dyes, *e.g.*, those from *m*-aminobenzoyl-J-acid. An example is:—aminoazotoluene sulphonic acid → E developed with *β*-naphthol gives bordeaux shades.[49]

The washing fastness of dyeings on cotton is increased by treating them with a monomeric poly-(N-alkoxymethyl)-amide of a polybasic acid or with a monomeric poly-(N-alkoxymethyl)-melamine, where the alkoxy groups comprise 1–5 C atoms, drying and heating to an elevated temperature, preferably in the presence of an acid catalyst. Examples of such agents are methoxymethyladipamide and trimethoxymethylmelamine.[50]

Dyes patented by American Cyanamid Co.

Blue, grey, violet and brown violet copper-containing dyes which are resistant to the effects of crease-proofing are prepared by treating a dye of the type:—*o*-hydroxy-coupling end component ← dianisidine $\xrightarrow{\text{alk.}}$ S-acid $\xleftarrow{\text{acid}}$ an aniline-sulphonic acid, with ammoniacal copper sulphate, which effects both triazole formation at the azo linkage of the acid-coupled S-acid and copper-complex formation in the one operation.[51] New diazo components for cotton dyes are (*a*) N-substituted derivatives of 6-amino-1 : 4-benzodioxan obtained by treating the dioxan with 2-chloro-5-nitrobenzenesulphonic acids and related compounds, followed by reduction;[52] (*b*) N-substituted derivatives of 6-amino-1 : 3-benzodioxan obtained by heating the latter with a *p*-nitrohalogenobenzene, which may or not contain a negative substituent *ortho* to the halogen, followed by reduction;[53] and (*c*) N-substituted derivatives of 5-aminocoumarins also obtained by heating the 5-aminocoumarins with a *p*-nitrohalogenobenzene, such as 2-chloro-5-nitrobenzenesulphonic acid, followed by reduction.[54]

Miscellaneous cotton dyes

Allied Chemical & Dye Corporation have described a process for coppering *o*-hydroxy-*o*′-methoxyazo-compounds with an aqueous ammoniacal solution of a copper salt at 85–100° in the presence of metallic copper. The resulting products are said to yield considerably brighter shades on cotton and show less tendency to stain organic derivatives of cellulose than similar products prepared in the absence of the added metallic copper.[55] The same firm has described an orange dye remarkably fast to chlorine, light and washing, obtained by condensing 2-aminonaphthalene-6 : 8-disulphonic acid → aniline with 4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid, the redness of shade being controlled by the extent of a sodium sulphide aftertreatment of the condensation product.[56]

They also phosgenate and thiophosgenate monoazo compounds of the type:—2-(aminoaryl)arylenethiazole disulphonate → aromatic amine of the benzene series to form symmetrical urea and thiourea disazo dyes for cotton.[57]

I. G. Farbenindustrie A.-G. make a mixed urea of the azo-anthraquinone series, giving green shades on cotton, by condensing the O-phenylurethane of 4-amino-4′-hydroxy-3′-carboxyazobenzene with 1-amino-4-(*p*-amino)-anilinoanthraquinone-2-sulphonic acid.[58] Imperial Chemical Industries Ltd. make olive and brown shade dyes by coppering condensation products of 4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid (A), certain aminostilbene-triazoles and certain benzenoid amino-monoazo compounds containing the *o*-OH-*o*′-OCH_3-azo grouping. The aminostilbene-triazoles employed are those obtained by coupling diazotized 4-nitro-4′-aminostilbene-2 : 2′-disulphonic acid with naphthylamine sulphonic or carboxylic acids coupling in *ortho* position to the amino group, oxidizing the *o*-aminoazo compound to the triazole and reducing the nitro group. Thus the coppered condensation product from equimolecular proportions of A, the aminostilbene-triazole for which 1-naphthylamine-4-sulphonic acid has been employed as intermediate coupling component, and the aminozao compound 2-aminophenol-4-sulphonic acid → *m*-anisidine gives brown shades of good fastness to light and washing on cotton.[59] General Aniline and Film Corporation use 1 mol. of an aryl-J-acid and 1 mol. of an acetoacetarylamide as coupling components for disazo grey, bluish-grey and brown dyes from tetrazotized benzidine-3 : 3′-dicarboxylic acid or benzidine-3 : 3′-diglycollic acid.[60]

Azoic dyes

A number of American patents have been taken out by the American Cyanamid Co. for new bases which can all be regarded as derivatives of 4-aminodiphenylamine and related to Variamine Blue B Base (I.G.) which is 4-amino-4′-methoxydiphenylamine. The N-substituted derivatives of 6-amino-1 : 4- and 1 : 3-benzdioxans and of 5-aminocoumarans referred to above in the section on azo dyes for cotton have also been used by this firm for diazotizing and coupling with arylamides of 2-hydroxy-3-naphthoic acid.[52, 53, 54] 4 : 4′-bis-(4-aminophenylamino)-diphenylether gives a golden tetrazonium salt which, in admixture with $MgSO_4$, $2H_2O$ and anhydrous Na_2SO_4 gives a water soluble product very stable to storage. Depending on the coupling component used, it gives azoic dyestuffs varying in shade from golden yellow to dark purple.[61] Diazo and tetrazo components which, with ice-colour coupling components, yield azo compounds giving blue to violet shades of good fastness to light, heat and washing, are provided by glycol (C_2-C_4) ethers of 4-amino-4′-hydroxydiphenylamine, *e.g.*, $NH_2.Ph.NH.Ph.O.CH_2.CH_2.O.Ph.NH.Ph.NH_2$,[62] 4′-tetrahydrofurfuryloxy-4-aminodiphenylamine,[63] ω-alkoxyalkyl ethers of 4-amino-4′-hydroxydiphenylamine,[64] 4 : 4′-bis[N-(4″-aminophenyl)-amino]-diphenylether,[65] and 4′-alkenyloxy-4-aminodiphenylamines.[66]

5-(4′-Aminophenylamino)-1 : 3-benzdioxoles, obtained by condensing 5-amino-1 : 3-benzdioxole with a *p*-nitrohalogenobenzene and reducing the nitro group, when diazotized and coupled to ice colour coupling components give novel colour shades and unusual light fastness. In the case of coupling with the anilide of 2-hydroxy-3-naphthoic acid a strong blue shade is obtained, with the urea of J-acid a direct cotton dye is obtained which gives deep brilliant blue shades.[67] Arylamides of picolinic and nicotinic acids containing a diazotizable amino-group in the arylamide residue have been used as bases by du Pont de Nemours & Co. Azoic couplings therefrom have good dischargeability and fastness to light and chlorine.[68] The same firm has also employed azotized metal and metal-free phthalocyanines in making azoic products.[69]

Investigations designed to produce new coupling components for azoic combinations have led du Pont de Nemours & Co. to use hydroxybenz-*a*-acridines, or halogeno derivatives thereof, in which the OH group is at one of positions 2, 9 and 10. With diazo components devoid of water-solubilizing groups these components lead to insoluble azo dyes having a wide variety of shades, including browns, and having good fastness, particularly to light and chlorine.[70] The Society of Chemical Industry in Basle have described the preparation and use as coupling components for ice colours of amides obtained by interaction of a 2-hydroxy-3-naphthoic acid and a 2-aminoarylene-thiazole, *e.g.*, 2-amino-6-methoxybenzthiazole. Specially valuable dyes are those from diazo components containing more than one phenyl nucleus, *e.g.*, diazo components of the phenylether group, especially phenyl or benzylethers of *o*-aminophenols or diazo components which are aminoazo compounds.[71] *o*-Hydroxy-carboxyarylides from *p*-aminophenylmorpholine are described by General Aniline & Film Corporation for use as azoic coupling components. Examples of the parent *o*-hydroxycarboxy compounds used as starting materials are 2-hydroxy-3-carboxy-anthracene and 2-hydroxy-3-carboxy-diphenylene oxide (OH *p*- to the O of the five-membered ring).[72]

A paper by N. Mehta and V. B. Thosar[73] describes experiments on the hydrolysis of Naphthols AS, AS-RL, AS-TR, AS-OL, AS-BG, AS-E, and AS-LB with alcoholic potash, varying the concentration of the potash and of the alcohol, the time and the temperature. The results indicated that hydrolysis does not occur at room temperature and is a function of the strength of the alkali solution and of time, being independent of the total quantity of the alkali added so long as this exceeds that theoretically required for hydrolysis. It is also a function of the concentration of alcohol in the alkali solution. In the case of Naphthols derived from 3-hydroxycarbazole-2-carboxylic acid, such as Naphthol AS-LB, hydrolysis was slow although the naphthol was comparatively soluble in alcohol.

A useful list of melting points of 26 unsulphonated azo compounds from Naphthol AS, their diazo components and the benzoyl derivatives of the latter is given in a paper by L. Koch and R. F. Milligan[74] relating to the identification of such azoic combinations.

du Pont de Nemours & Co. have reacted non-coupling aryl carboxylic acids such as benzoic acid or 3 : 5-dinitrobenzoic acid or a salt (Na) or anhydride of such an acid with a diazonium halide, such as that from 2 : 5-dichloroaniline, and used the products to form water-containing printing pastes which may be stable for several days.[75]

Stable diazoamino compounds from 3-aminocarbazoles and certain benzenoid primary amines containing negative groups, which may be isolated as insoluble salts by the addition of di-*o*-tolylguanidine hydrochloride, are obtained by the same firm by condensing the diazonium compound with 6-sulpho-1 : 2 : 3 : 4-tetrahydroquinoline-8-carboxylic acid in strongly alkaline solution.[76] Other stabilizers for diazo-compounds described by du Pont are hydroxyalkyl- or alkoxyhydroxyalkyl-cyanamides, -guanidines, -guanylureas and -biguanidines,[77] and aminobenzene-sulphon- or carboxy-N-hydroxyalkyl-amides.[78]

The American Cyanamid Co. employ organic nitrogenous bases, free from coupling capacity or ability to react with nitrous acid, containing 1 olefinic or acetylenic bond, *e.g.*, an alkylguanamine, and their soluble salts as stabilizers in the preparation of printing pastes of diazoamino compounds,[79] and, in another specification, di-alkylol- or -alkoxyalkylol-dicyandiamides,[80] whilst Messrs. Kuhlmann use 2-*cyclo*hexylamino-5-sulphobenzoic acid for the preparation of stable diazoamino compounds.[84] In order to prevent thinning of printing pastes containing diazoamino compounds the American Cyanamid Co. employ in one specification at least one ester of a di- or tri- basic carboxylic, sulphonic or sulphocarboxylic acid with an alcohol having at least one olefinic or acetylenic bond, *e.g.*, diallylsulphosuccinate,[81] and, in another, a soluble sulphonic acid or salt containing at least one olefinic or acetylenic bond, *e.g.*, sodium 2-propene-1-sulphonate.[82]

General Aniline & Film Corporation find that the stability of dyeing solutions and printing pastes containing a diazo salt is increased by incorporating therein an aliphatic mono- or poly-sulphonic acid containing ≯ 4 C atoms, *e.g.*, methane sulphonic acid or Na 2-chloroethane sulphonate.[83]

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IRON AND STEEL

By G. E. SPEIGHT, F.R.I.C., F.I.M.

The United Steel Companies Limited

STEEL production in 1947, though not fulfilling entirely the ambitious programme laid for it, nevertheless achieved the very creditable total production of 12,724,000 ingot tons, of which about 1,900,000 tons were exported. During the early part of the year the iron and steel industry, in common with most others, was seriously hindered by the fuel crisis, but during the closing months the steel production rate was more than 14,000,000 ingot tons per year; this has been fixed as the target rate for 1948.

Whether the 1948 target is achieved or not depends upon a number of factors, one of the most important again being the fuel position. This, however, is distinctly more encouraging than at the commencement of 1947, and during the year conversion of industrial furnaces to fuel oil burning has continued. Other factors, such as transport organization and availability of scrap, will have to be closely considered. Unless there is adequate response to the campaign for the speedy return of industrial scrap, the resulting shortage may well become serious. Consideration is being given to alternative raw materials for steel production such as the increased use of iron ore. In spite of such difficulties, however, the overall picture enables one to take a reasonably optimistic view of the prospects for 1948.

Mineral resources and treatment of iron ores

The iron ore resources of the world have been reviewed by R. Durrer,[1] who estimates that these are sufficient to meet the probable requirements for several hundred years, and are practically limitless if iron quartzites and titanium-bearing sands are included.

As the more accessible and richer deposits are being depleted and increasing use made of lower grade iron ores, interest has been directed towards methods of beneficiation. Considerable progress has been made in the United States and in Germany during the war, and methods of beneficiation have been the subject of several reports of the British Intelligence Objectives Sub-Committee. Concentration of low grade iron ores by removing the clay constituents, with an upward flow of air and water in a washing tower, was developed by Wiedelmann of Ilsederhutte.[2] By this method a product containing 38·9% iron is obtained from ore containing 21·6% iron, with a recovery of 91·5% of the iron originally present. In the Lurgi process,[3] hematite ores are reduced by blast furnace gas, in rotary kilns, to yield magnetite, which is subsequently concentrated and separated magnetically; concentration from 28% iron in the raw ore to about 40% in the final product is achieved, with a recovery of 83%. In the Renn-Wälz modification of the Krupp-Renn process, described by Tettenborn,[4] for the recovery of iron from waste materials produced in the smelting of zinc and lead ores, the material is heated to 1000° by the countercurrent gases and the volatile metals are removed as vapour, leaving behind 80–85% of the iron.

The influence of burden preparation on the efficiency of the blast furnace operation, has prompted considerable research on the properties and production of iron ore sinter. The basic requirements of good sinter, for the blast furnace, are that it should be mechanically strong but easily reducible. In 1945, Berger Hessle[5] described the production of good sinter from Swedish concentrates. Sintering time should be as short as possible, the sintering temperature kept under close control, the charge should be porous and well mixed with finely crushed fuel, and a large volume of air should be used for the combustion. By close attention to these conditions, appreciable increase in iron output from the blast furnace has been achieved at several plants with saving of fuel.

A valuable contribution to the theory of sinter production and behaviour has been provided by the laboratory investigation of Hay and McLeod.[6] One of the most important factors affecting the reducibility of a sinter is its permeability to gaseous diffusion, which, according to the Glasgow investigators, occurs in two stages: first, rapid diffusion into the macro- and micro-pores, followed by much slower diffusion from the pores into the solid. From this it follows that the better the microporosity of the sinter, the better will be its reducibility. Industrial sinters are often difficult to reduce because of low microporosity resulting from incipient melting and excessive glass formation. This may be avoided by using carbon in the sinter mixture in just sufficient amount to provide the required amount of reduction for rapid sintering, without producing large quantities of FeO which would form low melting point silicates such as Fayalite ($2FeO.SiO_2$). The formation of these silicates is decreased by a low excess silica content, obtained by having a $CaO : SiO_2$ ratio as high as possible without incurring the risk of producing calcium orthosilicate $2CaO.SiO_2$, which on account of its 10% volume change on cooling would cause crumbling.

A useful practical guide to the production of good sinter has been provided by T. W. Plante.[7]

Production of pig iron and ferro-alloys

During the war, much attention in Germany and Russia was devoted to the possibility of blowing blast furnaces with oxygen or oxygen-enriched air, and research on the production scale was carried out with a considerable measure of success. Inspired by this success and by the possibilities of cheaper oxygen, interest has now spread to this country and to America. The idea of oxygen enrichment, however, is not a new one; as early as 1909, P. Monnartz[8] described successful small scale experiments on the production of ferro-chromium by smelting chrome ore with an oxygen enriched blast in the blast furnace.

The advantage of oxygen enrichment lies in the partial elimination of nitrogen which, apart from carrying heat to the stack and so preheating the burden, serves no useful purpose and carries an excessive amount of heat out of the furnace. With removal of this ballast, the combustion temperature is raised, more heat at a higher temperature becomes available, and consequently higher hearth temperatures are possible. The reduction of oxides, such as those of chromium and silicon which require a high temperature, is therefore facilitated, and it should be possible to produce ferro-chromium and ferro-silicon in the blast furnace, instead of by the normal electric smelting process.

A natural corollary of the exclusion of nitrogen is a reduction in the temperature at the top of the stack. Since this should not be allowed to fall below 100° for efficient working, the stacks of furnaces designed primarily for smelting with oxygen-enriched blast would need to be lower than those using air blast. Such low-shaft furnaces have proved practicable both in Germany and Russia.

The advantages which theoretically should accrue from oxygen enrichment are discussed by Shapovalov,[9] who also describes a furnace campaign for the production of 10–11% FeSi with a blast containing about 30% oxygen. Further Russian work is described by Bardin,[10] while the foremost worker on the subject in Germany during the war was Lennings.[11]

Oxygen enrichment has been applied successfully to the production of ferro-chromium at the Suddeutsche Kalkstickstoff Werke,[12] where low grade chrome ore, too poor to smelt electrically, was smelted in a low shaft furnace, only 5·8 metres high with a 2 metre hearth, using a blast containing 55% oxygen, to yield ferro-chromium containing 28–32% chromium.

In America, considerable attention has been given to another line of approach to improve the efficiency and economy of blast furnace operation, *i.e.*, acceleration of the reduction of the ore by the application of high top-pressures to the exit gases. Although this has often been tentatively considered in the past twenty years, the development is still in its infancy. The principle is that, by increase of pressure to the exit gases, the reducing gases are in contact with the burden for a longer period and are consequently more effective. Slater[13] describes how top-pressures of 10–11lb. per sq. in. have been used in blast furnaces of the Republic Steel Corporation at Youngstown and Cleveland, with useful reductions in coke consumption of 130 to 255lb. per ton of iron and an overall reduction in cost of more than $1.00 per ton of iron. It is believed that further saving and increased efficiency will result from the use of still higher top-pressures, and equipment is being installed which will make possible pressures as high as 20–25lb. per sq. in.

Laboratory experiments carried out by Marek, Bogrow, and King,[14] have shown that the reduction of hematite ores takes place in two stages, to FeO initially and then to metallic iron, at a rate which, other things being equal, is proportional to the pressure. It is also shown that carbon deposition according to the reaction $2CO \rightarrow CO_2 + C$ is increased by increased pressure. Lyuban,[15] also studying the carbon deposition reaction, confirmed that it is catalysed by the active form of iron, produced by low temperature reduction of iron oxide. The effect of iron on this reaction ceases at a temperature of 685°, which is the point of intersection of the equilibrium curves of the reactions $2CO \rightleftharpoons CO_2 + C$ and $FeO + CO \rightleftharpoons Fe + CO_2$.

It was established a number of years ago by Holbrook and Joseph[16] that, due to lower viscosity, blast furnace slags of high magnesia content have a higher desulphurizing power than slags of the same basicity containing only lime. A recent application of such slags, described by Nickel[17], is to the production of low silicon basic iron, which is in great demand for basic open hearth steelmaking. By charging dolomite instead of limestone a slag containing approximately 20% magnesia is produced which, due to its lower melting point and greater fluidity, promotes adequate desulphurization at the relatively low temperature required for the production of low silicon iron. The product is a pig iron of reasonably low sulphur content containing an average of only 0·48% Si compared to 1·07% in the normal iron.

Foundry practice

A detailed study of the side-blown converter process, which is extensively used for the production of foundry steel, has been made by the Side-Blown Converter Practice Sub-Committee of the Steel Castings Research Committee,[18] whose first report was published in January of this year. It is shown that the steel produced in the side-blown converter is of a high quality comparable with open-hearth steel—this is attributed to the fact that the steel is refined essentially by slag-metal reactions in the side-blown converter, and not by air-metal reactions as in the bottom-blown Bessemer. The relatively small amount of silicon in the iron (about 1·0% compared with 2·5% in the normal Bessemer process) is not the main source of heat; its oxidation serves merely to raise the temperature of the metal to about 1450°, at which temperature carbon is rapidly oxidized and thereafter provides the requisite heat. There is actually a reversion of silicon to the metal towards the end of the blow.

A satisfactory solution to the problem of desulphurization of cupola iron is described in a report by a Sub-Committee of the Institute of British Foundrymen.[19] Treatment in the ladle with soda ash, followed by transfer to another ladle where a second soda ash treatment is given, results in a reduction of sulphur in the iron from 0·20% to 0·045%. If an oxidizing agent is added as well as the soda ash, dephosphorization to a similar degree may also be achieved. The problem of sulphur in cupola iron is aggravated by the necessity of using high sulphur coke. It is suggested by the Council of Ironfoundry Associations[20] that the best method of countering this is to charge high-manganese iron.

In an interesting discussion on the function and mechanism of moulding sand binders, Jeníček[21] enumerates the desirable properties of a binder. It is essential that the binder should wet the sand-grain surfaces; that there should be a strong adhesive force between the binder and the sand; and that there should be a strong cohesive force within the binder. The popularity of organic binders, in preference to clay, is growing, and the advantages of synthetic resins for bonding materials are discussed by Gebhardt,[22] who claims that shorter baking times, at lower temperatures, may be used to give moulds stronger, both in tension and compression, than clay bonded moulds. Sands, ready coated with a resin known as Westonite, are used by a grey-iron foundry at Lynchburg in Virginia.[23] Reports from Germany[24] mention the use that has been made of cellulose derivatives as bonding materials, while Shaw[25] describes the use of ethyl silicate, which in conjunction with a suitable condensing agent gives a range of setting times varying between 5 minutes and 5 hours.

Direct production processes for iron

Although sponge iron was one of the earliest forms in which iron was extracted from its ores, there is still much conjecture and research regarding the most suitable method for its production and commercial utilization. In the opinion of Specht and Zapffe,[26] some form of low temperature gaseous reduction offers the most promise. They have published an exhaustive survey of all previous work in this field and have investigated the reduction of magnetite with hydrogen and carbon monoxide. Their conclusion is that when hydrogen is used, reduction to the extent of 80% is attained most rapidly at temperatures of 700–800°; for complete reduction, however, lower temperatures (575–600°) are preferable. Using carbon monoxide, carbon is stated to be the active reducing agent, except in the initial stages, and the maximum rate of reduction occurs at temperatures of about 1000°. According to a theory, postulated by Wiberg,[27] the failure of hydrogen to effect rapid and complete reduction at elevated temperatures, is due to the pressure of H_2O formation being insufficient to break down the protective layer of fused iron formed around the ore particles. With carbon monoxide as reductant, CO_2 is evolved at a much higher pressure which is sufficient to break down this layer so that reduction may proceed unhindered.

Experiments in America on the reduction of iron ore to sponge iron by a carbon monoxide-hydrogen mixture produced from natural gas are described by Brown.[28] The natural gas, containing 94% methane is mixed with air and passed over a catalyst, nickel oxide on an alumina base, to yield carbon monoxide and hydrogen. The presence of excessive amounts of water vapour and carbon dioxide in the gas however, hinders the reduction, and the results obtained are not entirely satisfactory.

In the Krupp-Renn process,[29] which was operated in Germany during the war, reduction is effected, by means of a solid carbonaceous reducing agent, in a rotary kiln, fired with oil or powdered coal. The process is applicable particularly to the reduction of highly siliceous ores, which would require excessive quantities of limestone if smelted in the blast furnace (the optimum lime : silica ratio in the Krupp-Renn process is only 0·20–0·25 compared to 1·3 in the blast furnace). The iron is discharged from the kiln as small pellets or balls embedded in a pasty mass of slag. After cooling, the whole mass is crushed in ball mills, and the iron recovered by magnetic separation. Since sulphur removal is negligible and most of the phosphorus enters the metal, raw materials and fuel containing as little as possible of these elements must be used if the product is to be suitable for charging directly to steelmaking furnaces.

Buehl, Shoub, and Riott[30] describe the use of dolomite to control the sulphur content of sponge iron, which is produced by solid reduction of iron ore or mill scale in a rotary kiln, similar to that used in the Krupp-Renn process. Sulphur contents within the range 0·03–0·05% are obtained.

Production of steel

In both open-hearth and Bessemer steelmaking processes, as in the blast furnace, great interest has been aroused in the possibilities of improved furnace efficiency and output due to oxygen enrichment of the air used in these processes. There have also been suggestions for somewhat unconventional uses of oxygen.

The use of oxygen for acceleration of the open-hearth process has several applications in the two main periods, (*a*) melting the charge and (*b*) refining the liquid bath. During melting down, oxygen may be used to enrich the air used for combustion and so increase the flame temperature. Alternatively, oxygen may be injected directly on to the preheated scrap, with subsequent decrease in melting time. This is achieved by the extra heat, derived from the exothermic oxidation of a fraction of the scrap; the loss of iron is not great as much of the iron oxidized at this stage is subsequently reduced and returned to the metal during refining. The refining period may be shortened by injection of oxygen into the bath, thereby removing carbon much more rapidly than by ore or scale additions. Moreover, the oxidation of carbon with oxygen is exothermic so that less heat is required from the fuel than when the carbon is oxidized endothermically with ore.

Most of the development work on the utilization of oxygen in the open-hearth furnace has been carried out in U.S.A. In a large number of experimental heats, described by Slottmann and Kerry,[31] the melting period was shortened by 1 to 3 hours, and fuel consumption per ton of steel produced was reduced by about 8%, due to oxygen enrichment of combustion air. An account is given by Slottmann and Lounsberry[32] of the use of oxygen at the Allegheny-Ludlum Steel Corporation for acceleration of carbon removal. Oxygen is fed at a pressure of about 100lb. per sq. in. and a rate of 25,000–50,000 cu. ft. per hour through steel pipes into the metal bath. To reduce carbon from 0·20% to 0·10%, the volume of oxygen required for each 0·01% carbon is 5·1 cu. ft. per ton of steel; to reduce carbon from 0·20% to 0·06%, the corresponding oxygen required is 7·0 cu. ft. The efficiency of the oxygen thus decreases as the carbon content of the bath falls.

When using oxygen for the removal of large percentages of carbon, care must be taken that the bath does not become overheated. It has recently[33] been suggested that injection of compressed air might be used more economically than oxygen (and with almost similar success), for the removal of carbon; if this suggestion were adopted the problem of overheating would be less acute.

Some pioneer work on the use of oxygen for the acceleration of combustion has been done in Russia also, and is described by Mozharov.[34] In order to eliminate the undesirable nitrogen ballast, normally present in gaseous fuel, he suggests that the gas producers, which supply fuel to open-hearth furnaces using oxygen for combustion, should be operated by a blast composed of the exit gases from the furnace admixed with oxygen, rather than by the normal air-steam blast. The gas produced, containing no nitrogen, would return to the ingoing end of the steel furnace to form a closed gas cycle. The producer gas formed with such a blast could have any calorific value between 90 and 290 B.Th.U./cu. ft., depending on the composition of the exit gas from the furnace and on the amount of oxygen added to the blast. The advent of cheap " tonnage " oxygen would open out many such interesting possibilities in furnace design.

Oxygen-enriched air for the blast in the basic Bessemer process was used in 1939 at Sulzbach-Rosenberg as described by Eilender and Roeser.[35] Oxygen contents of 27–35% were used, the oxygen being supplied by a plant operating on the Linde-Fränkl principle. Since the war, suggestions for the blowing of the Bessemer with oxygen have been made, and trials have been carried out in both France and Russia. After describing experimental blows with 30% oxygen blast made as early as 1925, Shapovalov[36] discusses the advantages which theoretically should accrue from blowing with oxygen or oxygen-enriched air. Blowing times would be shortened; irons of low metalloid content (the source of heat in the Bessemer process) could be blown successfully; large amounts of scrap, which normally cannot be melted in the Bessemer, could be utilized, and the nitrogen content of the resultant steel would be reduced to a level approaching that of open-hearth steel. Kondakov[37] has described experimental acid Bessemer blows using 100%, 75%, and 50% oxygen blast which were made at the Stalin Kuznetsk Metallurgical Combine. Steel of superior quality was produced; with 100% oxygen blast, the nitrogen content was as low as 0·0010–0·0022%, and even when the oxygen in the blast was reduced to 50%, the steel produced contained only 0·006% nitrogen, compared with the normal 0·012 to 0·015% in bottom-blown Bessemer steel.

Preliminary experiments on the increased use of oxygen in iron and steel production have been made in this country; further commercial development depends to a great extent upon the large scale production of oxygen at an economic price.

A technical development in open-hearth steel melting, rendered necessary in this country by the difficult fuel position, has been the conversion of a large number of open-hearth furnaces from gas-firing to oil-firing. A similar conversion had already been carried out to a large extent in America. The advantages and disadvantages of oil-firing as applied to open-hearth furnaces have been discussed by many writers, including Bashforth.[38] In general, oil is more suitable than gas as an open-hearth fuel, thermal efficiency being higher, and combustion more easily controlled. Against these advantages must be set the higher cost of the oil and the extra storage equipment which must accompany oil-firing.

The efficiency of producer gas fired open-hearth furnaces, as a function of port design, was the subject of extensive study by Chesters and Thring.[39] For the purpose of their trials, three furnaces at the Templeborough shop of Messrs. Steel, Peech, & Tozer were investigated. Apart from port design, these furnaces are essentially similar; the ports however, are radically different, one being of standard type, another of Maerz type, and the third, a semi-Venturi type. It was found that the semi-Venturi type furnace is the most efficient of the three, and that the best port design is the one which gives the shortest flame. Recommendations are made for further improvement. The scope of the report is considerably wider than the title would suggest, being in effect an overall survey of the thermal efficiency of the open-hearth process. A point particularly stressed is the importance of instrumentation to ensure efficient operation; it is claimed that adequate instrumental control of a furnace will, other things being equal, reduce the melting time by as much as 10%.

Physico-chemical studies of different aspects of the steelmaking processes continue to be made. On the question of sulphur equilibria between slag and metal in the open-hearth process, the paper by Grant and Chipman[40] is of interest. From experimental heats in which Armco iron was melted in a small electric furnace in contact with synthetic slags under a nitrogen atmosphere, it was concluded that MgO and MnO have desulphurizing powers as marked as that of CaO, and that CaF_2 is neutral from the viewpoint of desulphurization. FeO in the slag, at concentrations within the range 3–70%, acts merely as a diluent with respect to the sulphur ratio; this conclusion would appear to invalidate previous theories that the controlling reaction for sulphur removal is: CaO (slag) + FeS→CaS (slag) + FeO (slag). However, sulphur removal is assisted when the FeO content of the slag is less than 3%. Change of temperature within the range 1540–1660° does not affect the sulphur ratio; temperatures higher than this have a slightly deleterious effect, and lower ones a slightly beneficial effect. The greatest factor in the distribution of sulphur between slag and metal is undoubtedly the ratio of bases to acids in the slag.

Chipman, in association with Winkler,[41] has studied also the phosphorus equilibria between metal and slag under experimental conditions similar to those of the sulphur melts. The rate at which equilibrium between metal and slag is achieved was determined by the aid of radioactive phosphorus as a tracer. The time required for restoration of equilibrium after its disturbance was found to be 10 to 15 minutes. Phosphorus removal is improved by relatively low temperatures, by a high state of oxidation, *i.e.*, a high FeO content of metal and slag, by increased CaO, MgO, and MnO contents of slag, and by decreased SiO_2 content of slag. Fluorspar additions have no detrimental effect on phosphorus removal.

Working on the effect of temperature on the phosphorus reactions, Balajiva and Vajragupta[42] have postulated that the phosphorus equilibrium constant, k ($= \frac{[P_2O_5]}{[P]^2 \times [FeO]^5}$) and the CaO content of the slag may be related empirically by the linear equation:—

$$\text{Log } k = n \log \Sigma \ [\text{CaO}] - c$$

in which the gradient, n, remains constant and c varies with temperature.

There have been several papers on the mechanism of carbon removal from liquid steel. Mackenzie[43] and Sarjant,[44] in two separate papers, use a correlation (depending upon the constancy of the product $[C] \times [O]$) between the FeO content and the rate of carbon drop to determine the FeO content of liquid steel. On the other hand, Sims[45] quotes data showing that the rate of carbon drop is a function, not of [C] as would be expected, but of log [C]; Jay[46] also presents some evidence to suggest that the rate of carbon elimination is independent of the carbon content, depending only upon the state of oxidation of the bath.

The oxygen content of liquid steel, and the effect on it of several operating variables, have been studied by Brower and Larsen,[47] who report that the oxygen content of the metal is independent of slag composition over the ranges commonly used in acid and basic furnaces. The oxygen content of the metal in excess of that in equilibrium with carbon at a carbon monoxide pressure of one atmosphere (referred to as $\Delta[O]$), is largely independent of the rate of carbon drop, the FeO content of the slag, or its viscosity. The main variable is the condition of the hearth which has a marked influence on the ease of bubble formation. Sims[45] also discusses the formation of carbon monoxide bubbles, he accepts Ranque's calculation that an evolution pressure of carbon monoxide of 55 atmospheres is necessary for the formation of bubbles in the body of liquid steel, but suggests that bubbles may be initiated at the hearth surface when the evolution pressure is much lower, owing to the presence there of suitable nuclei. In a later paper, Brower and Larsen[48] discuss the effects of special additions, stirring methods, and tapping on $\Delta[O]$. It was found that $\Delta[O]$ is not greatly affected by agitation of the bath either by stirring or by solid additions designed for that purpose. There is, however, a tendency for $\triangle[O]$ to decrease during tapping, with a simultaneous decrease in carbon content, promoted presumably by the movement of the metal over the refractories of the tap hole.

In regard to the basic electric process, Urban and Derge[49] conclude that the CaC_2 content of the reducing slag has little effect on the FeO content of the bath. Minimum FeO contents of metal and slag are achieved at approximately the same time, *i.e.*, 40–80 minutes after removing the oxidizing slag, but the minimum FeO content of the metal is related more closely to the carbon content of the metal than to the FeO content of the slag. No matter how long the reducing slag conditions are maintained, the oxygen in the bath never decreases much below the value required for equilibrium with carbon.

The Iron and Steel Institute has published two papers on hydrogen in steel and its effect on properties. Sykes, Burton, and Gegg[50] report that, irrespective of how carefully steelmelting conditions are controlled, hydrogen contents of 4–6c.c./100g. at tapping must be expected. If not removed by heat treatment to a figure below 2c.c./100g., the ductility of the product will suffer. It was found that hair-line cracks did not automatically result even from relatively high hydrogen contents. By calculation of hydrogen diffusivity, the authors have predicted the rate at which hydrogen should be evolved from steel at various temperatures above 400°. In the other paper by Andrew, Lee, Lloyd, and Stephenson,[51] the relationship between the hydrogen content and the transformation characteristics of steel is studied. It is shown that there is a pronounced increase in the rate of evolution of hydrogen from steel, corresponding to the $\gamma—\alpha$ change. The conclusion is reached that hydrogen embrittlement and hair-line cracks are closely associated, hydrogen diffusivity and solubility being the controlling factors for both. Whilst hydrogen is suggested by these authors to be the principal cause of hair-line crack formation, the importance of stresses is emphasized because of the possible effect upon hydrogen diffusivity and solubility.

Analysis

In routine metallurgical analysis increasing use is being made of physical and physico-chemical methods, which are frequently more rapid or less costly in man-hours than the established chemical methods. Of these newer techniques, the spectrograph, polarograph, and photo-electric absorptiometer have the widest application in metallurgical analysis, and much attention has been devoted to their development. It should not be supposed, however, that the conventional methods have been superseded; they must be employed for the calibration and standardization of these instruments, and there are still many estimations to which the physico-chemical methods have not yet been successfully applied. Development of suitable chemical methods is therefore still important. An exhaustive bibliography of the advances that took place between 1942 and 1946 in all spheres of iron and steel analysis, both chemical and physico-chemical, has been prepared by Pigott.[52]

The most rapid, and in many ways the most attractive, of the newer techniques is the spectrograph, which has been applied to the estimation of most of the constituents of iron and steel, with the exception of carbon and sulphur. An interesting new application of the spectrographic technique has been to slag analysis as described by Rozsa.[53] Using the spectrograph, complete analyses of open-hearth and electric furnace slags, including the contents of calcium, magnesium, manganese, silicon, phosphorus, chromium, titanium, nickel, and iron, may be obtained in only 11–18 minutes; this time is short enough to render the method applicable to control work.

A system for measuring directly the intensities of the spectral lines is described by Oldfield.[54] The spectrum is focussed on a photo-tube instead of the usual photographic plate, and the magnitude of the current produced when a given spectral line is incident on the cathode of the tube is a measure of the intensity of the line. Comparison is made between a line of the element under examination and a standard line. It is claimed that, by direct reading, the operating time may be reduced to a quarter of that required for photographic estimation. Hasler[55] discusses the possible application of direct reading spectrographic methods to the control of steelmaking processes.

Although, hitherto, the widest application of the polarograph has been to the analysis of non-ferrous metals, its use for ferrous analysis is growing. The fundamental laws of polarography have been elucidated by Heyrovsky,[56] whose work was largely responsible for the successful development of the polarograph.

The accuracy and speed of colorimetric estimations have been increased tremendously since the advent of the photoelectric absorptiometer. The most popular instrument of this type in this country is the Spekker, which has prompted the development of many new colorimetric methods. Vaughan and Whalley[57] describe a micro-chemical scheme of analysis for ferrous alloys, which would have been completely impracticable without some such absorptiometric instrument. Methods are described for the individual determinations of most of the elements commonly found in ferrous alloys. In addition, the authors have evolved a comprehensive scheme by which manganese, nickel, molybdenum, chromium, vanadium, cobalt, copper, tungsten, titanium, and iron may be determined on a single sample weight of only 15mg.

The accurate determination of small percentages of carbon in steel is a difficult procedure requiring special technique, and most workers have resorted to measurement of some physical characteristic to complete the estimation. In 1944, Ericsson[58] used the change in electrical resistance when barium is precipitated as carbonate from a solution of barium hydroxide. Carbon dioxide, from the combustion of steel in oxygen, is passed into barium hydroxide solution of known resistance, and the resistance measured again; the change in resistance is then related to the carbon content of the steel. Nesbitt and Henderson[59] describe a method for determining carbon contents lower than 0·1% with an accuracy within 0·0003% carbon. The sample is burned at 1140–1450° in a stream of purified oxygen, and after removal of sulphur gases by activated manganese dioxide the carbon dioxide is absorbed in sodium hydroxide solution. The absorbent is then acidified to liberate the carbon dioxide from the sodium carbonate, and the volume of carbon dioxide thus evolved is measured under reduced pressure to give a measure of the carbon content of the steel.

The vacuum fusion method for the determination of oxygen in steel is firmly established; minor modifications are periodically suggested for its improvement but the basis of the method remains unaltered.

Methods for the determination of hydrogen in liquid steel have been investigated by Wells and Barraclough.[60] The vacuum heating method proved satisfactory for the determination of the hydrogen content of a given steel specimen, but difficulty was experienced in retaining in the solidified sample the whole of the hydrogen which was present in the liquid steel. The conclusion reached was that rapid quenching of a pencil sample gave the most satisfactory results.

Properties and tests

Much attention has been given to the development of alloys suitable for high temperature service, particularly in gas turbines and jet-propulsion. The properties required of such alloys are discussed by Robertson.[61] The most important property is resistance to creep, but other factors that must be considered are fatigue, resistance to corrosion at elevated temperatures, resistance to embrittlement, structural changes and precipitation hardening. Sykes,[62] in the Second Hadfield Memorial Lecture, gave an account of the work, carried out since 1938 at the Brown-Firth Research Laboratories, on the development of ferritic and austenitic steels for high temperature work. In June, 1946, the American Society for Testing Materials held a symposium on materials for gas turbines. Among other interesting contributions to this symposium, mention may be made of the report by Cross and Simmons[63] on the materials that have been considered for gas-turbine parts. These materials range from modifications of 18/8 chromium-nickel steels to practically iron-free cobalt-chromium and cobalt-chromium-nickel alloys to which additions of various combinations of molybdenum, tungsten, columbium, tantalum, titanium, aluminium, boron, and nitrogen have been made. The stress-rupture and creep properties of these materials were examined; in general the cobalt-base alloys showed better properties in the cast than in the forged state. The metallurgy of two groups of alloys, one nickel-base and the other cobalt-base, which have been successfully applied to gas turbine construction is discussed by Badger and Sweeny.[64]

A symposium,[65] published by the Iron and Steel Institute, on the hardenability of steel describes the work carried out by the Technical Advisory Committee of the Special and Alloy Steel Committee (Ministry of Supply). The work includes a standardization of the Jominy end-quench hardenability test, with an examination of the fundamental principles involved, and concludes with a correlation of the results of the Jominy test with other mechanical properties on a representative series of B. S. En steels. The end-quench test is stated to give satisfactorily reproducible results which are not affected appreciably by slight changes in the testing conditions. It is shown, however, that there could be a wide variation in hardenability across the section of a bar and that hardenability is affected by the structure before quenching. Knowledge of the chemical composition and grain size does not provide sufficient data from which to calculate hardenability. Furthermore, the specifications permit such a wide range of composition that considerable differences are found in the hardenability of material made to the same specification.

Investigation is still proceeding on the influence on structure and mechanical properties of steel treated with boron, and the literature on the subject has been reviewed independently by Archer[66] and by Dean and Silkes.[67]

Contractor and Vatchagandhy[68] have studied the effect of boron up to 0·01% in medium carbon steels. They confirm that the hardenability is increased by increasing boron additions, but find that over the range 0·003–0·007% the increases are not so great as reported by other workers. In addition to the effect on hardenability, resistance to corrosion by acids and atmospheric attack is improved by additions of boron of the order 0·003–0·007%; additions of more than 0·007% give no further improvements. The possibility of replacing some of the molybdenum in Ni-Cr-Mo and Mn-Mo steels has been investigated by Udy and Rosenthal,[69] who conclude that, in aluminium-killed steels of the types 0·30%C, 0·85%Mn, 0·50%Ni, 0·50%Cr, 0·40%Mo and 0·30%C, 1·60%Mn, 0·40%Mo, the hardenability and notched-bar impact strength could be maintained if half the molybdenum were replaced by addition of 0·0015–0·003% of boron. It is emphasized that full deoxidation must be carried out before the boron addition, to obviate inconsistent hardenability resulting from loss of boron.

After a general discussion of gases in metals and their detrimental effect on the properties of metals, Hume[70] discusses and criticizes common methods of degassing, including freezing and remelting, alloy additions, decomposition of solid fluxes, melting *in vacuo* and melting in a hydrogen-free atmosphere. The flushing of gases from the metal by an inert gas free from hydrogen, is then described in detail. Gases suggested for the purpose include nitrogen, argon, sulphur dioxide, chlorine, and boron trichloride, the first two being generally employed for steel. This process is claimed to produce castings free from porosity due to gas, to eliminate flaking and to remove non-metallic inclusions by flotation. The separation of gases from metals during cooling and solidification is considered by Phillips.[71]

In a symposium on fatigue, held at the University of Melbourne in December, 1946, Evans[72] discussed corrosion fatigue as an electro-chemical phenomenon. He found that when a wire, subjected to alternating stress, is maintained wet with a mixture of potassium chromate and chloride, the electrode potential drops suddenly when the protective coating, formed by the chromate, breaks down. The life of the wire is shortened by increased stress range and chloride concentration, and lengthened by increased chromate concentration. Zinc coating of the steel either with zinc tape or by application of a zinc-rich paint lengthens the life of the specimen even though access of the corrosive medium is not prevented, showing that the protection is largely electrochemical.

The possibility of preventing corrosion fatigue by the application of a cathodic current is considered both here and in a later paper by Evans and Simnad.[73] When a cathodic current is applied to a wire undergoing corrosion fatigue in a solution of potassium chloride, it is found that as the applied current is increased the rate at which iron compounds are formed, and the number of cracks produced, decreases and ultimately becomes zero. The life of the wire is actually shortened however, by the application of weak cathodic currents but is greatly lengthened by stronger currents. This may be explained by the fact that owing to stress concentration, the presence of a few cracks is more destructive than many, so that increased life is not attained until the applied current is strong enough to prevent all crack formation. The magnitude of the current required for complete protection increases as the stress range increases.

Corrosion

Several useful general reviews and bibliographies on the subject of corrosion research have been published during the year. A survey by Evans[74] is confined to the work of British investigators, while a comprehensive bibliography and summary of the literature, mainly directed to prevention and protection, has been prepared by Morral.[75] Towards the end of 1946, Voigt[76] published an extensive bibliography of corrosion testing methods covering the period 1935–1945, and about the same time a useful glossary of corrosion terms was prepared by the Electrochemical Society.[77]

The mechanism of oxide and sulphide film formation has been studied in detail by Evans.[78] In a mathematical treatment he concludes that the outward migration of cations and electrons leads to a parabolic rate of film growth, though mechanical breakdown of the film may modify this to a rectilinear or logarithmic growth. The film may suffer different types of breakdown, *e.g.*, blistering, flaking, or sheer cracking, depending upon the relative strength of the adhesive, cohesive, and compressive forces.

Resistance to scaling at high temperatures is a property which is of extreme importance in gas turbines and, more recently, in jet-propulsion. A new apparatus for carrying out scaling tests in various atmospheres has been devised by Stauffer and Kleiber.[79] The apparatus incorporates a specimen holder consisting of a cylindrical framework which can carry as many as 18 specimens. This assembly is introduced into an electric tube furnace so that the specimens are completely surrounded by the corrosive gas mixture. Such simultaneous testing ensures truly comparable results. Avery[80] has prepared, from experimental data, a series of nomographs indicating the corrosion to be expected of iron-nickel-chromium alloys in air and flue gases at temperatures of 1600–2000°F. After a study of scaling of various steels in sulphur dioxide/oxygen/nitrogen atmospheres at high temperatures, Nicholson and Kwasney[81] find that increased temperature is a more serious factor in scaling than increased concentrations of oxygen or sulphur dioxide.

The present state of knowledge of atmospheric corrosion is summarized by Strong,[82] who discusses also methods of protection. Valuable information has been provided by tests in which chromium and chromium-nickel steels were exposed in an industrial atmosphere in Pennsylvania for a period of 10 years. The results of these tests, reported by Snair,[83] show that the corrosion resistance of straight chromium steels, containing 12–28% chromium, increases with increasing chromium content. In chromium-nickel steels, however, increase in chromium content above 18% and in nickel content above 8% produces no appreciable improvement in corrosion resistance. The corrosion resistance of chromium-nickel steels containing columbium, titanium, or vanadium, compared with the normal 18/8, was found to depend upon the heat-treated condition. Considerable improvement in corrosion resistance, as a result of such modifications, was evident in the samples heat-treated at 1200°F., but no similar improvement was observed in the fully annealed condition. Welding of stainless alloys had little or no effect on corrosion resistance. Binder and Brown[84] confirm the beneficial effects of increasing chromium content in straight chromium steels upon resistance to industrial and marine atmospheres.

An interesting phenomenon is described by Fontana and Beck,[85] who show that a passivated 18/8 stainless steel surface is activated by exposure to a vacuum; passivity returns again upon exposure to air. As electron diffraction methods could detect no trace of oxide layers on the passivated surface, it is concluded that passivity results from a physically adsorbed layer of gas molecules. Cone and Anderson[86] also consider the possibility of passivation due to an adsorbed layer of gas.

Cathodic methods are now generally accepted as being the most suitable for pipeline protection. The underlying principles of this method of protection are discussed by McRaven.[87] Those parts of a pipeline, to which air has free access become oxidized so that a cathodic surface is in contact with the soil; in regions where the oxygen supply is insufficient to maintain an oxide film, the bare steel surface behaves as an anode. The cell action, and the consequent corrosion, may be reversed by the external application of a suitable counter-current. Five year tests in badly drained swampland, in which corrosion of pipelines was successfully combated by cathodic protection, are reported by Huddlestone.[88]

In experiments on the corrosion of steel by boiling water, Gould and Evans[89] show that the form and severity of the corrosion depend upon the supply of oxygen to the surface. Under anaerobic conditions the steel reacts with water, with evolution of hydrogen, to form a continuous oxide film over the surface. This film, which initially is probably ferrous hydroxide and later is converted to magnetite, affords considerable protection to the steel against subsequent attack. However, in the presence of oxygen the oxidation of ferrous hydroxide to magnetite occurs at a distance from the metal causing discontinuities in the film, which in consequence is no longer able adequately to protect the metal from attack. With a supply of oxygen, the degree of corrosion is intensified by the presence of salts in the water and decreased by sodium hydroxide; no similar effects are operative under anaerobic conditions.

A subject closely related to the preceding is the investigation by Wormwell[90] on the influence of movement upon corrosion in a liquid medium. When a specimen of mild steel is rotated in 0·5N-sodium chloride solution, increased speed of rotation increases the rate of corrosion. It is suggested that rotation of the specimen increases the turbulence of the liquid and the supply of oxygen to the metal surface, with resultant intensification of corrosive attack. A greater effect upon corrosion rate is produced by initial motion than by a subsequent increase in speed. When the specimen rotates at 2 r.p.m. corrosion is three times as rapid as when the specimen is at rest; with the speed of rotation increased to 260 r.p.m. however, the corrosion rate is only 12 times the stationary value.

Information, not previously available, on the constitution and structure of oxide films, formed on alloys of iron, cobalt, nickel, and chromium, has been provided by the electron diffraction studies carried out on the films *in situ* by Hickman and Gulbransen.[91] This evidence shows that iron and chromium diffuse more rapidly to the surface than ions of the other metals; nickel oxide, for instance, is never found on the surface even of alloys containing large percentages of nickel. Except for iron and chromium, metals occurring to the extent of less than 5% in the alloy never appear as simple oxides on the surface.

The extensive and important work carried out by the Joint Corrosion Committees of the British Iron and Steel Research Association has been summarized and correlated by Hudson.[92]

Surface treatment

In a brief consideration of the mechanism of steel pickling, Reavell[93] postulates an electrochemical theory, according to which, scale and base metal in contact in the presence of an electrolyte set up various electrolytic cells such as Fe-Fe_2O_3, Fe-FeO-Fe_3O_4, and Fe-Fe_3O_4-Fe_2O_3. This cell action causes some of the higher oxides present to be reduced to the ferrous state, in which form they react with the acid ions present to form ferrous salts which pass into solution. Bablik,[94] also discussing the chemistry of pickling, includes a short account of the effect of inhibitors. An extensive review and bibliography of the work done on inhibitors in pickling baths has been prepared by Imhoff.[95] Methods for the disposal and utilization of waste pickle liquors are described by Hoak,[96] who includes processes developed in the laboratory but not yet applied in industry.

Electrolytic polishing of steel is receiving much attention, and the methods available, with a brief consideration of the theory involved, are reviewed by Honeycombe and Kemsley.[97] Evans and Lloyd[98] find that, for the production of decorative finishes on 18/8 stainless steel, an electrolytic bath containing 37% phosphoric acid, 56% glycerol, and 7% water by volume gives the best results. Sparks[99] concludes that stainless steels may be polished in any bath containing more than 50% free sulphuric or phosphoric acid, or both, but that for the polishing of carbon steels, only baths containing 9–28% of water are suitable. The application of electrolytic polishing for metallographic purposes is considered by Merchant,[100] who does not recommend solutions containing phosphoric or sulphuric acids because of the possible pitting that may result. Acids preferred for metallographic polishing are perchloric, nitric, and chromic acids, diluted where possible with acetic anhydride, acetic acid, or alcohol. Specimens containing the graphite phase, large amounts of slag or other discontinuities do not respond to electrolytic polishing.

The relative efficiency of different forms of powdered carbon as carburizing agents has been investigated by Stäger, Brandenberger, and Kobel.[101] Graphite and various forms of lampblack precipitated from gases under different conditions have been tested as carburizing agents at 1200° *in vacuo.* It is found that there is marked migration of the graphitic carbon into the steel, but no carburization occurs with the amorphous powders which, however, develop carburizing power after graphitization at 2000°. Carburization of steel in cyanide baths is discussed by Komarnitsky,[102] who advocates the addition of alkaline earth catalysts, such as barium cyanide, to the sodium cyanide bath, which should be operated at a temperature of 840–950°.

Development work on the application of protective phosphate coatings to steel continues, and the work done has been reviewed by Darsey and Cavanagh.[103] Other coating processes of interest include Calorizing, described by Sayles,[104] in which a corrosion resistant alloy of aluminium and iron is formed on the steel surface, and nickel-zinc Corronizing, described by Conradi[105]; this process is used to protect metals such as steel, brass, or bronze from attack by sulphurous gases. The base metal is electroplated, first with nickel and then with zinc, and finally heat-treated at 700°F. to permit inter-diffusion of the zinc and nickel.

Heat treatment, metallography, and welding

The application of controlled atmospheres to heat-treatment processes such as bright annealing, carburizing, malleablizing, nitriding, and gaseous deoxidation is discussed by Jenkins.[106] Increasing use is being made of synthetic atmospheres to control the metal/gas reactions that occur during heat-treatment. Two main types of controlled atmospheres are used in the heat-treatment of steel, those derived from synthetic ammonia and those from the partial combustion of hydrocarbon gases such as town's gas. The production of heat-treatment atmospheres from the combustion of town's gas is described elsewhere by Jenkins.[107] The gas is initially burnt with an air/gas ratio of less than 1·75 : 1, though its composition may subsequently be modified by further treatment, *e.g.*, reheating, after drying, lowers the carbon dioxide content and consequently decreases the decarburizing power of the gas. The bright annealing of high carbon steels at 680° illustrates the effect of such modification; when partially burnt town's gas is used as produced, excessive decarburization occurs; if however, carbon dioxide and water vapour are eliminated, the atmosphere becomes carburizing. Liedholm[108] describes the occurrence of quench-cracking, which results from too high a hydrogen concentration in the heat treatment atmosphere.

Application of the electron microscope to metallographic purposes is comparatively recent. Its development, severally described by a number of authors including Davy,[109] Haine,[110] and Cosslett,[111] has made possible the examination of many of the finer structural details that are beyond the resolving power of the optical microscope.

The transformation of austenite continues to provide the basis for investigation, and McReynolds[112] describes a method for observing the austenite-martensite transformation in a specimen, by measuring the change in its electrical resistance. To ensure uniform temperature and correlation of temperature and electrical resistance, small wire samples are used. From *X*-ray and microscopic studies of the transformation of iron-carbon alloys, Wrazej[113] concludes that austenite is not homogeneous but contains three pseudo-phases which are designated γG, γS, and γE, in accordance with the G, S, and E points of the equilibrium diagram. These three pseudo-phases differ in their crystal structure and in their behaviour on quenching, when γG is transformed to ferrite, γS is transformed to martensite, and γE is retained as austenite.

The mechanism of graphite formation in cast irons and in nickel-carbon and cobalt-carbon alloys has been extensively studied by Morrogh and Williams,[114] who find that the behaviour of graphite in these materials is closely analogous. Graphite in cast iron may occur in the form of flakes, spherules or nodules, or alternatively as very fine " undercooled " graphite. The mode of solidification determines the structure of the precipitated graphite. The coarse graphite structures are formed when solidification produces a eutectic of solid solution and graphite; the fine " undercooled " graphite occurs when solidification produces a eutectic of solid solution and carbide, which subsequently decomposes after solidification to yield fine graphite. It was found that of the three carbides involved, iron carbide is the most stable, nickel carbide the least, and cobalt carbide intermediate between the other two. As a result of this, many properties show a corresponding gradation from iron-carbon alloys, through cobalt-carbon alloys to nickel-carbon alloys. Graphite nodules, for instance, are easily formed in nickel-carbon alloys, with some difficulty in cobalt-carbon alloys and only with great difficulty in cast irons. Similarly in cast irons and cobalt-carbon alloys, the carbide may be stabilized by the addition of such elements as tellurium; corresponding carbide stabilization cannot be effected, however, in nickel-carbon alloys.

Much investigation has been devoted to attempts to prevent graphitization resulting from welding. In steel, deoxidized with heavy aluminium additions, precipitation of graphite in a continuous brittle film occurs in those regions that have been subjected to severe heating to the Ac 1 point during welding, according to Hoyt, Williams, and Hall.[115] They suggest that graphitization may usually be prevented by heat treatment at 705–745° after welding. As pointed out by Smith, Urban, and Bolton,[116] however, no heat treatment method of preventing graphitization seems to be entirely satisfactory, and therefore it is advisable to stabilize the carbides with alloy additions to the steel.

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NON-FERROUS METALS

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THE year has seen the publication of a large number of papers of considerable practical and theoretical interest, but it is not easy to pick out any for special mention. A well-attended symposium on powder metallurgy was organized by the British metallurgical societies and produced some excellent discussions. In theoretical metallurgy, both French and British workers have claimed that by careful attention to technique it is possible to reveal the existence of slip lines on surfaces prepared after straining, and attention has been drawn, apparently for the first time, to the general and, now that it is pointed out, rather obvious, fact that the grain size produced in a metal by annealing is limited by the thickness of the specimen. The embrittlement of phosphorus-deoxidized copper by small amounts of bismuth has been studied in great detail; and careful experimental work on the bright annealing of brass strip has enabled a satisfactory process for this difficult operation to be worked out. Among the engineering applications of non-ferrous metals, important developments have been recorded in alloys for high temperature service in gas turbines and turbo-superchargers.

Ore dressing and process metallurgy

An important contribution to the literature on milling and concentration practice has been published by the American Institute of Mining and Metallurgical Engineers as a special volume commemorating Dr. Robert H. Richards, " the father of the modern art of ore-dressing," who was Professor of Mining Engineering at the Massachusetts Institute of Technology from 1873 to 1914 and who died at the age of 100 on 26th March, 1945. The memorial volume collects 68 papers and discussions presented at meetings of the Institute from 1943 to 1947. Among the recent papers is a new study[1] by Rogers and Sutherland, of the Commonwealth Council for Scientific and Industrial Research, Melbourne, of the theory of the flotation process. The view is taken that earlier theories, such as those due to Taggart, Dean, and Wark are oversimplified and too generalized; and that each example of flotation needs to be considered as a separate problem. A detailed critical examination of the factors which affect flotation is supplemented by the results of experimental work and a set of principles is formulated which, it is claimed, determine whether any specific reagent behaves as an activator or a depressant and any organic electrolyte as a collector. A further paper[2] by the same authors with E. E. and I. W. Wark draws attention to the value of paraffin chain salts as collectors for silicates and other minerals not responsive to the familiar flotation agents, such as the xanthates. The unusual properties of the paraffin chain compounds are attributed to micelle formation. If the new agents are added in excess, flotation does not take place, probably as a result of the armouring of the bubble with an excess of the collector, which then hinders contact between the mineral and the bubble. The use of chelate-forming organic compounds as flotation agents has been described by G. Gutzeit.[3] These act as depressants for the common gangue minerals because they bind the activating cations into practically undissociable complexes and so remove them as factors in the process. Examples of compounds which have been found effective when added in small quantities before the alkali to the flotation cell are aspartic, glutamic, and ethylene diamine tetra-acetic acids. The importance of considering the solubility products when assessing the factors influencing bubble-formation in flotation has been emphasized by Taggart and Hassialis.[4]

Some Russian[5] work on the widely-used xanthate flotation agents explains their action as due to interaction between the anions of the xanthate and the dissolved cation of the galena, chalcopyrite, pyrite, blende, or similar mineral under treatment. This leads to the precipitation of the heavy metal xanthate and to its selective attachment to the sulphide particles in the pulp. In the flotation of calcite, barytes, fluorspar, and similar polar non-metallic minerals the action is more complex.

The use of laurylamine hydrochloride as an alternative to the more expensive xanthate flotation agents has been studied.[6] Contact-angle measurements were made in dilute solutions for sphalerite, galena, quartz, and pyrites and the results used in working out various flotation procedures. Good separations were secured from sphalerite-quartz and galena-quartz mixtures; and differential flotation of a Pb-Zn ore was achieved by first floating the galena with K ethyl xanthate and then floating the sphalerite with the cheaper amine.

In Australia, attention has been given to improved methods of concentrating and treating some of the potentially important tin deposits. At Mt. Bischoff,[7] the ore contains 1·46% of cassiterite and 0·87% of stannite; and although relatively clean sulphides can be liberated readily, the cassiterite is intimately associated with quartz. The present practice is to crush the ore in stamps; but it has been shown that recovery could be improved by 10% by using roll crushers and so preventing excessive sliming. A sulphide-cassiterite concentrate is produced by gravity concentration on shaking tables and subsequently roasted. It is not satisfactory to roast before crushing, but the possibility of removing sulphides by flotation has been investigated. At Aberfoyle[8] (Rossarden, Tasmania) deposits containing 1·5% of tin and 0·25% of WO_3 are crushed, dried, sized, and passed through a magnetic separator to recover a tungsten concentrate. The non-magnetic product is treated in flotation cells and a tin concentrate collected, the calculated recovery of tin being 86%. The deposits at the Greenbushes tinfield[9] in West Australia are of special interest, as they contain a high proportion of tantalite (for which there is an increasing demand) in association with the cassiterite. The gravity concentrates contain about 32% of Ta_2O_5 and 56% of SnO_2, and laboratory tests indicate the possibility of separating a marketable product containing about 73% of $(Ta,Cb)_2O_5$ and 2·6% of SnO_2 by magnetic separation. The general problem of the flotation of cassiterite and associated minerals has been the subject of a detailed study by Herzt, Rogers, and Sutherland.[10] They find that sulphated and sulphonated paraffin chain compounds are excellent collectors and promise to be selective. A process for floating cassiterite from ores containing iron sulphides, quartz, and more than 0·2% of tin has been worked out and consists in (*a*) grinding in an alkaline circuit of $p_H > 10$, (*b*) reducing the iron sulphide content to $< 1\%$ by flotation with xanthate, and (*c*) conditioning with sodium cetyl sulphate at p_H 3·0–5·0 and then floating the cassiterite.

In the field of process metallurgy, attention has been given to the production of lithium. During the war, this metal was used in Germany in appreciable quantities for Bahnmetall, a bearing metal containing 0·04% of lithium; and more recently it has found an increasing application elsewhere as a degassing agent in the founding of copper and copper alloys. A survey[11] of the extraction methods followed in Germany shows that the main source was the tailings left after extraction of tungsten and tin from the zinnwaldite deposits at Zinnwald, near Freiberg. These were magnetically concentrated from 0·2–0·5% Li to 1·5% Li, and roasted with K_2SO_4 at 900° in a rotary kiln. On leaching with hot water, crude Li_2SO_4 was extracted, and this was purified and converted to lithium salts. The metal was prepared by electrolysis of a fused 48 : 52 KCl–LiCl mixture. More recently, Kroll and Schlechten[12] have shown that very pure lithium may be readily prepared by reducing a mixture of Li_2O and CaO with silicon or, preferably, with aluminium in a vacuum of less than one micron at 950–1000°. The chief item of expense in these and all methods previously proposed is the high cost of the lithium salts; and the possibility of producing the metal directly from the mineral spodumene (which contains about 5% of LiO_2) by a modification of the Pidgeon magnesium process—heating a mixture of spodumene with lime and either ferrosilicon or aluminium in a vacuum furnace and distilling off the lithium metal—was investigated by Stauffer[13] under an American Government research contract. A substantial excess of lime is needed; and lithium begins to distil at about 1000°, though for high yields it is necessary to run at 1050–1100°. The pressure should be below 100 microns. The lithium which has so far been produced by this process is of lower purity than that obtained by electrolysis.

Attention continues to be given to the production of electrolytic manganese. The U.S. Bureau of Mines investigators[14] have studied the effects of impurities on the current efficiency in a diaphragm cell. Additions of cobalt, nickel, copper, zinc, or manganese may reduce the efficiency, but arsenic, lead, and vanadium have no effect. The performance of various lead alloys as anodes has also been studied.[15] For some reason, still obscure, the nature of the anode has a marked influence on the efficiency of electrodeposition. Lead containing 1% each of silver and arsenic was found to have the best combination of properties. It corrodes only 12% as rapidly as the lead-silver alloy currently used in production, it has the effect of reducing oxidation of the manganese by 55%, and is at least as good as regards physical properties and performance in the cell. The pilot-plant of the United States Bureau of Mines at Boulder City, Nevada, has been engaged in examining the possibility of producing electrolytic manganese from (*a*) the metals reserve stock piles at Deming, N. Mexico, Cushman, Ark., and Phillipsburg, Montana,[16] and (*b*) nodules (containing manganese, iron, and lime) at Chamberlain.[17] A satisfactory product was obtained from all of these ores.

The production of titanium and zirconium, among the minor metals, has been reviewed by Kroll and Schlechten,[18] who have made important contributions to the work on these metals sponsored, again, by the United States

Bureau of Mines. A simple method of producing tantalum and columbium as reasonably pure powder has been proposed [19] by Wulff and his colleagues at the Massachusetts Institute of Technology. A mixture of solid powdered tantalum (or columbium) pentachloride with potassium chloride is reacted with magnesium chips at 450–470°. The magnesium chloride which is produced forms a liquid bath with the potassium chloride and prevents reduction from proceeding too rapidly. After reaction, the salts are readily leached from the reduced metal.

Melting and casting

The process of solidification of an ingot, in some ways the most important of all metallurgical operations, has been subjected to mathematical analysis by Fell.[20] The shapes of the pipes formed by shrinkage in an upright cylindrical mass when cooling proceeds (*a*) from the vertical sides only and (*b*) from the sides and from a flat base, were determined by calculation. The results were in good agreement with those found in specially cast ingots of aluminium alloy containing 12% of silicon. Fell points out that information, otherwise unobtainable, about the changes taking place within an ingot during solidification may be obtained from observations of the surface level of the still-molten liquid. The cooling ingot is, in effect, its own dilatometer.

A welcome addition to the rather scanty literature on centrifugal casting is contributed by Lee and Northcott, of the Armament Research Department, Woolwich, in an account[21] of the centrifugal casting of copper alloy wheels in sand moulds. Few advantages were found for centrifugal casting with aluminium bronze or high-tensile brass, since with these alloys sound castings were readily obtained by static methods. On the other hand, the soundness of phosphor-bronze or tin-bronze castings was increased by up to 35% by centrifugal casting since the process largely eliminates both shrinkage and gas porosity, and quickly closes up any dispersed gas porosity resulting from the metal-mould reaction.

The complex problem of obtaining sound static castings in bronzes, phosphor-bronzes, and gunmetals continues to attract attention, and a useful summary has been given by Pell-Walpole[22] of the results of his investigations on the effects of the rate and temperature of pouring and of mould conditions on shrinkage porosity in chill-castings. The rate of pouring was found to be by far the most important factor affecting the production of sound castings, and the harmful effects of shrinkage porosity can be minimized by pouring at the slowest rate which will just avoid the formation of cold shuts. The critical pouring rate is directly proportional to the periphery of the ingot section for any given alloy composition, and the relationship was established for all the standard bronze compositions. The pouring temperature is of little importance providing the ingot is poured slowly, but high pouring temperatures accentuate the unsoundness found in quickly-poured ingots. The temperature and wall-thickness of the mould and the type of mould dressing have little effect on porosity, but considerably influence the quality of the surface of the ingot. The effects of a number of both refractory and combustible mould dressings have been studied,[23] and it is concluded that many commonly-used dressings do not prevent blowing, particularly under unfavourable mould and pouring conditions, unless applied so thickly as to induce exudations (tin-sweat) and entrapment of charcoal.

Stockholm tar and one commercial refractory dressing are fairly resistant to blowing, but best results were obtained with a thick coat of a resinous aluminium paint containing about 20% of aluminium. The effects of additions of 2·5–10% of zinc to tin bronzes cast by Pell-Walpole's technique have been investigated by Winterton,[24] who finds that zinc is generally a disadvantage, particularly since when it is present it is impossible to pour sufficiently slowly to prevent the formation of interdendritic shrinkage cavities. The effects of additions of phosphorus to an 88 : 8 : 4 gunmetal made from pure virgin metals in an induction furnace have been studied by Colton and Loring,[25] in America. Additions of less than 0·02% increased the density of sand castings and definitely improved the running characteristics of the alloy, as observed in test melts sand-cast in spiral " fluidity " moulds. Larger additions were detrimental to the mechanical properties and reduced the density of the sand castings, probably because they widened the freezing range and so encouraged the formation of interdendritic cavities. Segregation in both chill-cast and sand-cast ingots of 10% tin-bronze has been studied by Pell-Walpole and Kondic.[26] Chill-cast ingots show marked inverse segregation, which is explained by relating the changes which occur in the constitution of the still-liquid portion of the cooling ingot during the process of solidification to the movements of this liquid, and particularly to the intercrystalline feeding which must occur to compensate for shrinkage. Segregation in a sound ingot of this type can be greatly reduced by annealing at about 800°. Sand-cast ingots show normal segregation and a high density in the surface layers, but marked inverse segregation and porosity in the interior. Apparently the inverse segregation here is caused by an outflow of tin-rich liquid from the centre at a late stage of solidification as a result of evolution of hydrogen which is absorbed from the sand mould during pouring.

Good reviews of the principles of foundry practice have been presented for aluminium- and magnesium-base alloys by Hinchcliffe,[27] and for magnesium-base alloys by Gray.[28] A new method[29] for simultaneously cleaning, degassing, and grain-refining magnesium alloys, tried so far only on a laboratory scale, consists in treating the molten metal at 675–690° with chlorine which has first been bubbled through carbon tetrachloride at about 27°. If, after treatment, the metal is solidified and remelted, it will still give fine-grained castings without the need for the superheating operation which is normally necessary with these alloys. Coarse-grained castings result if the treated metal is held at a low temperature for a few minutes, but the grain-refining effect of the treatment may be restored simply by reheating the melt to a proper pouring temperature.

Powder metallurgy

The important symposium on powder metallurgy organized by the Iron and Steel Institute and held in June, 1947, should as Jones[30] remarked in his introductory survey, " do much to win again for Britain the leading position in the industry." In all, 28 papers were presented and covered a wide range of interests, particularly those more closely allied to practical applications of the process. Theoretical and fundamental aspects received, perhaps, rather less attention. A general review of the methods employed in the production of metal powders was given by Miller,[31] and Meyersberg[32] dealt very fully with modern methods of manufacturing flake powders of aluminium, copper, and bronzes by the stamp and " modified ball mill " processes for the paint, lightweight concrete, and pyrotechnics industries. Later in the year, the first account to be published of the " atomization " process for producing aluminium powder was presented by Thompson,[33] together with an unusually detailed study of the effects of process variables on the output and quality of the powder. In modern equipment, molten metal is transferred to a gas-heated clay-graphite crucible from which it flows to a refractory " atomizing " nozzle, the special feature of which is that compressed air is blown through an annulus concentric with the metal orifice. The " atomized " powder is carried by the air stream into a large-diameter tube, the mouth of which is encased in ½in. armour plate (as a precaution in case of explosion) and then passes through trunking to a cyclone, where the majority of the powder is deposited and continuously collected. Coarse grade 36/dust powder is produced at a rate of 6–7cwt./hour, and fine grade 200/dust at up to 1cwt./hour. The powder is surprisingly free from oxide and of uniform shape, the length of each particle being about twice as great as the other dimensions. Control of size characteristics is achieved principally by altering the area of the metal orifice; most other process variables are of minor importance.

The application of powder metallurgy methods to the production of dust cores for telecommunications equipment was described by Buckley,[34] who dealt especially with the properties of 3·5% molybdenum permalloy cores, and an account of present practice in making sintered Alnico magnets was given by Garvin.[35] Early efforts to compact and sinter the crushed cast alloy were unsatisfactory owing to the hardness of the particles, and later attempts to sinter a mixture of powders of the constituent metals failed owing to the thin oxide films on the aluminium particles. The turning point in the development of the process was the discovery that powders prepared from master alloys of aluminium with cobalt, nickel, or iron, were sufficiently free from surface films to sinter well together. Extreme precautions are nevertheless necessary to avoid oxidation during sintering, and the compacts may be packed with iron-aluminium or titanium-aluminium powder to prevent traces of residual oxygen from the furnace atmosphere (of dry commercial hydrogen) from reaching them. The production by powder metallurgy of an alternative magnetic material, Permet, which unlike Alnico, can be readily machined, has also been described.[36] The material contains cobalt 30, copper 45, and nickel 25%, and after heat-treatment has a maximum energy value (BH max.) of 700,000.

The production of hard-metal carbides was described by Brownlee, Geach, and Raine (who dealt with the preparation of carbides), and by Burden (who gave an account of the pressing and sintering operations). In addition, Sandford and Trent[37] contributed an exceptionally detailed study of the physical metallurgy of the sintering process which, they point out, is unusual, even in the field of powder metallurgy, since " after a single pressing and sintering cycle, the density of the sintered piece approaches closely to the theoretical." Five stages are recognized in the heating process. In the first, up to about 1000°, the cobalt particles recrystallize and some welding occurs. In the second, as the temperature is raised to 1320°, solid solution of tungsten carbide in cobalt is observed and is accompanied by appreciable contraction, even though no liquid phase is present. Then, at 1320°, the cobalt-tungsten carbide eutectic is formed and wets the carbide grains, completing contraction by the action of surface-tension forces. At 1400°, residual porosity is eliminated after a short period, probably by solution of gas in the liquid phase with subsequent diffusion to the surface. If the compacts are heated above 1600° large holes appear, probably as a result of reaction between carbon and impurities such as silica. The changes which occur during cooling, the effects of an excess or deficiency of carbon, the probable form of the tungsten-carbon-cobalt system, and the properties of sintered carbides are also considered. A further contribution to the theory of the sintered carbide process has been made by Metcalfe,[38] who has investigated by *X*-ray diffraction methods the mutual solid solubility of tungsten carbide and titanium carbide. Titanium carbide has little solid solubility in tungsten carbide, even at temperatures as high as 2500°, but it dissolves 73% by weight of tungsten carbide at 1400°, and 95·5% at 2450°.

Three[39, 40 41] of the symposium papers dealt with porous metal components made by powder metallurgy, and in the final section detailed investigations were reported on the manufacture and properties of many types of ferrous and non-ferrous sintered components. Sintered iron-copper compacts were studied by Northcott and Leadbeater[42] and by Chadwick[43] *et al.* The strongest sintered compacts are those pressed from mixtures of iron with about 25% of copper, and have a tensile strength of 32–40 tons per sq. in. Northcott draws attention to the fact that compacts of exceptionally high density can be produced by impregnating compressed iron skeletons with molten copper, a process which has received some commercial exploitation in America. Finally, copper compacts were studied by Cook and Pugh,[44] copper-lead and similar bearing metals by Tait,[45] and some brass and bronze engineering components by Lennox.[46] Experiments at the Royal Aircraft Establishment on sintering copper-aluminium powders were described by Bickerdike.[47]

Some valuable studies of the fundamental operations of powder metallurgy have been reported elsewhere. The pressing operation is considered by Seelig and Wulff[48] to comprise three overlapping phases. In the first, when the compact is consolidated, the shape of the particles is of major importance, and most of the applied energy is absorbed by interparticle friction. In the second, when the pressure rises, die-wall friction absorbs most of the energy and undesirable density gradients tend to be set up; and in the third the particles may be cold-worked or even broken up. A further paper by Seelig[49] emphasizes that the shapes that can be pressed by powder metallurgy are limited because the powders do not flow as liquids and, when compacted, have restricted plastic flow. Friction on the die-walls is more important than inter-particle friction, and proper lubrication is essential to produce compacts of reasonably uniform density, to prolong die life, and to assist ejection. The operation of hot-pressing has been examined by Strauss,[50] who points out that above a certain temperature (related to the melting point of the metal) there is a sudden contraction of volume, the material assuming a degree of plasticity unobtainable in conventional cold-pressing. By making use of this " moment of active deformation " very light pressures can give very dense compacts in a very short time. A theory of fritting of metal powders has been developed by Huttig and his collaborators at Prague for many years, and a series of 13 of his papers has been summarized by Jones.[51] In his most recent statement,[52] Huttig considers that, on being heated, a crystal successively passes through stages at which self-diffusion in the surface, self-diffusion in the lattice, melting or loss of order in the surface, and melting in the lattice take place; and that there is a direct relation between the absolute temperatures at which these changes occur and the absolute temperature of melting. These conceptions are applied to explain the sintering of two or more crystals in contact. The views of Huttig are not, it may be noted, universally accepted, and the current American point of view, in which much stress is laid on the effects of surface-tension forces, has been expounded by Rhines[53] in a " seminar on theory of sintering."

Constitution and metallography

In the theoretical study of alloy systems, and in dealing with almost any of the properties of the component alloys, it is invariably necessary to go back to the constitution diagram as a basis of reference. The major constitutional investigations reported during the year have all been concerned with ternary systems. From the Dept. of Metallurgy of the University of Birmingham, Raynor and his associates have published a series of papers dealing with aluminium-rich alloys of aluminium with iron and nickel,[54] cobalt and nickel,[55] and manganese and cobalt.[56] The aluminium-rich aluminium-nickel-iron alloys contain a ternary compound which appears from crystallographic evidence to be based upon the composition $FeNiAl_9$ and to be isomorphous with Co_2Al_9. The results of micrographic and *X*-ray examination of the system, supplemented by the analysis of primary crystals extracted from the slowly-cooled alloys, give strong support to the view that, along the aluminium-rich boundary, nickel replaces iron atom for atom in this compound over a range of about 11% by weight, and the limiting composition, representing the maximum solubility on nickel in $FeNiAl_2$ occurs at 2·58% iron and 28·03% nickel, corresponding (on the basis of Raynor's general theory of the behaviour of transitional elements when alloyed with aluminium) with an electron : atom ratio of 2·285. It was therefore expected that, in the aluminium-cobalt-nickel system the compound Co_2Al_9 would dissolve a large amount of nickel by atomic replacement up to a limit corresponding to the same electron : atom ratio. This prediction was borne out by the results of the experimental work, calculated and observed solubilities being in excellent agreement. It was further suggested by the theory that the system should contain no ternary compound in equilibrium with the primary solid solution and that the solubility of cobalt in $NiAl_3$ should be low; both of these predictions were verified. This work provides an unusual example of the success of theoretical reasoning in forecasting the form of an unknown equilibrium diagram. The agreement of the experimental results in the aluminium-manganese-cobalt system with theory are, however, at first sight rather less convincing. Here, it was expected that a ternary compound similar to that occurring in the aluminium-manganese-nickel system should be formed. However, no evidence for its occurrence was obtained. It is possible, however, that the compound may be present without ever coming into equilibrium with the primary solid solution, and could only be found by examining alloys rich in manganese and cobalt. On the other hand, it is possible to argue that the compound $MnCoAl_6$, analogous to $FeAl_3$, might be expected to form at the expense of a compound with the arrangement $MnCoAl_8$; and further work will be necessary to establish which view is correct.

The aluminium-chromium-manganese alloys have also been studied by Raynor,[57] and it is found that solid solutions of chromium and manganese in aluminium show a greater lattice contraction than is to be expected from considerations of the atomic diameters of the elements. This may be caused by the lower valency of the solute reducing the overlap across of (200) faces of the Brillouin zone of the aluminium structure, an effect which is conceivable if the unfilled *d*-shells of the atoms of the transition elements take up electrons from the aluminium atoms.

The copper-rich alloys in the copper-manganese-aluminium system have been studied by Dean *et al.*[58] in America as part of a general study of alloys which may provide an industrial application for electrolytic manganese; and the constitution of slowly-cooled aluminium-rich alloys in the same system has been investigated by Day and Phillips[59] as part of a general programme of work on the constitution of aluminium alloys under conditions of metastable equilibrium such as are likely to be met with in commercial practice.

The discovery, by Jacquet, some years ago of the process of electrolytic polishing introduced an important new tool to the technique of metallography. During the war, Jacquet continued research in France on methods of micrographic examination of metals—particularly of copper and copper alloys—and has now published[60] a detailed review of this work. Some slight modifications have been made in the original polishing solution, and it is emphasized that electrolytic polishing is particularly suited for revealing inclusions of all kinds. By etching, after electrolytic polishing, for a very short time (1–3 sec.) in a special reagent, prepared by saturating aqueous ammonia with hydrogen sulphide and keeping the solution until it turns yellow in colour, it is claimed that extremely fine discontinuities or " microfissures " are revealed in cold-worked silicon- or manganese-deoxidized copper. Microfissures have not been observed in oxygen-free high conductivity or vacuum-melted copper, and it is thought that oxides and other impurities are concerned in their production. The most remarkable claim made by Jacquet, however, is that it is possible by " electrochemical attack " after etching to reveal slip-lines in cold-worked copper. Hitherto, it has always been considered that the traces of slip-lines could be observed only on surfaces which have been polished *before* straining; and that they could not be revealed by any process of etching on surfaces prepared after straining. However, examples are now illustrated of slip-lines in many samples of cold-worked copper, and the structures are compared with the *X*-ray diffraction patterns obtained from the same specimen. Slip-lines were detected after deformations so small in amount that they had no influence on the *X*-ray patterns, and it is shown that they are not distributed uniformly throughout the crystals. The " electrochemical attack " used to reveal these slip-lines is carried out after electrolytic polishing by short-circuiting the terminals for a minute or longer so as to allow a polarization current to flow and bring about a very even and slight degree of etching. Markings of a similar type have been observed independently by McLean[61] in lightly-deformed brass on sections electrolytically polished and then etched in alkaline copper ammonium chloride solution or in hot, very dilute, orthophosphoric acid, and are termed by him "striations." Electron-microscope photographs support the view that these are in truth slip-lines, and it is suggested that failure to observe the markings in the past has probably been due to the imperfections of mechanical polishing.

The process of thermal etching has been examined afresh by Shuttleworth, King, and Bruce Chalmers,[62] with special reference to its application to the study of crystal growth and of the movements of crystal boundaries in pure silver. Electrolytically polished silver, when heated at 920° in vacuum, hydrogen, or nitrogen develops grooves at grain boundaries and twin boundaries. By means of a special technique, devised to permit microscopic observation of the surface of a heated polished specimen, it was found possible to follow the progress of grain growth, since the curious feature was established that the grooves moved with the boundaries. It is suggested that the surfaces tend to alter so as to meet at angles determined by surface tension forces; at equilibrium the surfaces of adjacent grains curve inwards and a groove appears. Methods for the production of etch figures of perfect geometric form on electrolytically polished surfaces of pure aluminium have been developed by Lacombe and Beaujard,[63] and their use in studying the nature of grain boundaries, the progress of deformation, and imperfections in the structure of single crystals demonstrated in some extremely beautiful photomicrographs. It is shown that the attack of the etching reagent on the grain boundary may be very slight if there is only a slight difference between the orientation of two adjacent crystals, although the boundary may be distinctly revealed if the difference in orientation is greater. This observation explains the great difficulty often encountered in determining the grain size of a sheet having an oriented texture. Further instances of the influence of the state of dis-registry of the atomic lattice at a grain boundary have been described by Forsyth *et al.*[64] Precipitation, for example, might be expected to occur most readily in those boundary regions where there is most atomic disorder; and it was in fact found that in aluminium-magnesium alloys the degree of precipitation varies from boundary to boundary. Further, in a copper-beryllium alloy, an abrupt change in the relative orientation of two grains caused by twinning was observed to correspond with an abrupt change in the amount of precipitate. The process of grain growth in high-purity aluminium when the metal was annealed for periods of 20 sec. to 11 days at constant temperatures between 350° and 650° was studied by Beck[65] and his collaborators at the University of Notre Dame. The results can be expressed in the form $D = D_0 t^n$, where D is the average grain size at time t. Thus, although the rate of growth slows down as the grains become larger, the grain size does not tend to approach a finite limit. The relation, however, holds only if the grain size is well below the thickness of the specimen. In the past, it has not been generally recognized that sheet thickness may limit grain growth, and much earlier work is thus vitiated. A theoretical study of the mechanism by which pointed crystals may grow in aluminium as a result of "stimulation" by another crystal has been reported by Burgers and May.[66] The orientation of the two crystals in this case is almost always that of spinel twins.

The embrittlement of phosphorus-deoxidized copper by small amounts of bismuth has always presented a number of puzzling features, and these have now been investigated by Voce and Hallowes,[67] of the British Non-Ferrous

Metals Research Association. As little as 0·001% of bismuth may cause some embrittlement at temperatures between 450° and 600°, although specimens tested at room temperature after quenching from this range only showed embrittlement when more than 0·002% of bismuth was present. It was established that bismuth can be transferred from specimen to specimen by way of the vapour phase. It is concluded that the agent responsible for embrittlement is elementary bismuth, present in the form of a thin film at the grain boundaries of the copper, and that at temperatures above 600° an increasing amount of bismuth passes into solid solution in the copper. This conclusion has been supported by the results of examination of electrolytically polished samples by the optical and electron microscope by Schofield and Cuckow[68] at the National Physical Laboratory. The solid solubility of bismuth in copper was assessed by Voce and Hallowes to be less than 0·001% below 600° but to increase rapidly at higher temperatures, becoming about 0·01% at 800°. Some anomalous results were obtained, and it is believed that these may be associated on the one hand with a relatively high phosphorus content (which appears to counteract the embrittling effect of small amounts of bismuth in quenched specimens) or with inefficient deoxidation of the melt, which has the same general effect.

Two other, quite different, examples of embrittlement of metals have been examined. Atkinson and Gladis[69] have reported that platinum-ruthenium alloys may be rendered brittle when heated in a blowpipe flame, as in a soldering operation. The trouble is attributed to opening of the grain boundaries by reaction with the atmosphere of the heating flame, but the detailed mechanism remains unknown. The Liquid Steel Temperature Sub-Committee of the Iron and Steel Institute have presented a series of papers[70] as a symposium on the contamination of platinum thermocouples. In recent years, outbreaks of thermocouple embrittlement have been reported by users of the quick-immersion method for measuring the temperature of liquid steel. It is now clear that the trouble is due to the sulphur content of traces of oil in the thermocouple assembly. Platinum is not embrittled by heating in contact with carbon or sulphur alone. If, however, small amounts of sulphur and carbon are present together in a siliceous refractory thermocouple tube, gaseous silicon sulphide may be formed, and this attacks the rare-metal wires forming one or more of a number of silicides of platinum at the crystal boundaries.

Further study of the curious type of deformation which may be produced in non-cubic metals by cycles of alternate heating and cooling has been reported by Boas and Honeycombe.[71] In tin-base bearing alloys containing antimony or antimony and copper, as in pure tin, plastic deformation (resulting from anistropy of thermal expansion) occurs mainly near the grain boundaries, and is characterized by the rumpling of a previously smooth surface. The effect may contribute to the failure of tin-base bearings. It is considered that the absence of the effect in the cubic metal lead may help to explain the success of the war-time substitution of lead-base for tin-base alloys.

Heat-treatment and age-hardening

The bright-annealing of brass strip is one of the most troublesome of industrial heat-treatment operations, owing to the difficulty of preventing oxidation and staining by traces of oxygen-bearing and sulphurous gases and to the rapid rate at which the surface loses zinc by volatilization. The factors involved in these surface changes have been very thoroughly investigated by Jenkins,[72] and it is found that a bloom is formed on brass strip heated in cracked ammonia at 550° even when every precaution is taken to free the furnace tube from absorbed gases and to maintain the purity of the cracked ammonia atmosphere. This effect is due to carbon dioxide and carbon monoxide evolved from the brass itself. It is found that a degreased brass coil can be bright annealed perfectly by first heating up to 500° at a low pressure of about 4mm. of mercury to remove absorbed gases, and then maintaining the brass at 575° under static cracked ammonia for sufficient time to permit zinc to diffuse to the surface from the interior of the strip and restore the surface colour.

The theory of the age-hardening of duralumin-type alloys continues to receive attention. Rohner[73] has advanced a theory of vacant lattice sites based on the view that, before rejection of solute atoms from a supersaturated solid solution, there must be an egress of solute atoms to the interstitial lattice space. The gaps caused by the migration of the solute atoms are held to be the chief cause of the increase in strength and electrical resistivity on ageing. Gayler[74] has continued her very thorough and already classic work on this subject, with a further study of the ageing of a high-purity aluminium alloy containing 4% of copper. Evidence is brought to prove that age-hardening of this alloy is due to precipitation of copper or a copper-rich phase, and the simultaneous formation of crystallites of the aluminium-rich solid solution which is stable at the ageing temperature. It is not due to precipitation of either the α or β forms of $CuAl_2$. The process of precipitation in aluminium alloys has also been followed in America[75] by means of an electron-microscope technique. Thin oxide films were formed by anodic oxidation and then stripped by the mercury process for examination in the electron microscope. In alloys aged at room temperature, the size of the particles were very small (less than 0·03 μ.), but particles up to 0·3 μ. in mean diameter were detected in alloys aged to maximum strength at elevated temperatures.

In a general survey of age-hardenable alloys, Gayler[76] has drawn attention to the existence of two types of precipitation—" discontinuous precipitation," which commences in the grain boundaries of the alloy and generally spreads inwards, and " continuous precipitation " which occurs more or less uniformly throughout the grains at much the same rate at every point, without much regard to grain boundaries. The relation between these processes has been studied[77] by experiments on the age-hardening of standard silver (silver 92·5, copper 7·5%). Both types were observed, and it is shown that normally " discontinuous " precedes " continuous " precipitation. The controlling factor governing the type produced by any given heat-treatment is the degree of supersaturation at the temperature of ageing.

High-temperature alloys

Industrial research into new alloys has, during the last ten years or so, been very largely concentrated upon the development of high-temperature alloys for service in gas turbines. The alloys which have shown greatest promise are nearly all non-ferrous. In this country, " Nimonic 80," a nickel-base alloy containing 19–22% of chromium, not more than 5% of iron, 1·5–3%

of titanium, 0·5 to 1·5% of aluminium, not more than 1% each of silicon and manganese, and not more than 0·1% of carbon has, according to Sir William Griffiths[78] been the standard material since 1942 for aircraft rotor blades. The alloy will withstand 12·5 tons/in.^{2} for 300 hours and 9·5 tons/in.^{2} for 1000 hours before rupture at 750°, and shows a total elongation in creep of 0·1% in 1000 hours under a load of 5·5 tons/in.^{2} at the same temperature.

In America, an extensive programme of co-operative research on high-temperature alloys was undertaken during the war years, and the results obtained have been recorded at a symposium on Materials for Gas Turbines organized by the American Society for Testing Materials. Data on 46 alloys are summarized by Cross and Ward.[79] Stress-rupture tests at 805, 870, and 1090° are presented, and complete creep curves at 730, 805, and 870° given for many of the more promising materials. The results, taken as a whole, suggest that the precision-cast cobalt-base alloys have a longer creep life than any of the heat-resisting steels or other alloys which were tested, or of any wrought materials. One of the best of the cobalt alloys is that known as X–40, containing cobalt 55, chromium 25, tungsten 7, nickel 9, carbon 0·5, and iron 0·55%, with small amounts of manganese and silicon.

Chromium-base alloys were studied by Parke and Bens,[80] who took the view that the brittleness which has hitherto hindered the use of these materials is due to the presence of impurities. In order to reduce the amounts of carbides, nitrides, and oxides in the melt to a minimum, melting and casting were carried out in beryllia or zirconia crucibles in a specially designed vacuum furnace, incorporating a centrifugal casting device. The pressure was maintained below 0·1mm. of mercury, and nitrogen was then readily removed. Carbon and oxygen were removed as carbon monoxide, the composition being adjusted so that the alloys contained 0·02 to 0·05% of carbon. The most promising alloys appeared to be those in the chromium-iron-molybdenum system in the range 15–25% of iron, 25–15% of cobalt, and 60% of chromium. The alloy with 60% of chromium, 25% of iron, and 15% of cobalt was the strongest at 870° of any examined.

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ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES

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In the field of electrodeposition of metallic coatings the trend has been in the direction of improved control of the properties of electrodeposited metals, owing to the stimulus of new engineering applications where strong adhesion and high strength, both at ordinary and at elevated temperatures, are required. For example, aluminium alloys were regarded as difficult to plate with a strongly adherent coating, whereas now there is abundant evidence that the difficulty has been overcome. Chromium, attractive for its high hardness, low coefficient of friction and chemical inertness, has been the subject of much research and development for engineering purposes. Nickel, the most important coating in decorative electroplating, has received much attention in the search for improved methods of control of its adhesion and porosity and of impurities in its plating solutions while, on the more academic side, the discovery of its ability under certain conditions to grow to a smoother surface, both on a macro and a micro scale, may have important practical implications. An increasing amount of attention is being directed towards alloy deposition and a comprehensive research has demonstrated the important properties of cobalt-tungsten alloy coatings. Polishing represents the most costly item in decorative electroplating and, partly for this reason, considerable attention has been given to electrolytic polishing processes which are increasingly being used in industry, often as an aid in metal finishing rather than as the sole method of producing a bright finish. Many developments in primary batteries have been released, giving a clearer picture of the mechanism of the reactions in Leclanché-type dry cells and describing the development and behaviour of cells of the types—silver oxide-zinc, lead dioxide-zinc (or lead), and the Ruben cell.

A number of these publications are probably the outcome of war-time investigations, but the progress they represent or forecast is appreciable.

Electrolytic processes

Extraction, refining, plating, and polishing of metals

Aluminium.—German anodizing practice has been surveyed by a British team[1] who visited 14 firms in West and South Germany. The sulphuric acid process using d.c. probably accounted for 70% of the anodizing done in Germany; some firms used a.c. with sulphuric acid, and some used an oxalic acid electrolyte with d.c. or a.c., or d.c. followed by a.c. A fairly detailed abstract of a document on the Seo-Foto process is appended.

Aluminium and its alloys have always been considered difficult to electroplate with other metals, but recent work has shown that strongly adherent coatings may be formed on many of the alloys by first precipitating a film of metallic zinc on the surface by dipping into a solution of sodium zincate and then plating as if the metal were of zinc; an essential preliminary to the treatment in sodium zincate is etching to remove noble constituents, such as $CuAl_2$, from the surface. This method has been investigated in Great Britain for a wide range of alloys by a quantitative study of the adhesion of nickel deposits.[2] With the duralumin alloys, the adhesion approached the tensile strength of the metal but it was somewhat less strong, though more than three-quarters the tensile strength, with alloys containing appreciable amounts of magnesium, for which a modified cleaning method was proposed. There is some need for such a method for hardening the surface of aluminium alloys, but an alternative to the electrodeposition of a hard coating like chromium might consist in electroplating with copper and heating at 500° in an atmosphere of nitrogen;[3] by suitably prolonging the time of treatment to remove the more brittle $CuAl_2$ and leave only CuAl, a coating with a Knoop hardness of about 550 may be produced.

The production of aluminium by electrolysis of a fused mixture of $AlCl_3 + NaCl$ in equi-molecular proportions at 400°, instead of 1,000° for the usual cryolite type of electrolyte, has the potential advantages (in addition to the saving of fuel) of using readily available materials, only slowly consuming the carbon anodes and producing no corrosive attack on the nickel container and cathode.[4] A pure product is claimed to be produced at a cathode efficiency of 92% with a cell voltage of 5–6. Various engineering difficulties (such as the removal of the deposited aluminium) remain to be solved.

Two reports[5, 6] on aluminium reduction and refining in Germany have indicated the German processes to be relatively efficient but lacking in mechanization. The aluminium produced was not of high purity, due mainly to impure raw materials. Refining of virgin aluminium and of re-melted scrap by the three layer process was highly developed and gave a pure product but at high cost. The process consisted in electrolysis with a layer of molten heavy alloy containing 20–35% Cu as anode; over this anode layer floated the fluoride electrolyte at a temperature of 740–750°; the cathode layer of pure aluminium floated on top and the metal to be refined was added as required to the bottom layer.

Beryllium.—The production and applications of beryllium and beryllium alloys in Germany and Italy have been investigated and the results have been published.[7, 8, 9, 10] The F.I.A.T. report[7] gives a detailed account of the Degussa processes used at Frankfurt and Rheinfelden and of the Sappi process at Chivasso; the applications of beryllium metal, alloys and refractories are described. The B.I.O.S. report,[8] which is complementary and to some extent repetitive of the other, includes an amplified section on methods of analysis. The Degussa process, which gave products of poor quality compared to the American material, involves the extraction and purification of the oxide, its conversion to chloride, which is mixed with sodium chloride and electrolysed at 350° in a nickel crucible with a graphite anode; the beryllium is thereby produced in the form of flakes which are melted and cast.

Chromium.—Various engineering applications of hard chromium plating continue to be described. Large Diesel engine cylinders (400–600mm. in diameter) plated with " porous " chromium by the Van Der Horst process were found to wear only 0·0002in. per 1000 running hours.[11] High speed and carbon steel tools of various types are found to last much longer between regrinds and to need much less metal removing in grinding when thinly plated with chromium (0·0001in. or less).[12] The building up of chromium coatings thicker than about 0·015in. is usually regarded as uneconomic, but a repair of a turbine rotor journal has been described,[13] in which a much thicker coating was applied in stages with intermediate grinding to smooth the deposit. Chromium plating of the bores of guns is practised at the U.S. Naval Gun Factory at Washington, D.C., and the method has been described.[14] The extending engineering uses of electrodeposited chromium which are indicated by these and other publications have encouraged studies of the properties and structure of the deposit. All types of electrodeposited chromium appear to be brittle, and the relatively slight differences in ductility are difficult to evaluate. They have been studied by extending strips of steel plated with chromium coatings of even thickness and determining the number of cracks in the coating;[15] a modification of the Dubpernell test was used for this purpose, consisting of depositing copper at controlled potential and using the current density as a quantitative measure of the area of the cracks. This investigation showed that grey chromium coatings deposited from chromic acid solutions at about 25° were least susceptible to cracking on extending. As a result of an *X*-ray investigation of the structure of thin, hard chromium deposits on steel, the suggestion has been made[16] that the lattice of the steel is expanded temporarily by hydrogen to dimensions which nearly correspond to the lattice of chromium; subsequent contraction of the steel lattice by diffusion of hydrogen then leaves a strained condition near the interface which promotes high resistance to wear.

Developments in the technique of chromium plating have consisted mainly in improvements in the control of solutions. The determination of sulphate is much accelerated by adding picric acid, which allows the precipitated barium sulphate to be filtered off within a few minutes;[17] other authors have described the use of the " Spekker " for the rapid analysis of chromium plating solutions for Cr^{VI}, Cr^{III}, Fe and SO_4.[18, 19]

Cobalt.—A method of electro-winning cobalt[20] from cobaltite ores, operated in a pilot plant producing 5lb. of cobalt per day, involves deposition from sulphate solution congaining 40g. of cobalt per litre with insoluble anodes. The ore is treated to produce cobalt carbonate which is used to regenerate the electrolyte. The cathodes, from which the deposited cobalt is peeled as required, consist of roughened sheets of stainless steel which are passivated in nitric acid before use. A previous publication[21] indicated the advantage of adding 1% of silver to the lead anodes to reduce the formation of cobalt peroxide during electrolysis. The cobalt deposit contained 99·1% Co with nickel as the chief impurity.

Copper.—The most generally used solution for the electro-deposition of heavy copper coatings (copper sulphate and sulphuric acid) suffers from the drawback of needing addition agents for the production of smooth deposits of good properties at high current densities. Many attempts have been made to find a reliable and easily controllable addition agent but without complete success. An alternative bath has been investigated[22] and is stated to produce semi-bright plate without addition agents at 150 amp./sq. ft. and to be capable of being worked at current densities up to 1000 amp./sq. ft.; it is made by dissolving copper carbonate in alkanesulphonic acids to give a copper content of 25–100 g./l. and a free acid content of 5–10 g./l.

Iron.—Increasing use of powder metallurgy in the manufacture of components has stimulated attempts to make iron powder by electrodeposition, either by the deposition of a brittle iron which is ground to powder,[23, 24] or by direct electrodeposition of powder from a ferrous ammonium sulphate solution at 200 amp./sq. ft.[24] Subsequent annealing in a reducing atmosphere (hydrogen) is desirable to soften the particles and to reduce the oxide content. Whilst such methods can produce powder of suitable properties, the cost of production tends to be high, largely because of the cost of labour in collecting, washing and drying the product.

Magnesium.—An electrolytic process of producing an oxide coating on magnesium alloys, now known as the Manodyzing process, consists[25] of electrolysis with a.c. at 25 amp./sq. ft. or, as anode, with d.c. at 15 amp./sq. ft. for 25 minutes in a hot (85–90°) solution of sodium hydroxide (24%) with water-glass (3% of 41° B. solution) and an addition of 0·3% of phenol. For alloys containing 1·5% Mn. a.c. is used; either a.c. or d.c. may be used for alloys containing aluminium according to the properties required of the film, which is thinner (0·0004in. a.c., 0·0008in. d.c.), harder and more compact when formed with a.c., but is darker in colour. The film may be dyed to almost any desired colour when formed with d.c., but the a.c. film can only be dyed with dark colours. The process is claimed to have numerous advantages over the conventional acid dichromate finish used in America as a foundation for paint.

Manganese.—In continuation of previous work on the electro-winning of manganese, tests by the U.S. Bureau of Mines in a pilot plant showed[26] that electrolytic manganese could be successfully produced from ore from three reserve stock piles by the usual method at current efficiencies of 62–66%. In another paper[27] from the same source, results are recorded of the effects of the following cell variables in a plant with a daily capacity of 2000lb. of manganese and operated for a period of five years—electrode spacing, rate of feed to cells, Mn concentration in cell catholyte, length of time of cell operation between cleanings.

Nickel.—It is well known that surface irregularities are faithfully copied or sometimes exaggerated by electroplated coatings, but the reverse process of covering up or smoothing out rough or scratched areas in the basis metal has only recently been recognized as a possibly controllable process. An elegant demonstration of this effect has been given[28] on a macro scale by photomicrographs of sections of nickel deposits on roughened surfaces and on a micro scale by light reflectivity measurements. Additions of zinc or cadmium to matt nickel depositing solutions had a " smoothing action " which was specially marked on a macro scale; depressions in the original cathode surface of a depth of 0·004in. were not apparent in the surface of a deposit 0·002in. in thickness, although without the zinc or cadmium addition the depressions were just as apparent after plating as before. Bright nickel solutions which showed no macro smoothing action had a marked micro smoothing action, as shown by reflectivity measurement. The mechanism of the brightening action of organic sulphonates in nickel depositing solutions has been further studied[29] and has been attributed to a micro smoothing action caused by increase of deposition potential at the high spots where more sulphonate is absorbed.

The relative properties of nickel and chromium for engineering applications have been compared;[30] the value of nickel and the uselessness of chromium for preventing fretting corrosion were emphasized.

The American Electroplaters' Society has initiated a research project on the determination of impurities in electroplating solutions; the first six publications[31, 32] are concerned with impurities in nickel solutions. The plan of the research and colorimetric technique are described in the first two; the next four deal with the determination of lead, iron, manganese and copper respectively—all by colorimetric methods. Methods of analysis of bright nickel-cobalt baths for Ni, Co, Cl, formate and formaldehyde have been described.[33] Tests of the effect of copper in nickel baths have indicated that the safe maximum content of copper in a nickel anode is of the order of 0·13–0·17%.[34] A study of the effects of zinc on nickel deposition has been reported.[35]

Silver.—The second and third of a series of three papers on heavy silver deposits have been issued to record the American development of aircraft engine bearings consisting of a steel shell with a silver lining 0·02–0·06in. in thickness finished with lead and indium plating. The first of these papers was reviewed in the previous report.[36] The second paper[37] gives an account of the process used at Oneida Ltd., where over 2½ million bearings of this type were produced. Most of the bearings were silver plated at a current density of 60–70 amp./sq. ft. in a potassium argentocyanide solution containing ammonium thiosulphate as a brightener. The silver deposits produced under these conditions had a tensile strength of 48,000lb./sq. in., an elongation on one inch of 12–14% and a Rockwell 15W hardness of 90–92; the tensile strength was halved and the elongation more than tripled by annealing. The third paper[38] gives a brief outline of a method of plating used elsewhere.

Tin.—The method of continuous electro-tinning of steel strip in an acid halogen solution at the Weirton Steel Company's works has been described.[39] The strip travels at a speed of 1000ft. per minute near the surface of the plating solution and is plated first on one side and then on the other at a current density of 225 amp./sq. ft. The various stages of the process—alternate cathodic and anodic treatment in alkali, pickling in sulphuric acid, plating, flow brightening, chromate treatment and oiling in a fog of cotton-seed oil—are briefly described and illustrated by diagrams and photographs. This publication, coupled with those mentioned in the previous report,[36] provides information on three of the American methods for electro-tinning steel strip.

Investigations of the factors affecting the protective quality of electrodeposited tin coatings (in the range of thickness used for tinplate) on cold-rolled steel have given interesting results. The quality of the coatings was assessed by thiocyanate and hot-water porosity tests and by corrosion tests in a humidity chamber and outdoors. The stannous sulphate bath gave the least porous deposits with the following conditions[40]:—Sn 30–40 g./l., cresolsulphonic acid 10–40 g./l. (plus the usual H_2SO_4 50 g./l., β-naphthol 1 g./l., gelatin 2 g./l.); current density 20 amp./sq. ft. without agitation; temperature $< 30°$. The shape of the curves relating coating thickness and behaviour in the porosity and corrosion tests[41] was similar for both the stannous sulphate and sodium stannate baths and showed a marked change in the region of 12oz. of tin per basis box (0·000045in.), below which the quality of the coating deteriorated markedly. The quality of deposits from the sodium stannate bath was less affected by the method of pickling used in preparation for plating than from the stannous sulphate bath.[42]

Zinc.—The brightening action of sodium sulphide in zinc cyanide plating baths has been attributed[43] to a specific effect rather than to the precipitation of heavy metal impurities, since very pure baths were found to give a dull deposit without the addition and a bright one with it. The recommended concentration was 2 g./l.

A German process[44] for the electrolytic extraction of zinc from burnt pyrites consists in roasting the cinder with sodium chloride, leaching and purifying the extract to give a solution carrying 60g. of zinc and 180g. of sodium chloride per litre. This solution is electrolysed with a mercury cathode to produce a zinc amalgam from which the zinc may be recovered by electrolysis in an acid zinc sulphate electrolyte with aluminium cathodes.

Technique for the electroplating of zinc-base die-castings with a chromium finish has been the subject of several papers. A symposium of three papers[45] dealt with the manufacture of die-castings, the method of plating used at the Fisher Body-Ternstedt Division of the General Motors Corporation, and the causes of failure of the coatings in service. The importance is emphasized of producing castings with a good surface finish which only need buffing, and of efficient cleaning methods which remove the minimum amount of metal from the surface. Microscopic examination of plated zinc-base die-castings taken from automobiles after five years' service in Chicago showed that insufficient thickness of coating was the most important factor leading to failure by blistering or corrosion at pinholes. The rapidity of failure can be accelerated by unsatisfactory composition of the casting leading to inter-granular corrosion, by poor adhesion leading to more rapid blistering around perforations in the coating and by pinholing of the nickel which is believed to occur as a result of corrosive attack. There are several other publications on the same theme.[46, 47, 48, 49]

Zirconium.—Powder generally containing 70–80% Zr was produced[50] by the electrolysis of molten mixtures of: (*a*) $AlCl_3$, KCl, NaF, ZrO_2; (*b*) K_2ZrF_6; (*c*) KCl, NaCl, K_2ZrF_6; (*d*) $ZrCl_4$, NaCl. A grey powder containing 90–93% Zr was however obtained from electrolyte (*c*) at 700° with a current density of 0·5 amp./sq. dm. A compact layer of Zr was formed on a molybdenum cathode by electrolysis of K_2ZrF_6 at 0·5 amp./sq. dm.

Alloy deposition.—A comprehensive investigation of the electrodeposition of alloys of tungsten with metals of the iron group, with special reference to cobalt and nickel, has been described.[51] The best solution for the deposition of cobalt tungsten alloys contained: Co (as chloride or sulphate) 25g., W (as sodium tungstate) 25g., Rochelle salt 400g., ammonium chloride or sulphate 50g. per litre, with the addition of ammonium hydroxide to give a p_H of 8·5. The recommended operating conditions were: temperature 90° or above, p_H 8·5 or above, current density 2–5 amp./sq. dm. The current efficiency under these conditions was over 90% and the deposits contained 20–30% W. *X*-ray examination showed the deposits to be solid solutions. Their diamond pyramid hardness was more than 400 and was increased to over 600 by a precipitation hardening treatment at 600° for one hour. The hardness at elevated temperature (*e.g.*, 700°) was comparable to that of stellite. It is concluded that these alloy deposits should find applications where high hardness, particularly at elevated temperatures, is required; they may be competitive with chromium deposits for engineering applications especially as the throwing power of the solution is superior to that of the chromic acid bath. The paper includes a review with bibliography (27 references) of previous work on the deposition of tungsten alloys. Another publication[52] is devoted to an annotated bibliography of the electrodeposition of nickel alloys.

The properties of copper-lead deposits have been investigated[53] with special reference to the effects of annealing on their hardness and structure in connexion with their deposition on steel liners to make bearings. Alloys containing 10–12% Pb were hard as deposited (200–300 Vickers) and the hardness increased on low temperature treatment at temperatures below 300°; appreciable softening only occurred at temperatures above the melting point of lead.

Electrolytic polishing.—Electrolytic polishing has attracted a considerable amount of attention during the period under review, partly because of the special importance under present conditions of its potentialities for saving labour in the finishing of metals; in addition, however, electrolytically polished surfaces have specific properties which are of technical and scientific importance to chemists, engineers and physicists. Technical applications of the process to steels for engineering purposes[54, 55] refer mainly to its uses for super-finishing, for increasing the fatigue limit of highly stressed parts and for reducing friction and wear. The scientific applications of electrolytic polishing to metallography and to the study of the properties of surfaces have been authoritatively reviewed[56] with reference to optical, electrochemical, chemical and magnetic properties and to hardness and crystal structure; 161 references are given. Methods have been described for electropolishing various metals for microscopical examination (steel, zinc and zinc alloys and lead and lead-tin alloys,[57] aluminium alloys,[58] magnesium alloys).[59] A brief description of a portable brush electrode for local polishing or for metallurgical examination and of an electrolytic lapping disc are included in a general survey of the subject.[60]

A description has been given[61] of the development of a method of electrolytically polishing small, 70 : 30 brass pressings, which were successfully nickel and chromium plated without mechanical polishing at any stage. Electrolytic polishing of silver plated articles in a cyanide solution has supplanted the normal scratch-brushing operation with economy in labour and in silver.[62, 55] Stainless steel and nickel-silver cutlery ware have been electropolished on an experimental scale in a solution of orthophosphoric acid and glycerine; good results were obtained except with nickel-silver of low nickel content, but the polish tended to be marred by inclusions in the metals.[63] Experiments on the use of fluorosulphonic acid in conjunction with phosphoric and chromic acids for electropolishing stainless steel, nickel and nickel-silver are claimed to have given good results.[64] An electrolytic method, akin to electrolytic polishing, for pointing fine tungsten wires for rectifiers in micro-wave radar apparatus consists in anodic treatment in a solution of KOH containing $CuCl_2$.[65]

Miscellaneous

Structure and properties of coatings.—Two properties of fundamental importance to the satisfactory behaviour of electrodeposited coatings are adhesion and porosity (*i.e.*, pinholes extending through the coating to the basis metal). An exhaustive review of the adhesion of electrodeposited metals has been undertaken as one of the co-operative researches of the American Electroplaters Society.[66, 67] The review includes a bibliography of 134 references, a discussion of the nature of adhesion of coatings, and a summary of information contained in communciations resulting from a circular letter sent to members of the Society and others. Quotations from published and private communications are made freely and the report is profusely illustrated. Another research in the same series is being carried out on the porosity of electrodeposited metals. The first report[68] contains a critical evaluation of the causes of porosity and methods of testing, with a bibliography of 226 references to 1946.

Cleaning.—Satisfactory cleaning of metal surfaces prior to electroplating is well known to be essential to the production of adherent deposits. Various methods have been used to study the removal of oil and dirt, for example, fluorescent technique and a fine water-spray which forms droplets on unclean areas.[69] Examination by electron diffraction of steel panels after electrocleaning in various solutions has demonstrated[70] the presence of a film of ferroso-ferric silicate on panels cleaned cathodically in silicate solution; anodic cleaning in the same solution did not leave silicate on the surface.

Electroforming.—Electroforming—one of the earliest applications of electrodeposition for reproducing coins, artists' designs in plaster, etc.—has lately been employed as an engineering tool for the production of precision parts of various types for radar equipment, Venturi tubes for jet propulsion engines, three-dimensional cams, moulds for pressing plastics, etc. Precision work of this type where, in addition to dimensional accuracy of the part, the deposit must have suitable mechanical properties for the service required of it, demands precise control of the electrodeposition process. Examples of this type of application, the methods used and an outline of the properties of the deposits are given in two papers;[71, 72] elsewhere, a process of making copper ball floats by building up a metallized ball of paper pulp has been described.[73] Methods of metallizing glass and plastics have been comprehensively reviewed with a bibliography of 126 references[74] and general accounts of the process of electroforming for the production in quantity of small parts have been given.[75, 76]

Electrodeposition plant and practice.—Periodic reversal of the plating current in the electrodeposition of copper from cyanide solutions is reported[77] to result in smoother deposits, consequently in lower polishing costs, and more rapid plating. The period of reversed current may be for one second after every five seconds plating or for 0·5–5 sec. after every 2–40 sec. plating.

The German electroplating and metal finishing industries have been reviewed in two reports[78, 79] which confirm the findings of an earlier team that, in general, the standard of development of the German electroplating industry was inferior to that of the British—less organized and more dependent on the Supply Houses for information on methods of control; a possible exception was hard chromium plating, the standard of which was relatively high. In an unusual strip plating process, separate layers of copper and zinc were plated on steel and the coiled strip was heated to 600–700° to alloy the two coatings. (This process is also described elsewhere).[80]

Rectifiers.—A fourth report on the German rectifier industry describes the process of manufacture of selenium rectifiers at S.A.F. plants at Nurnberg and Weissenberg, and reviews the results of previous investigations;[81] a translation is given of an important paper by R. Brill and H. Krebs on the results of *X*-ray investigations of A.E.G. and S.A.F. rectifiers. This paper, which affected German methods considerably, indicates the existence of a transitional barrier between the base plate and the selenium, a definite relationship between the structure of the selenium and the usable load rating of the rectifier and shows the effects of conditions of application on the structure of the selenium.

A general review of rectifiers for electroplating has been given,[82] and covers the action of rectifiers, an account of different circuits for supplying electroplating current, methods of voltage control and the practical advantages and disadvantages of various systems.

An investigation of the electrolytic valve action of zirconium[83] showed that this metal was suitable for electrolytic rectifiers using sulphuric acid as electrolyte. The behaviour of zirconium was similar to that of tantalum, but its break-down voltage was lower. Obstruction to the passage of electricity was due to a potential barrier of approximately six volts and current capacity was limited by the rate at which heat produced in this process could be dissipated.

Electrochemical processes

The production of perchlorates in U.S.A. expanded by twenty times during the years 1941–1945. Papers describing the processes used at three plants have been published. In the first,[84] the manufacture of potassium perchlorate at Claremore, Oklahoma, is described. Details of the construction of the plant and operating data are given. Similar information, but more detailed on the chemical side, is given for a large scale plant operating at Henderson, Nevada;[85] the theory of the mechanism of the process is reviewed and factors affecting its efficiency are described. A third paper[86] discusses the chief factors influencing efficiency and economy in the electrolytic manufacture of perchlorates, and gives a description of the process and equipment of the International Minerals and Chemical Corporation.

A survey has been made of the possibility of producing sulphuric acid by electrolysis;[87] electrodes of platinum and tantalum, separately and in combination, were tried. It was concluded that the large irreversibility associated with the reaction—$SO_2 + O_2 + H_2O \rightarrow H_2SO_4$ made its commercial development a doubtful possibility.

The development of the production of fluorine by electrolysis in Germany during the war is described elsewhere.[88] Operating details are given for two types of German cells, viz., the high temperature type (245°) at Falkenhagen and the low temperature type (75°) at Leverkusen. The best anode material depends on the temperature of electrolysis; nickel is best below 100°, although a specially prepared carbon anode can be used in the range 65–90°; graphite is a suitable anode material in melts free from HF at temperatures around 250°.

The general survey of German electrochemical operations in the Bitterfeld area, referred to previously,[36] has been supplemented by a further, more detailed account of the electrolytic production of chlorine, hypochlorite, chlorates, hydrogen and calcium in this area.[89] The amalgam plant at Bitterfeld North was reported to be one of the most modern in Germany and worth studying for plant lay-out and successful operating procedure. The calcium hypochlorite process was only notable for the production of calcium chloride in granular form from waste liquor, while the processes for production of chlorates and perchlorates differed from U.S. practice and were accordingly reported carefully. Another report[90] describes six alkali-chlorine cells and four hydrogen-oxygen plants in Germany. Four German processes for making sodium (two of them new) have been described[91] and compared for cost. A new I.G. process consisted in making lead-sodium alloy by electrolysis of sodium chloride at 850° with a molten lead cathode and a graphite anode, the yield being nearly 100%; the product was used for the production of tetra-ethyl lead and of sodium hydroxide; the yield in the production of tetra-ethyl lead could be much improved (from 66 to 88%) by the inclusion of 1% of potassium in the lead-sodium alloy. The other new process was the production of sodium from sodium amalgam by electrolysis in a fused halide plus hydroxide electrolyte containing NaOH 53%, NaI 28%, NaBr 19% at a temperature of 230°; the lower temperature possible with this ternary eutectic electrolyte resulted in a lower mercury content in the sodium. Degussa plants for the production of sodium in the Downs cell at Knapsack[92] and of lithium at Rheinfelden[93] have also been described.

Primary and secondary cells

The p_H change in the region of the cathode has been found[94] to be one of the most important factors contributing to the decline in working voltage of Leclanché-type dry cells; in addition to the previously reported formation of $ZnCl_2.2NH_3$ at the cathode, it was found that, during heavy drains, the compound $ZnCl_2.4NH_3$ may also be produced. *X*-ray diffraction and the petrographic microscope were used in another investigation[95] to identify solid phases formed in dry cell reactions; the most important reaction is $2MnO_2 + Zn \rightarrow Zn.Mn_2O_3$ (hetaerolite). Hetaerolite has been identified in used dry cells and was produced in the laboratory by the reduction of MnO_2 in the presence of Zn. In a study of the relationship between capacity and drain, it was found[96] that, on light or moderate loads, the current is uniformly distributed between the different particles of manganese dioxide; accordingly, a diffusion process within the particles determines the behaviour of a dry cell on light or moderate loads. An *X*-ray study of various types of MnO_2 with markedly different chemical and physical properties has been made[97] with particular emphasis on those prepared chemically; the role of potassium in determining the course of the various transformations and the manner in which lead is combined in a commercial MnO_2 by-product are discussed. A method of preparing a dry cell depolarizer consists in the air-oxidation of freshly precipitated manganous hydroxide in the presence of some sodium hydroxide (0·03–3·0N.);[98] the alkalinity must be controlled and the oxidation must be done quickly after precipitation before ageing takes place, for example, by slowly adding manganous sulphate solution to the strongly aerated alkali. The product corresponded to $MnO_{1\cdot85-1\cdot90}$ and was suitable for high-capacity, heavy-duty cells when mixed with African MnO_2. The addition of lithium chloride to the dry cell electrolyte enabled a capacity of 10–20% (according to the rate of drain) of the normal to be obtained at −40°, whereas the ordinary dry cell is useless below −23°;[99] cells designed for use at −40° sacrifice some capacity at higher temperatures and the composition of the electrolyte should therefore be adjusted according to the minimum temperature at which the cell is required to operate. The shelf-life of dry cells at 55° was extended from a few weeks to 3–6 months by spraying them with vinyl resin plastic, due presumably to the low transmission rate of moisture through the plastic.[100]

Where high capacity and a well-sustained operating voltage are important, the air-depolarized primary cell with a caustic alkali electrolyte (Zn|NaOH|C) has attractive possibilities;[101] an improvement in the method of removing dissolved zinc by lime has reduced the volume of the electrolyte by 60% below that otherwise required for cells of equal capacity.

So-called amorphous carbon blacks (*e.g.*, acetylene black made at high temperature) have been found[102] to have a crystalline structure when examined by the electron microscope; this finding, together with the results of *X*-ray and electron diffraction examination, indicated that the particles have a graphitic structure. A study of the electrode potential of carbon in acid electrolytes has shown[103] that, when carbon is exposed to oxygen in the presence of acid, it develops oxidizing characteristics measurable as potential or as capacity to oxidize reducing agents; sorption of both acid and oxygen is essential to the development of oxidizing properties.

The method of construction and characteristics of a cell of the type: $Ag\text{–}AgO_2 \mid KOH \mid Zn$ – have been described.[104] The use of asbestos as a separator produces silicates which inhibit attack on the zinc during storage and cells retained most of their capacity when stored at 54° for two months; to prevent excessive attack on the asbestos, the electrolyte (a 40% solution of KOH) was buffered with boric acid. The potential remained constant at 1·5 volt almost throughout discharge, even at high rates of drain (*e.g.*, 30 amp./sq. dm.); at low rates of drain, the cell delivered 80% of theoretical capacity. In another study of a similar type of cell,[105] the performance at low temperatures, *e.g.*, −24°, was found to be unsatisfactory due to rapid polarization.

A detailed description of the design, method of manufacture, electrochemical principles, performance and applications has been given[106] of the Ruben cell: $Zn\text{–}Zn(OH)_2 \mid KOH\ aq. \mid HgO\text{–}Hg$. The rated capacity is 200 m.amp. hours for each 1·6 g. unit of active material. The normal open circuit voltage is 1·34 and the initial closed circuit voltage is 1·24–1·31. Flat discharge curves are obtained with 80–90% utilization of active material. Compared with other commercial types of dry cell, the life obtainable at high current drain is 4–7 times that of conventional cells of equal volume discharged to the usual cut-off voltages of 0·75–1·0 volt. The adaptation of this type of cell, developed for war-time use, to civilian use, in which a fixed capacity is available over the entire load range, with collapse of voltage following closely at the end of effective life, has been discussed in another paper.[107] The evolution of a new " balanced " dry cell with the same voltage as the original and a capacity of 5·43 amp. hr./cu. in. (0·331 amp. hr./c.c.) is described.

Several papers have appeared describing investigations of cells based on the lead dioxide cathode with zinc or lead anodes. The discharge characteristics of the cell Pb | $HClO_4$ | PbO_2 have been investigated[108] at various temperatures (from −40° to 40°), current densities and acid concentrations. The best results were obtained with 60% acid, which gave good efficiencies down to −20° at low current densities. At high current densities, *e.g.*, 17·2 amp./sq. dm. 60% acid did not give useful results below 0°. A comparison of various electrolytes (perchloric, fluoboric, fluosilicic and some sulphonic acids), made in a similar type of cell, indicated that perchloric acid gave the best performance and that the sulphonic acids were the least useful.[109] The performance, especially the capacity, of the zinc-lead dioxide cell has been studied as a function of the type of lead dioxide—whether made by electrolytic forming or by direct electrodeposition—and of the electrolyte.[110] The dependence of capacity on the type of dioxide, on the nature and temperature of the electrolyte and on the rate of discharge is explained by the coating of the particles of the dioxide with a protective film of some substance formed in the course of discharge. In a parallel investigation,[111] an account is given of variations in the method of preparation of the lead dioxide electrode on the capacity of the zinc-lead dioxide cell when discharged under standard conditions.

The advantages of lead-calcium alloy over lead-antimony alloy for the grids of secondary cells have been established by the results of tests of cells on floating service over a period of nine years.[112] Grids of lead-calcium alloy containing 0·077–0·137% Ca delivered more than 115% of their rated capacity compared with 70% for lead-antimony grids; the trickle current on float was only one-third to one-fifth of that required for lead-antimony alloys, and the rate of growth of positive grids of lead-calcium alloy containing 0·07–0·10% Ca was less than half that of grids made of lead-antimony alloy with 12% Sb. Variable corrosion of positive grids and posts which occurred in early trials of lead-calcium alloy has been traced to inaccurate control of calcium content. A rapid method of estimating calcium content by the appearance of test ingots is demonstrated in a subsequent paper.[113] The method depends upon the quantitative removal of calcium by interaction with antimony with which the alloy is " titrated " until the characteristic effects on the appearance of test ingots produced by traces of calcium just disappear.

Reports of surveys[114, 115, 116] of the manufacture of nickel-cadmium storage batteries in Germany have included descriptions of the manufacture and tests of Durac cells having sintered plates, a development designed to give a light-weight battery of low internal resistance. The positive plates were made by pressing nickel powder (made from carbonyl) into a wire mesh, sintering and impregnating *in vacuo* with nickel nitrate solution and forming by electrolysis in hot sodium hydroxide solution; the negative plates were made similarly but using a mixed powder of copper (70%) and nickel (30%) and impregnating with cadmium chloride solution. This development was not perfected, and difficulties in meeting production requirements and in the loss of capacity of the negative plate on standing and in use, led to the rejection of the cell by the Luftwaffe.

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ACIDS, ALKALIS AND SALTS

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THE need for increased food production throughout the world is reflected in the large demand for both nitrogenous and phosphate fertilizers, which continues to exceed the supply. Deficits equivalent to a million tons of nitrogen and over two million tons of phosphate are estimated, in spite of the efforts being made everywhere to increase production, sometimes by methods which under pre-war conditions would have been considered quite uneconomic. It is clear that for some years to come a considerable proportion of the effort of the chemical industry will be devoted to the expansion of plants for the production of these materials, and at present the reconstruction and reconditioning of plants damaged and neglected during the war is by no means complete.

The total world production of nitrogenous products during 1946-47 is estimated as equivalent to 2,550,000 tons of nitrogen, which is slightly higher than the pre-war level of 2,242,000 tons (an average over the years 1936-38). Canada and the U.S.A. have together increased their output to 537,000 tons above pre-war level, but European production has fallen short of pre-war figures of 359,000 tons—an indication of the extent to which the after-effects of war are still being felt. Of the total world production during the year under review 80% was derived from synthetic ammonia, 10% from by-product ammonia, and 10% from Chilean nitrate. These supplies are being apportioned between the various consumer-countries by the International Emergency Food Committee, in Washington.

The world production of phosphate rock has continued to rise, and new deposits are being developed, for example, in the United States (Montana, Utah, and Idaho), in Canada, in South Africa, and near Fengtai, in China. The last of these is estimated to be capable of yielding 2,500,000 tons of phosphate. A comparison with war-time production is afforded by the figure for the total North African production for the first eight months of 1947, which was 3,552,400 tons, as against less than 4,000,000 tons for the whole of 1945. As a result of these increases in the output of rock there has been a corresponding increase in the production of phosphate fertilizers, a large proportion of which still consist of ordinary superphosphate. In the United States the total output of phosphate fertilizer during 1947 was 9,506,000 tons, an increase of 13% over the previous year, and a further 10% increase is estimated for 1947-48. The United Kingdom production fell during 1947, however, from 603,700 tons (the 1946 figure) to 567,100 tons. The fuel shortage at the beginning of the year was largely responsible for this, but there were, and still are, many other difficulties facing the manufacturers, such as shortage of labour, raw materials, and steel for the erection of new plants.

Figures have recently been published of the output of sodium chloride in Great Britain, showing that while output has increased by nearly 10%

since 1938 (the 1946 figure was 896,000 tons), the quantity exported fell by more than 25% (232,000 tons in 1938 to 169,000 tons in 1946). This gives an indication of the extent to which the British alkali industry has increased its efforts, and other figures show that the total home production of alkalis (mostly sodium carbonate) has increased by 32% over this period. Calcium chloride, the principal by-product of the ammonia-soda process, is finding an increasing number of industrial outlets, so much so that in the United States supplies obtained in this way are proving inadequate, and manufacture by direct reaction methods is being undertaken. Uses include the acceleration of the curing of concrete, filling of tractor tyres, dust-laying in coal mines, consolidation of soil roads, and (in Australia) the production of artificial rain.

Ammonia and ammonium salts

During the past year no major developments in the ammonia synthesis process have been reported. The catalytic decomposition of ammonia gas has been studied by the Japanese workers, T. Koyano and R. Ito,[1] using an iron catalyst containing 9·8% Ni. Working over the temperature range 400–610°, they found that the rate of decomposition was accelerated in the region of 600°. A general account of this process, including the uses of cracked ammonia, has been described by C. V. Snell.[2]

No outstanding developments have been reported from Germany for the recovery of by-product ammonia.[3] It is interesting to record, however, that a widely adopted procedure was to fertilize soil by the direct addition of weak ammonia liquor. Similarly in the U.S.A., more than 150,000 acres of crops have been fertilized with anhydrous ammonia,[4] which was released under the soil; loss to the atmosphere is claimed to be negligible.

The unusual properties of anhydrous liquid ammonia as a solvent are well known in the laboratory, but little use has been made of them in industry. It has now been disclosed that liquid ammonia was used as a solvent on a large scale during the war. Nitroguanidine, required for use in flashless powder, was made by the American Cyanamid Company by reacting ammonium nitrate with dicyandiamide in anhydrous liquid ammonia[5] at 160° and 1500lb. per sq. in. The previous method was fusion or reaction of these materials in aqueous solution, both of which were difficult to control and tended to proceed with explosive violence. Use of liquid ammonia gave better control of the reaction, produced a higher yield and a purer product.

The world shortage of ammonium sulphate has led to investigations into methods of producing it from various waste liquors, often by methods which, under pre-war conditions, would have proved quite uneconomic. The Shell Development Company have claimed a process for converting waste sulphuric acid from petroleum refining into free-flowing ammonium sulphate.[6] Neutralization of this acid with ammonia normally forms ammonium sulphate of little commercial value, as tar and oily matter (organic sulphates, etc.) are precipitated with it, adversely affecting the purity and handling properties. In the process described the acid is neutralized in the presence of quinoline or pyridine, in which any organic impurities dissolve, forming an oil phase, which is then separated from the ammonium sulphate solution. The pyridine is subsequently regenerated from the oil phase and recycled. The Mellon Research Institute and others have been working on the production of ammonium sulphate from waste pickle liquor, and describe processes[7, 8] which surmount one of the main difficulties, namely, filtration of gelatinous ferrous or ferric hydroxide. In the processes described, ammonia and pickle liquor are fed continuously to a reactor of special design in which the precipitated ferrous hydroxide is oxidized, under carefully controlled conditions, to ferroso-ferric oxide. Precipitation of iron is claimed to be complete, and the iron oxide settles out so rapidly that it can be separated from the ammonium sulphate liquor by continuous decantation.

A plant for the production of 150 tons per day of ammonium sulphate has recently been completed in Travancore, India, utilizing, for the first time on record, the Merseburg process of reacting gypsum with ammonium carbonate, combined with direct neutralization of acid.[9] For the maintenance of a continuous and steady level of output this dual type of process has marked advantages. In this plant, Lurgi filters are used for removing the precipitated chalk, and continuous Bird centrifuges for separating the ammonium sulphate.

A novel type of drier, suitable for installation on plants making by-product ammonium sulphate, has been patented by G. Royston.[10] Wet sulphate is fed on to a turntable into a stream of hot air and blown up a vertical pipe into an expansion chamber, where it impinges on a baffle plate to break up aggregates. From the expansion chamber it falls down a tower fitted with a series of louvres up which passes a current of hot air. From the lower end of the tower it falls direct into an enclosed storage bin. The air, preheated by steam heaters, is circulated by two fans, the stream from one being used for drying whilst the other stream is used for elevation of the sulphate. The drying time is only a matter of seconds, and fracture of crystals is minimized because there are no moving parts in contact with the sulphate.

Nitric acid and nitrates

W. J. Cotton, of the Pennsylvania Coal Products Company, has described a method of producing oxides of nitrogen from their elements in a low-temperature electrical discharge.[11] A special feature of this work is the use of a " crossed " discharge which causes a marked improvement in the yield. Highest efficiencies are obtained with the discharges at right angles. One discharge is of low frequency, 60 cycles, and one of high frequency, which in the experiments varies from 16·7 to 0·485 megacycles. It was observed that the wavelength of the high frequency discharge is critical, and dependent in many cases on the electrode materials. Electrode gaps of 20–30mm. are used, the voltage for the low frequency discharge being of the order of 800 volts, and for the high frequency 500 volts. A deficiency of energy makes the discharge unstable, but energy supplied to the system in excess of that required to maintain the discharge is dissipated as heat and does not affect the course of the reaction. The inlet gases, at 25°, only show a rise of 0·2° after activation. A clearly defined glow is apparent from the discharge, which is at a maximum intensity under the optimum operating pressure. For the production of oxides of nitrogen this pressure is 335mm. Hg absolute. The best yield quoted by W. J. Cotton is 920g. equivalent HNO_3 per kilowatt hour, which was obtained with a measured power factor of about 0·3, so that the yield is 276g. HNO_3 per kilovolt amp. hour. These figures correspond to a power consumption in the discharge of 1,100 kw. hr./ton of equivalent HNO_3 produced in the gas. This does not seem excessive, and if the process can be developed successfully on a large scale it may be possible to produce nitric acid at a cost which compares favourably with established processes.

The oxidation of ammonia at pressures of between 10 and 50 atmospheres has been studied by V. I. Atroshchenko,[12] who finds that, contrary to previous reports, the yield of oxides of nitrogen is not decreased upon increasing the pressure to 50 atmospheres. He suggests that by the use of such a process it may be possible to construct a plant using cooler-condensers instead of absorption towers. Work on the catalytic oxidation of ammonia at low temperatures has been reported from Japan.[13] In the temperature range 260–440° the activity of various catalysts decreased in the following order: $Cr > Ni > Co > Mn > Fe > V > Cu > Cd$.

H. Zborowski has described the use of highly concentrated nitric acid as an oxygen carrier in rocket power units.[14] Nitric acid is preferred to liquid oxygen or hydrogen peroxide because of its smaller specific volumetric consumption. It is made more efficient by the addition of nitrogen dioxide or pentoxide.

The kinetics of nitrous gas absorption in aqueous nitric acid (10–60%) have been studied[15] in order to determine the effect on absorption rate of gas composition, acid concentration, and temperature. It was found that the absorption per unit area of interface could be expressed in the form $V = kd[(N_2O_4) - C(N_2O_4)^{\frac{1}{4}}(NO)^{\frac{1}{2}}]$. Here (N_2O_4) and (NO) refer to the concentrations in the gaseous phase, and C is a constant which can be calculated from the known equilibrium constant of the reaction. The main effect of acid concentration is on the constant C, and therefore increase of acid concentration decreases the absorption rate. Increase in temperature causes a considerable decrease in the rate of absorption of the dioxide, mainly due to a shift in the equilibrium between NO_2 and N_2O_4.

The production of ammonium nitrate, either pure or mixed with a suitable diluent, for use as fertilizer often entails some method of granulation. An improvement on the usual spraying process has been claimed,[16] using the outside of a heated drum, rotating rapidly about a horizontal axis, to form a spray. A weir adjacent to, but not quite touching, the ascending side of the drum is used so that the fluid is continuously in contact with only a limited area of the drum. The spray falls down a tower 70–90ft. high. A uniform granular product is obtained, and it is claimed that crushing and screening are unnecessary.

The disastrous explosions of ammonium nitrate at Texas City, and at Brest, have demonstrated only too clearly the hazards associated with the handling of large quantities of ammonium nitrate. A result will, no doubt, be the application of more stringent safety precautions for the transport of ammonium nitrate. The chief causes of the two explosions at Texas City were (*a*) fire resulting from carelessness, and (*b*) high temperature and pressure due to confinement of the nitrate in the hold.[17] An excellent review of the explosion and fire hazards of ammonium nitrate has appeared recently,[18] and the precautions recommended are similar to those made by the Fire Prevention and Emergency Bureau of Dallas, Texas, and the National Board of Fire Underwriters in the United States.[19]

Phosphates

Superphosphate in the form of granules, as opposed to powder, is becoming increasingly popular in many countries, since it is easier to apply to the soil, and wastage due to soil fixation is reduced. The methods in general use for granulation entail production of a powder form of superphosphate which is then mixed with water in a granulator.[20] In a process patented by Procter and the Sturtevant Company,[21] however, granulation is carried out immediately after the phosphate rock has been treated with acid. He overcomes the disadvantage of low extraction of P_2O_5 due to reduced reaction time by certain alterations in the reaction technique.[22]

The production of triple (or double) superphosphate is now receiving some attention. Whilst superphosphate may be regarded as a mixture of $CaH_4(PO_4)_2 . H_2O$ and $CaSO_4$, double or triple superphosphate consists essentially of $CaH_4(PO_4)_2 . H_2O$. The production of this material in the U.S.A. increased from 282,000 tons in 1945-46 to 359,000 tons in 1946-47,[23] and a further increase of 25% is expected for 1947-48.[24] To meet the increased demand for triple superphosphate two additional plants are to be erected. Triple superphosphate has not been manufactured in the United Kingdom for several years, but a plant for the production of 100,000 tons a year of this phosphate is being erected (for Fisons Ltd.) at Immingham.[25]

Processes employing nitric acid for extraction of phosphate rock have engendered a lively interest in Europe owing to the shortage of sulphuric acid.[26] Although many claims have appeared in the patent literature[27] there have been no significant developments during the period under review. The disadvantages of using nitric acid are (*a*) the plant required is more elaborate and therefore more costly, (*b*) the nitrogen efficiency is often low, and (*c*) the products are usually hygroscopic. In some countries, notably Germany and the Low Countries, the demand is such that the disadvantages are outweighed, and various modifications of the original Odda Process, involving separation of calcium nitrate, are being worked.

There is an increasing tendency to incorporate magnesium in phosphatic fertilizers. One of the functions ascribed to magnesium is that of a carrier for phosphorus, and the relatively high content of magnesium and phosphorus in seeds suggests that magnesium may be the best cation to use in combination with phosphorus.[28] The addition of magnesium silicate, in the form of olivine or serpentine, to superphosphate is reported to have given favourable results in Russia and New Zealand.[29] Crop yields from the mixtures were higher than from superphosphate alone. A plant at Permanente, in America, is now producing up to 200 tons per day of a fused phosphate made from phosphate rock and serpentine.[30] A similar product, made from phosphate rock and olivine, is also being developed at the University of Washington for the Oregon Manganese Development Company.[31] Agronomic studies indicate that both these new products give good results when used in acid soils. The production of magnesium ammonium phosphate for use as a fertilizer has been the subject of a recent

French patent.[32] It is claimed that this compound is an excellent fertilizer which, whilst being readily available to plants, is not washed away by rain water.

A continuous process for the production of red phosphorus has been described by the Tennessee Valley Authority[33] in which the time required to convert white to red phosphorus is reduced from several days to a matter of hours. White phosphorus is maintained at its boiling point in a reaction vessel for 5–6 hours, and the resulting slurry, containing 30–50% of solid red phosphorus, overflows continuously into a heated screw conveyor in which it is carried counter-current to a stream of hot inert gas. The white phosphorus is vaporized, condensed, and recycled, whilst the finely divided red phosphorus is discharged and requires no further treatment.

Although nothing of importance has been reported on the preparation of phosphate salts for industrial purposes, certain uses are worthy of mention. Organic phosphorus compounds are becoming increasingly important, and among new chemicals available to industry are triethyl phosphate,[34] triethyl hexyl phosphate,[35] and hexaethyl tetraphosphate.[36] Triethyl phosphate is a useful solvent, and is also a raw material for the manufacture of organic phosphorus insecticides. Triethyl hexyl phosphate is being produced by Carbide and Carbon Chemicals Corporation as a plasticizer under the trade name "Flexol T.O.F." Subsequent to its successful use in war-time experimental work the industrial demand has been so great that a new plant is being built for its production.[35] Hexaethyl tetraphosphate, manufactured by Monsanto Chemical Corporation, is a powerful insecticide, being effective in dilutions ranging from 0·25% to 0·025% against various species of insects. The use of monoammonium phosphate for the fire-proofing of timber is well known, but the use of diammonium phosphate[37] and urea phosphate[38] for this purpose has recently been described. The last of these materials, in alcoholic solution, has been shown by the Admiralty Chemistry Department to be effective in fire-proofiing plywood and soft timber. Ferrous ammonium phosphate has been used as an anti-corrosion pigment,[39] and ferric phosphate, recovered from waste pickle liquor, has been described as an effective coagulant in water and sewage treatment.[40]

Sulphur and sulphuric acid

A process has been reported for producing sulphur from sulphur dioxide, such as might be present in dilute pyrites burner gases, by reacting the sulphur dioxide with carbon monoxide to form carbon dioxide and sulphur. In this process there is a tendency for secondary reactions to give carbonyl sulphide, but this can be lessened by the use of a vanadium pentoxide catalyst at 600°. The best carbon monoxide/sulphur dioxide ratio is 2.[41]

In the production of sulphur dioxide there is no progress to report. Emphasis has been laid on the need to use indigenous sources of sulphur; the extraction from coal gas by various methods, and the possible recovery as hydrogen sulphide from coke oven gas,[42, 43] have been discussed. The methods depend on absorption of the hydrogen sulphide in organic reagents such as *n*-phenylaminoacetic acid or triethanolamine, or in inorganic reagents such as sodium carbonate, ferric oxide in sodium carbonate, or sodium disulpho-arsenite. An aqueous suspension of nepheline can be used for extracting 1–4% sulphur dioxide, and the sulphur dioxide can be recovered by boiling.[44]

A German process for producing sulphur dioxide sufficiently concentrated for liquefaction was to absorb the sulphur dioxide in cement kiln gases (8%) in xylidine and water. The resulting xylidine bisulphite when heated to 100° gave up its sulphur dioxide as a concentrated wet gas.[45]

The theoretical aspects of the chamber process have been reviewed by H. Stevenius-Nielsen.[46] He states that in the Glover tower sulphur dioxide is oxidized by nitrous acid in the liquid phase to sulphuric acid, and sulphuric acid is also formed by hydrolysis of $HNSO_5$, which he regards as a sulphate, properly written $NOHSO_4$. The $NOHSO_4$, H_2SO_3, and HNO_2 are the results of absorption of sulphur dioxide or nitrogen trioxide in water in a gas-liquid phase, as is the desorption of NO. The oxidation of the NO to NO_2 is a gaseous phase reaction. An alternative view of Kuz'minykh[47] is that the reaction of NO_2+SO_2, $NO+O_2$, and SO_3+H_2O all take place in the gas phase, the rate being determined by the first. He also suggests that chambers could have a much greater capacity if they could operate at 120°, which is, of course, only practicable if a more resistant material than lead can be found for lining the chambers.

N. Titlestad and L. N. Allen[48] have described a step in the contact process in which the hot sulphur dioxide gases from the roaster are cooled by scrubbing with water. The gases are thereby dehydrated to such an extent that they and the admitted air subsequently form 98% sulphuric acid. The warm water from the cooler is blown with air to remove the sulphur dioxide, and these exhaust gases are admitted to an intermediate point of the sulphur dioxide cooler.

A method of recovering sulphuric acid from contaminated 80–96% acid from organic processes[49] is to spray it into an oil burner fed with air at 430°. The acid decomposes at about 900° into sulphur dioxide, oxygen, and hydrogen. The water is removed by cooling, leaving a gas containing 8–8·5% sulphur dioxide and 11–11·5% oxygen suitable for the contact process.

During the past year the commercial production for sale of sulphur trioxide has been announced by the General Chemical Co., of New York. There are stabilized and partly stabilized forms, the former being the *gamma* modification and the latter the *beta*.[50] The stabilizers are not disclosed, but another company has claimed the use of thionyl chloride for this purpose.[51]

The reaction of sulphur dioxide and methane over calcium sulphide at 775–1020° has been studied[52] for various gas ratios and space velocities. The hydrogen sulphide yield increases with temperature, and appears to depend on the rate of decomposition of the methane. The effect of space velocity is negligible at sulphur dioxide/methane ratios of 0·5 and at 800/1000°, but free sulphur appears at high-space velocity and low temperature for higher ratios. Conversion of 90% of the sulphur dioxide to hydrogen sulphide is obtainable.

The production of sulphides has received some attention. The I.G. process for production of a pure grade of sodium sulphide by reaction of sodium amalgam from an electrolytic chlorine cell has been described.[53] The amalgam is withdrawn from the cell to react with sodium tetrasulphide to form sodium sulphide and mercury, which is returned to the cells. An anhydrous grade of sodium sulphide was also made in Germany by reduction of sodium sulphate by hydrogen and coal.[54] G. A. Peirce describes a somewhat similar process.[55] A mixture of sodium sulphate and coal is charged into a rotary furnace through which are passed combustion gases containing 1–5% carbon monoxide and about 12% carbon dioxide. The heat content of the gases is sufficient to melt the charge and finally to yield a dry product. The charge is retained in the revolving furnace long enough to reduce impurities and also until the carbon dioxide content of the exit gases is steadied at 12–14%, after which it is cooled out of contact with air. In a study of the reduction by various gases the influence of catalysts was examined, and iron was found to be the most effective. Up to 700° hydrogen was the most efficient gas, and above 800° methane was quite reactive.[56]

Sulphamic acid, sulphamide, and the relationships of the various nitrogen derivatives of sulphuric acid have been discussed.[57, 58, 59] In addition to compounds made by action of ammonia on chlorine derivatives of sulphuric acid, direct addition of ammonia to sulphur trioxide forms ammonium amido sulphate; by using the appropriate amine, *n*-substituted sulphamic acids can be prepared. While these compounds are generally still uncommon, sulphamic acid and sulphamide are commercially available and have uses in agriculture, in electroplating and in chemical manufacture, and some resins have been formed from sulphamide, analogous to the related urea-derived resins.

The problem of disposal of waste sulphate pickle liquor has been met by the Sharon Steel Corporation,[60] who use it to make a cellular building material which it is claimed has particular value for heat and sound insulation. The ferrous sulphate liquors are mixed with milk of lime and diluted. During reaction the mixture is brought to complete neutralization, at which point precipitation of the iron as hydroxide is complete. The suspension is filtered at high pressure, and the resulting press cakes are fed through a pug mill and extruded on to trays, which pass through a drier. During drying the cake oxidizes and sets to a material of high porosity. Fibrous material may be added to the slurry. The final product is a mixture of iron oxide and calcium sulphate, though it is suggested that it may be a " ferroxy calcium sulphate " as distinct from a mixture. Under present-day circumstances it may present a useful outlet for an otherwise waste product.

Another process for recovery of sulphuric acid from waste pickle acid or titanium liquors[61] is to add to the waste liquors sufficient iron sulphide or alkaline earth sulphide from a previous cycle practically to neutralize the free acid. The hydrogen sulphide evolved is collected for oxidation to sulphuric acid. When liquors containing titanium are thus treated hydrated titanium oxide is precipitated, which may be separated for recovery. The iron sulphate in the mother liquor is reduced by addition of the sulphide of any metal above iron in the electromotive series with a greater solubility product than iron sulphate, *e.g.*, alkali and alkaline earth sulphides. In general a mixed precipitate of iron sulphide and alkaline earth sulphate will result, which may be prepared for re-use by calcining and leaching the sulphide. Calcium sulphide may be reduced by hydrogen sulphide to the soluble hydrosulphide.

Fluorine and fluorine compounds

Some American reports on the recovery of calcium fluoride from various ores have appeared, but they concern standard methods, of interest only as indications of the search for fluorine-containing minerals. The chief interest in fluorine was the disclosure of part of the vast amount of work carried on in U.S.A. during the war and reported at conferences held in 1946 and 1947. Most of this work was on organic fluorine compounds, and only that reporting work on fluorine and its inorganic compounds will be summarized here.

Various types of fluorine cells have been described, all depending on the electrolysis of potassium hydrogen fluoride. They differ in working temperatures, however, some being relatively low at 60–80° and some as high as 275°.[62] The electrolyte is regenerated by addition of anhydrous hydrogen fluoride either continuously or at intervals. Cells up to 2000 amp. have been described.[63] The addition of lithium fluoride or aluminium fluoride to the electrolyte is said to give improved operation.[64] Various materials are used for construction, usually steel for the cathode, and carbon, which may be impregnated, for the anodes.[65, 66] With the generation of fluorine on such a large scale it has been necessary to develop the technique of handling this extremely reactive gas, so that there has been a general examination of its behaviour in various metallic and non-metallic containers.[67] The important points to be observed are freedom from moisture and hydrogen fluoride. The gas has been compressed, and can be stored in nickel or steel cylinders,[68, 69, 70] but it is important to ensure complete absence of organic substances with which it reacts extremely vigorously.

Of the compounds of fluorine, hydrogen fluoride has naturally received a good deal of attention. The methods of preparation in Germany have been described. Furnaces are of two types, one with fixed tube and rotating internal shafts and the other with rotating tubes. The former are limited by the length of shaft which can be supported, and the latter by difficulties in obtaining a satisfactory gland, which make it necessary to produce an aqueous acid and concentrate it by distillation.[71, 72] Purification of the acid is of some importance, and two processes for removal of sulphur dioxide have been patented. In one the sulphur dioxide reacts with hydrogen sulphide to reduce it to sulphur,[73] which is removed, and in the other the hydrofluoric acid is digested with heavy olefinic oil formed in the alkylation of olefines with hydrofluoric acid. The resulting mixture is distilled.[74]

There has been considerable interest in the handling of hydrofluoric acid at various concentrations; a surprisingly large number of materials are suitable if conditions are correct. Monel metal is said to be generally the most useful metal over a wide temperature range and for all concentrations, including anhydrous acid, while steels are also useful for high concentrations.[75] A very interesting development in this line, however, is a new type of glass containing no silica and based on phosphorus pentoxide; this is claimed to be completely resistant to hydrofluoric acid.[76]

A use for hydrogen fluoride which is of some interest is as a liquid medium for oxidation of organic compounds under pressure. In this medium it is claimed that high conversions can be obtained of, for example, benzene to phenol.[77]

Among other fluorine compounds chlorine trifluoride is of particular interest. This chemical is made by direct reaction of chlorine and fluorine, and was made in large quantities in Germany. It has most of the reactions of fluorine, but as it is a liquid boiling at 11° it avoids the disadvantage of requiring the high-pressure containers needed for fluorine itself, and, moreover, allows the reactions of fluorine to be controlled more easily.[72, 78]

Boron trifluoride can be made by the reaction of boric acid on fluorosulphonic acid at 85–135°, as an alternative to the usual route from sodium borofluoride.[79] After reaction with hydrocarbons it can be removed from the gaseous hydrocarbons by absorption in anhydrous hydrofluoric acid, from which it is, in turn, recovered by heating.[80]

Sulphur hexafluoride production has been described. The process is to burn molten sulphur in a stream of fluorine in a steel pipe, the reaction being extremely rapid and exothermic. Several other compounds are formed, but a pure stable hexafluoride is obtained by water washing, hydrolysis with caustic soda, and drying. It can be compressed into steel cylinders, and has interesting possibilities as a gaseous dielectric.[81, 82]

Other compounds of fluorine which have been reported are the fluorophosphoric acids. Anhydrous monofluorophosphoric acid was prepared by reaction of anhydrous metaphosphoric acid with liquid anhydrous hydrofluoric acid.[83] It can also be made by heating phosphorus pentoxide and 69–100% hydrofluoric acid in a closed system until the reaction is complete.[84] It is an oily, colourless liquid.[85]

Another compound of fluorine is fluorine perchlorate, produced by reaction of fluorine and concentrated perchloric acid. It is a highly reactive explosive gas boiling at −15·9°. Oxygen difluoride is also produced in the reaction.[86]

Chlorine and chlorine compounds

The most interesting information which has been disclosed on chlorine production in the last year or two has been that obtained by examination of German factories. Various types of cell have been described, including mercury cells with horizontal, vertical and rotary denuders, and diaphragm cells with rotating cathodes. A comparison of diaphragm and mercury cells based on this information has been published.[87] The technical data are compared, and the possibilities of using mercury cells for production of other compounds, such as sodium methoxide, hydrogen peroxide and hydrazobenzene, are considered.

It has been shown that in cylindrical chlorine cells there is a straight line inverse ratio between current efficiency and cell liquor concentration. Higher current efficiencies tend to give longer anode life. It was cheaper to renew the diaphragm during the life of an anode, and the total cell product costs still declined even after three diaphragm renewals.[88] Methods of reducing anode consumption in cells, which may represent as much as 10% of the total cost, are to lower the temperature and increase the salt concentration. Lower temperatures also increase current consumption, however, and are not therefore admissible.[89]

A new stationary mercury cell has been announced by the Mathieson Alkali Co.,[90] in which it is claimed that stronger caustic soda solutions can be obtained direct, that it can operate successfully in presence of calcium sulphate in the brine and with lower current consumption. The denuder used is of the tower type packed with graphite, which acts as the cathode; the floor space required is much less than in the horizontal type.

A reduction of the voltage required in a mercury cell with a moving cathode is obtained by addition of a wetting agent, such as a sulphonate of chlorinated paraffin, to the sodium chloride solution.[91] It is stated that chlorine free from carbon monoxide may be obtained by using electrodes of silicon carbide, or carbon coated with silicon carbide.[92] Another improvement is the use of an auxiliary anode whereby the cell may be maintained at a suitably low potential isolated from the main current during cleaning.[93] The production of chlorine by electrolysis of by-product hydrochloric acid in a diaphragm cell has been worked out by the I.G. Farbenindustrie A.-G.[94]

Methods of making chlorine by other processes than electrolysis have also received some attention, particularly those involving the use of sulphur dioxide. In one process salt is reacted with sulphur dioxide, steam, and air at red heat. The reaction liberates hydrogen chloride, which is absorbed in water to give a concentrated hydrogen chloride, and oxidized over a copper chloride catalyst at 400° to give chlorine.[95] In another process sulphur trioxide and salt are reacted to form sulphur dioxide and chlorine.[96] Part of the sulphur dioxide is removed and the rest passed over a catalyst to form sulphuryl chloride, which is separated, leaving chlorine to be recovered. The sulphuryl chloride is decomposed to sulphur dioxide and chlorine, and mixed again with the reactants. In a Russian process[97] salt is treated with a mixture of sulphur tri- and dioxides (30–50%) at a temperature above the melting point of the pyrosulphate. The product is a fused pyrosulphate and a gaseous mixture of chlorine and sulphur dioxide. To the fusion enough salt is added to form the sulphate and liberate more chlorine and sulphur dioxide.

A method of separating sulphur dioxide and chlorine is to absorb the sulphur dioxide on zirconium tetrachloride at −10 to 0°, when an additive compound is formed, leaving chlorine to be separated. The complex decomposes at about 100°, to regenerate the sulphur dioxide and the absorbent.[98] An alternative method is to use silica gel to absorb the chlorine from gas mixtures. Three absorbers with inter-coolers are used, and the chlorine is recovered by reduction of pressure.[99]

Hydrochloric acid, which is often available as a by-product of organic chlorine reactions, and which may be contaminated with organic impurities, is of some importance as a source of chlorine. The I.G. Farbenindustrie A.-G. operated a process in which a preheated mixture of hydrochloric acid and oxygen at 200° was passed through molten anhydrous ferric chloride and potassium chloride.[100] After drying the chlorine was recovered by absorption in sulphur monochloride and fractional distillation at 7 atm. In another process[101] contaminated dry hydrochloric acid was subjected to catalytic combustion with air over copper chromite. This oxidized the organic impurities but not the hydrochloric acid. After drying the purified hydrochloric acid was oxidized in a Deacon reactor. Hydrogen chloride may be oxidized by use of a copper oxychloride catalyst between 475 and 600°,[102] or by use of chromium sesquioxide supported on silica gel at 340–450°, this catalyst being regenerated by air blowing at 420–480°.[103]

Purified hydrochloric acid may be recovered from waste gas containing hydrogen chloride by absorption in an anhydrous metal salt such as copper chloride or sulphate in an inert solvent,[104] or by absorption in liquid anhydrous organic oxy-compounds such as dioxane or an ether.[105] A method of obtaining more concentrated hydrochloric acid from aqueous acid is to mix it with ethylene glycol with which hydrochloric acid forms a complex. Water is then boiled off at a temperature below the complex decomposition point, and at a higher temperature the complex decomposes to give ethylene glycol and concentrated hydrochloric acid as a distillate.[105a]

In the production of hypochlorites the most interesting event is the announcement of the production of lithium hypochlorite in a solid form. It is prepared by reacting an aqueous solution of calcium or other alkaline or alkaline earth hypochlorite with lithium carbonate or sulphate. The solution obtained after filtering is cooled to separate a substantial part of the lithium chloride and the solution of lithium hypochlorite is then evaporated. Solid lithium hypochlorite is obtained by drying above 20° but below decomposition temperature under a pressure not exceeding one-tenth of the water vapour pressure at the temperature used.[106] Precipitation of insoluble lithium compound can be prevented by mixing with the solid lithium hypochlorite not less than an equal weight of a water soluble polyphosphate, *e.g.*, $(NaPO_3)_6$ or $Na_4P_2O_7$.[107] It is claimed that the lithium hypochlorite has advantages over other hypochlorites in its greater stability, its compatability with soaps, its complete solubility, and in that it does not form grey soap films on fabrics.[108]

Basic calcium hypochlorite ($CaOCl_2 . Ca(OH)_2$) can be made by passing chlorine into an aqueous suspension of calcium hydroxide at about 30° until crystalline basic calcium hypochlorite separates.[109] Another method of making calcium hypochlorite is to react lime slurry with an excess of *tert.*-butyl hypochlorite. If the reaction is carried out in the vapour phase using calcium hydrate, butyl alcohol distils, leaving solid calcium hypochlorite behind.[110]

In the pulp trade there seems to have been some progress in the use of chlorine dioxide generated at the mill from sodium chlorate and acid in presence of a reducing agent, rather than from sodium chlorite. Chromium sulphite is a particularly suitable reducing agent for this reaction, and it can be recovered for re-use by reduction with sulphur dioxide.[111]

A new use for sodium chlorite is in the preservation and bleaching of raw sugar, a process developed by the National Bureau of Standards.[112] The sugar is sprayed with the chlorite solution, which is allowed to remain in contact with it during storage and transit. The reagent exerts a slow bleaching effect and protects the sugar from bacterial fermentation. It is claimed that it is more effective than chlorine or hypochlorites.

Alkali and alkaline earth compounds

Sodium compounds

Alkalis are not only an essential raw material for some industries, but are also used in small amounts in most industries, so their consumption can almost be taken as a guide to the total industrial output of a country.

During recent years the total U.K. output of alkalis, mostly sodium carbonate, based on 1938 = 100, has been 114 in 1944, 118 in 1945, and 132 in 1946; of these units, 27, 32, and 34 respectively were for export.[113]

The ammonia-soda process for making sodium carbonate had tremendous difficulties to overcome when it was first introduced nearly 80 years ago, but so much attention has been paid to technical details that the large plants now in use are very efficient. Progress in the sodium carbonate industry is therefore generally shown only by minor improvements or adjustments and by increases in output.

Several variations of the ammonia-soda process have been published during the year under review, especially in Russian patents, and three typical variations are mentioned here. In one,[114] instead of absorbing ammonia in brine and then absorbing the carbon dioxide in towers in which sodium bicarbonate is precipitated, it is proposed to absorb the ammonia and carbon dioxide simultaneously in a spray of brine. This may well avoid much of the pressure drop which occurs in the conventional absorption towers, but it has not been shown that it will produce good enough crystals of sodium bicarbonate for satisfactory operation. In the second[115, 116] proposals are made for combining sodium carbonate manufacture with ammonium chloride manufacture. The ammonium chloride is in the mother liquor, which also contains unreacted salt and the little sodium bicarbonate which is soluble; the usual procedure is to recover ammonia from it by distillation with lime. Reinders and Nicolai have shown that, by adding solid salt and ammonia gas, and cooling, the mother liquor yields ammonium chloride and leaves a liquor which is suitable for use instead of brine in making sodium bicarbonate. Ammonium chloride has been made for some years by a somewhat similar process, the only important difference being that the proposed method provides a completely cyclic process giving equivalent yields of sodium bicarbonate (or carbonate) and ammonium chloride. Unfortunately, the uses of ammonium chloride are far fewer than those of sodium carbonate, and unless some large outlet for it can be found there is little prospect of this cyclic process being adopted to any large extent. The third variation[117] is to convert the ammonia and carbon dioxide gases into solid ammonium carbonate, which is then dissolved in brine, and the resulting solution is carbonated with more carbon dioxide to precipitate sodium bicarbonate. This involves handling the solid carbonate, and it is not clear what compensating advantage is obtained to offset this additional operation.

The vital need for more caustic soda has also been exemplified by the publication of various processes intended to provide alternative sources, yet electrolysis of sodium chloride, either in mercury cells or diaphragm cells, and causticization of sodium carbonate with lime are the only processes of industrial importance. The Löwig process for roasting sodium carbonate with iron oxide and then leaching out caustic soda has recently been patented in Russia,[118, 119] and a similar process in which sodium formate is roasted with iron oxide has been patented in Germany.[120] Several German patents[121] have also been obtained on variations in the Kiflu process, in which sodium chloride is converted into fluoride and then causticized with lime, and the fluoride is recycled as K_2SiF_6. An interesting process in which salt, lime, and coke are heated *in vacuo* in an induction furnace to yield sodium vapour which is reacted with water to give caustic soda has also been described.[122] A process[123, 124] has also been described for decomposing sodium sulphate at 1000° with CO_2 and steam, or with reducing agents in the presence of copper oxide, to give SO_2 and fused caustic soda. None of these processes seems to have any possibility of competing with the established processes.

Calcium compounds

In the large limestone burning plants much attention has been paid to the efficient burning of fuel and the production of high quality quicklime.

V. J. Azbe has suggested[125] that better control of lime burning, and consequently less hard-burning of small lumps and underburning of large lumps, can be achieved in a producer gas-fired vertical kiln by recirculating a substantial amount of hot kiln gas, thereby lengthening the burning zone and lowering the maximum temperature which must be reached in the kiln for adequate burning of the limestone. He has also[126] dealt in detail with the four principal factors which need to be controlled if rotary lime-kilns are to be efficient; these are:

1. proper flow of material through the kiln;
2. draught;
3. a proper balance between the superficial temperatures of the lime mass and of the individual lime particles; and
4. full recovery of waste heat by proper pre-heating and cooling.

Modernization of quarrying equipment is important for efficient working, and that the importance of this is realized is demonstrated by recent descriptions of Guest, Keen, and Baldwin's mechanized quarry at Porthcawl[127] and of the Beecroft quarry of Settle Limes Ltd.[128]

Several processes have been put into operation in recent years for making finely divided calcium carbonate of particle size and shape desired for a filler in rubber, paint, and paper. One method, used by the Wyandotte Chemical Co.,[129] is to precipitate calcium carbonate from solutions of calcium chloride and sodium carbonate. This method was chosen because it dovetailed with the sodium carbonate activities of the Company, and permitted easy removal of the impurities in the limestone used in making the raw materials. Another method used in Canada[130] for making a newsprint filler is to carbonate milk of lime and send the resultant slurry direct to the paper mill. For this purpose, which is to make the paper whiter and more opaque, the amounts of magnesia and sulphur compounds must be small. Attempts have also been made to obtain by-product calcium carbonate from other processes, in a form in which it can be used as a filler. For instance, in the reaction of sodium carbonate solution with lime to give caustic soda solution and a precipitate of calcium carbonate, careful control of the lime slaking and causticization reactions can yield a calcium carbonate filler.[131, 132] However, the output of caustic soda is limited by the output of calcium carbonate filler, and the separation of fine calcium carbonate from caustic soda liquor is not easy. Carbonation of milk of lime has the advantage of simplicity with no need to wash out a by-product, but the other methods have the advantage of using solutions and thereby avoiding the presence of insoluble impurities in the product.

Other alkaline earth compounds

An improved method of making barium carbide has been patented[133] which involves passing a porous agglomerated mass containing powdered coke and barium oxide or carbonate through a tubular furnace at 1600°. This avoids the corrosive action of the barium oxide. Carbon monoxide is removed as it is formed by passing hydrogen through the furnace. It might be economic to substitute barium carbide for calcium carbide in the manufacture of acetylene, despite the extra cost of barium compounds, because baryta, being water-soluble, could be recovered by dissolving it from the residue from the acetylene generator. Impurities such as silica and alumina, however, reduce the yield of carbide, and there are probably other difficulties to be overcome.

There has been little published on magnesium compounds except on the oxide. The output of magnesia during the war was expanded considerably for the manufacture of magnesium for light alloys and flares. Established methods were used, such as dissolution as magnesium bicarbonate from calcined dolomite followed by decarbonation to precipitate magnesia, or precipitation of magnesia from sea water by lime or calcined dolomite. An acid extraction process from North Carolina olivine (MgO 47%, SiO_2 43%, FeO 7%), has been investigated at the U.S. Bureau of Mines.[134] The process involves dissolution of the magnesia by hydrochloric acid, followed by evaporation of the solution and calcination of the resultant magnesium chloride to give magnesia and hydrochloric acid; laboratory tests have shown that there would be difficulties in filtering off the iron hydroxide-silica residue from the magnesium chloride solution.

For electrolysis the magnesia must be converted into anhydrous magnesium chloride. Hydrated magnesium chloride cannot be used because it hydrolyses. It may be dehydrated by heating with ammonium chloride at a temperature above 250°, at which reaction occurs and any basic hydrolysis product is reconverted into chloride.[135] Usually, however, magnesia is reacted with carbon and chlorine in a furnace, and Magnesium Elektron Ltd. have published some details of methods of carrying out this operation.[136] Powder containing at least 20% of hydraulically setting magnesia is mixed with water or magnesium chloride solution, a reducing agent such as coal or peat added, and the mixture formed into spheroidal pieces and chlorinated in a furnace to fused anhydrous magnesium chloride for the electrolytic cells.

Industrial gases

Hydrogen.—The large-scale production of hydrogen and hydrogen-bearing gases is considered here in its relation to ammonia, methanol, and hydrocarbon synthesis. Whilst technical developments in water gas and producer gas generation are reported under the " Gas " section there is one important development which is mentioned here, as the principles involved may be found applicable to other reactions between solids and gases. This new process[137] for the production of water gas and producer gas is based upon the fluidized powder technique of catalyst cracking.

The process involves supporting a mass of finely divided solid particles in a rising gas stream, under conditions of flow controlled to ensure a high degree of turbulence and a high concentration of particles without loss by entrainment. Avoidance of local overheating and better control of reaction conditions are some of the many advantages claimed for this process. The "fluidizing" technique has already been applied to the steam-iron reaction for the production of hydrogen of 99% purity.[138] The method should allow the use of a much smaller plant for this reaction because of the higher ratio of gas to catalyst.

In a review of present-day processes for the manufacture of hydrogen[139] the construction of a large plant for the direct pyrolysis of hydrocarbons to carbon black and hydrogen is described. The hydrogen obtained by this process is, however, of low purity. L. Tronstad has claimed a method for producing electrolytic hydrogen for ammonia synthesis[140] which is part of a multi-stage process for the preparation of heavy water and metals or alloys of low carbon content. Some of the hydrogen-deuterium mixture which is produced is used for the reduction of metallic oxides, the resultant $H_2O + D_2O$ being recycled to the electrolysis unit.

The kinetics of the reaction between carbon monoxide and steam, using a zinc oxide catalyst, have been studied.[141] Velocity constants and activation energies were determined, and it was found that over the temperature range 270–400° the reverse process is negligible.

The purification of ammonia synthesis gas, by treatment with water under pressure for removal of CO_2, and scrubbing with copper liquor for removal of CO, is well known. The theoretical considerations underlying these reactions have been discussed,[142] and performance data for water scrubbing on a Russian plant have been disclosed.[143] The details of operation of a proposed two-stage scrubbing unit are also given. It is claimed that this can be operated more economically than the normal single-stage unit, and reduces loss of the nitrogen-hydrogen mixture.[143] A new absorbent for carbon monoxide[144] is promoted silver oxide in which the silver is at least partly in the bi- or multivalent form, *e.g.*, as $(Ag_3O_4)_2$. It is doubtful whether the use of this absorbent would prove economic in the purification of ammonia synthesis gas.

Argon.—The residual gases from the manufacture of synthetic ammonia may contain up to 40% of argon mixed with nitrogen and hydrogen. The process employed by the Soc. Ammonia e Derivati for the production of argon from these gases[145] is first to obtain crude argon by liquefaction. Hydrogen and methane are then removed by treatment with granulated copper oxide at 800°, and the resultant carbon dioxide removed by scrubbing with potash solution. The oxygen liberated by the cupric oxide during the above process is removed by potassium pyrogallate and caustic potash. The resulting argon, after drying with phosphorus pentoxide, conforms to the specification of maximum impurities permissible for electric light bulbs. 100% argon is obtained by passing this product slowly through calcium containing 10% of potassium at 500°.

Oxygen.—Although no novel principles or procedures have been reported from investigations of modern liquid oxygen plants operated in Germany it is worthy of note that the only steel which was found to be suitable for replacing copper in low-temperature construction was an alloy containing 18% Mn, 3–5% Cr, and 0·4% C.[146] The Linde Air Products Company of America have patented a process[147] for producing oxygen of high purity from air. Air and steam are passed alternately over a contact mass consisting of sodium manganate, which collects oxygen from the air and releases it to the steam.

Some attention has been directed to the improvement of ozonizer performance in the U.S.A.[148] Reducing the moisture content of the inlet air from 0·02 to 0·001 g. per g. of dry air increased the output of an ozone generator sixfold. The yield of ozone was found to be unaffected by the relative humidity of the inlet air below a moisture content of 0·001 g. per g. of dry air. For maximum output, therefore, the dew point of air used in the production of ozone should not exceed −17°.

Carbon dioxide.—The Air Reduction Co. Inc. have described[149] an apparatus and procedure for producing pure liquid carbon dioxide from "dry ice." This entails separation of the oil, used as a plasticizer in "dry ice," after melting the solid carbon dioxide above the triple point pressure. The vapour is filtered from the impure liquid carbon dioxide, at a pressure of 60–150lb. per sq. in., and then condensed, using the impure liquid as coolant. Considerable interest has been aroused in the application of "dry ice" for the production of artificial rain. Several experiments have been carried out during the past year[150] in which "dry ice" has been dropped from aircraft on to cumulus clouds, sometimes successfully.

The well-known catalytic reaction of hydrogen and carbon monoxide, to give methane or other hydrocarbons, has been the subject of a recent literature survey[151] and a review.[152] The production of methane by biochemical synthesis from non-fibrous carbohydrates[153] is a process which is now in the pilot plant stage. A new culture (*Methanosarcina barkerii*) capable of effecting the biochemical synthesis of methane from carbon monoxide and hydrogen has been described,[154] but it is difficult to visualize this being adopted on a large scale in preference to the catalytic process.

Miscellaneous

Peroxides

While there is nothing of interest to report on the usual electrolytic route to hydrogen peroxide, there has been some activity on alternative methods of production. The German process operated at Hollriegelskreuth has been described.[155] At this factory hydrogen and oxygen were combined in a silent electrical discharge. Hydrogen, oxygen, and water were passed at 160° over banks of quartz plates, spaced 5mm. apart. One side of the plates was coated with aluminium and the other etched. Alternate plates were connected in parallel and ionization was carried out at 12,000v. 9500 cycles, 0·96 kw. per pair of plates. The exit gases were cooled and scrubbed to recover 10% hydrogen peroxide solution. The product could be stored without stabilization before distillation. A 2000kw. unit was planned, for which the power consumption was estimated to be 62·6kw. hr. per kg. of hydrogen peroxide. The reaction of hydrogen, oxygen, and water by passing the gaseous mixture through a reaction vessel lined with fused boric acid at 5 to 35 atm. pressure and 400–600° is also described.[156]

Instead of hydrogen, hydrocarbons may be used for the preparation.[157] For instance, they may be burned incompletely in an apparatus of non-crusting steel with a wall cooled below 300°; 90% propane and 10%

oxygen may be preheated and then burned at 470°. The products of combustion are cooled to give a solution of hydrogen peroxide with lower aldehydes as by-products. Fractionating this mixture may cause explosions, which are avoided by converting the organic peroxides to carboxylic acids by heating. In another process hydrocarbons are oxidized at 300–600° in a vessel with a smooth non-porous interior surface coated with boric acid, keeping the temperature below the point at which all the gaseous oxygen reacts.[158]

A method of production of hydrogen peroxide from alkali amalgam is to react the amalgam with a watery liquid continually provided with oxygen. The method suggested is to use potassium amalgam from an electrolytic cell and to dilute it with mercury till the potassium content is only about 0·0003%.[159]

Aluminium Compounds

The development of methods whereby alumina can be economically extracted from clays and low-grade bauxites continues to attract attention. Mechanical methods of removing silica from low-grade bauxites seem to be popular in America, and the U.S. Bureau of Mines[160] has published details of investigations in which acceptable concentrates containing less than 7% of silica and 6% of iron were made. The methods involved were classification and tabling to remove iron oxides, flotation with caustic soda, oleic acid, and talloil to remove silica, and sometimes magnetic separation of magnetite. The silica content may also be reduced to 7% by allowing the surface gangue to hydrate during wet grinding of the crushed bauxite, followed by de-sliming.[161] Acid extraction of alumina from clay or felspars has also been tried, partly because other valuable products can be isolated at the same time. One method[162, 163, 164] involves stewing calcined clay with hydrochloric acid, removing insoluble materials, crystallizing aluminium chloride from the solution, and calcining the chloride to yield alumina and hydrogen chloride. Soluble by-products accumulate in the mother liquor and can be removed periodically. Clays can also be mixed to a stiff paste with sulphuric acid and then roasted for an hour at 200–250°, after which aluminium sulphate can be extracted with water.[165] The large amount of clay which must be treated, and the difficulties of operating such processes, are among the reasons why the Bayer method of aqueous caustic soda extraction of bauxite remains the most important process for making alumina industrially. Clay has also been roasted with calcium carbonate and sodium carbonate, and the alumina leached from the ground product by sodium carbonate solution and precipitated by treatment with CO_2.[166, 167] Gelling sometimes occurs during the leaching, and it was found that gelling always occurs eventually, the rate increasing rapidly with caustic soda concentration. The nature of the gel seems to be a suspensoid based on calcium silicates and colloidal alumina, and gelling can be inhibited by sugars and by sodium hexametaphosphate.

At Ludwigshafen-am-Rhein[168] alumina was produced by treating bauxite with sodium sulphate, lime, and anthracite, to give sodium aluminate, sulphur dioxide, and carbon dioxide. The process was interlocked with the Bayer process, and gave alumina and sodium carbonate decahydrate. Part of the alumina was converted into aluminium sulphate and alum.

Silicon compounds

Silica sols have been known for a considerable time, but have not achieved any real importance until recently. They can be made by neutralizing sodium silicate solution, but the resultant sol is unstable unless part of the alkalinity remains free and the silica content is below about 3%. The neutralization can be carried out with sulphuric acid, but as the sols have been considered largely for coagulating suspended matter in raw water, neutralization with chlorine so as to give a hypochlorite/silica liquor with sterilizing properties has been tried. Treatment with ammonium sulphate, sodium bicarbonate, and alum have also been investigated as a means of giving more stable sols useful in water treatment, and these sols, particularly the Bayliss sol, are becoming more and more important. Recently an improved method has been patented[169] whereby silica sols of silica content as high as 18% and total sodium content below 0·5% can be made, ion-exchange resins being used to remove the alkalinity from sodium silicate solution. It is claimed that these sols are much more stable than those hitherto available, possibly because of their low electrolyte content. The absence of electrolytes introduces other potential benefits and makes it possible to use silica sol instead of the more expensive ethyl silicate. The adhesive properties, high silica content after drying, and absence of fluxing compounds permit its use for bonding refractory materials and in the recently introduced precision casting method of making accurately dimensioned small metallic castings. It may well also be useful either as a filler or for surfacing in the paper industry. Most of the developments have so far taken place in U.S.A., and it is too early yet to judge whether the promising forecasts are likely to materialize. A silica sol which it is claimed will change reversibly from sol to gel by heating in an autoclave, and back from gel to sol by shaking, has also been made by dialysis.[170]

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FUEL

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THE past year has been notable for fuel in this country for a number of reasons. It has seen the National Coal Board take over the coal mines and certain ancillary industries from 1st January, 1947, whilst the British Electricity Authority[1] has been set up to exercise similar functions for the electricity undertakings. The year has also seen a recrudescence of activity of various organisations in arranging conferences, amongst the more important of which, from the fuel aspect, have been the Ministry of Fuel and Power "Fuel and the Future" Conference, October, 1946, the Smoke Abatement Conference in March, 1947, jointly by the Institute of Fuel and the National Smoke Abatement Society, the Institute of Fuel Pulverized Fuel Conference in June, the Royal Institute of Chemistry Symposium on Coal, Petroleum and their Newer Derivatives in July, the Eleventh International Congress of Pure and Applied Chemistry also in July, and the National Smoke Abatement Society's Annual Meeting in October. The first post-war conference of the World Power Conference at the Hague in September was also of great interest to this country.

One of the first acts of the National Coal Board was to take over the responsibility of the Mining Association for the support of the work of the British Coal Utilisation Research Association[2] and this was followed by negotiations for the transfer to the Board of the Coal Survey[3] of the Fuel Research Station of the Department of Scientific and Industrial Research.

The year was also notable for the fuel crisis in the spring, when severe weather accentuated the parlous state of the country's fuel position. A similar position also arose due to bad weather in the eastern states of the U.S.A., although the fuel affected particularly was natural gas. In both cases inability effectually to control domestic consumption led to curtailment of supplies to industry. An upward trend in this country's coal output is, however, now clearly visible, and the target of 200 million tons for 1947 should be realized.

Steps are also being taken in other countries to secure adequate regulation of fuel industries. Australia has passed the Coal Industry Act[4] and appointed a Commission to report upon the Coal Mining Industry.[5] A Canadian Royal Commission has reported against nationalization of the Coal Industry.[6] South Africa, by the Liquid Fuel and Oil Bill,[7] is aiming to assist the production of liquid fuel from low-grade coal.

The two councils, for Domestic and Industrial consumers respectively, to be set up in this country under the Coal Industry Nationalization Act have been duly appointed.[8]

The P.E.P. organization has published "British Fuel and Power Industries,"[9] which surveys in a comprehensive manner all aspects of fuel and power, national resources and production, consumption and organization.

Fuel resources and production

The world's coal reserves have been surveyed by C. A. Carlow,[10] who considers that substantial reduction should be made in the previous estimates, and concludes that a new appraisal is overdue since reserves may be perilously small. What is virtually the only lignite deposit in Great Britain is now being worked,[11] and is considered to be a potential source of hard wax similar to German montan wax.

A survey of the Australian coal reserves[12] gives the total as more than 16,000 million tons of black coal and 40,000 million tons of brown and sub-bituminous coal. The Blair Atholl field in Queensland, now being exploited, is estimated[13] to contain actual reserves of 116 million and a probable 90 million tons. South Australia possesses deposits of bituminous coal,[14] but they are inaccessible owing to depth of cover and to water. The only accessible deposit is of sub-bituminous coal at Leigh Creek, and contains about 380 million tons. Steam drying of this coal by the Fleissner process,[15] briquetting and cleaning have been investigated. The brown coals of Victoria have been surveyed by A. B. Edwards,[16] who traces their change in moisture with depth of burial and variation in the chemical composition of the ash with conditions of sedimentation. The reserves of coal in New Zealand have been reconsidered,[17] and it is concluded that previous estimates were not reliable. Substantial reserves can be mined by opencast methods. Deposits of bituminous coal of the order of 2·5 to 5 million tons are reported from Tanganyika, and their geology is described.[18] Canadian coals are reviewed by R. E. Gilmore and E. J. Burrough.[19] Coals of all ranks from semi-anthracite to lignite are produced, chiefly in Alberta, but 70% is bituminous. Reserves are estimated at 99 billion tons. Coal consumption[20] is 41 million tons of bituminous coal and 4 million tons of anthracite, of which more than half is imported from the U.S.A.

The U.S. Bureau of Mines has reported[21] that in Alaska coals occur in Permian, Cretaceous, and Tertiary rocks. The reserves are estimated as lignite and sub-bituminous 69×10^7, bituminous 25×10^9, and anthracite 2×10^9 short tons. The analyses of typical samples are given. Chinese coal reserves are given as 240,847 million tons according to the latest estimate,[23] which places her fourth in world reserves. Coal is found in nearly every province, and 78% is high rank, bituminous. Details of the reserves are given in a series of papers.[24] Large but inaccessible coal reserves, 18,000 million tons, are reported in Columbia.[25]

French coal production [26] in 1946 at 49·5 million tons was greater than in 1938, 47·5 million. The South Limburg field of Holland has been the subject of renewed war-time study.[27] Japan's reserves are given[28] as 16·7 million tons, and those of Manchuria as 17,400 million. Coal production in Poland in 1946 is estimated[29] at 46 million tons. Spain's resources of coal are given[30] as 140 million tons of anthracite, 4000 million tons of bituminous, and 8000 million tons of lignite. Total coal production in 1946 was 13·8 million tons,[31] compared with a pre-war maximum of 7·5 millions in 1937. The Spitzbergen coal output[32] in 1946 was 60,000 tons.

A. C. Fieldner[33] estimates the coal reserves of the U.S.A. as 3200 million tons, of which 0·6% is anthracite, 56·4% bituminous coal, 23·1% sub-bituminous, and 18·7% lignite. The U.S. Bureau of Mines has studied the washing characteristics of Pittsburgh[34] and of Nevada coal.[35] It also estimates[36] the reserves at Coalcreek, Colorado, at 65 million tons of coking and 35 million tons of non-coking coal.

The need for a practical classification of British coals based on quality has been stressed,[37] and E. S. Grumell[38] has proposed a system of pricing based on the heat units in the coal, the efficiency with which these units are used, and a utility or convenience factor.

Peat

Methods of winning and drying are discussed by Clement and Robertson,[39] and the Ivanov system of combustion of powdered peat is described. Tomter[40] describes a technically successful method of winning peat by scraping off layers ¼ – ½in. in depth, and which is economic on a scale of 50,000 tons per year. The peat formations of Holland have been examined in detail.[41] No regular variation in successive layers of the Drente bog was found. The character of peat is concluded to be a function of its physical structure. A change in oxidation-reduction potentials with depth has, however, been found by Apushkin.[42] Analytical data for peat assembled over eleven years have been used to study the variations in moisture, ash, and calorific value.[43]

Physical and chemical properties of fuel

Flora and fauna of coal

A new classification of " spore types " has been proposed.[44] Jongmans has dealt with the correlation based on fossil plants of the British coalfields[45] and of the coal basins[46] of the U.R.S.S., China, and other Eastern countries. As a result of a bore near Ashington, Northumberland, it is considered[47] that the Ashington Marine Bed corresponds to the Skipsey Marine Bed of Scotland and the Bolton Marine Horizon of Cumberland. A revision of the data from a much earlier boring has led[48] to the identification of the Top Busty Seam with the Tilley Seam, and that recorded as Bottom Busty is in reality the Top Busty. The faunal sequence of the Kent coalfield has also been studied,[49] and Trueman has published two parts of a monograph on the zonal classification of the British Coal Measures.[50] New South Wales coals have received the attention of Dulhunty,[51] and the coal measures of Belgium have also been studied.[52] The flora of the Kaiping (China) coal basin are found to be of an age corresponding to the Westphalian of Europe.[53]

Physical properties of coal

A general review of the theories of coal constitution has been undertaken by Cassan.[54] The importance of the capillary structure of coal has been stressed by Wilkins,[55] who shows that the free space within the coal substance varies systematically with its rank. Fusain bands and durains are more permeable than vitrains. *X*-ray powder photographs of bituminous coals and of the products of their partial and complete carbonization[56] has shown that this process with coking coals is analogous to the carbonization of certain pure organic compounds, *e.g.*, dibenzanthrone. The *X*-ray patterns of Tertiary lignite[57] and Tertiary anthracites have been found to be different, the latter showing more free carbon.

A detailed study[58] of coal/methane systems shows that below 100 kg. per sq. cm. pressure most of the methane is adsorbed; above 200 kg. per sq. cm. the amount of compressed free gas exceeds the adsorbed.

Chemical properties of coals

Inorganic constituents.—The inorganic constituents normally present in coal have been classified[59] into shales or clays, sulphides and carbonates. Their effect on the behaviour of the coal, *e.g.*, towards cleaning, and their changes on heating are considered. Producer and boiler flue dusts may in certain cases contain concentrations of the less commonly occurring constituents, *e.g.*, vanadium, germanium, or gallium. The relations of the chemical composition of coal ash with its softening temperature and the viscosity of the molten slag have been reviewed[60] in connexion with the clinkering behaviour of coal and the use of slag tap furnaces.

Pyrolysis.—Gillet[61] has continued his studies of the pyrolysis of coals from 7–31% in volatile matter. The resulting changes are regarded as simulating the natural progression of coals of successively higher ranks, and a theory is developed according to which coals are macromolecular derivatives of a polynuclear hydrocarbon in the neighbourhood of C_{26}.

Sulphur and nitrogen.—The reaction of elementary sulphur with coal which can be readily followed through its gaseous products is being used[62] to elucidate its internal structure. The forms in which nitrogen and sulphur occur in organic combination in coal have been shown[63] not to be uniform since some concentration can be effected by specific gravity separations.

Oxidation of coal.—The oxidation of coal by elemental oxygen has been reviewed by Kramers.[64] The products are classified into (*a*) peroxidic complexes, (*b*) alkali soluble, water insoluble "humic acids," (*c*) "water soluble acids," or (*d*) gaseous end products. The need is emphasized for further study, particularly of the "humic" and "soluble acids," with a view to technical applications. Oxidation,[65] particularly by oxidizing reagents, is considered to have been the most productive method of obtaining information on coal constitution. Humic acids are an intermediate stage leading to hydroxy acids, which finally give simpler end products, *e.g.*, acetic, oxalic, and benzenoid acids. Connexions have been traced[66] between the yield of acetic acid on oxidation and the behaviour of a coal on carbonization.

Humic acids.—The humification of organic matter and its subsequent conversion to coal is considered by Sandor and Smith.[67] Both the cellulosic and lignin constituents of the original vegetation are now regarded as participating in the formation of humus and of the alkali-soluble humic acid. In recent work methyl glyoxal has been advanced as an intermediate in the humification of cellulose. The thermal decomposition of peat-bog dopplerite[68] and of pure humic acids[69] has been shown to give rise to bitumens similar to those extractable from coal and possessing coking properties, and it is concluded that bitumens are formed from peat during its coalification. Over 250 solvents have been tried[70] for the separation from mineral matter and fusain, of humic acids from oxidized coal. The nitrogen in such humic acids has been found[71] to exist in two main forms, one which yields NH_3 with alkaline permanganate and the other nitrate ion.

Hydrogenation studies.—The volatile oils arising from the action of hydrogen on Pittsburgh seam coal have been preliminarily separated[72] chromatographically and the chemical nature of the fractions further investigated. The hydrogenation of lignin[73] over Raney nickel has also been studied.

Solvent extraction.—According to a review[74] a satisfactory ceramic filter for separating Pott-Broche coal extract from the residue has been developed. About 2400 tons of coal were extracted per month in Germany, giving 52·7% of extract, which was used in the manufacture of electrode carbon. It has been proposed[75] to determine the quality of coal on the basis of its solubility in different organic solvents. Peat has been shown[76] to contain from 3–17% of ester wax similar to montan wax, but it contains more resinous material and has a melting point lower by 10–15°. The German production[77] of montan wax and of the preparation therefrom of the synthetic I.G.[78] waxes is described.

Coal-mining and preparation

Well-illustrated reports[79] on the methods adopted in the German open-cast brown coal mines are now available, and the Mechanization Advisory Committee has published[80] reports on German deep-mining in the Ruhr. Recent developments in coal mining in the U.S.A.[81] and in Britain[82] have also been described.

Demart[83] estimates the economy in man-power in underground gasification to be about 80%, and that electricity generated by a gas turbine using the gas produced would cost 0·045 francs, against 0·256 francs for a coal-fired steam plant. The first officially known experiment in underground gasification outside the U.R.S.S. has taken place at Gorgas Mine, Alabama.[84] No difficulty in maintaining combustion was experienced, but gas quality was low even with the use of oxygen. Production by underground gasification in the U.R.S.S. is planned[85] to reach 33,000 million cubic ft. by 1950.

Dust problems.—Further evidence for the value of both finely powdered aluminium[86] and dry hydrated alumina[87] in the treatment of pneumokoniosis has been obtained. The theory and principles of dust sampling[88] have been surveyed together with the methods in use. A study[89] of the composition of air-borne dust in S. Wales has been published. Great variations are found in the dust from anthracite workings.

In general, water sprays at appropriate points have been adopted to suppress dust,[90] but the use of wetting agents[91] and of foams[92] are also being tried. A special study[93] of the wettability of coals shows them to be variable in this respect. The danger that imperfect mixing of stone dust with coal dust will not prevent explosion is emphasized by the Safety in Mines Research Board.[94]

Handling and storage of coal.—A bulletin has been prepared advising how to handle and stock coal to avoid losses by overheating.[95] The successful storage of non-coking bituminous coal (40% V.M.) in a compacted layer 13ft. deep is reported.[96]

Coal preparation.—A report has been prepared[97] on the vexed question of coal sizes and classification, and recommendations are based upon existing preferences. Seven sizes of graded coals are proposed, from "large cobbles" (6in.–3in.) down to " grains " (¼in.–⅛in.). In this connexion the " Inconsistency Factor "[98] has been introduced to indicate the range within which will lie 90% of the samples of coal of a certain size. The fundamentals of coal sampling have been considered by Badger[99] and Visman,[100] and the statistical methods used in sampling surveys and their interrelations have been reviewed.[101]

The Fleissner system of drying has been applied successfully[102] to Victorian brown coals. A turbine-type drier made by Büttnerwerke has been described.[103] For fine coal drying the thermo-Venturi type has been developed.[104]

Coal cleaning.—Grumell and Dunningham[105] have shown that the averages for British coals of the ash in "pure" coal ($d<1{\cdot}35$), middlings ($d<1{\cdot}60$), washed coal ($d<1{\cdot}60$), and dirt ($d>1{\cdot}60$) are 2·8, 14·4, 4·4, and 60–70%. The efficiencies of coal washing plants have been discussed by Hancock[106] and by MacLaren.[107] The separation[108] of certain Yorkshire coals into a float fraction ($d<1{\cdot}29$) largely consisting of bright coal possessing coking properties and a higher gravity fraction comprising largely durain has been shown to be possible. Several general reviews of developments in coal preparation and washing have appeared. Richardson[109] refers to the increase in refuse, in fines, and in top size of the material coming from the mines. Driessen[110] regards the heavy medium method of separation of fine coal <¼in. as still under development, and refers to the cyclone washer, which uses centrifugal force in place of gravity.

Froth flotation[111] is regarded on the Continent as best for fines below ½mm. Centrifuges drying fines to 10% moisture show promise. Jig washers handle 87–88% of the coal washed in the Ruhr,[112] including that under 8 or 10mm. size. Sizes below 10mm. are dedusted before washing, with benefit on the dewatering of the coal and clarification of water. Dust under 0·75mm. is commonly handled by froth flotation.

Scholes[113] has described a development of heavy medium washing in which the floor of the tank consists of an upwardly sloping band conveyor. Developments in Rheolaveur Trough washing in Belgium are also considered.[114]

A countercurrent system of spraying for " desliming " a slack coal has been developed,[115] and may serve as an alternative to dedusting for damp coals.

Lessing[116] has advocated that all coal should be crushed to <4in. dedusted and then separated by gravity washing into bright coal, $d<1{\cdot}35$, dull coal and middlings, $d=1{\cdot}35$–$1{\cdot}6$, and mineral refuse, $d>1{\cdot}6$.

In this country, as in Germany, the preparation of ultra-clean coal has been undertaken to provide coke for electrode manufacture. Nelson[117] describes the froth flotation of a coal which yielded a coke of not more than 1% ash. Details have also been given[118] of an electrostatic cleaning method which the Germans were developing.

Briquetting.—J. B. Reed[119] has reviewed the principal types of press used in briquetting and the great variety of materials suggested as binders. The importance in briquetting of the wettability of the coal by the binder is emphasized. For brown coals the humic acid content is also of importance. The drying of peat preparatory to briquetting for use in gas producers and for carbonization is described.[120] Briquettes made from peat after explosive disintegration by superheated steam are said to yield excellent coke.

Coke properties and production

Coke quality

The physical behaviour of coke in a blast furnace is stated to be[121] predictable from an index which characterizes its resistance to gas flow. That the particle size should be sufficient to permit gas flow is agreed[122] to be important besides the resistance to shatter and abrasion. Drum stability tests are discussed. A method of evaluating the binding power[123] of the bitumens in coke by means of a point attached to a swinging pendulum has been devised.

In the U.R.S.S. electrical conductivity is being used to assess coke quality and to study the coking process. Thus Obukhovskii[124] uses the method to measure the uniformity of a coke charge from an oven. Study of the conductivity[125] during coking suggests that coke shows the characteristics of an electronic semi-conductor in which the carbon lattice is influenced by mineral admixtures. The same authors[126] have studied the heats of wetting with methyl alcohol of coke obtained from the separate petrographic constituents of coals.

Coking practice

In order to produce a coke satisfactory from the point of view of ignition and combustion characteristics for domestic open grate purposes carbonization of low ash, $>4\%$, coal preferably cleaned at the colliery is essential.[127] The increased use of cleaning coupled with blending of high and low-volatile coals for metallurgical coke results[128] in greater uniformity in its physical and chemical properties. A semi-coke from low-temperature carbonization[129] of Silesian weakly-caking coal has been found to give a satisfactory metallurgical coke when blended with the same coal, and a similar effect has been found with certain American coals[130] from Utah.

Agroskin reports[131] that for three years some coke ovens have been washing coal with petrol—as has also been reported in the U.S.A.—with the object of increasing coke yield. Coke and tar quality are also improved. Anthracene oil may also be used. In this connexion studies[132] of the wettability of coals by hydrocarbons have been made. The effect of the wetting is to increase the weight of coal charged to an oven.[133]

The slight changes in coal composition which are sufficient to change a coking coal of normal behaviour into one showing dangerous swelling properties have been described.[134] The difficulty was particularly acute when endeavouring to prepare a low-ash coke of the required density for electrode carbon manufacture. Addition of 5% of breeze assisted.

Carbon

Long and Norrish[135] conclude that 125 kcal./g.atom is the correct value to take for the latent heat of sublimation of carbon into mono-atomic vapour in the ground state. Electron micrographs and *X*-rays have been used[136] to study charcoals and soots. The behaviour of graphitic oxide black suggests that not only the unsaturated carbon atoms in the prismatic planes are active in adsorption and catalysis. Calculations by Coulson[137] lead to the conclusion that graphite may be called a true electronic semi-conductor. A carbon isotope C^{13} is now available[138] for use as a tracer element.

An active carbon has been prepared[139] by chlorinating 6–20 mesh coal until a 100% gain in weight has taken place. The residue was pelleted with hydrolysed starch as a binder, and baked, crushed, and steam activated at 800°. Active carbons for respirators, solvent recovery, and decolorizing were prepared[140] by the Germans from peat. The peat was mixed with 45% $ZnCl_2$ solution to give a paste of peat: $ZnCl_2$ of 70:30, which was extruded and activated at 700°, followed by leaching with HCl and treatment with $CuSO_4$ and K_2CO_3. An active carbon of fair to good activity can also be prepared[141] from raw unbriquetted anthracite and semi-anthracite.

Low-temperature coke

Additional information relative to the Krupp-Lurgi low-temperature carbonization process, which produces a smokeless domestic fuel, has been secured.[142] The price secured as domestic fuel was 20–22 marks per ton, as compared with high-temperature coke 16–18 marks.

A novel method of carbonization is reported by Carter,[143] according to which slack Utah coal in a layer ½in.–1½in. thick is heated to 400–510° whilst being vibrated. The residence time is 1–3 minutes, after which the semi-coke is compressed into cylinders called "coal logs." The fluidization technique has now been applied to carbonization. Singh[144] reports the low-temperature treatment of powdered bituminous coal. The removal of volatile matter can be controlled to a considerable extent, and the "char," which consists of hollow spheres, may be blended with coal to yield satisfactory cokes, or may be used as powder for cyclone-type firing or in complete gasification.

Combustion of solid fuels

The processes involved in the combustion of fuels have been reviewed by A. C. Egerton[145] and D. T. A. Townend.[146] At low temperatures the oxidation of coal and carbon is conditioned by the formation of a carbon-oxygen-water complex. At high temperatures the initial product in fuel beds is carbon monoxide. The reactions taking place in a producer have been considered by Prettre,[147] and a simplified kinetic theory advanced. The rate of combustion of carbon between 900° and 2650° has been studied.[148] A study of the kinetics of the steam/carbon system[149] at temperatures of the order of 700° and up to 1 atm. pressure has shown that the steam/carbon reaction, the primary product of which is carbon monoxide, is of fractional order with respect to steam and is strongly retarded by hydrogen. The carbon dioxide/carbon reaction is likewise of fractional order with respect to CO_2 and is strongly retarded by CO. The resultant rate for both these reactions takes the form, rate $= \dfrac{k_1p_1}{1+k_2p_2+k_3p_1}$ where p_1 and p_2 are the pressures of steam and hydrogen or CO_2 and CO respectively. This expression is found to provide a consistent interpretation of earlier conflicting results. The reaction between water and charcoal at substantially lower pressures of the order of <1mm. Hg has also been studied.[150] The proportions of the CO and H_2 in the product gases were found to vary in a manner which was explainable in terms of the adsorption of water vapour, hydrogen, and CO.

Vulis[151] has considered the absolute rate of combustion of carbon, and proceeds to calculate the time required for the radius of a burning coal particle to decrease from one value to another. The effect of a growing layer of ash on the rate of combustion is also calculated. A study of the combustion of coal particles has also been reported by Orning.[152] Preliminary data indicate that the rate of combustion is not directly proportional to the partial pressure of oxygen. The work of the U.R.S.S. Thermotechnical Institute has recently been summarized.[153] Studies of the combustion of definite coal shapes, *e.g.*, cylinders and spheres have been made and mathematical analysis attempted, but the latter have so far only proved solvable by making simplifying assumptions. The mathematical study of fuel beds has proved even more intractable, but certain characteristics of the dynamics of gasification have been graphically presented. In continuation of their studies of the combustion of coal on a chain-grate stoker, Marskell, Miller, and Joyce[154] have found that a small-scale pot-furnace gives an accurate picture of the process on a full-scale unit. The degree of correlation between the combustion characteristics of representative Illinois coals and their chemical properties and petrographic composition has been examined.[155]

Fuel utilization

Industrial boilers

According to a survey[156] of British water-tube boiler practice, units from 10,000 to 1 million lb. of steam/hour are now made, and, with full heat recovery, 90% of the net heat in the fuel is presented as steam to a turbine. Forced circulation is becoming more common, and grates in which the grate itself is carried on a driving chain are being adopted. The tendency is towards pulverized fuel firing. The various types of forced circulation are described by Patterson.[157]

Most of the recent German[158] boilers were of forced circulation type. Brown coal was the fuel for 65% of the stations, and in many cases in pulverized form. Fouling of gas passages in superheaters and deposits inside the boilers were commonly experienced. Burst water tubes in the German Navy led to an extensive investigation,[159] and was largely traced to unsatisfactory water circulation. The development of German types of rotating boilers is described.[160] Experience with the mercury boiler in the U.S.A. has been so satisfactory[161] that a further boiler is to be installed. C. S. Darling has reviewed[162] British fuel-burning developments: (1) equipment to burn a wide range of fuels; (2) chain-grate stoker to burn filter cake; (3) spreader-stokers; (4) equipment for shell-type boilers; (5) Meldrum sprinkler-stoker; (6) Oldbury chain-grate stoker; (7) Doby stoker. A substantial saving in coal is to be expected[163] from the conversion of hand-fired shell boilers to mechanical firing, as well as other advantages. A review of underfeed stokers has been prepared by Tinley,[164] who discusses the suitability of coals for these stokers. The spreader-stoker has found increasing use[165] in the U.S.A. by reason of the fact that it will handle a wider range of coal than other stokers.

The Cyclone burner has also been developed[166] to use efficiently coals containing much ash of low fusion temperature, but at the same time reducing the emission of fly ash, by operating so that the ash is fused. The need for adequate instrumentation in boiler houses has often been stressed, and a Bulletin[167] has been issued describing the types available and their correct positioning.

The use of mechanical stokers on locomotives has been reviewed.[168] Better fire control, rapidity of grate cleaning, and increased availability results.

Partridge[169] reports on trials of slurry blended with other fuels, such as washed pearls, coke breeze, anthracite gum, etc. The Mining Association[170] describe and discuss practices at boiler plants in colliery districts. The work of the Shell-type Boiler and Firing Equipment Committee has shown[171] that the efficiency of a shell boiler decreases with increase in rating, and such boilers should not be operated at more than 70% of the normal maximum rating. The problems of heat transmission in shell boilers[172] and of heat transfer from submerged surfaces to boiling liquids[173] have been reviewed.

Pulverized fuel firing

Official statistics[174] show that the consumption of pulverized fuel in Great Britain has increased since 1939 by 2·8 million tons to 9·3 millions tons.

A study has been made[175] of the physical characteristics of the pulverized fuel resulting from grinding five representative British coals in a variety of mills. The need for a satisfactory grindability test for coal is still felt. Brown, Ivison, and Birney[176] suggest an index based on the work done in grinding 90% of the coal through a test sieve. Heywood[177] is concerned with the scale effect between laboratory tests and large-scale mills. Non-mechanical methods of size-reduction have been reviewed.[178] In a statistical survey it is concluded[179] that the power used in industrial milling is related to the transport of material rather than to the energy required for size reduction. An apparatus for the explosive pulverizing of coal with steam, analogous to " puffed " cereals, has been developed.[180] Expansion takes place through a throat, and, besides pulverizing, considerable drying is effected, so that wet coal can be used. The methods available for the determination of particle-size distribution and specific surface have been reviewed.[181]

Recent literature on pulverized coal burners has been reviewed by Allan.[182] Burners are classified on the length of luminous flame. The mathematical analysis of burner jets is considered. Hard pitch (m.p.$>$100°) is particularly suitable[183] as pulverized fuel in metallurgical furnaces on account of low ash and sulphur. C. H. Sparks[184] points out that the present tendency to divert poor quality coal to pulverized fuel firing reduces availability of boilers and restricts rating. For units in excess of 400,000lb./hour liquid ash-removal seems advisable. Disposal of fine dust from arresters is difficult and expensive. Accounts of methods of disposal have recently been given.[185, 186, 187]

Boiler deposits and corrosion

Internal deposits.—The deposition of a magnetic boiler scale was found[188] to be due to reduction of iron compounds by tannins used for water conditioning. The chemical descaling of boilers by means of inhibited acid is described by Burns[189] and Powell.[190] Investigation shows[191] that stressed metal is more readily attacked by inhibited acid than stress relieved, and treatment should be carried out below 60° and with acid of $<5\%$ strength.

External deposits.—The work of the Boiler Availability Committee which was set up in 1939 to investigate and alleviate external deposits has recently been reviewed.[192] At British power stations a correlation between alkali chlorides in the coals and severity of boiler deposit trouble has been observed. Similarly there is a correlation between sulphur content and air-heater trouble. These correlations do not apply to pulverized fuel boilers, which are relatively immune. Suitable methods of cleaning boilers have been devised which have lengthened boiler operation periods from less than 1000 hours to more than 5000. Chemical "smokes" to remove SO_3 are under investigation. The analysis of boiler deposits has been described.[193] External corrosion of water tubes due to sulphur in the presence of alkali under reducing conditions is reported.[194]

Industrial furnaces

The fundamentals of industrial furnace design and operation which affect fuel consumption and thermal efficiency are outlined by Southern.[195] A new type of metal recuperator which prevents accumulation of deposits has been described.[196] The need for a more scientific design of open-hearth furnaces has led to a detailed long-term investigation[197] to accumulate the necessary fundamental data at a large number of steel works. A laboratory furnace for experimental work has also been installed and a number of variables studied.[198] Increase of the order of 40% in open-hearth output as a result of oxygen enrichment of the blast is reported from Canada;[199] 32% of oxygen doubled production in the U.R.S.S.[200]

Other fuel utilization

Domestic heating and cooking.—New designs of solid fuel appliances are appearing, which have been reviewed by Hales.[201] Such appliances are designed primarily to burn smokeless fuels, and can be combined with water-heating. The importance of insulation of the structure of domestic dwellings is supported by experimental evidence.[202]

District heating.—The supply of space heating and domestic hot-water by a public utility service of piped steam or hot-water has been reviewed by Margolis.[203] Stubbs[204] has costed a typical scheme for 250,000 people. Technical details for five specimen schemes for small housing estates have been calculated,[205] and it is concluded that district heating cannot be economic when tenants are satisfied with pre-war standards of heating and hot-water supply. A scheme is described[206] in Iceland, where hot-water from deep borings is employed for district heating.

Large-scale hydrogenation of coal.—Developments in Great Britain are described by Gordon.[207] Overall coal consumption worked out at 5–6 tons per ton of final petrol. Treatment of creosote and gas oil is also considered, as well as the manufacture of *iso*octane. A very detailed account of the hydrogenation processes employed in Germany, with costs, is given in a report of the Ministry of Fuel and Power.[208] The chemical nature of the light oil[209] and heavy oil[210] obtained from coal has been reported.

Pulverized fuel gas turbines.—Development of an open-cycle gas turbine locomotive fired with pulverized coal is actively proceeding in the U.S.A.[211] The chief problems are pulverization, combustion within limited space, and removal of fly ash to give adequate life to turbine blades. The latter is accomplished by means of Aerotec filters.[212] Karthauser has reviewed[213] pulverized fuel firing for gas turbines, and it is concluded that the method will become economic.

Coal in oil suspensions.—Work early in the war on coal in oil suspensions has been described,[214] and it is concluded that such may yet have a place to fill in fuel technology.

Atmospheric pollution

The methods adopted for the measurement of smoke in the atmosphere have been described by Meetham.[215] The work of the Fuel Research Station on the measurement of smoke emission from both domestic and industrial chimneys has been reviewed, and the steps taken to reduce both described.[216] This has included smoke consuming domestic fireplaces and appliances, industrial grit arresters, and smoke eliminators for hand-fired boilers consisting of secondary air tubes arranged over the fire. Trials are reported of such smoke eliminators in a merchant ship,[217] which resulted in fuel lost as smoke and unburnt gas being reduced from 10·7 to 5·4%. In the U.S.A. steam-air jets are employed with similar objects.[218]

The properties of the dusts carried by the flue-gases from furnaces have been discussed and methods of removal described.[219] In general, cyclones are used on stoker installations, whilst electrostatic precipitators are more popular with pulverized fuel firing, for which spray washers are inadequate. Wagner gives a comprehensive account of such electrostatic precipitators,[220] including costs and energy consumptions. A development in cyclone collectors, the Aerotec, already referred to, is as efficient as the electrostatic precipitator, and has been installed with success[221] at Peterborough power station. The disposal of the collected dust is a nuisance since it is necessary to use a wetting agent to ensure proper[222] control of wetting.

Mathematical expressions have been derived[223] for the variation in SO_2 concentration and in dust deposition in the neighbourhood of a chimney stack, and recommendations made for siting to avoid nuisance.

Fuel efficiency and economy

Two conferences have been primarily concerned with Fuel Economy, firstly the " Fuel and the Future " Conference of the Ministry of Fuel and Power (London, October, 1946), and, secondly, the World Power Conference (Hague, September, 1947). At the former it was shown that considerable fuel savings result from the work done to increase the availability of large boilers. In shell-type boilers there was need for better design of convection heating surface and more mechanical firing. The great savings possible by balancing demands for power and steam in works and by linking up steam-using processes were emphasized. Wider adoption of heat recovery was necessary on furnaces particularly in the iron and steel industry, and greater use should be made of insulation. A number of the Conference papers have already been reviewed in this Report. Others of direct fuel economy interest are listed.[224]

An important part of the Hague Conference consisted in receiving Fuel Economy Reports from the National Committees in 19 countries. These Reports describe the many varied ways in which fuel stringencies were partially or completely overcome, and have been reviewed by Lulofs.[225] In addition to those papers of the Conference to which reference has already been made are papers on fuel economy.[226]

The recovery of waste heat from industrial furnaces has been reviewed by Critchley.[227] A plant in this country for the recovery by dry cooling of the sensible heat in coke discharged from coke ovens has been described[228] by Pearson, and other dry cooling plants in Switzerland by Hersche.[229]

Analytical methods

Progress in the last two years in the analysis and testing of solid fuel has been reviewed.[230] Simek and Ludmila[231] criticize existing methods of moisture determination in solid fuels, and prefer dry xylene distillation in metal apparatus for easily oxidized material. A rapid method using high-frequency current is favoured by Liplavk.[232] The Millin technique for the determination of C and H in coal in 20–35 minutes has been tested and found satisfactory.[233] Another time-saving technique for the same determination has been described.[234] The direct determination of oxygen in coal by carbonization in a stream of N_2 and reduction to CO of the gaseous products with carbon activated by alkali carbonate has been reported.[235] Hydrogenation for the determination of oxygen is also readvocated.[236]

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MINERAL OILS

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AN outstanding feature of the petroleum industry is the phenomenal increase in the consumption of petroleum products in the last year or two. In the United States alone more than two thousand million barrels of oil were consumed in 1947, that is 8½% more than was consumed by both the civilian population and armed forces in the peak year of the war.[1] This increased consumption of petroleum products has overtaken the crude oil production in the United States, and, as a result, that country has become, on balance, an importer of oil.[2]

In the past a large proportion of the petroleum requirements of the Eastern Hemisphere was supplied from the Western Hemisphere, but in future these supplies will be largely provided by the Middle East.[3] Extensive construction of refinery capacity for the treatment of the crude oil from the Middle East is being undertaken, particularly in the United Kingdom, where refineries are to be constructed on the banks of the Thames and the Manchester Ship Canal. For the same purpose it is proposed to extend the refineries at Llandarcy,[4] at Fawley,[5] and at Grangemouth,[6] while at Heysham part of the refinery used for the manufacture of aviation gasoline during the war is to be converted for the treatment of crude oil.[7]

Another important development of the petroleum industry in the United Kingdom is the construction of plant for the manufacture of chemicals from petroleum. Such development is the direct result of the removal of Customs duties on imported hydrocarbon oils[8] and, in addition, has a beneficial effect on Britain's financial position.[9]

Natural gas

An aeroplane has been flown in the United States using butane as fuel.[10] The liquid butane was passed near the hot air lines, which caused vaporization of the fuel, which was then passed through the carburettor and into the cylinders. This fuel is much cheaper than aviation gasoline, but the necessary containers for liquid butane are heavier than gasoline tanks.

The consumption of liquefied petroleum gases (propane and butane) is increasing steadily. In the United States the consumption in 1947 was 30% greater than that in 1946.[11] It is interesting to observe that the increase for domestic purposes was 31·8%, for industrial uses 11·6%, for utilities (electric supplies) 55·8%, and for chemical manufacture 34·9%.

Petroleum substitutes

Considerable expansion is contemplated in the research work carried out by the United States Bureau of Mines on synthetic liquid fuels.[12] The main work is being carried out on adaptations of the Fischer-Tropsch process in order to obtain a supply of gasoline to supplement that obtained from crude petroleum by the conventional processes. The development of gasoline manufacture from natural gas by this process has reached the stage when it can compete, under suitable conditions, with the usual methods of manufacture.[13]

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The Swedish shale oil industry is of particular interest at the present time as the oil shale is radioactive and contains about 220g. of uranium oxide per ton.[14] The centre of production of shale oil in Sweden is at Kvarntorp, where 2000 barrels per day are refined.

It is proposed to develop the lignite deposits at Bovey Tracey, in Devon, to produce lignite for fuel purposes. It is also planned to produce ester wax of the montan wax type. A production of about 3000 tons per year of montan wax is envisaged, of which 2000 tons will be for export.[15]

Another type of ester wax which is being investigated is that from British peat.[16] This kind of wax requires treatment by solvent extraction to render it miscible with paraffin wax of petroleum origin.

Refinery plant

In addition to the large extensions to refinery capacity which are under construction in the United Kingdom, new construction in the United States is the greatest in the history of the petroleum industry.[17] Large extensions and new refineries are being built near Rotterdam.[18] The extensions at Haifa refinery[19] are being constructed to handle the increased volume of crude oil from Iraq, which will be available in the spring of 1949, when the new Kirkuk-Haifa pipeline is expected to be ready for operation.[20]

Details have been published of the underground storage tanks built during the war.[21] A typical tank is of mild steel, all welded with open top, erected on a concrete foundation and protected by a cylindrical reinforced concrete chamber with a roof of concrete supported on columns inside the tanks.

In order to minimize corrosion in refinery equipment, steel alloys are used in such parts of the plant which are subjected to high temperatures or corrosive material. In the catalytic dehydrogenation of *n*-butane, a step in the manufacture of butadiene, severe conditions are met, both with regard to high temperature and alternate oxidizing and reducing atmospheres in the furnace. Under such difficult conditions it was found that alloy steel containing 27% of chromium withstood corrosion better than a large number of other alloys which were tried in this service.[22]

A method of retorting oil shale using the "fluidized" solids technique has been investigated.[23] The experimental work was carried out on Australian shale of a very rich type containing 63% carbon and 8% hydrogen. The spent shale was obtained by removing oil at a temperature of 850°–1000°F. by a fixed-bed type of operation. This spent shale was used in the form of a fluidized bed to heat fresh shale to a temperature of 850°–1000°F. Heat for the distillation was provided by burning, in the reactor, carbon and hydrogen left on the spent shale and some distilled oil vapours. At this stage the cost of carrying out the process on a commercial scale cannot be estimated, but it may be competitive with the conventional methods of distilling oil shale. American shales can be treated by this process as well as those from Australia.

In fractionating towers, the use of cascade ("Kaskade") type of trays is claimed to increase the capacity of the plant quite considerably.[24] In existing towers the bubble trays can be replaced by these cascade-type trays, and the new trays are claimed to have 36% greater capacity and 25% greater efficiency than bubble trays of the same diameter.

Comparative figures have been given for the present-day cost (in the United States) of plant required for the manufacture of gasoline.[13] A conventional refinery charging crude oil costs \$2000 to \$2500 per barrel daily of product. A natural gas synthesis plant (Fischer-Tropsch process) costs \$4000 to \$4500 per barrel daily. A synthesis plant (Fischer-Tropsch process) using coal costs about \$8000 per barrel daily.

A vacuum distillation unit of unusually large capacity has been erected at Wood River, Illinois.[25] The plant has an intake capacity of 35,000 barrels of topped crude oil daily. The flash tower is spherical in shape, having a diameter of 30 feet. The transfer line taking hot oil and vapour from the furnaces to the flash tower has an inside diameter of four feet. Operating at 770°F. and 60mm. pressure, this unit will flash 80% of the topped crude overhead.

A new process for manufacturing lubricating greases by a continuous method[26] gives products of better quality than those obtained by the conventional method of batch production. The components are fed continuously to the kettles and then through a homogenizer, leaving the plant and being pumped continuously into suitable containers.

Cracking

The conversion of a thermal cracking unit into a Thermofor catalytic cracking unit has been successfully carried out in the United States at an overall cost of \$250 per barrel per day throughput capacity.[27] The plant was designed for 3000 barrels per day, and has handled 5000 barrels per day with good yields.

A method has been proposed for predicting the activity of cracking catalysts from a determination of the heat of wetting of the catalyst when contacted with pure methanol. In the absence of catalyst poisons, accurate correlation of activity with heat of wetting is claimed.[28]

The effect of the temperature of catalytic cracking, the severity of cracking, and the chemical nature of the feed stock, on the composition of the cracked gasoline produced, has been investigated.[29] The gasoline produced from naphthenic type of feed stock contains a higher proportion of aromatic hydrocarbons than that obtained from paraffinic feed stocks when cracked under similar conditions.

Motor spirit

Gasoline produced by catalytic cracking is usually subjected to a hydrogenation treatment to make it suitable for aviation purposes. It has been found that this hydrogenation step has practically no effect on the aromatic hydrocarbons in the product.[30] In the catalytically cracked product the lower boiling fractions have a high olefine content, and, therefore, require hydrogenation, whereas the higher boiling fractions are more aromatic and less olefinic in nature. The higher boiling fractions may, therefore, be allowed to by-pass the hydrogenation stage and given a suitable acid treatment to obtain a stable gasoline of good anti-knock quality.

The presence of " gum " in gasoline may give serious trouble due to sticking of valves and deposits in the induction system. The use of about 0·5% by volume of " Paradyne Fuel Improver " is claimed to have a beneficial effect on fuels which are known to have valve-sticking tendencies.[31] The additive consists mainly of a high-boiling petroleum fraction, having a flash point of 340°F. and a distillation range of up to 840°F. This fraction is a good solvent for gummy deposits and for materials which tend to form such deposits.

Tests carried out on a full-scale engine have shown the effect of volatility of gasoline on the performance of the engine.[32] The uniformity of fuel-air mixture distribution among the cylinders decreases with lower volatility or lower carburettor air temperature. The distribution of tetraethyl lead and ethylene dibromide (constituents of ethyl fluid) among the cylinders does not always correspond to the distribution of the total fuel. This accounts for different amounts of lead deposits in the cylinders and differences in the tendency to detonation in the various cylinders.

An experimental automobile engine designed with the very high compression ratio of 12·5, approaching that of diesel engines, gave satisfactory results in road trials when using gasoline of octane number approximately 100 (research method).[33] The increased efficiency shown by the high-compression engine corresponded to 35–40% better fuel economy compared with a standard car. There is no likelihood of such high-compression cars being produced for some years to come, but it is of interest to note that it is a possibility of the future.

Tests have been carried out on a series of substitute fuels to measure their ability to start up under low temperature conditions.[34] The tests were carried out in a refrigerated chamber, a reconditioned 1939 Ford V8 engine being used for the purpose. Operation on ethyl alcohol was found to be practicable over a wide temperature range if a small percentage of more volatile compounds is added. The most effective additive for this purpose was diethyl ether.

Lubricating oils

A special problem during the war period was the supply of lubricating oils suitable for the lubrication of delicate instruments. The chief requirements for this purpose were chemical stability, that is, freedom from oxidation and corrosive effects, low pour point ranging from –40° to –80° F., and high viscosity index. Synthetic compounds were found to be suitable for this purpose, long straight-chain diesters having one or more short alkyl branches being the most effective.[35] These synthetic oils having viscosities of 10 to 15 centistokes at 100° F. were tried under all conditions in the Services and in industry in connexion with instruments and similar mechanisms. They gave very good performance over a wide range of temperatures, giving good rust preventive service and low foaming tendency.[36] These diester oils are also suitable for use as dielectrics and as damping fluids.

Selenium dioxide has been found to be a good antioxidant, but it is insoluble in mineral oils. In the presence of suitable alcohols, this additive will dissolve in lubricating oils and give good oxidation resistance.[37] In order to prevent bearing corrosion it is necessary to add another component. Best results are obtained when using a combination of 0·15% selenium dioxide in benzyl alcohol and 0·07% triphenyl phosphite.

The A.S.T.M. pour test (D97-39) is useful as a control test in connexion with the addition of pour point depressants, but in actual practice it is found that it cannot be relied upon to predict the temperature at which an oil becomes solid. Certain oils go solid in the field at temperatures above their A.S.T.M. pour point, others remain fluid well below it. An accelerated test has been worked out in which the lubricating oil is subjected, after a preliminary heating treatment, to a cycle of cooling treatments in a refrigerating cabinet. The oils under test are immersed in an *iso*propyl alcohol bath to minimize fluctuations in the oil temperature. It was found possible, by the use of this test, to estimate the quantity of pour depressant required to enable the treated oil to remain fluid in service at any particular temperature.[38]

Tests have been carried out on heavy duty motor oils in Service vehicles in order to find out whether the filtration of these oils during service in the field removes any of the additives used in the lubricating oils. A variety of filters were used in these tests, and it was found that there was direct adsorption of detergent additives to a greater or less extent.[39]

In addition to the adsorption of detergent additive by the filter medium, adsorption by the retained sludge also takes place. The effect of oil filters on the removal of other additives, such as oxidation inhibitors, corrosion inhibitors, and wear reducers, requires further investigation. Claims have been made that certain kinds of filters are suitable for detergent oils, and the subject is receiving a great deal of attention.[40]

Fuel oil

An attempt has been made to indicate the burning properties of distillate fuel oil by means of the " Burning Index." This is based on the A.P.I. Gravity of the oil and the temperature at which 50% distils over, and can be taken from a nomograph[41] which applies to No. 2 fuel oil—a grade used for domestic burners in the United States. The burning index for such fuels should exceed 65 for satisfactory operation. The burning index of blends can be predicted from those of the constituents and their proportions in the blend.

The consumption of diesel fuel is increasing at a rapid rate, particularly in the United States,[42] where it is expected to be about 135,000 barrels per day in 1948, compared with 65,000 barrels per day in 1939. The large increase in consumption is due to applications for the railways, armed services, gas and electric companies, manufacturing, mines, trucks and buses.

The British railways are planning extensive developments in the use of diesel-electric locomotives, particularly for main line express trains.[43] The units to be constructed for three of the railway systems are 1600 h.p. diesel-electric generators, which will work normally in pairs. These locomotives are expected to haul express trains at speeds of 100 to 120 miles per hour. At present, weight and length in relation to tractive power favour the steam engine in comparison with the diesel-electric locomotive. If, however, a practical and efficient form of direct drive could be evolved for a diesel locomotive in the 3000 h.p. range, the saving in length made possible by the abandonment of electric transmission would put diesel locomotives in an even better position relative to steam locomotives than that already attained.[44]

The world's largest locomotive is the diesel-electric locomotive on the Kansas City Southern Railway. It has a total of 8000 b.h.p., and is used for freight traffic only.[45]

The first attempt to use a gas turbine burning fuel oil in a railway locomotive is being made in a new type of passenger locomotive under construction for the Santa Fe Railway in the United States.[46] The unit is expected to develop 3000 h.p., and will be capable of speeds in excess of 100 miles per hour.

Special products

The production of chemicals from petroleum, referred to as the petroleum chemical or petrochemical industry, is expanding rapidly in the United States,[47] in Europe, and particularly in the United Kingdom. The hydrocarbons available for chemical processing range from methane and other saturated hydrocarbon gases in natural gas to unsaturated hydrocarbons from cracked gases and higher molecular weight hydrocarbons, including aromatics, in liquid petroleum fractions. In the United States over 30% of all organic chemicals manufactured are derived from petroleum.[48]

Two Fischer-Tropsch plants being erected in the United States for the production of gasoline from natural gas[49] are expected to produce annually over 300,000,000lb. of alcohols, acids, ketones, and aldehydes. It is of interest to note that all the products obtained from this source are *normal* compounds, such as *n*-propyl alcohol, *n*-amyl alcohol, etc.

Extensive new construction is planned in connexion with the manufacture of chemical products from petroleum in the United Kingdom.[50] The plant at Stanlow, which produces 24,000 tons yearly of the synthetic detergent sodium higher alkyl sulphates (Teepol),[51] is to be extended, and the production is expected to reach 50,000 tons yearly in 1948.[52] At Thornton-le-Moors a large plant is in course of erection, and will shortly have an initial output of about 24,000 tons a year of a wide range of chemical products, such as acetone, methylethyl ketone, methyl*iso*butyl ketone, *iso*propyl alcohol, diacetone alcohol, *sec.*- and *tert.*-butyl alcohols, *iso*propyl ether, and other chemicals.

At Shell Haven the manufacture of a range of insecticides, fungicides, and other products used in agriculture is being carried out. This plant is being extended so that the annual output of these products will amount to 30,000 tons. In connexion with the manufacture of agricultural products, an experimental farm has been acquired at Woodstock, Sittingbourne, Kent, where research work is being carried out on the development of insecticides and similar products.

Another scheme for the manufacture of chemicals from petroleum is being planned in the neighbourhood of the refinery at Grangemouth,[53] but no technical details are yet available.

Developments in Holland[54] in the petroleum chemicals industry involve the construction of two factories near Rotterdam, in the neighbourhood of a large petroleum refinery. One of these will be for the production of synthetic resins, with an initial output of about 2000 tons annually, based on vinyl and vinylidene chloride. The other plant is for the production of synthetic soaps of the Teepol type. The initial output of detergents from this factory will be 25,000 tons annually.

One of the intermediate stages of the manufacture of synthetic glycerine is the production of allyl chloride and allyl alcohol from propylene. In addition to these, a new allyl product to be marketed is diallyl phthalate, which is a base for synthetic resins.[55] Another allyl product under investigation is allyl sucrose, which is a varnish resin.

A practical method has been worked out for the production of thiophen from normal butane,[56] which is subjected to dehydrogenation in the presence of sulphur, followed by cyclization with sulphur to form the thiophen ring.

Among some of the newest developments in the production of chemicals from petroleum should be mentioned the production of benzene by the hydroforming process,[57] propylene glycol as a glycerine substitute,[58] and hexylene glycol.[59]

The use of chlorine for treating water containing harmful bacteria is somewhat unpleasant, but a less objectionable method is to use chlorinated lower hydrocarbons, such as trichlorobutane, trichlorohexane, etc.[60]

Analysis and testing

In the eighth edition of the *Standard Methods for Testing Petroleum and Its Products,* published by the Institute of Petroleum in 1947, there are several new methods. Among these new methods is the estimation of metals in used lubricating oils, the tendency of grease to corrode copper, the flashpoint of liquid asphaltic bitumen, and the estimation of tetraethyl lead in motor fuel. A number of the standard methods have been amended, among others the procedure for determining kinematic viscosity in absolute units and the details of knock-rating estimation.

In the testing of petroleum products, both for control during manufacture and investigations on the application of these products, extensive use is made of the latest advances in physical methods.[61] Among the methods used are the application of electron diffraction in thin films for the study of lubrication, and *X*-ray diffraction and infra-red absorption spectra for the analysis of mixtures of hydrocarbons.

The separation and identification of the hydrocarbons in a Mid-Continent crude petroleum has been carried on since 1926 at the National Bureau of Standards under Project 6 sponsored by the American Petroleum Institute. From the gas, gasoline, and kerosene fractions 72 hydrocarbons have been isolated.[62] The methods in use comprise fractional distillation, extraction with various solvents, adsorption, and fractional crystallization. The lubricating oil fractions from this crude oil are also being investigated for hydrocarbon composition.

Some of the hydrocarbons recently separated from the Mid-Continent petroleum are 29 compounds, including nonanes, alkyl*cyclo*hexanes, alkyl*cyclo*pentanes, and butylbenzenes.[63] The fraction distilling from 102° to 108°, after separation of aromatic hydrocarbons, has been found to consist of ethyl*cyclo*pentane boiling at 103·5, 1:1:3-trimethyl*cyclo*pentane boiling at 104·9°, and 2:2-dimethylhexane boiling at 106·8°. The amounts of these hydrocarbons in the original crude petroleum are estimated to be, respectively, 0·1, 0·3, and 0·01% by volume.[64]

The alkybenzenes in the C_9 fraction of seven representative crude petroleums have been examined by a number of different laboratories by distillation and spectrographic analysis. It was found that the alkylbenzenes in the C_9 fraction of petroleum are present in relative amounts of the same magnitude in all, except one, of the different crude oils tested.[65]

A sub-committee of Committee D-3 of the American Society for Testing Materials, in co-operation with thirty laboratories, has undertaken the standardization of analysis of gaseous fuels. The volumetric analysis of a standard sample of natural gas by absorption and combustion methods carried out by the various laboratories confirms the fact that standardization of methods of analysis is necessary.[66] The co-operating laboratories have also analysed a standard sample of natural gas using the mass spectrometer.[67] Results showed that this method of analysis is capable of good reproducibility and, to some extent, accuracy.

A method of estimating the quantity of antioxidant, such as alkyl-substituted *p*-aminophenol and *p*-phenylenediamine, used in gasoline, is to extract the additive with aqueous hydrochloric acid, neutralize the extract with sodium carbonate in the presence of Folin and Dennis reagent, which consists of phosphotungstic acid solution, when a blue coloration is produced which is proportional to the concentration of inhibitor present in the gasoline.[68]

A simplified method for the determination of carbonaceous deposits on cracking catalysts[69] consists of burning 20 g. of the sample heated to $1100 \pm 25°$ in a stream of oxygen at the rate of 75 ml./min., and passing the gases over heated CuO-clay catalyst to a brine-filled graduated receiver, so that 4 litres are collected in 90 minutes, by displacement of the brine to a second receiver. The CO_2 content of the gas is determined by an Orsat apparatus, and the volume of the gas is corrected to N.T.P. and for the partial pressure of the water vapour. From the corrected volume of the CO_2 the weight of carbon present in the catalyst is calculated. The accuracy is $\pm 3\%$ of the total carbon present in the range of 0–7% by weight on the catalyst. The advantages of the method are (1) the sample need not be ground, (2) the equipment is simple and inexpensive, (3) five estimations can be made simultaneously with a total elapsed time of 2 hours and an expenditure of 1 man-hour.

A new micro-worker for mechanically working 5 g. samples of lubricating greases has been proposed.[70] The instrument consists of two 5 c.c. hypodermic syringes connected together tip to tip by means of a shearing element, which is composed of two cut-off hypodermic needle hubs soldered together with a fine mesh screen across the joint. The consistency of the grease is measured by means of the conventional micropenetrometer needle with a small cup for holding the grease.[71] The present standard A.S.T.M. worker requires a much longer time to give the same information as the new method.

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FATS, FATTY OILS AND DETERGENTS

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PROGRESS during the past year has been steady and has extended knowledge on lines of development similar to those of previous years without any definitely new fields of research appearing. Many papers have found their way into the technical literature, and they have dealt with a very wide variety of subjects.

Detergents

Commercial Soaps.—A number of papers have dealt with the manufacture of soap, and among them may be mentioned one by D. Bachrach[1] who has shown that the addition of phosphates increases the lathering power of liquid soaps, so that such salts are useful when coconut oil is scarce. J. W. McCutcheon[2] has briefly correlated the properties of soaps with physico-chemical concepts and with peculiarities of the cation. P. A. Winsor[3] has shown that very small quantities of sodium soaps exert a strong foam-breaking influence on neutral or alkaline solutions of certain sodium alkyl sulphates. The sensitivity of the reaction may be influenced by the position of the attachment of the SO_4Na group to the carbon chain, and a stable foam may result from the use of either a larger or a smaller amount of soap than causes foam-breaking. The detergent properties of sodium alkyl sulphates diminish as the SO_4Na group recedes from the end of the hydrocarbon chain.

Recent developments in factories in the United States are described by R. Latour.[4] W. J. Govan, jun.,[5] claims that by the use of a counter-current washing system, in which successive alkaline washes from the soap are returned to another soap kettle in an earlier stage of processing, more complete recovery of glycerine is achieved. The neutralization of soaps is controlled by G. DeW. Miles *et al.*[6] in the continuous manufacture of soap so as to yield a product of uniform free alkali content by adjusting the potential between an antimony electrode wet with the soap against a standard calomel electrode to balance a second potential in a potentiometer circuit. Variations in the free alkali content then cause a deflexion of the galvanometer from zero position; the proportions of the reactants supplied are altered from time to time to keep the deflexion at zero. Light coloured soaps are made from relatively dark fats in a patent of Lever Bros. and Unilever Ltd.[7] by bleaching the raw material with small percentages of an acidic phosphoric compound such as phosphoric acid or a salt thereof, and of an oxygen-liberating per-compound at a temperature between 90° and the melting point of the fatty material; separating the sludge, drying, bleaching with a bleaching earth, filtering to remove the latter, saponifying the bleached stock to form soap, and bleaching this with sodium sulphoxylate or sodium hydrosulphite. B. Clayton[8] produces substantially anhydrous soap by saponifying fats with a slight deficiency of alkali, removing glycerol and other volatile matter by distillation, mixing with a little water, and extruding hot under pressure so that the water evaporates as the extrusion pressure is released to give a porous product.

C. Berti[9] has described the Mazzoni soap drying process which consists of a flash drying of soap by first spraying it into a vacuum chamber, then causing it to adhere as a thick film to a metal surface where a high degree of heat transfer can be effected. A few pages later in the same journal[10] is a review of the causes of cracking in milled soaps. The factors that must be considered include the titre of the fatty acids, moisture content of the soap, homogeneity of the batch, thickness of the flake, plodder pressure, unnecessary heating or chilling and mistakes in pressing.

Synthetic Detergents.—The alkyl aryl sulphonates have been reviewed by L. H. Flett;[11] those with alkyl groups of from 10 to 16 carbon atoms are washing and foaming agents. They can be made by combining alcohols, olefines or chlorides with benzene, phenol or other aromatic compounds to give products which are easily sulphonated. Commercial uses of the products are reviewed. A study has been made with the "Detergency Comparator" by S. F. Sylvester *et al.*[12] to compare the scouring efficiency of soap and synthetic anionic, non-ionic, and cationic detergents. The variables studied were bath-to-cloth ratio, and additions of sodium carbonate or bicarbonate, sodium sulphate and sulphuric acid. Sodium carbonate appeared to be the best assistant although all the salts had some value. Their effect was to drive the detergents to the oil-water interface.

D. Burton and L. F. Byrne[13] have discussed the constitution of sulphated oils, giving methods for determining $-COOH$, $-OSO_2OH$ and $-SO_3H$ groups and their salts. A. F. Guiteras and R. L. Shapiro[14] point out that where cation-active agents are used as bactericides in detergent compositions, it is essential for the detergent to be emulsifying in character and not saponifying. If its alkalinity is sufficient to saponify fats, the resulting soap will inactivate the cation-active agent and render it non-germicidal. The same authors with L. H. Flett and R. C. Haring[14] have shown that anionic detergents are bactericidal at hydrogen ion concentrations varying from p_H 2 to p_H 12. Nacconol NR killed 99% of the organisms of *Staphylococcus aureus* within five minutes at a concentration of 1 in 500 in the range from p_H 2 to p_H 11·9.

Analysis.—S. R. Palit has put forward[15] a direct volumetric method for the analysis of soap. Ethylene or propylene glycol, preferably in admixture with *iso*propyl alcohol or chloroform, is a powerful solvent for soap, and in such a solution soap may be titrated directly and accurately by a standard solution of a strong acid in the same solvent medium. The end-point is determined either potentiometrically or by an indicator. If a mixture of phenolphthalein and methyl red or methyl orange is used, both free alkali and soap may be titrated. Potentiometric determinations have shown that true end-points are yielded by the indicator method. The fatty acids present may be recovered after the titration by adding hydrochloric acid, water and chloroform (if not already present), separating the chloroform layer and evaporating off the solvent. Borates and carbonates are slightly soluble in the solvent mentioned above, and if they are present the method needs to be modified.

Report No. 6 of the Sub-Committee on Methods of Soap Analysis of the Analytical Methods Committee of the Society of Public Analysts and other Analytical Chemists[16] deals with the determination of phenols in soaps. When high-boiling tar acids are absent, it recommends the use of a modification of the method of H.M. Govt. Dept. Specifications for General Stores, T.G. 23—Soaps. In other cases the soaps are precipitated with calcium nitrate solution from alkaline solution, the clear filtrate is acidified and extracted with benzene, and the benzene extract is extracted with 15% sodium hydroxide solution. The volume of phenols is measured directly after acidifying and saturating with salt. The Soap Analysis Committee (A.O.C.S.-A.S.T.M. Committee D-12, 1945)[17] has put forward certain minor revisions of tentative methods for soaps containing synthetic detergents.

J. P. Sisley[18] has determined the difference between various detergents in scale-removing power and effect on the dispersion of lime soaps by four empirical methods: the amount of detergent necessary to create a permanent foam in a lime soap solution, the amount required to remove the turbidity from a lime soap solution, the amount of lime soaps remaining in a filtered mixture of detergent and lime soap solution as determined by titration with hydrochloric acid, and the behaviour of vat dyes sensitive to the hardness of the water such as Solanthrene Blue NB. The methods proved to be comparative rather than absolute.

The Krafft point is described by M. Demarcq[19] as a fundamental notion in the physico-chemistry of soaps. The point is defined as the temperature at which a soap solution becomes opaque, or at which cogel or crystal formation takes place. This is a definite characteristic of soaps which varies but little with soap concentration in the solution; it increases with increasing number of carbon atoms in the chain, and with sodium soaps is a little less than the titre. The Krafft points of the alkali stearates were found to be: lithium soap, 145–150°; sodium soap, 79°; potassium soap, 48°; rubidium soap, 52·5°; caesium soap, 49°. For other soaps the points were: lithium oleate, 72°; sodium laurate, 38°; potassium palmitate, 30·5°.

Extraction and processing of fats

General.—The manufacture of synthetic fats is described by P. N. Williams.[20] He divides synthetic fats into three categories: those in which glycerol and fatty acids, both products of industrial treatment of natural fats, were re-esterified; those in which glycerol was replaced by other alcohols which were esterified by fatty acids; and those in which glycerol was esterified with fatty acids prepared by the oxidation of hydrocarbons. The first method was in use in Italy and other Mediterranean countries before the war, and had been in use for a short time in England some years before. The second method had been used on a considerable scale on the Continent before the war, particularly for the esterification of rape oil acids with ethyl alcohol. The esters so formed were used in margarine to the extent of from 5 to 10%. They were however liable to hydrolyse and produce a bad taste; they are not likely to be used again.

The third method involves first the formation of fatty acids from hydrocarbons, which is carried out in the following stages: oxidation of the hydrocarbon, saponification and recovery of part of the unchanged hydrocarbon, heating to decompose certain compounds and separation of more unsaponifiable matter, acidification of the soap and liberation of the fatty acids, and finally their fractional distillation. The hydrocarbon used in Germany during the war was a fraction boiling at 320–450° from the Fischer-Tropsch process. It was oxidized in cylindrical aluminium vessels of 10 or 20 tons capacity, fitted with stainless steel covers. 0·2 to 0·5% of potassium permanganate was added as aqueous solution; water was evaporated at 110°, and after cooling to 105° air was passed in through an aluminium distributor, at the rate of 50 cu.m. per hour. After about 24 hours from 30 to 35% of fatty acids were present and the saponification value reached 130. The reaction was then stopped. The acids produced are reported to have carbon chains from 6 to over 19 atoms long, the percentage of most of the acids tending to be in the range 5–10%. Esterification of the fatty acids was carried out in 6-ton stainless steel vessels in which about 1% excess was heated with the glycerine in the presence of 0·2% or tin or zinc catalyst for about 8 hours at from 120 to 180°. The pressure aimed at was 2 mm. mercury pressure, but the author believes that this is the final pressure and that the pressure is lowered and the temperature raised as the reaction proceeds. When the free fatty acid content has fallen to about 1% the reaction is stopped and the catalyst is washed out with dilute acid. The product is then treated by the usual methods of fat refining. Margarine was made from the product in the usual manner; it is stated to have a poor taste, but not so bad a one that hungry people would not eat it; when fresh it has a creamy consistence and spreads easily. Tests made by colleagues of the author show that these synthetic fats were not so well utilized by animals, though no definite injurious effect was observed.

Mention must also be made of the excellent review of fat splitting given by D. Allan.[21] After a historical introduction, the author deals with the theoretical principles of fat splitting and then details processes operated at atmospheric pressure, including the process of lime saponification in which the fat is emulsified with lime and water at 100° and allowed to stand over-night; the mass is ground and the glycerine liberated by the hydrolysis is extracted with water; the lime soap is transformed either direct to fatty acids by acidification or reacted with sodium carbonate to form sodium soaps and calcium carbonate. In the acidification process, fats are treated for about 12 hours at 120°, after previous drying, with 4 to 8% of concentrated sulphuric acid by the injection of dry steam. The resulting acids are of very dark colour and are distilled. The enzyme process has usually been carried out with the enzyme lipase, obtained from the seeds of the castor bean. These are ground to a paste with water and, after incubation at 23° for a day or two, form two layers of which the upper contains the hydrolytic agent and has the consistence of cream. This is mixed with the prepared oil and the mixture is kept at about 30° for 1 to 2 days, yielding a partly separated emulsion from which glycerine and fatty acids are recovered. In the Twitchell process, which has been extensively used both in Europe and in the U.S.A., the fat is mixed with water and a small quantity of the fat-splitting agent, a sulphonated oily mixture, a material now usually prepared from petroleum products.

Processes used at moderate pressures are all batch operated, and consist in the autoclaving of the fat with steam in the presence of a catalyst, such as zinc, magnesium or calcium oxide. Splitting starts slowly and becomes more rapid as the proportion of soap in the mix increases. At high pressures continuous processes have been proposed, and indeed operate in the U.S.A. They appear to involve passing an emulsion of fat and water through a series of splitting vessels at 260 to 320° under a pressure of 3,500lb. per sq. in. The mixture passes to a flash chamber in which partial evaporation of water takes place, and separation of the aqueous and fatty phases occurs. The latter pass to storage, and the sweet water is evaporated to form crude glycerine. Alternatively, water and fat may pass through the splitting stage in countercurrent. The paper concludes with a review of the uses of fatty acids.

Extraction and expression of oilseeds.—M. Bonotto[22] has explained the difficulties that may be caused in the operation of continuous extraction processes by the presence of " fines ", and has sketched methods by which their formation may be minimized. W. H. Goss[23] illustrates and describes various forms of plant used in Germany and America for the extraction of oilseeds. J. Pominski *et al.*[24] deal with a portable batch solvent extraction apparatus. W. H. Baskervill *et al.*[25] describe a study of factors affecting the pressure extraction of oil from cottonseed. The tests were made on flaked meats of 7% moisture cooked in a laboratory cooker and pressed in a cylinder of which the cylinder temperature was 200°F., pressures of 2000lb. per sq. in. being used. The oil content of the cake decreased to a minimum of 4% as the pressure of the steam used for cooking rose from 5 to 45lb. per sq. in. No advantage was secured by decreasing the thickness of the cake below that of common milling practice. Increased pressing time reduced the residual oil in the cake from 5·2 to 4·4%. E. L. D'Aquin *et al.*[26] show that the crude cottonseed oil obtained by solvent extraction of either the cooked or the uncooked meats, with removal of solvent below 140°F., compared favourably with expressed oil. Uncooked meats yielded the lightest oils. The authors believe that the solvent extracted oils refined better and gave comparable colour and refining tests. Pressed oil was noticeably less affected by heat than solvent extracted oil.

M. L. Karon and A. M. Altschul *et al.*[27] of the U.S. Dept. of Agriculture have determined the pattern of respiration for 17 lots of cottonseed with moisture contents ranging from 10 to 17%. The average R.I. was found to be an exponential function of the moisture content. Free fatty acids in immature seeds were found to decrease in proportion during storage; the lipolysis rate constant for mature seed could be converted to a linear relation with moisture content of the seed. Treatment of mature seed with ammonia inhibited respiration and lipolysis; it also reduced the light absorption of the oil at 360 mμ. Vapours of Nacconol N.R. and of 2'-Me-1-maleanil inhibited lipolysis in cottonseed under conditions where there was a stimulation of respiration. Certain fungicides and germicides had no effect on the lipolysis rate. Most of the deterioration of stored cottonseed is believed to be due to enzyme action rather than to microbial activity.

L. H. Downs and R. H. Bellwood[28] have patented a process for the extraction of oil from whale meat in which the meat is submerged in hot water or aqueous extraction liquor and subjected to changes of mechanical pressure; it may be conveyed through a number of troughs at different levels, the troughs being provided with conveyor worms of special design which produce local compression.

Refining and bleaching of oils.—An interesting process is due to R. H. Fash;[29] a glyceride oil and a solution of sodium hydroxide (only slightly more than is sufficient to neutralize the oil) are separately converted to aerosols and the mists are mixed. It is claimed that neutralization is exactly effected and that the negative charges of the alkali neutralize the positive charges of the colloidal colouring matter in the oil. The emulsion is said to be easily broken as a consequence, and the soap plus impurities separated.

The same author[30] reports a study of the caustic refining of vegetable oils from which the amount and kinds of phosphatides present in the crude oil would appear to be dominant factors in selecting the conditions of refining and in controlling the composition of the by-product soap-stock, both in liquid-liquid and in mist refining.

J. M. Martinez Moreno[31] describes the extraction of oleic acid from olive oil by means of 96% alcohol in a tower packed with Raschig rings or broken glass, the latter being the more effective. After passing through the tower the mixture separates into an oil phase and an alcoholic phase, the latter containing 75–90·5% oleic acid. This process is reminiscent of the processes used in Manchuria before the war for the extraction of soya bean oil from the beans which resulted in oils of comparatively low acidity.

The evaluation of the effect of earths and active carbon on oils is dealt with by A. Paleni[32] who points out that the decolorization of vegetable oils does not imply their purification since many impurities which must be removed by adsorption on active earths and carbon are not coloured. He advocates a measurement of the actual weight of impurities removed by adsorption.

E. R. Woodward and G. P. Vincent[33] describe the bleaching of fats by wet or dry ClO_2. The fatty matter may be treated with 1% of sodium chlorite and enough 20% sulphuric acid to give 10% of water in the mixture and a p_H not over 4. Alternatively, a mixture of ClO_2 and air is passed through the fat or into it. The ClO_2 is produced by the action of chlorine on sodium chlorite, and 100lb. of the latter suffices for 300 tons of tallow. This dry process is the more economical. Lever Bros. and Unilever Ltd.[34] bleach dark-coloured fats and oils by treatment with 0·25 to 2% each of an acidic phosphoric compound and an oxygen-liberating compound such as hydrogen peroxide for about an hour, or for as long as there is improvement in the colour. The fat is afterwards given an ordinary earth bleach. It is claimed that by this process colour reversion, when the fat is converted to soap, is at a minimum.

Other processing of oils and fats.—The practical preparation of mono-and diglycerides is the subject of a study by R. O. Feuge and A. E. Bailey[35] who have obtained the compositions of the products produced by heating cottonseed oil with glycerol at various temperatures in the presence of 0·1% of sodium hydroxide as catalyst. At temperatures below 200°, and within the range of glycerol concentration in which the reaction product becomes homogeneous, the proportions of free glycerol, monoglycerides, di- and triglycerides at equilibrium agree closely with those expected on a basis of random distribution of fatty acid radicles on OH groups esterified. Temperatures of the order 250° were needed to obtain complete miscibility when the glycerol amounted to about 20 to 30% of the OH groups esterified, and the random distribution of the products was not then followed. What are thought to be polymerization products were found under these conditions. If the products of the reaction are steam-deodorized, there is a tendency for the formation of diglycerides and a reduction in the percentages of mono- and triglycerides.

The fractionation of glyceride oils has been patented[36] by Lever Bros. and Unilever Ltd. who separate oils into more and less unsaturated fractions by rapid chilling of a solution of the oil in a non-polar solvent to between —30 and —60°, followed by centrifuging. The systematic crystallization of lard and tallow has been followed by R. W. Riemenschneider and others[37] who crystallize the fats from acetone at temperatures from —20 to —45° and determine the compositions of the six fractions obtained. The proportions of fully saturated triglycerides in lard and tallow were found respectively to be 1·9 and 15·0%, figures close to the theoretical ones for random distribution of the available fatty acids over the glyceryl radicals for each fat.

S. B. Radlove *et al.*[38] describe the catalytic isomerization of linseed, soya bean and dehydrated castor oils, of the methyl esters of their fatty acids and of methyl linoleate by heating with nickel (reduced by hydrogen) on active carbon at 170 to 190°. The contents of diene and triene conjugated acids then rise to between 30 and 40%, or in some cases higher. Catalytic activity was shown only by carbons made from waste sulphite liquors. Maximum activity was obtained with a ratio of nickel to carbon of 1 to 3 and with about 7% of catalyst. Products of the process had reduced drying time and increased resistance to water and alkali.

Glyceride oils are decolorized and, if desired, hardened in a patent granted to Lever Bros. and Unilever Ltd.,[39] by treatment at a high temperature with hydrogen in the presence of a catalyst consisting of co-precipitated oxides of iron with copper, silver or gold in approximately equimolecular proportions alone or with nickel, cobalt, platinum or palladium. The process may be carried out continuously; time of treatment is from 15 to 30 minutes.

A development of the continuous process for hydrogenation of oils appears in an American patent of L. H. Manderstam and L. W. Warner[40] in which a group of hydrogenating tubes is arranged in a temperature controlling chamber with the necessary means for adding hydrogen, oil, catalyst, etc.

A process for the synthesis of glycerol patented by N. A. Milas[41] consists in reacting allyl alcohol with hydrogen peroxide in an initially anhydrous inert organic solvent in the presence of osmium tetroxide as catalyst, and directly recovering glycerol from the reaction mixture. New techniques for the distillation of glycerine are described by W. A. Peterson.[42]

Drying oils

The mechanism of the oxidation and reduction of unsaturated groups in drying oils has been studied by T. P. Hilditch[43] who argues that anomalies previously noticed in the selective hydrogenation of unsaturated groups are explained on the basis of the different reactivities of diene systems in which the carbon atoms of a chain enclosing a double bond are separated by a single CH_2 group and of isolated double linkings. Initial attack of oxygen on the unsaturated system is most likely to take place at the double linkings, followed by migration of hydrogen from a neighbouring CH_2 grouping to form a hydroperoxide. The author also discusses the polymerization of autoxidized oils and the synthesis of linoleic and linolenic glycerides in oilseeds. J. C. Cowen, W. C. Ault, and H. M. Teeter[44] show that polyesters of polymeric fatty acids with glycol may be compounded and cured with sulphur and other reagents to yield vulcanizates having improved properties as compared with factice. Raw materials may be soya bean oil, linseed and tall oils. The authors prepared simple moulded products on a large scale. Used as a tread surface, the esters showed fair resistance to abrasion, and were approximately equal to Thiokol for wear. Modified drying and semi-drying oils are described by Raybestos-Manhattan Inc.[45] and H. Plimmer *et al.*[46] In the former patent a mechanically refined oil is treated with an oxygen containing gas at 25–70° until it is converted to one having a conjugated system, when it becomes soluble in synthetic resins at room temperature and insoluble in alkali, yet remains fluid. Index of conjugation is measured by the increase in refractive index, the required increase being 40 points (*sic*) on the Abbê instrument. In the second patent, drying oils, etc., are heated at 90 to 150° with maleic acid or a derivative of it in the presence of oxygen containing gas. Excess of acidic groups may be esterified with a di- or polyhydric alcohol, or a partly esterified polyhydric alcohol; alternatively, any hydroxy groups in excess may themselves be esterified. The products may be heated with resins to check gelation on storage.

A catalytic process for dehydrating and heat-bodying castor oil is due to A. E. Rheinbeck and S. B. Crecelius[47] who heat it progressively to 250 to 300° with from 0·005 to 0·2% of a heteropoly-acid of tungsten. The process requires about three hours when applied to castor oil; it may also be applied to other oils.

Fume condensation and removal are dealt with both by Younghusband, Barnes & Co. Ltd.[48] and by J. C. Dittmer.[49] In the patent of the former, the fume is withdrawn from an open kettle by using ejectors to create a current of air over the surface of the heated oil. The second author describes the difficulties of the removal, which are chiefly due to the small size of the oily droplets; he regards burning as satisfactory in certain cases but not in all, and refers to the use of a water spray.

X-ray examination of the products of vulcanization of linseed oil have suggested[50] that sulphur has been added to each double bond and that the molecules are linked by sulphur atoms. A. Steger, J. van Loon and P. J. van Limmeren[51] have studied the course of the hydrogenation of tung oil and its methyl esters and of oiticica oil, discussing changes in iodine values, diene numbers and other constants from the standpoint of reaction mechanism. Oximes and semicarbazones of couepic and ketostearic acids were prepared and constants recorded for them. R. T. O'Connor *et al.* deal with the spectrophotometric determination of the α- and β-isomers of elaeostearic acid.[52] F. A. Kummerow and E. I. Green[53] find that the β-linoleic acid prepared by the de-bromination of liquid tetrabromostearic acid is not uniform by chromatographing the methyl esters on alumina and eluting with a petroleum fraction and acetone. The acid was found to contain a small amount of a viscous yellow material, which appeared to be monobromo-oleic acid. The bromine could not be removed with zinc in absolute alcohol. α-Linoleic acid prepared from the crystalline tetrabromide on the other hand proved to be homogeneous.

W. O. Lundberg and J. R. Chipault[54] have investigated the early stages of the oxidation of the methyl esters of linoleic acid at 40, 60, 80 and 100°. Almost all of the absorbed oxygen was found as relatively stable linoleate peroxides. Up to a level of 300 m.e./kg. of peroxide, a constant fraction of the total peroxides is present as conjugated dienes. Secondary products believed to be of a ketonic nature, absorbing at 2775A. were formed in proportion to the oxygen uptake. D. Cannegieter[55] has studied the kinetics of the polymerization of linseed oil both with and without SO_2 as catalyst. He has derived equations relating the increase in viscosity to time, and finds that the bodying of tung and oiticica oils follows similar equations.

The fatty acids of dormant tung buds have been analysed by H. M. Sell and S. G. Gilbert[56] who have prepared the methyl esters of the fatty acids in the wax and separated them to fractions. Cameline oil, derived from " false " or wild flaxseed, and its use in paints are described by M. Carrière.[57] Paint made from the oil dried more slowly than similar paints made from linseed oil, but it is nevertheless considered to be a substitute for the latter.

Antioxidants

The effect of storage conditions and antioxidants on the keeping quality of packaged oils has been investigated by J. E. W. McConnell and W. B. Esselen, jun.,[58] who have decided that the most important factors influencing deterioration are exposure to light and the original quality of the oil. Storage in the dark, or at least in amber glass containers is desirable, and temperature of storage should be as low as possible. Several antioxidants, including catalase, gallic acid and maize germ oil, were slightly active in diffused daylight, but in no case were they as good as darkness. Neither deodorization nor de-aeration improved the stabilities of oils in daylight.

The mechanism of oxidant effects of commercial salt and water in butter fat has been studied by G. L. Hills and J. Conochie.[59] They find that dispersed water in butter fat accelerates oxidation and that both halide and hydrogen ions catalyse the oxidation when it is caused by commercial salt in acid solution. B. M. Watts, T. J. Cunha and R. Major[60] describe the effect of feeding and injecting hogs with tocopherols. Addition to the diet resulted in a slight decrease in the susceptibility of the lard to rancidification, but the effect was too small to be of practical significance. Injection led to no improvement. On the other hand L. O. Buxton[61] shows the tocopherols, alone or in conjunction with lecithin, to be effective preservatives for vitamin-*A*, though they have little effect on the formation of peroxides.

S. Kaloyereas[62] has shown the Wheeler test to be relatively the most reliable for the examination of olive oil for rancidity. The Issoglio test is of no value for this purpose but can be used to help in differentiating natural oils from refined ones. He mentions that infestation of the olives with moulds increases the susceptibility of the oil to rancidity.

Attention is drawn to an important review by W. O. Lundberg[63] which surveys the present knowledge, researches and practices in the United States concerning the stabilization of fats. It forms a pamphlet of 44 pages and includes some 217 references to the bibliography of the subject.

Vitamins and nutrition

Vitamins.—The recovery of vitamin-*A* in the unsaponifiable matter of fish liver oils is described by M. M. Black *et al.*,[64] and this series of papers is continued by E. R. Roux and C. J. Molteno[65] who deal with variations in the oil and vitamin-*A* content of the Cape hake. Extraction of fish liver oils with solvents, including *iso*propanol, acetone and methanol by L. O. Buxton[66] has led to a concentration of the vitamin and of associated antioxidants in the solvent fraction.

The factors affecting the reliability of the spectrophotometric determination of vitamin-*A* are discussed by H. W. Rawlings and G. H. Wait[67] who outline the use of simple statistical methods. The authors prefer the Beckmann instrument to the Hilger spectrograph as giving greater precision, and note certain precautions that they have found necessary. A. E. Sobel and H. Werbin introduce[68] a new reagent, activated glycerol dichlorhydrin as reagent for vitamin-*A*; it is prepared by distilling 1 l. of β-dichlorhydrin with 10 to 50 g. of antimony trichloride at from 4 to 40 mm. pressure. The colour produced from the reagent and vitamin-*A* in chloroform is stable for from 2 to 10 minutes and obeys Beer's law over a wide range. The chromatographic method for separating free and esterified vitamin-*A* on defatted bone meal is described by J. Glover, T. W. Goodwin and R. A. Morton,[69] who claim the method to be satisfactory in the presence of large amounts of sterols. A chromatographic technique is also used by J. B. Wilkes[70] with kieselguhr as absorbent. A. R. Kemmerer[71] uses magnesium carbonate and calcium phosphate.

Nutrition.—G. Popjak[72] deals with the effect of feeding cholesterol without fat on the plasma-lipids of the rabbit, inferring that it acts as a regulator of the plasma-lipid levels by determining the rate of mobilization of the fat from the depots, and the synthesis of plasma-phospholipids. The absorption of fat from the intestine has been reviewed by A. C. Frazer[73] who regards it as a cytological problem. Fatty acids, bile salt and monoglycerides form the essential constituents of an intestinal emulsifying system. Of these, fatty acids and monoglycerides are formed in adequate quantities in the first 5 hours of pancreatic lipolysis. Hydrolysis of long chain triglycerides may be restricted in the upper two-thirds of the intestine, and more extensive hydrolysis occurs in the lower part of the ileum. Tributyrin and other short chain fats are more easily hydrolysed. The author discusses the possibility of particulate absorption and the chance of phosphorylation in the intestinal cell. He presents a working hypothesis of the fat absorption mechanism. Anomalies of intestinal absorption are dealt with by W. T. Cooke *et al.*[74], and K. F. Matil *et al.*[75] study the comparative digestibilities of plastic shortenings made from lard and from hydrogenated vegetable oils. The authors of the latter paper conclude that both are equally digestible when fed to rats. V. Augur and colleagues have shown[76] that the addition of lecithin to fats causes them to be absorbed more rapidly than the same fat without lecithin; this would appear to be in accordance with the theory of A. C. Frazer, *supra*.

Composition of oils and oilseeds

A review of the production and composition of tomato seed oil is given by M. Carrière[77] and one of the oil and linamarin contents of linseed varieties by E. André and M. Kogane-Charles.[78] A bromide of a linoleodilinolenin has been isolated from the fatty oil of kurchi seeds by R. J. Irani.[79] The probable glyceride structure of the oil of the fruits of *Terminalia belerica*, Roxb. is stated by B. K. Singh and A. Kumar[80] to be: palmito-oleolinolein 35·24, stearo-oleolinolein 43·51, palmitodiolein 1·07, stearodiolein 1·95, dioleolinolein 9·54, and triolein 8·69%. Analyses and compositions of a number of chaulmoogra oils from the Belgian Congo are given by L. Adriaens.[81] The chemical composition of a shark liver oil from a small shark caught in Bengal waters has been determined by I. M. Gajjar[82] who has shown it to contain 171,500 i.u. of vitamin-*A* per gram. The mixed fatty acids contain 32% of oleic type acids, 15 of linoleic, 2·6 of linolenic and 8·6% of clupanodonic type. The iodine value of the unsaponifiable matter was 173·2 and that of the oil 90·3.

Oil of chia (*Salvia hispanica*, L.) is described by F. Palma *et al.*[83] as derived from a wild plant of Mexico used for the manufacture of a soft drink. The seed contains about 24% of a liquid oil having: sp. gr. 0·9330, n_D 1·481, cloud point —13·0°, titre —14·7°, unsaponifiable matter 1·21%, sap. value 192·0, iodine value 191·4, CNS value 118·6. The oil is computed to contain 54% of linolenic acid, and the extracted seed meal to contain 23% of protein on a dry basis.

The crushed, decorticated seeds of *Sideroxylon tomentosum* (N.O. Sapotaceae) contain, according to M. D. Nadkarni,[84] 41% of oil having: d^{25}_{28} 0·912, n^{25} 1·4675, sap. value 189·3, iodine value 80·4, unsaponifiable matter 1·66%. The same authors have examined the seeds of *Mappia foetida* (N.O. Olacaceae) and find 48% of oil to be present. The oil has: d^{28}_{25} 0·9310, n^{28}_D 1·4781, sap. value 185·4, iodine value 123·7, unsaponifiable matter 0·81%.

M. Lewy[85] has obtained the oil from kenaf seeds (*Hibiscus cannabinus*, L.) in a yield of 20%. It had: d^{15}_{15} 0·9175, n^{40}_D 1·4657, sap. value 189·8, iodine value 99·7, unsaponifiable matter 1·7%. The oil has a positive Halphen reaction.

Calabash seed, *Crescentia cujete*, L., contains [86] about 35% of oil, having sp. gr. $^{25}_{25}$ 0·913, n^{25}_D 1·4676, saponification value 191·2, iodine value 88·7, CNS value 71·2, titre 27·8°, unsaponifiable matter 0·81%.

The free fatty acid fraction of human hair fat has been investigated by A. W. Weitkamp and others[87] and found to contain normal saturated and unsaturated fatty acids ranging in chain length from 7 to 22 carbon atoms. Normal acids having an odd number of carbon atoms appear to have been obtained from a natural source for the first time. The double bond is located characteristically in the 6 : 7 position in the unsaturated acids, but 8 : 9 and other isomers are present as well.

T. P. Hilditch and others have studied further the composition of commercial palm oils, separating the glycerides of an oil from the Belgian Congo with the aid of crystallization from solvents at low temperatures.[88] With other collaborators, T. P. Hilditch[89] has examined the oil of *Tetracarpidium conophorum*. This is a drying oil that may achieve considerable importance as a linseed oil substitute. It has an iodine value of 200–205 and contains: linolenic acid 64–68, linoleic acid 10–12, oleic acid 10–11, saturated acids 10–12% (wt.). The oil forms a hard clear film on exposure to air. The shrub which it is obtained from is of fairly rapid growth and is already cultivated for native edible purposes in Southern Nigeria. The seed tissues are apparently unusually rich in lipase, and formation of free acidity is rapid in the dried kernels, but treatment at 100° to destroy the active enzymes allows the seeds to be stored and exported to this country without too marked an increase in acidity.

Professor Hilditch[90] has further applied the technique of low temperature crystallization to a study of the glycerides of rapeseed oil. With F. D. Gunstone[91] he has dealt with the component acids and glycerides of Australian lumbang oil, and with H. C. Dunn[92] with the acids of West African ben and mango oils.

U. S. Kini and K. Chidambaram[93] describe the liver oils of elasmobranch fish of South Indian waters in a comprehensive paper. They list 27 species of shark and 30 of skate and ray represented in these waters, and note that 20 of these species are economically important as sources of food and for their liver oils. Analytical data are recorded for the liver oils of 12 different species.

Analysis

J. L. Trauth[94] points out that while calculations of potential yields of glycerine and fatty acids from the ester value, etc., are valid for high-grade fats, they are not for material of low grade owing to the possible presence of mono- and diglycerides, so that the yields should always be arrived at by actual determinations. W. D. Pohle and V. C. Mehlenbacher[95] determine glycerol by acetylation with acetic anhydride in pyridine after the manner of West *et al.* (A. 1934, 510). In a later paper, which would appear to have the highest importance, these authors[96] have worked out a scheme for the determination of glycerol, propylene glycol and trimethylene glycol in mixtures. Periodic acid is used to oxidize glycerol to formic acid and propylene glycol to aldehydes; it does not react with trimethylene glycol. Total acetylizable matter being determined by the use of acetic anhydride in pyridine, the percentages of the three hydroxylated compounds may be calculated.

Semi-micro methods for the determination of saponification values and equivalents are described by A. N. N. Trenité[97] and D. Ketchum[98], the latter author using the Riemann double indicator method; after saponification with 0·5N-alcoholic potash the solution is titrated with 0·5N-hydrochloric acid to phenolphthalein, and then with 0·025N-acid to bromphenol-blue; the last titre is equivalent to the potash required for saponification. The determination of unsaponifiable matter by the A.O.A.C. and the S.P.A. methods has been reviewed by G. Kirsten.[99] He finds the latter method to give the higher results if large amounts of unsaponifiable matter are present. The titratable acidity of the final residue is, however, appreciable and should be corrected for. M. L. Karnovsky, W. S. Rapson and M. Black[100] have applied the S.P.A. method to South African fish products, and find that a greater number of extractions than three of the aqueous alcoholic soap solution is necessary in certain cases to ensure the complete extraction of the unsaponifiable matter. It is concluded that the difficulty of securing complete extraction in three extractions with ether is associated with a high content of α-glyceryl ethers in the oils. M. L. Karnovsky and W. S. Rapson[101] have applied the method described as the Fitelson method, namely the determination of the iodine value of the fraction of the unsaponifiable matter passing through a chromatographic column of aluminium oxide, to the determination of squalene in a number of marine oils.

A report of the A.O.C.S. Colour Committee is of interest in showing[102] a desire to supplement the visual determination of the colour of an oil by photoelectric measurement. Collaborative measurements were made on 12 samples of oils and tallow/grease mixtures by various means. Very good agreement is noted between visual colour gradings, Lovibond red values and readings on the Klett-Summerson colorimeter using a No. 50 filter. L. K. Whyte[103] looks further into the possiblities of a photoelectric method. He measures the optical density of a 1-cm. depth of the oil with blue, green and red filters and calculates the ratios of blue to green and green to red, and has devised several systems of colour grading based on these ratios. It is somewhat doubtful whether this method will lead to better results than an application of the method of G. Forsyth and T. I. Pound[104] who worked out a system for the conversion of photoelectric data obtained with the Bolton & Williams colorimeter to red and yellow units. The work of the latter authors was carried out mainly on tanning extracts, but in the writer's hands it has proved equally successful for determination of the colours of oils, and anticipates the work of the American investigators by some years.

J. P. Kass and others[105] emphasize the empirical nature of the determination of hexabromides. C. H. Lea points out the effects[106] of dissolved oxygen on peroxide values, and develops two procedures in which oxygen exclusion is adequate.

K. Schmidt-Nielsen[107] discusses difficulties in the determination of the melting point of human fats arising from their low values. He suggests that these are avoided if the fat is first cooled to —70° to produce a microcrystalline mass. He points out that, while the melting point of visceral fat is from 30 to 35°, that of the peripheral organs is lower. Fat from the feet often has m.p. 0 to 10°. A person exposed constantly to high temperatures was found to have fat of extremely high melting point.

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GLASS

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THIS report differs from those published over the past few years in that it deals with those aspects of glass chemistry which are likely to be of interest to the chemist rather than the glass technologist. It is not a complete review of all the advances in the field of glass technology, and greater emphasis than formerly has been given to those publications concerning the fundamental nature of the structure of glasses. Some outstanding work on this subject has been published, and it is significant that attempts are now being made to elucidate the finer structures of glasses.

The constitution of vitreous systems

During the year under review a considerable amount of fundamental work on the constitution of glasses has been published. Over the past few years the random network theory based on *X*-ray diffraction studies has been developed to give a broad picture of the constitution of glasses. The recent studies direct attention to the more detailed aspects of the theory and to the interpretations of the physical properties of glasses in terms of the theory. Although this work is due mainly to physicists and chemists closely associated with the glass industry, it is worthy of wider attention as it has an important bearing on the nature of the liquid state.

R. W. Douglas[1] has considered the relationship between the physical properties and the structure of glass, particularly the variation of physical properties with time and the variation of viscosity as a function of temperature. After reviewing the present state of knowledge of the structure of liquids and glasses, Douglas suggests that the crystallite theory which has been proposed as an alternative to the random network theory is inconsistent with the experimental evidence, and adopts the liquid-like structure as the basis for his argument. In the development of this argument, Douglas summarizes the theory of J. D. Bernal on the structure of monatomic liquids and the change of atomic configuration with temperature to an equilibrium configuration, and suggests that as liquids and glasses give the same general form of *X*-ray diffraction pattern their atomic configurations are capable of description in similar terms. The work of Bernal leads to four conclusions concerning the free energy, the specific heat and the equilibrium configuration of a liquid, and the free energy of the liquid as compared with that of the corresponding crystal. Glass is then defined as a super-cooled liquid in which the viscosity remains so high that the configuration remains fixed at a state not corresponding to the equilibrium configuration, but one determined by heat treatment and the time elapsed. This definition is regarded as concerned only with temperatures far below the crystallization temperature, that is, temperatures at which the rate of attainment of equilibrium is so slow as never to reach completion. In the light of the theory, Douglas examines the experimental data on the variation of viscosity with time at constant temperature and the phenomenon of heat absorption in glass in the transformation region, and shows that they are compatible with the equilibrium configuration hypothesis, without the necessity for assuming the existence of aggregations or crystallites. The idea of a state of aggregation has also been used to explain viscosity-temperature relationship in glasses, mainly on account of the fact that the simple equation relating viscosity with temperature for unassociated liquids does not hold for glasses. Again, Douglas[2] shows that the random network has an equilibrium configuration corresponding to each temperature; such equilibrium is attained instantaneously at elevated temperatures.

The fundamental conditions of glass formation have been enumerated by K. H. Sun.[3] The essential condition is the existence of strongly bonded large networks or long chain molecules in the liquid which prevent orderly orientation of the atoms within the chains or networks. For long chains or large networks to exist it is necessary (*a*) that the bond strengths of the atoms should be high, (*b*) that the small ring formation of these strongly bonded atoms is at a minimum, and (*c*) that the relative numbers are such that the continuous chain or network is possible. At the same time, the co-ordination numbers should be small. Sun tabulates the bond strengths of a number of M-O single bonds, and shows that for glass formers this is of the order of 80 k. cal. per Avogadro bond, 60-80 k. cal. per Avogadro bond for intermediates, and below 60 k. cal. for the modifiers. Sun[4] has also given a brief review of the chemistry of glass formation, and deals with elementary glasses, such as sulphur, selenium, and tellurium glasses, oxide glasses, halide glasses, and sulphide glasses. The review contains a considerable number of references on the structure of glasses.

An important series of papers dealing with the bonding of the atoms in glasses has been published by H. Cole. The first of these[5] deals with the structure of glass based on evidence from the effect of composition on colour, and is considered from the point of view of the electronic theory of valency. The effects of increasing the alkali content of sulphur amber glasses at the expense of silica are similar to those produced by increasing the reducing agent, and, conversely, the behaviour of manganese in soda-silica glasses of increasing silica content is similar to that of increasing oxidation. Since an oxidizing agent is one which can accept electrons, and an acid is a substance whose molecule can accept a pair of electrons to form a covalent bond, the two processes both involve electron transfer. Another effect of structure on colour can be demonstrated by composition changes in soda-boric oxide glasses containing cobalt; the colours ranging from blue to pink cannot be ascribed to the oxidation-reduction effect, but the possibility of fundamental structural changes is indicated. In this case it is suggested that the formation of a co-ordinate link occurs when soda is added to a boric oxide glass, and added metals may under certain conditions actually take part in the structure. This point of view is supported by the added tendency to attach reservations to the random network theory of Zachariasen, and to assume that many of the metals in glasses take part in the network. In fact, there seems to be no precise line of demarcation between the network former and the network modifier, but the effect of structure on the colour given by a colouring metal seems to be related to the degree of covalent character of the colouring atoms.

In his second paper[6] Cole has discussed the constitution of coloured glasses based on the analogy between glasses and solutions. It is considered that the division of coloured glasses into two types, one containing "ionic" colouring agents and the other containing "colloidal" colouring agents, is inadequate, and coloured glasses may be treated on the solution analogy if consideration is given to modern theories of liquids. On the basis of solution, coloured glasses may be divided into two classes, (1) liquid phase colours, and (2) solid phase colours, and each class may be sub-divided respectively into (1a) atomic (ionic and covalent), (1b) molecular, (2a) colloidal, and (2b) crystalline. Transitions are possible between these types. Cole discusses particular cases of these classes on the basis of structural arrangements. In a further paper Cole[7] discusses the different criteria which have been put forward by various workers to determine whether a glass constituent is likely to take part in the structure as a network former, as a network modifier, or as an intermediate. The numerical values which have been derived by various authors are based in general on crystallographic data involving ionic bonding, which Cole considers to be arbitrary, and is probably an over-simplification for glasses. For this reason and on account of the work of K. Fajans[8] on the formation of the covalent bond it is considered that the Si-O bond is partly covalent in character, and a quantitative factor may be deduced which is a measure of the amount of covalent character between the atoms concerned. This covalency factor is a measure of the extent to which an atom will take part in the network. The factor may be modified owing to interaction with other atoms in the structure, but it is considered that the factor may be of importance in devising mixtures which will yield a vitreous product with little tendency to crystallize.

An important series of papers by J. M. Stevels on the physical properties of glasses has been published. These papers deal in particular with the calculation of density from composition, and the two original papers[9, 11] on which the recent work is based were published in Holland during the war and have only recently become available in this country. A brief review of these two papers is therefore given here. In the first place, Stevels objects to the formula given by Huggins[10] for the calculation of the volume of a silica glass containing one gram atom of oxygen on the grounds that the constants of the Huggins' equation have no physical meaning. Stevels shows that this volume V can be expressed simply as

$$V = \frac{V_0}{1-R\chi} \text{ where } V_0 \text{ and } \chi \text{ are constants}$$

and R is the ratio of the number of oxygen atoms to the total number of atoms of the glass-forming elements. V_0 is the volume of an amount of glass containing one gram atom of oxygen for $R \rightarrow O$, and χ is connected with the extent to which the oxygen network is contracted by the different glass-formers.

Stevels' second paper[11] deals with the derivation of this formula which is based on the present knowledge of glass structure, and it is shown that for a large number of glasses the deviation between the calculated and the experimental value, is not greater than 1%. These are called normal glasses, for which R, the ratio of the number of oxygen ions to the number of glass-forming ions, is less than 2·5, and P, the ratio of the number of oxygen ions to the number of metallic ions, is greater than 3·9. The former does not hold for abnormal glasses where $P < 3\cdot9$, and for glasses where $R > 2\cdot5$, and the theory of the departure from normality is discussed in terms of the breaking of network linkages as oxygen is introduced. The subsequent papers published recently consist of an extension of the formula to vitreous systems other than the silicate system. In the soda-boric oxide system[12] it is found that the value of χ decreases with increasing R up to a value of 16% Na_2O. Although very complete data are not available, this behaviour does not appear to be confined to the B_2O_3–Na_2O system, but occurs also in the systems BaO–B_2O_3 and PbO–B_2O_3.

In dealing with systems containing more than one glass-former[13] it is possible to set up arbitrary rules concerning the value of χ, and these rules are used to calculate densities of glasses in these systems. Similar rules are found to apply to phosphate and germanate glasses, and the values of χ for the different glass-formers are summarized. Its value is shown to be roughly inversely proportional to the "field" of the glass-former as defined by Dietzel.

In a further paper[14] Stevels discusses the abnormalities in the density of the B_2O_3–Na_2O system at 4% Na_2O. The relationship between density and Na_2O content is an S-shaped curve which differs from the curve derived by the methods previously developed. A possible explanation of the divergency is that the increase in volume which would be expected from the formation of tetraheda on the introduction of sodium oxide is taken up by irregularities in the network.

In Paper VI of the series[15] Stevels shows that there are no perceptible differences between the volumes of the non-bridging and the bridging oxygen ions, and from the volumes of the interstices in the oxygen network deduces the volume of a block of glass containing one gram atom of oxygen. These volumes are practically identical with those obtained using the formula developed earlier. Paper VII[16] deals with the molecular refraction of glasses, and it is shown that, provided distinction is made between bridging and non-bridging oxygen ions, data for atomic refractions may be used to calculate the molecular refractions of abnormal glasses in an additive manner. In this paper Stevels reviews the methods put forward in recent years by various investigators for the calculation of molecular refractions.

Although the structure of glass has been elucidated to the extent that it can be used as a basis for understanding and explaining many physical properties, there is still difficulty in correlating with the structure those properties which depend chiefly on the surface of the glass. W. A. Weyl[17] has surveyed this important aspect of glass chemistry, pointing out that the configuration of the ions in the surface layer is not identical with that in the bulk, and the incomplete co-ordination of these surface ions calls for a readjustment either by the attraction of water molecules forming OH groups, by the attraction of greasy impurities, or by a migration to the surface of those cations which are more easily satisfied by incomplete co-ordination. Weyl deals with the various chemical changes that may occur and, after outlining the methods available for studying the phenomena, discusses the bearing of the phenomena on many practical problems, including glass-metal sealing, surface devitrification, base exchange reactions, reduction processes, the deposition of non-metallic compounds, copper and silver, and deposition of fluorides from the gaseous phase. Weyl's paper contains many references to the literature on the surface chemistry of glass.

An approach to the problem of the constitution of glass by chemical methods has been made by A. W. Bastress,[18] who considers that the chemical reaction between dry hydrogen and powdered glass at different temperatures offers possibilities for investigation. Glass compositions containing 5% Sb_2O_3, Bi_2O_3, and PbO, or 0·1% Ag_2O were studied, and it was found that silver ions were reduced at lower temperatures as basicity increased, while an increased ratio of B^{+++} to O'' or Si^{++++} to O'' increased stability. It was concluded that Ag_2O plays the same role as Na_2O, that is as a network modifier. The electronic structure of lead, bismuth, and antimony ions is such that they compete with the network-forming cations and they show maximum stability as B_2O_3 is added to Na_2O–SiO_2 glass. The stability of the lead ion introduced into sodium-titanium silicates increases rapidly if the titanium oxide content is increased above 15% by weight.

The function of aluminium in silicate glasses in the system Na_2O–CaO–Al_2O_3–SiO_2 has been investigated by H. W. Safford and A. Silverman.[19] From a study of the silicate minerals it appears possible for aluminium to assume fourfold co-ordination, replacing to some extent silicon of the same co-ordination number. Safford and Silverman have determined the densities and refractive indices of glasses within the system investigated, and the partial molecular refractions of the component oxides were evaluated, using the Lorentz-Lorenz equation. The refractions are found to be sensibly additive for both the glasses and the isomorphous series of soda-lime felspars. The partial molecular refractivity of Al_2O_3 in the glasses agrees closely with that calculated for crystals. This leads to the conclusion that the Al ion is in fourfold co-ordination.

J. E. Stanworth[20] has found that the introduction of RO oxides into the system Al_2O_3–R_2O_3–P_2O_5 is advantageous in promoting glass formation. The range of possible compositions for the formation of glasses is extended considerably by the use of both RO and R_2O oxides.

During recent years new optical glasses of high refractive index and low dispersion have been developed, and lanthanum oxide has been used in substantial proportions in such glasses. A quantitative study of the relative effects of lanthanum and barium on refractive index and dispersion has been published, and several glass-forming systems based on the networks of SiO_2, B_2O_3, P_2O_5 and containing lanthanum have been investigated.[21]

M. L. Huggins and K. H. Sun[22] have published the energies of formation of oxygen-containing crystals and glasses from dilute gases composed of metal and oxide ions.

Glass melting

The processes of chemical oxidation and reduction of the metals in glasses have engaged the attention of a number of workers recently. Both processes play a very important part in glass-melting reactions, but in practice their control is often very difficult. Temperature alone has an effect in that the state of oxidation tends to a lower valency with increasing temperature. In the conventional type of glass-melting furnace, therefore, it is only possible to maintain a balance between the oxidation and reduction processes, and very rarely can complete oxidation or reduction be achieved.

G. E. Rindone, E. C. Marboe, and W. A. Weyl[23] have recently carried out some experiments on the oxidation and reduction of a soda-lime-silica glass by electrolysis. The passage of direct current leads to oxidation and reduction processes at the anode and the cathode respectively, and if the portion of the melt round the anode can be separated from that round the cathode by a refractory diaphragm, zones of almost complete oxidation and reduction can be obtained. Weyl and his co-workers describe the various methods which may be adopted in practice, and they describe a number of experiments with colouring ions in low-temperature-melting borate and phosphate glasses. Since the oxidation or reduction process is almost complete in the neighbourhood of the electrodes, the method affords interesting possibilities for the study of the effects of colouring ions in various stages of oxidation. It is also suggested that electrolytic reduction may be used to remove gases such as CO_2, SO_3, and H_2O, which participate in the glass structure as anions CO_3'', SO_4'', and OH'. The possibility of complete removal of H_2O from a glass suggests that glasses with high infra-red transmissions might be obtained.

P. Gilard[24] has presented a review of the present-day knowledge of oxidation and reduction reactions and their importance in connexion with the release of dissolved gases and the equilibrium colours obtained with colouring ions in different valency states.

The blackening of lead glasses heated in a reducing flame is usually ascribed to the reduction of lead oxide to the metal by the hydrogen or carbon monoxide in the gas flame. Since, on the structural theory, lead oxide *per se* cannot exist in the glass, A. J. Monack[25] has considered this phenomenon from the point of view of a reaction in which lead ions acquire electrons from the negatively charged flame. The production of blackening by electrolysis of glass can be explained by the migration of sodium ions which replace lead ions at the cathode.

The influence of surface tension on glass melting is not in general appreciated by the glass chemist, and some work reported on this subject by L. Shartsis and A. W. Smock[26] is therefore of considerable interest. These workers found a positive correlation between surface tension and seed quality, pot attack, and the amount of gas liberated during melting for a number of optical glasses, and although the work may be criticized on the grounds that the correlation data are open to subjective error, it offers an interesting approach to many melting problems.

Devitrification

The study of the devitrification of vitreous systems is of importance both in the investigation of glass structure and in the practical side of glass making. The rates of growth and the rates of solution of crystals are usually linear with time, and H. R. Swift[27] has shown that above and below the liquidus temperature the curves relating rate of crystal disappearance and rate of crystal growth with temperature are continuous. The determination of these curves affords a precise method for the determination of the liquidus temperature. Swift has applied these methods to the investigation of the effects of magnesia and alumina on the rate of crystal growth in glasses of general composition, SiO_2 74%, Na_2O 16%, $(CaO+MgO)$ 10%, MgO replacing CaO in 2% steps.[28] In this series the rate of crystallization was minimum for 6% MgO. A series of glasses of general composition ($SiO_2+Al_2O_3$) 71%, Na_2O 17%, CaO 12%, in which Al_2O_3 replaced SiO_2 in 2% steps up to 8%, was also investigated. In this case the observed devitrification was rather complex; as the alumina content was increased the rate of growth of devitrite, the primary phase, decreased, but the rate of growth of wollastonite tended to increase at the high alumina compositions. The data obtained on these glasses are examined in relation to the equation put forward by various observers for the crystallization rate in terms of other variables,

$$R=\frac{K}{\eta}(T_{liq}-T)$$

where R is rate of crystal growth at temperature T, T_{liq} is the liquidus temperature, and η is the viscosity. Swift suggests that the equation may be written in the form $R=\frac{KM}{\eta}$, where M is the amount of material available for crystallization.

S. M. Cox and P. L. Kirby[29] have deduced the variation of the rate of crystallization with temperature from a consideration of the vibrational energies of the ions of the glass and of a crystal at a plane glass-crystal boundary, and the expression thus obtained has been applied to glasses in which cristobalite is formed as the crystalline phase.

A useful guide to the identification of inclusions in glass (stones) which occur in practical glass making has been published by M. A. Knight.[30] Much valuable information on the technique of stone recognition is given, and the paper includes a table which summarizes the properties of crystals which are found to occur in commercial glasses.

Glass melting furnaces

During the last few years the problem of the efficiency of glass-melting units has received increasing attention. Apart from the question of glass-making economics, the problem of the efficient utilization of fuels has become one of universal importance, and recent progress in this field has been significant. Probably the most important papers dealing with this subject are those due to I. Peychès. In the first of these[31] Peychès discusses the thermal balance of glass furnaces deduced from the measurement of convection losses at many points round the furnace. In particular, the effect of insulation is examined, and the effect of increased temperature due to insulation on the corrosion of the refractories is considered in specific cases. On this account optimum working conditions must be based on a compromise between heat economy and refractory life. In a second paper[32] the effect of convection currents on the heat loss from a tank and on the attainment of homogeneity is discussed in very great detail. It is impossible in this report to give an adequate summary of the ideas put forward in this paper, but it is probably the most important survey of the subject which has yet appeared, and detailed study is recommended.

B. P. Dudding[33] has continued his statistical studies of the thermal performance of glass-melting tanks, and his recent discussion is concerned with four different furnaces. The importance of plotting some measure of furnace performance against statistically determined limits in order that changes in performance can be detected at the earliest possible moment is emphasized. It is shown that for all practical purposes the calculation of the thermal efficiency factor Q, put forward by the Society of Glass Technology, is a good measure of thermal performance.

The formula for Q has been examined by C. E. Gould,[34] who has shown that the formula can be used to deduce the relationships between glass output and temperature when the heat input to the furnace is constant, and also the relationship between the calorific value of the fuel and temperature when constant weight of fuel is used. A form of the performance formula is given which enables Q to be calculated when values of the coal/glass ratio and the sq. ft. per ton per day figures are known.

A British Standard Specification for determining the efficiency of fuel-fired regenerative tank furnaces has been published.[35] This provides for two forms of test, (1) a short simple series of industrial tests, and (2) a comprehensive series of tests for a complete evaluation of performance.

A useful review of the fundamental laws of radiation and the derivation of the emissivities of flames and flame constituents has been given by G. Ribaud.[36] The heat transfer in a glass tank is dealt with in a quantitative manner. W. E. S. Turner and his associates have described further results of studies on the distribution of temperature in the molten glass in a tank furnace. In their most recent work[37] they show that for colourless glasses of widely different compositions the fuel consumption is practically constant for the maintenance of a given surface temperature. The temperature gradients through the depth of the glass are very similar, being of the order of 5–10° per inch compared with 85° per inch for coloured glass of high iron content. A series of experiments on the temperature gradients in cobalt glasses showed that the heat transmission of normal commercial types of cobalt blue glasses more nearly approaches that of colourless glass than do other coloured glasses.[38]

An electric furnace for experimental melting of glasses at temperatures about 2000° has been described by J. Fortey and E. M. Haines.[39]

Mechanical properties

Over the past few years J. B. Murgatroyd has been responsible for a number of important investigations concerning various aspects of the problem of the strength of glass. At room temperature certain glasses show an anomalous elastic response to loading, an " instantaneous " deflection being followed by a slowly increasing deflection which may vary from 2–10% of the "instantaneous" deflection. Conversely, on removal of the load a slow recovery follows an " instantaneous " recovery. Some experimenters have failed to observe this phenomenon, and Murgatroyd's recent experiments[40] show that the amount of the delayed effect is dependent on the rate of loading. If rapid loading is carried out, then the delayed portion of the strain obeys Hooke's law, and the strain is almost completely reversible. Murgatroyd attempts to explain the experimental results on the basis of his hypothesis that glass consists of a continuous elastic matrix with inclusions of viscous material. The assumption that the viscous material obeys the Nutting stress-strain equation is found to be not in agreement with the experimental results, but the phenomena can be explained if the viscous component is a complex of several substances having different Newtonian viscosities. The effects obtained by loading a mechanical system consisting of an elastic body coupled in parallel with four bodies each having different Newtonian viscosities are shown to be similar to those obtained with glasses.

Murgatroyd and Sykes[41] have also considered the relation between the delayed elastic effect and the decay of the strength of silicate glasses at room temperature. Murgatroyd's hypothesis of brittle rupture[42] lead to an expression relating the breaking stress with the strain, and in deriving the expression a number of assumptions were made. The expression is now shown to be applicable to results obtained experimentally on three different glasses, and it is therefore considered that the underlying assumptions are justified. Further results may also be explained on this theory. Thus the assumption is made that there is a local stress concentration in glasses subjected to load, and the stress concentrating factor tends to increase as some component of the glass relaxes under constant load. The rate of strength decay is therefore connected with the appearance of delayed strain. The type of bond involved in such a process cannot be a primary atomic bond, and this may account for the low strength of glasses. Murgatroyd and Sykes suggest that their theory can be used to explain the experimental observations of T. C. Baker and F. W. Preston[43] that under certain conditions the strength of glass rods can be the same for duration of loading varying from 0·1 sec. to 10 sec. Baker and Preston argued that the decay of strength under prolonged loading is due to the presence of atmospheric moisture, and if this is removed then the strengths are identical. Murgatroyd and Sykes suggest that the opposite viewpoint may be taken, that the glass surface under ordinary atmospheric conditions is normal and the strength of the glass is normal. Under these conditions the surface may form a soft solid phase with little ability to resist stress. On the other hand, when heated *in vacuo* a hard skin of some new compound may remain on the surface. This may not in itself be a glass, and therefore have no viscous component, and its failure under stress would have no dependence on the duration of stress.

In recent years the use of routine specific gravity measurements as a means of quality control for glass-making tanks has found increasing favour, particularly in America. R. O. Duff[44] has reviewed the method of specific gravity determination in the light of variations in the technique suggested by M. A. Knight.[45]

A means of measuring the elastic constants and internal friction of glasses by an electrical method has been described by R. Cabarat.[46]

P. Giraud and P. Abadie[47] have suggested that there are interesting possibilities in the application of low-frequency spectra determinations to glass technology. In their paper the effect of annealing and humidity on tan δ, measured at frequencies ranging from 30 cycles to 30 megacycles per second, is demonstrated for a number of glasses.

Many of the important properties of glasses, such as annealing temperature, softening temperature, working range, etc., are usually defined in terms of viscosity, but there is no precise agreement throughout the industry on the viscosity values to be adopted for the various properties. The Glass Division of the American Ceramic Society has put forward a series of standard definitions which, if universally adopted, would go far to avoid some of the confusion which occurs at present.[48]

The development of hard glasses for use as instrument bearings has been described by A. E. Pavlish and I. Mockrin.[49] Hardness is discussed in relation to the random network theory, and a very useful summary of the previous literature on this neglected subject is given. The authors describe their own experimental work using the system Al_2O_3–CaO–B_2O_3–SiO_2 as their starting point and making substitutions of the various components. From the network theory, Si, Al, Be, Mg, and Ca seem to be good " hard glass " constituents, of which Be is the most striking. The results show that the Knoop hardness depends to a high degree on factors other than the strength of the glass structure. Low expansion, high softening point, and high chemical resistivity have been associated with strong structure, but the comparative hardnesses of vitreous silica and soda-lime-silica glass afford a good illustration of the danger of explaining hardness wholly on the structural strength.

Optical properties and coloured glasses

The computation of refractive index and dispersion as functions of composition is of importance to the glass technologist, particularly in the case of glasses made specificially for optical purposes. Many factors have been put forward by various authors, but the differences between the computed and measured results are often too great for the factors to be used with confidence. K. H. Sun[50] has now published a series of factors for 36 oxides which are linearly additive with composition for a region of composition and structure defined by the ratio of silicon to the total number of oxygen atoms. Sun also gives factors for the contribution of component oxides to the dispersion.[51]

It has been shown[52] that the dispersion of some optical glasses in the near infra-red (0·6–2·4 μ.) can be expressed by the Ketteler-Helmholtz dispersion formula provided that sufficient wavelengths are taken to calculate the constants of the formula.

In the manufacture of selenium ruby glasses the glass-maker encounters many difficulties, and the functions of some of the constituents which are considered essential to the batch are not well understood. Owing to the importance of such glasses it is not surprising that they form the subject of a considerable amount of work which is being done at the present time. Thus R. R. Shively and W. A. Weyl[53] have recently carried out experiments to determine the functions of zinc oxide, fluorine, bone ash, and minute amounts of copper and nickel oxides. These experiments indicate that zinc oxide helps to retain sulphur and selenium in the melt, and the introduction of fluorine facilitates molecular rearrangement because of the weaker forces exerted by the monovalent fluorine ion as compared with the divalent oxygen ion. The mobility of the glass at low temperatures is increased, thus facilitating the molecular rearrangement necessary for the striking process. The presence of phosphate in combination with fluorine leads to an insoluble phase which enhances the striking of the ruby. If copper or nickel oxides are present, sulphides of these metals are formed at the high temperatures and nuclei for the low-temperature formation of cadmium sulphoselenide are provided. In batches containing strong reducing agents alkali sulphoferrite and selenoferrite may be formed, and the deep colour of some glasses containing small amounts of cadmium sulphoselenide may be ascribed to these compounds.

Work on selenium ruby glasses has also been reported by A. E. Pavlish and C. R. Austin,[54] who have examined the conditions for the retention of selenium and cadmium in the melt. They find that conditions favourable for the retention of selenium have an adverse effect on the retention of cadmium, and that the introduction of silicon as a reducing agent is effective in controlling the amount of selenium retained. The use of metallic cadmium was also found to have a considerable effect in this connexion. These authors also report some interesting colours obtained with selenium in combination with metallic cations such as bismuth, iron, and arsenic, and give transmission curves for some glasses containing these substances.

The fluorescence and solarization of glasses is dealt with by W. A. Weyl[55] in part V of his monograph on coloured glasses. After surveying the fundamental theory of fluorescence, glasses are classified according to the role which the vitreous phase plays in producing fluorescence. So far as glasses are concerned the most important groups are those in which the glass provides an inert rigid medium for separating atoms or molecules which fluoresce because they are energetically isolated and the group in which glass-forming ions fluoresce. This is analogous to the group of coloured glasses containing cations or anionic groups as colour centres. The section on the solarization of glasses is an excellent survey of the present knowledge on this subject.

The investigation of the solarization of manganese-bearing glasses at different temperatures as a means of studying structure has been discussed by R. L. Collins and A. E. Badger.[56] The variation in colour produced by irradiation of the glass at the different temperatures is associated with the ionic environment of the trivalent manganese ion.

The use of titanium oxide as a colouring agent leads to some interesting coloured glasses, and for this reason a paper by P. Beyersdorfer,[57] published in Germany in 1941, should be mentioned. Intense colours are reported when active reducing agents are used with glasses containing titanium in combination with magnesium, aluminium and zinc, and also with sodium thiosulphate as a batch constituent. At the same time A. Dietzel and R. Boucke[58] reported the effects of titania on other colouring oxides.

A photosensitive glass recently developed in America has created considerable interest among glass technologists. The effects produced depend on the differential precipitation of particles within the glass after irradiation by ultra-violet light, the size of the particle and hence the resultant colour depending on the degree of irradiation. It is possible by exposure through a photographic negative to produce three-dimensional images within the glass. The glass has been described in various journals,[59] and R. H. Dalton[60] has given further details in the patent literature.

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CERAMICS, REFRACTORIES AND CEMENTS

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As a result of the fuel situation, the installation of new gas and electric continuous kilns, which are so greatly needed, has been delayed. The supply of new plant and machinery and other construction materials for modernization has also been impeded. The production in the pottery industry, considering all the difficulties of lack of machinery for modernization, and of labour, has been extraordinary. The supply of pottery to the home market is still restricted, but the value of the exports has exceeded expectations.

In the porcelain industry the titanate group of ceramics is still attracting attention. Sintered alumina is being used for many types of porcelain, and is probably the most valuable high-temperature ceramic oxide.[1] Prior to 1940, zircon porcelain was used to some extent for spark plugs, but the alumina plugs are likely to hold the field for some time to come. Recent war years, however, saw a much more intensive study of porcelains of the zircon type, with the result that their potentialities have begun to be realized. They are found to offer good high-frequency electrical characteristics, to possess excellent thermal properties, which are only exceeded by the high refractory oxides type, such as sintered alumina. There is much current interest in this new class of electrical porcelain, and there is every reason to believe that a permanent addition has been made to this field.

The success of many metallurgical operations depends to a large extent on the refractories used in construction of the furnaces. With possible higher heat temperatures it is likely we shall hear more about pure oxide refractories.[2] In the year under review the research work has been chiefly concerned with the basic refractories, both raw materials and finished products.

The position in the enamelling industry is about the same as last year, very few papers having been published in this country. Some co-operative research work is being done, and several first-class new enamelling installations have been constructed, which compare very well with modern plants in the U.S.A.

Clays and other raw materials

The plasticity of clay-water mixtures is obviously due to the clay-water structure; dry clay will disintegrate in water, but dry clay goods will maintain their shape when immersed in paraffin. The clay-water structure is of fundamental significance in the preparation of ceramic ware. Although this subject has received much attention previously, there is still much research work to be done. The plastic properties of clay may be explained in part by the concept of a film of water around the clay particles. Some water is also "bound," and is released when the clay is deflocculated.

The amount of water taken up by the clay is influenced by the nature and concentration of the available ions. The question arises as to whether water is adsorbed on the clay surfaces or if the ions are fixed on the clay lattice and become hydrated; both processes may operate. A. C. Siefert and E. C. Henry[3] have studied the effect of exchangeable cations on the hydrophilic nature of kaolin and a montmorillonite-type clay (bentonite). Both types of clay were surface saturated with hydrogen, calcium, sodium, and potassium ions. The hydrogen and calcium clays show a greater affinity for water than the sodium and potassium clays. It would be expected that the more highly hydrated hydrogen and calcium clays would be more plastic than the sodium and potassium clays. The attraction of these clays for water apparently decreases as the space occupied by the exchangeable cations increases; the smaller the number of the adsorbed ions, the greater will be the space available for water molecules in the system. Two monovalent ions are required to replace one divalent ion. From this statement it might be concluded that the adsorbed ion will determine the amount of water taken up, but Siefert and Henry (*loc. cit.*) show that the hydration varies with the type of clay as well as the adsorbed ion. Although the percentage of water adsorbed by bentonite, whether saturated with hydrogen, calcium, sodium, or potassium ions, is greater than that of kaolin saturated with the same ions, when they are compared on the basis of equivalent amounts of adsorbed cations, less water is adsorbed per milliequivalent of exchangeable cations in bentonite than in kaolin. If the adsorption of water by clays is attributed solely to the hydration of exchangeable cations, it would have to be concluded that these ions are hydrated to a greater degree in kaolin than in bentonite. On the other hand, another explanation is possible; a greater fraction of the surface of bentonite contains active areas on which cations would be adsorbed, with the result that proportionally less surface would remain exposed to water alone. Kaolin has only a comparatively small base exchange capacity; the adsorbed ions are held on only a small portion of the surface, and therefore there is exposed a larger surface for water films. It was found, some years ago,[4] that a proportion of certain organic cations were held on the surface of bentonite, and such clays do not exhibit the marked swelling which characterize this type. The water content of amine saturated bentonite is less than that of sodium and calcium saturated clays. The study of adsorption of organic cations has been extended to kaolinite clays,[5] and it is found that certain organic cations can be adsorbed in excess of the base exchange capacity of the clay. The three organic materials used were *n*-butylamine acetate, dodecylamine acetate, and ethyldimethyloctadecenylammonium bromide. *n*-Butylamine ions, with the smallest molecular size of the three organic bases, are not adsorbed in amounts greater than the base exchange capacity of any clay, but both dodecylamine and ethyldimethyloctadecenylammonium ions are readily adsorbed in excess of the base exchange capacity. The indications are that all adsorption in excess of the base exchange capacity is due to adsorption of undissociated molecules. Some further evidence of the peculiar effects of clay and water is given by W. O. Williamson,[6] who suggests that the warping in clay is not due entirely to differences in the clay-to-water ratio in adjacent parts of the piece. In some ceramic materials there are connexions between the water content and the degree of perfection of the particle orientation; further, differences in the water contents of neighbouring portions of a specimen may be associated with the operation of Reynolds' dilatancy. Certain pressed discs of earthenware body, consisting of clay, quartz, and felspar, show cracking radially; the cracks run inwards from the periphery. As soon as radial cracking occurs, however, the outer annulus becomes moister than the area nearer the centre of the disc. This is explained by Reynolds' dilatancy; the peripheral cracking accompanies the passage from a close to a more open packed structure and water is drawn from nearer the centre of the disc to fill the augmented pore space. This dilatancy is manifested by the non-plastic content of the body, but is not obvious in the ball clays and china clays. Williamson suggests that the relationship between moisture content and dry porosity shows that a completely homogeneous moisture content may be unobtainable.

An attempt to study in detail the crystal structure of the clay mineral in a number of fire-clays has been made by G. W. Brindley and K. Robinson.[7] Previous thermal analysis studies have shown the mineral to be intermediate in character between true kaolinite and true halloysite. This is confirmed by *X*-ray analysis. It is pointed out that there may well exist a series of minerals ranging from an ideal kaolinite at one extreme to an ideal halloysite at the other extreme, fire-clays appearing to occupy an intermediate position in such a series. Fire-clay is not a mixture of kaolinite and halloysite minerals, but a type of clay intermediate in characteristics between these clays.

The problem of increasing the plasticity of clays implies an increase in the base exchange capacity; the addition of various colloids and humus substances should have a positive effect. J. Hedvall, B. Lunden, and F. Sandford[8] tried many materials, and find particularly favourable results can be obtained with lime and aluminium sulphate. The addition of 0·2% lime and 0·01% aluminium as aluminium sulphate reduces rejections attributable to poor plasticity from 31·2% to 13·8%.

The addition of alunite[9] (theoretically $K_2O. 3Al_2O_3. 4SO_3. 6H_2O$) up to 20% to certain clays, increases the strength, firing shrinkage and density, and decreases the porosity and after-contraction. In some cases it causes a permanent expansion, especially on reheating to 1600°. The expansion is due to bloating caused by liberation of sulphur gases. If low-grade clays are used the refractory properties are adversely affected.

Grinding efficiency has been improved by the study of ball ratio, closed circuits, control of classifier and mill density, and speed of mill, but laboratory control in a mill is needed to indicate day-to-day consistency.[10] In size analysis the sub-sieve composition can provide an important controlling factor in relation to grinding cost and efficiency.

All millers have not changed from the pan grinding to cylinder grinding. The change will be gradual. Attention is directed to the electrical equipment for the grinding process;[11] for cylinders, which contain loose pebble flints, a protected type slip ring motor, capable of exerting one and one-quarter times full-load torque, is necessary to overcome the out-of-balance load when the cylinder is started up.

Vermiculite is an alteration product of phlogopite and biotite mica, due to the oxidation of iron compounds or to a change in their water content by hydration. It is characterized by expansion on heating to as much as twenty times the original volume. Its most important use at present is considered to be as an aggregate for lightweight concrete and as a sound and heat insulator. The objection for heat insulation has been its high after contraction, but a new development[12] is to use 25% of Eyrite (a colloidal magnesium silicate) as the bond which reduces the after-contraction at 1150° to 3%. Vermiculite is now being suggested for use in enamels.[13]

Calcined alumina has been introduced into whiteware bodies;[14] the alumina can be incorporated either as an addition or as a partial substitution for flint. Up to 20% of flint may be replaced by alumina in plastic-made bodies without affecting the shrinkage or vitrification, but bodies for semi-dry pressing require an increase in the flux content. The substitution of flint by 20% alumina increases the thermal expansion of the fired body and eliminates the expansion of the α–β quartz change. This may be useful for certain types of vitreous bodies, but it would be interesting to have some information on the effect of alumina in porous bodies, because we normally rely on the quartz content, which changes to cristobalite on firing, to give the necessary compression in the glaze for crazing resistance.

Ceramic bodies and making processes

Although zirconia has been used for many types of ceramics for a number of years, many papers have appeared during the period under review. Zircon porcelain has been known in the spark plug industry for some time, but it was during 1943 that zircon porcelain was found to have promising mechanical and high frequency electrical properties.[15] These porcelains should have at least 50% (wt.) of mineral zircon, under 30% of fluxes, which are usually added as double zirconium silicate of alkaline earth oxides, and clay is added in amounts generally not exceeding 30% (wt.). Small additions of bentonite are added to increase plasticity and dry strength. The low thermal expansion of the fired porcelain necessitates special glaze composition. Some of the suggested uses of this type of porcelain are components for radio, radar, and miscellaneous high-frequency equipment.

Zirconia is suggested as an addition to high titania bodies[16] which are particularly suitable for use in high-capacity condensers. The practical difficulties which may be experienced in the casting of bodies containing a high percentage of zircon have been overcome. A casting slip can be prepared from a suspension of finely ground zirconia silicate in water containing 0·002 to 0·5% colloid, such as starch, dextrin, albumen, tannin or gelatine, and 0·002 to 0·5% of an alkali.[17] The uses of zirconiferous nepheline syenite in special glasses, glazes, enamels, and high-voltage ceramic insulators, and as a source of zirconia, are discussed by I. I. Kitargorodski.[18]

A fusion cast refractory for use in contact with molten glass has been prepared from zirconia with other oxides.[19]

The use of powdered ceramic material mixed with a thermoplastic binder, which is then shaped and heated to drive off the binder, is suggested.[20] For the production of thin sheets, or when high shaping pressures are necessary, large proportions of binder are required, and the removal of it is liable to produce defects due to the violent evolution of products of the binder, which may leave liquid or gas entrapped in the ceramic body, subsequently giving rise to blisters. Poly*iso*butylene is chosen because it depolymerizes at a regular and controllable rate. This material has physical characteristics similar to those of rubber, and mixing can be effected by the technique used for compounding rubber with dry powders. The binder is worked up to about 100° on hot rolls, when the powder is added. Sheet material so made can be readily cut, pierced or otherwise shaped. The formed article is then gradually raised in temperature in a furnace, the rate of heating depending on the article concerned.

The titanate group of ceramics continues to attract most attention from the research worker.[21] The dielectric properties of barium titanate by oscillograph have been studied by E. N. Bunting, G. R. Shelton, and A. S. Creamer.[22] The addition of 1·5 to 2·5% magnesium fluoride to barium titanate produces a material which increases the dielectric constant to twice the normal value.[23]

A new material in the field of low-loss ceramics is introduced under the name of "Alsimag," which is a forsterite body, having magnesium orthosilicate ($2MgO.SiO_2$) as the main mineral constituent.[24]

A method for coating ceramic insulating surfaces with metal is suggested.[25] The metal is fired on to a ceramic body by the induction of eddy currents in the metal from a high-frequency electromagnetic field and by the generation of capacity currents in the ceramic from a high-frequency electrostatic field.

This year the literature on drying deals largely with the newer types of drying technique. Few new developments have taken place in infra-red drying. It has been suggested previously by Dr. H. W. Webb and the author that a combination of infra-red and convection drying may have advantages over either method by itself. Dryers are now being constructed using this principle. Clay ware can be dried in contact with moulds by a low-temperature radiant gas-heated panel, with a convection drying section using air heated to 60° by the exhaust from the radiant section. The dryer can deal with up to 50 dozen pieces per hour, requiring 30 dozen moulds per cycle. The complete drying of the ware can be effected in 30 to 40 minutes.[26] The limiting factors in dielectric heating are also discussed.[27] The high internal vapour pressure which is produced by the instantaneous heating of the interior of the body will almost certainly result in cracking or disruption, particularly with thick and dense articles. It is now being suggested that dielectric heating be used to warm the goods before transferring to a convection-heated oven to continue evaporation at a much slower rate.

Glazes

Opaque glasses consist of a clear glass matrix in which are suspended particles with a different refractive index than the surrounding medium. Because the ceramist is working with transparent materials in opacifying glazes it is necessary for him (1) to select an opacifier with a refractive index as far removed from that of the glass matrix as possible, (2) to maintain a low solubility of opacifier in glaze (this depends on the composition of the glaze), and (3) to maintain proper fineness and dispersion of opacifier in the medium. Certain materials suitable for opacifying enamels are not satisfactory in glazes. This is due mainly to the higher temperature necessary to mature a glaze, with a consequent greater solubility at the higher temperature and also volatilization of certain materials. Glazes suitable for a ceramic body of the earthenware type can either be of the lead or leadless, and the one most usual is a glaze of the lead borosilicate type. A glaze maturing at 1000° or slightly less is suggested,[28] in which lead oxide is replaced by barium, strontium, and zinc oxides with a zirconium opacifier. The glazes are a bright opaque. Barium oxide is the best substitute for lead oxide, although moderate amounts of strontium and zinc oxide can be used.

Chinese potters still prepare ash glazes by the traditional method of blending clay-slip with ash-slip. The ash is prepared by calcining lime and rice husks, only the fine portion being used. This is mixed with clay-slip.[30]

The copper red effect is still sought after by the studio potter. Details of the production are given by F. A. Ford and P. E. Cox.[31]

A black colour can be obtained by firing a mixture of chrome ore and alkaline earth in the ratio range of 1:1 to 3:2.[29]

Owing to the variation in the mineral rutile, with consequent variation in colour and effects, W. Busch and H. Strumm-Bollenbach[32] suggest using purified titanium oxide of definite crystalline characteristics mixed with the necessary iron oxide. By this means they are able to control both crystallization and colour.

An interesting and practical paper on the application of under-glaze lithos is published.[33] Faults in under-glaze transfers can be caused by wrong application and conditions, and quite high losses can occur. Such faults as frizzling can be traced to an excessively heavy coating of " size," a further contributory cause being a fast firing schedule in the hardening-on kilns. Another fault is curling of the transfer, which is due to the " size " not being of the correct tackiness, which varies with the temperature and humidity.

In the application of colour by spraying, the addition of a little methyl alcohol to the water facilitates the operation.[34]

Enamels

Numerous investigations are recorded in the literature on enamels which show the important effects of soluble salts on the properties of enamel slips. This is a very complex subject, and will depend on the type of clay used, as well as the variety of soluble salts. In some commercial enamels investigated by B. W. King, Jr., M. D. Carter, and H. C. Draker,[35] the four elements, sodium, boron, fluorine, and oxygen, comprise the greatest proportion of the soluble salts in the mill liquors. The soluble salt content increases with ageing, and it is difficult to maintain the same degree of coagulation for long periods of time. This change in coagulation affects the suspendability and " pick-up " of the enamel. For an enamel to be satisfactory it is suggested that the Na_2O to B_2O_3 ratio must be right, and then only a small quantity of fluorine is necessary. The difficulty with this suggestion is that one is limited to the composition of the frit, for the percentage of salts will depend on whether the frit is highly insoluble or not, and also if the right proportions of salts are dissolved.

The dark specks found in enamel coatings which have been applied after dipping in nickel solution have been shown to be due to traces of oxidized iron salts.[36]

The oxidation characteristics of steels influence the selection of the enamel to be applied to them.[37] It appears that with a given enamel adherence is subject to variations of the steel. Where adherence develops there is a metallic precipitation at the metal surface, and adherence may be associated with the oxidation characteristics of the steel and with the relative solubility of the enamel for this oxide. It is also pointed out that the composition of the enamel influences the properties of adhesion. Enamels lacking in cobalt and nickel do not have good adherence. Cobalt-bearing enamels are deficient in cobalt and rich in iron after firing, and it is evident that cobalt functions in replacing iron at the interface.[38]

The appearance of a wavy surface, sometimes referred to as "orange peel" in porcelain enamels, has long been recognized as a spraying problem.[39] Although the defect is a minor one, and in no way affects the serviceability of the product, it does detract from the appearance.

The composition of enamels suitable for application to aluminium and aluminium alloys appears in the literature.[40]

One of the most important properties of porcelain enamel as a finish is its ability to resist physical and mechanical wear. Such properties as hardness, texture, and structure of the surface have received much attention, but the determination of hardness of enamelled surfaces is not an easy matter.[41] A scratch test under light load tests only the resistance of the surface layer, and tests based on loss of gloss may be misleading. The durability and reflectance of enamelled surfaces are not related to the abrasion resistance, which appears to be determined largely by the bubble structure.

The advantages of firing ground coat and cover coat ware together are discussed by J. T. Irwin.[42] Molybdenum has proved outstanding as a surface tension reducer in an enamel, and is a valuable material in the development and advancement of the technology of one-coat white enamels.[43]

The thermal shock resistance of enamelled ware in relation to the thermal expansion of the cover coat and ground coat, and to enamel thickness, has been further investigated.[44] The results confirm that the total thickness and the expansions of the ground coat and top coat control the thermal shock resistance.

The use of titania in porcelain enamel compositions is not a recent development. With a high refractive index it is of particular interest in developing opacity. One big objection to titania in a white enamel is the yellow coloration which it is usual to get with this oxide. In the production of an opaque enamel with titania[45] the discoloration was found to be worse with overmelting of frit, but did not affect the colour of enamel. The composition of the enamel plays an important part in the producing of opacity. For opacity the Na_2O to B_2O_3 ratio is critical; it is necessary to have a high Na_2O to K_2O ratio, and MgO is beneficial. The MgO decreases the solubility of TiO_2 at the firing temperature. The best combination of ZnO, MgO, and CaO is 1% ZnO, 1% CaO, and 2% MgO, with about 15% TiO_2.

Opacifiers as mill additions are produced by calcining mixtures of finely divided calcium titanate and calcium antimonate in very definite proportions.[46]

Some improved qualities of enamel by the addition of lithium manganite and lithium cobaltite are described by R. A. Huppert.[47] There have been some differences of opinion on the effect of lithium on the expansion coefficient of an enamel. The above author finds that lithium manganite produces a frit with a higher coefficient of expansion than its counterpart without lithium.

In 1939 the German enamelling industry was forced to discontinue the use of borax and boron-containing compounds. As most enamel frits, particularly those maturing at low temperatures, contain some borax, it was necessary to employ some substitute flux. A flux known as V26 was developed, and is credited with having kept the industry alive during the war years. It is not considered a temporary substitute but rather a new material. It is a sodium-titanium-silicate in vitreous condition, whose composition corresponds to $Na_2O.\ TiO_2.\ SiO_2$. The materials to produce this are fritted at 1050°.[48] While this frit covers the melting point of enamels, it increases the surface tension and causes considerable trouble. A surface tension reducer would probably be effective.

Refractories

The fact that there has been no revolutionary change in design since Siemens built his first furnace is due in a large measure to the limitations of available refractories.[49] The ideal is still the " all basic " furnace which has led to faster melting and longer furnace life. Research still proceeds on the properties of the materials used in an all basic furnace.[50] Reports are also being received of the advantages and disadvantages of these materials in use.[51] Advantages claimed for the all basic open-hearth furnace include a roof temperature 100° above that of the silica brick roof, absence of silica drip, increased production and furnace life. Sensitivity to temperature changes after a short period of use is the principal disadvantage of chrome magnesite brickwork, which crumbles if the temperature falls below red heat. J. H. Chesters (*loc. cit.*) suggests that bricks having greater durability than the normal chrome magnesite brick are required, and agrees with Birch[52] that pure magnesia, alumina, and zircon offer considerable promise. Purification rather than bonding by additions should be the keynote of such developments, together with higher firing temperatures.

The development of basic insulating bricks for use as hot face in the roof of the open hearth furnace is a comparatively new suggestion, and much work is necessary before these are proved to be better than the dense bricks.[53] The production of lightweight bricks by the addition of certain organic[54] compounds is a most interesting development. An examination of the list of compounds effective in producing the desirable porous structure reveals certain molecular structure characteristics to be common to all of them. All of these compounds furnish an organic cation, having one or more hydrocarbon radicals of relatively large size, attached to the basic nitrogen atom. No groups are present such as OH, SO_3, or others that might be expected to make the molecules more hydrophilic. When clay-slips containing such materials are mixed with a high-speed mixer, air is incorporated. The air is held and the structure does not collapse on drying. Insulating bricks are very liable to slag attack, and further work is reported on gradated bricks with a dense face and a porous backing.[55] Such bricks permit the use of different types of slag resistant materials in the face. It is suggested that the firing shrinkage of the porous backing can be matched over a considerable range with that of the face.

As no refractory can be expected to possess all the theoretically desired attributes, a compromise must be accepted. A brick to be resistant to slag attack depends largely on the chemical composition and physical structure of the refractory, including low porosity with small pore size. Knowledge of the composition of any slag or slag-forming material present at operating temperatures is necessary. To resist spalling, other things being equal, usually means more open texture than for maximum resistance to slag attack. To decide on the most suitable brick for any installation means knowing the conditions the refractory has to withstand. The question of service life of refractories has been examined in the carbonizing industry[56] for regenerators[57] and for ladles.[58] Alkalis affect the life of refractories both in the carbonizing industry and in regenerators. The action of the alkalis in the two cases appears to be different. In the carbonizing industry the alkali vapours are absorbed, resulting in the formation of a material of different physical properties from the original material. This results in alteration of the properties of the surface expansion and causes ultimate disintegration. The regenerator bricks absorb the alkalis, which lower the refractoriness sufficiently for the bricks to deform. Bricks to use in contact with MgO up to 1540° should contain over 60% of alumina, or should be chrome, chrome magnesite, forsterite, or magnesite. Silicon carbide and zircon bricks are slightly attacked, and low-heat duty silica-alumina bricks severely attacked.[59] Firebricks containing free ferric oxide are attacked by reducing gases and will gradually disintegrate. The iron compounds which resist attack and those which influence the disintegration have been subject to *X*-ray analysis.[60] The spots which are attacked by methane and carbon monoxide contain iron mainly as ferric oxide with some magnetite. In the bricks which resist attack the iron is present as a glassy phase. Traces of hercynite ($FeO. Al_2O_3$) and fayalite ($2FeO. SiO_2$) can be found. The composition of " carbon deposits " with methane varies with temperature. *X*-ray diffraction photographs have shown that at 700° the " carbon spots " are metallic iron mixed with graphite, at 800° metallic iron with trace of iron carbide mixed with graphite, and at 880° all the iron is present as iron carbide. *X*-ray observations of the carbon deposit from carbon monoxide attack at 450° show the presence of magnetite with some iron carbide.

To obtain a silica brick with the lowest expansion has always meant a high tridymite content, but it is now reported that the glassy bond influences the expansion in a remarkable manner.[61] By deglassing a silica brick with hydrofluoric boric acid the value of linear thermal expansion is increased. The theory is advanced that the accepted values for the expansion of tridymite, which it is claimed has been prepared in its purest form, are too low, and it has been suggested that a cristobalite brick, in which the expansions are largely suppressed by the glassy bond, may be as good as or better than the tridymite brick. It is unfortunate that sodium tungstate was chosen as the bonding material to determine the expansion on the deglassed brick. This flux is very highly reactive towards silica. It has been shown that sodium tungstate will transform silica into the tridymite modification at 850°. As the thermal expansion pieces were bonded with sodium tungstate (although it was only a small percentage), and then fired to 1000°, there is a risk that the silica in the expansion pieces was not in the same form as in the original brick. It was not found that any alteration in crystalline form, by expansion method, had occurred before or after fluxing with sodium tungstate.

Analytical and physical measurements

The analysis of materials by thermal methods has not gained much ground in the ceramic industry, and in many instances the information yielded from the thermal analysis could be more conveniently obtained by *X*-ray examination. Thermal analysis appears to be very limited and the data somewhat approximate; for mixtures containing more than 50% of quartz the accuracy is in the order of ±3%. For lower quartz contents the accuracy is less.[62]

A useful and quick alternative method to the ordinary thermal conductivity method is given by J. R. Barrett, J. Vyse, and A. T. Green.[63] It should be a useful addition to the existing tests.

Energy absorption from high-frequency fields forms the basis of a new method of conductometric analysis. The distinct advantages are that this method eliminates the use of electrodes, and values may be read directly on a meter. It is very flexible and highly sensitive.[64] The use of the electron microscope is well established. It may be used to determine the structure of substances, either by photomicrographs or electron diffraction patterns, with particular reference to the change of phase occurring in clay minerals when subjected to heat.[65]

The velocity of reaction between solids is very important in ceramics. In the preparation of colours the constituents are calcined to obtain a particular tint. In many calcinations there is a reaction in the solid state between constituents, although no sintering takes place, *e.g.*, green chromium oxide with white zinc oxide forms brown $ZnO . Cr_2O_3$ when calcined, although there is no sign of actual fusion. It is interesting, therefore, that the subject is receiving some attention.[66]

An instrument for measuring the reflecting properties of surfaces of low and medium gloss[67] and one for the determination of the moisture content of a material by the measurement of its specific inductive capacity are now available.[68]

The classical analytical methods for clays are very long. What is badly needed are shorter methods with an accuracy similar to the old methods. The polarograph is being used for the determination of certain metals, but, unfortunately, this instrument has not yet been found suitable for the analysis of clays. The determination of Al_2O_3, TiO_2, and Fe_2O_3 in clays by the hydroxyquinoline[69] separation has been tried, and the method is slightly quicker than the classical method with about the same accuracy.

Firing

There are indications that tunnels of small cross section may be more efficient than large ones.[70] A tunnel of small cross-sectional area can be run faster than one of the same length of larger cross-sectional area, but there is a limit to the speed at which the ware can travel through the kiln. Every kind of ware has its own maximum rate of heating, so the optimum time cycle will be the least which the particular ware itself can tolerate, and, furthermore, it must be in the firing zone long enough to raise the temperature of the ware to its finishing temperature to produce the necessary degree of vitrification without warping, cracking, etc. The introduction of bodies and glazes which will develop strength and resistance to crazing without long soaking would help in the quicker throughput. A tunnel kiln with a narrow cross section, and in which the material as soon as it is fired is cooled to about 1000° by compressed air, considerably reduces the overall firing period.[71]

The correlation of results between laboratory trials and commercial kiln firing is difficult. The vitrification of a clay depends on time and temperature. The fired properties of a clay fired to the same temperature but at different rates will vary. A series of clays fired in a commercial kiln and a laboratory kiln have been examined and the relationship between the two methods of firing has been determined.[72]

The continuous type of kiln is more economical on fuel than the intermittent type, and, due to fuel shortage, it can be expected that much is published on this subject.[73] A furnace adapted for continuous fritting is claimed[74] comprising a rotatable refractory bowl mounted in relation to a stationary heat radiating bowl so that the material to be fritted can be fed to the space between the bowls. A continuous kiln for burning blue bricks has been patented.[75]

A high-temperature electrically heated furnace is claimed[76] in which the rod-like heating elements are of rare earth oxides with a negative coefficient of electrical resistivity. The advantage of electricity compared with other types of kilns for pottery firing are many.[77] Higher thermal efficiency is possible. The temperature is somewhat restricted by the type of elements, but it is expected that soon elements that can withstand temperatures in the region of 1400° will be available.

Cements

The manner in which the added gypsum controls the setting of cement has been the subject of many investigations and some controversy. In the absence of precise information relative to the function of gypsum in regulating the initial hydration, and in order to provide ample protection against the abnormal expansion that might result from the use of excess amounts of gypsum, it has been the custom to limit the SO_3 content of Portland cement to 2·5%. Some investigators have suggested that the gypsum forms a protective film of a calcium double salt[78] which hinders hydration. It is reported[79] that with some cement compositions the gypsum retards the initial hydration and set, while with others it acts as an accelerator. The gypsum content should therefore be varied, depending on the composition and fineness of the cement. The alkalis as well as the $3CaO . Al_2O_3$ content influence the gypsum requirements, more being required the higher the alkalis and $3CaO . Al_2O_3$. If a cement is low in $3CaO . Al_2O_3$ gypsum will accelerate the hydration, while in the cements with high $3CaO . Al_2O_3$ gypsum retards the early hydration. When the calcium aluminate content is high an increase in specific surface of the cement will increase the aluminate phase available for reaction with water at early stages, so that a greater amount of added gypsum is needed for proper retardation. The physical properties are also altered by the gypsum addition, and it is possible to increase the strength and to decrease the contraction on drying or the expansion in water storage.

The thermal conductivity of concrete varies with temperature, composition, density and water content. By altering the mix from the ratio of 1:5 to 1:7 the conductivity decreases 10%. A much greater effect is obtained in the presence of water. Increasing the water content from 0 to 10% increases the conductivity by 46%.[80]

It is well known that the method of preparation of concrete blocks for testing in compression, whether in steel or wooden moulds, influences the result. B. Mather[81] has further investigated this subject by varying the type of specimens, and concludes that the choice of specimen considerably affects the compressive strength value for the concrete.

The use of air entraining agents to control the air voids in concrete has been previously suggested; the air voids should be kept between 3 to 5%. The amount of these materials necessary depends on the cement and sand mix.[82] When the air voids are kept within the prescribed limit the concrete will have improved plasticity strength, surface texture and durability.

There are various opinions on the reactions which take place when cement hardens. T. C. Powers and T. L. Brownyard[83] consider hardened cement paste to be chiefly of microcrystalline texture. The $Ca(OH)_2$ formed, though theoretically unstable, does not become microcrystalline over a period of two years, although it is constantly reported as microcrystalline in the cement gel. The hydrates formed in Portland cement differ from the separately prepared hydrates of calcium aluminate. The available data indicate that the water is not held as microcrystalline compounds, but rather as in silica gel. Another investigator[84] suggests that the rapid shrinkage during the first 24 hours is due to volume changes arising from hydration of the cement constituents, whereby the original gel structure is partly replaced by a rigid crystalline complex of calcium sulpho-aluminate and $Ca(OH)_2$. Subsequent differential shrinkage occurs continuously over years, and arises mainly from volume changes in the gel (or from its partial conversion into crystals) due to progressive variations in water content of the concrete. He also discusses the factors which influence shrinkage, and explains the reasons for the variable results of different investigators.

The advantages of grinding hydraulic slags in water is given by L. Chassevent,[85] who suggests that after grinding they are then hardened by the addition of alkali. When crushing hydraulic slags in the dry state in ball mills very hard crusts form on the walls and balls of the crusher, which decrease fineness and reactivity. The slags can be ground under water without changing the hydraulic properties, and the paste can be made basic for setting. Supersulphated cements may be prepared from slags with added gypsum or anhydrite. The calcium sulphate is crushed separately or with the slag; the paste in the latter case is made alkaline before use, generally by adding lime in a very small quantity. An economy in fuel is achieved, but filtration of the slurry needs careful control.

An investigation[86] into the reasons for the disintegration of the surface of pavements has shown that the scale, which is approximately 1/16 to 1/32in. thick, consists mainly of cement, hydrated cement, and very fine aggregate. It is structurally weak and friable, very porous, and expands very differently from the parent concrete. Separation of the scale and subsequent disruption due to freezing and chemical action thus readily ensue. Calcium hydrate and calcium carbonate occur in fine cracks throughout the scale. Calcium chloride has been found to be present in sufficient concentration to promote the growth of calcium hydrate, and may even remove this from the cement gel by forming calcium oxychloride.

Some recent theories suggest that glass should be a normal constituent of Portland cement clinker. The presence of vitreous substances in cement clinker is associated only with conditions of exceptionally rapid cooling, which are never met with in industrial clinker production,[87] but the cooling rate, which introduces stresses, influences whether or not the clinker is difficult to grind.[88]

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THE PROTEIN FIBRES

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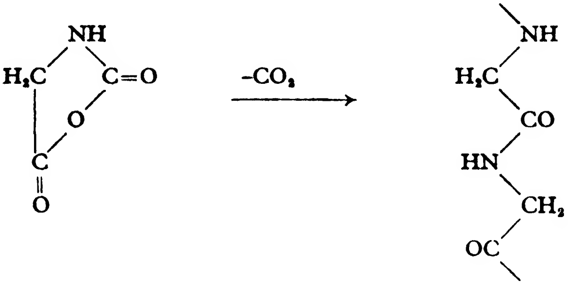
WORK on protein fibres, reported during 1947, has followed normal lines, but one interesting development has been reported by Woodward and Schramm[1] who state that they believe they have achieved the first successful synthesis of molecules having, like fibrous proteins, the structure

$$HOOC.CH(R)\text{-}NH-[COCH(R_1)NH]_n - COCH(R)NH_2$$

with very large values for *n*.

They used an ionic chain polymerization reaction which had been observed before inadvertently but whose scope and generality do not appear to have been realized hitherto.

In 1908, Leuchs discovered that an amino acid derivative, the cyclic anhydride, is readily transformed into polypeptides of high molecular weight with the liberation of CO_2,



and some were of the opinion that proteins are synthesized in this way by the animal organism.

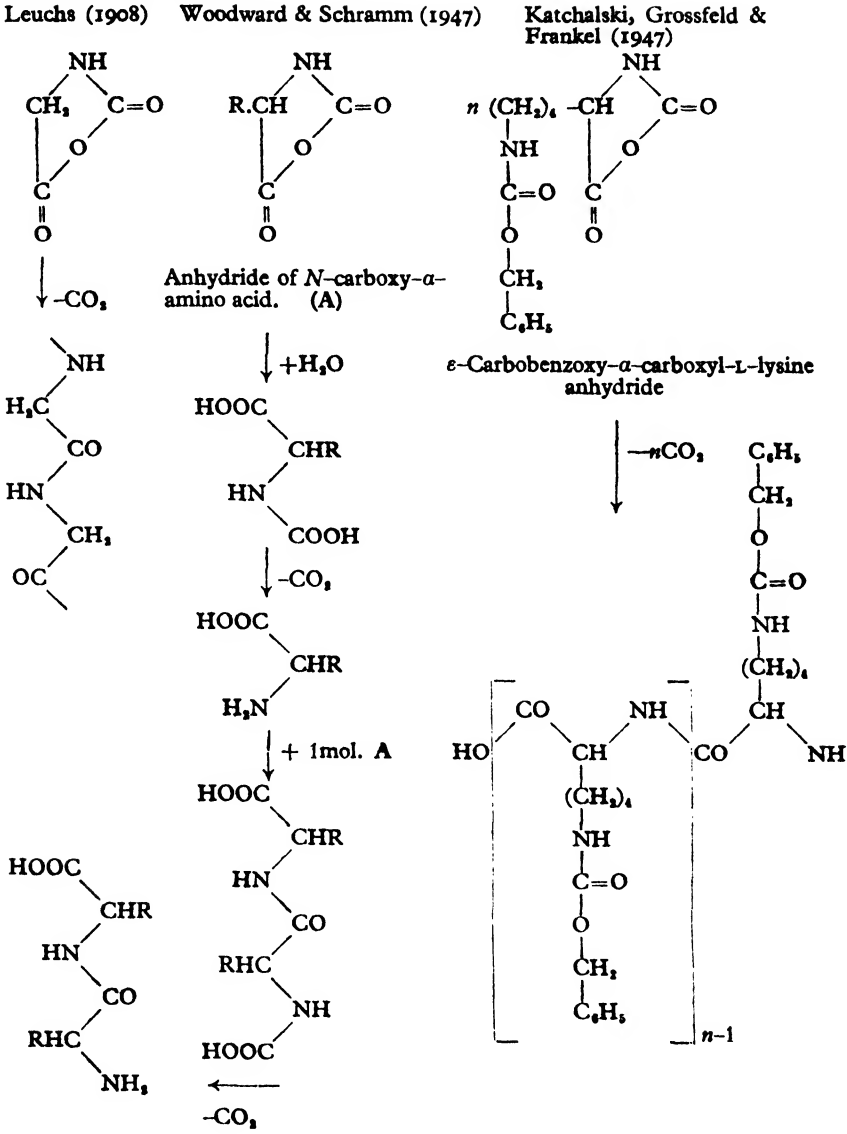
The monomers made by Woodward and Schramm are anhydrides of *N*-carboxy-α-amino acids and the initiator is water or any substance XH, in which H is an active H ion.

Each time a new peptide link is formed by the reaction of the active centre (NH_2) with a monomer molecule, a new, like, active centre is generated by the spontaneous loss of CO_2 from the unstable grouping (—NH—COOH).

Shortly afterwards another group of workers, Katchalski, Grossfeld and Frankel,[2] reported the synthesis of a polymer which they think represents the first synthetic basic α-polyamide. ε-Carbobenzoxy-α-carboxyl-L-lysine anhydride undergoes polymerization similarly to that of *N*-carboxyl-anhydrides of other amino acids studied previously. The above anhydride, dried *in vacuo*, undergoes at 105° melting and rapid polymerization yielding polycarbobenzoxy-lysine, which is soluble in water and may serve as a useful model in protein research. The average chain length is 32 units. The respective systems are shown opposite.

Wool

The greatest activity amongst workers on wool is still concerned with the problem of unshrinkability and it is therefore worth while reviewing



the present situation.

The production of " unshrinkable " wool

The shrinkage of wool garments is normally due to a combination of relaxation and felting shrinkages. Chemical methods of treatment aim at destroying the felting power of wool, which is a property associated with the elasticity of the fibre and the physical characteristics of its surface.

It has long been known that wool treated with solutions of hypochlorites and then acidified shrinks less than normal wool. This led to the development of processes to render wool unshrinkable. Wet chlorination includes processes in which aqueous solutions of chlorine and hypochlorous acid are the chief reagents. The weakness of such processes lies in the rapidity with which wet wool and chlorine react. The exposed fibres of a sliver may thus become over-treated. Technical methods have been developed to improve the uniformity of treatment.[3] These fall into four classes. The first depends on the gradual addition of the hypochlorite or the acid, or both, and became almost universal. The second involves the use of sulphonamides to withhold the chlorine from the wool and was commercialized in U.S.A. as the " Hypol " process. The third involves entering the wool dry and in oil, and controlling the p_H—the " Negafil " process of Clayton and Edwards. The action of the chlorine is retarded by the oil and control of the p_H at 4·0–5·5 ensures that the fibres are not swollen and so speed of penetration is reduced. The fourth class involves the control of p_H. The rate of uptake of chlorine is rapid and falls off as the p_H value of the chlorinating liquor increases and the slower reaction allows better penetration. At lower p_H, however, the wool is less likely to be discoloured and as the p_H of chlorination decreases the shrink-resistance increases. A recent process uses strongly acid aqueous solutions of 1 : 3-dichloro-5 : 5-dimethylhydantoin.[4]

The dry chlorination method was developed because the danger of the rapid reaction between wet wool and chlorine was recognized. King advocated dry chlorination at low pressures, with reduction in pressure to assist penetration. This method was developed to a commercial scale by the Woollen Industries Research Association. The wool is dried to 8% regain and then placed in a vulcanite lined autoclave, connected to a circulating pump which abstracts the gas from the bottom of the autoclave and returns it to the top. The air is pumped out before chlorine is added. An extensive examination, made on Army socks during the war, showed that no loss of wool substance is caused by dry chlorination, but that a 4% loss is experienced by wet chlorination. The efficiency of this method of chlorination is shown by the almost complete absence of untreated fibres.[5] Fabrics milled for the equivalent of 250 washes show no appreciable shrinkage nor wear into holes.

Wet and dry chlorination form the fundamental bases of most commercial shrinkproof processes for wool. More recently alkaline methods have been developed. Many years ago it was observed that it is possible to treat wool fibres with ethyl alcoholic KOH at elevated temperatures without changing the wool structure other than by substantial yellowing. Hall and Wood in this country, and Freney and Lipson in Australia, have worked concurrently on alkaline methods of reducing the felting power of wool. The methods developed by Hall and Wood involve the use of binary mixtures of alkali and, *inter alia*, alcohols[6] and also the use of ternary mixtures.[7] Under strictly comparable conditions it has been shown that ternary mixtures produce greater resistance to felting than the binary mixtures, as the non-solvent forces alkali on to the wool and causes the wool to absorb more alkali from such a ternary mixture than from an equivalent concentration of alkali in a binary mixture.[8]

Freney and Lipson's process is based on the treatment of wool with KOH in methylated spirits, followed by neutralization in a solution of sulphuric acid.[9] This process has not yet been perfected. Its chief disadvantage is a hardness of handle conferred on the wool and a tendency to " boardiness " in highly twisted yarns. The advantage over dry chlorination is that the shade of white is unaffected. Time of treatment varies from 2 minutes for 7% NaOH in 95% alcohol at 75° to 16 hours for 0·05% NaOH in 95% alcohol at 25°. Again the regain has to be reduced to about 8% to preserve the alcohol at the correct moisture content. The effect of alcoholic KOH on the handle of wool is described by Mercer and Makinson[10]. The harsh handle of the wool can be restored to normal by treatment with a dilute solution of cationic soap.

Many investigations have been carried out on this problem of reducing the felting of wool, and while some of these have as yet no commercial use, the methods of attack are of great interest and have been reviewed by Freney.[11] In 1935 sulphuryl chloride in solution in white spirits was introduced in a process to reduce shrinkage. The moisture content of the wool must be controlled, for there is a tendency for water to pass out of the wool into the liquid and react with the sulphuryl chloride. If too high a concentration of sulphuric acid results, the wool is damaged. The sulphuryl chloride method does not appear to give as uniform a treatment as dry chlorination, despite fairly high resistance to shrinkage.[5]

Treatment of wool with benzyl chloride in light petroleum *increases* the rate of felting on subsequent washing in soap solutions.[12]

An enzyme process for increasing the shrinkage resistance of wool was developed by Middlebrook and Phillips.[13] While papain digests wool very slowly, it has an intense action on wool in the presence of a 1% solution of sodium bisulphite. The sodium bisulphite does not act solely as an activator of papain but must be used in sufficient quantity to react with the wool to produce combined thiol and *S*-cystein sulphonate groups. Thiol groups are known to activate papain and their production, from the disulphide cross-link, assists the degradation of a layer of protein with which the felting properties are associated. The process is carried out at neutrality in a stainless steel dyeing or bleaching plant at a temperature of 45–65°. Finer wools are bleached with peroxide before the papain treatment. The wool thus treated is called " Perzymed " wool, is less wettable than chlorinated wool and dyes level. If dry chlorinated wool is treated with papain (" Chlorzyme " process), the fibre becomes soft and has a silky gloss through the removal of the scales without the breakdown of the fibre.

Hudson and Alexander[14] studied the direct fluorination of wool at various humidities and concentrations. Gaseous fluorine mixed with nitrogen was passed over a scoured knitted fabric under varying conditions. The anti-shrink effect was maximum with dry grease-free wool and a concentration of not less than 20% fluorine in the nitrogen stream, the time of operation being 30 min. It is considered that the action is confined totally to the cystine linkage, as a volatile sulphur fluoride is the only product of the reaction on mild treatments. This is confirmed by the fact that if wool is first treated with 0·1 N-sodium hydroxide for 24 hours, in order to replace the disulphide linkages by more stable cross-links, the felting powers of the wool are unaffected by fluorine treatments. Analyses employing cobaltic fluoride as a source of fluorine have shown that a minimum of 0·5% fluorine on the weight of wool is necessary to produce non-felting wool. In most cases 0·5–1·0% is required. The most important conclusion to be drawn is that complete unshrinkability can be obtained by the removal of sulphur as volatile hexafluoride.

Speakman, Nillson and Elliot have pointed out that manganese heptoxide, potassium permanganate and permonosulphuric acid can all impart an unshrinkable finish to wool and consider that any oxidizing agent capable of breaking the disulphide link is a potential agent for producing unshrinkable wool.

Another line of approach to this problem has been the impregnation of wool fibres with resins, but care must be taken not to affect the shade of the dyes. Dudley and Lynn[15] have described the nature of the condensation products of melamine and formaldehyde and the type of resin intermediate required for the treatment of wool to achieve shrinkage control. Nute[16] has also described the application of an alkylated melamine-formaldehyde condensate, miscible with water, to which an accelerator is added before impregnation of the fabric and heating to 300°F. to set the resin. After a six minutes cure, formaldehyde and unused resin are washed out. Shrinkage is stated to be reduced from 40% to 2%.

Barr, Capp and Speakman[17] have made use of the fact that the side chains of wool are capable of reacting with *iso*cyanates. It was known that wool may be made unshrinkable with cross-linking agents and cross-linking with di*iso*cyanates was therefore tried. Fabric was treated with di*iso*cyanate, *m*-phenylene di*iso*cyanate or hexamethylene di*iso*cyanate in solution in white spirits or cresol. The fabric is immersed in buffer solution at p_H 8, centrifuged and treated for six hours at 70° with 20% (by weight) of *m*-phenylene di*iso*cyanate dissolved in white spirits. The fabric increases 7·5% in weight. To attain a similar degree of unshrinkability an 80% solution of hexamethylene di*iso*cyanate is necessary and a weight increase of 20%. From a study of the elastic properties of human hair treated with the above solutions and the effect of water and p_H on the treatment of the fabric, it is concluded that the unshrinkability is due, not to the anticipated cross-linking of peptide chains, but to the masking of the surface scales by a deposit of the polymer arising from the conversion of the di*iso*cyanate into diamine by the water in the wool, followed by the co-polymerization of the di*iso*cyanate and the diamine. Another method of building up films of polymer on the reactive side-chains of wool[18] employs anhydrocarboxyglycine. The polymer is soluble in lithium chloride but the unshrinkable finish is not destroyed by this agent, so there is evidently a chemical combination with the wool. A confirmation of this lies in the fact that deaminated wool cannot be made unshrinkable with anhydrocarboxyglycine. Silicon tetrachloride in carbon tetrachloride solution can also be used to reduce the shrinkability of wool.

In the chlorination, alkali and enzyme treatments described, the cuticle of the fibre is attacked or its surface character changed. Microscopic examinations may not detect this, but Mercer and Rees[19], using the electron microscope, have demonstrated the difference in the cuticular profile of wool treated with trypsin and untreated wool. In treated wool the edges of the scales have been rounded. The chemical methods should cause disorganization of the fibre surface without affecting the bulk properties of the fibre. This disorganization is produced by the controlled degradation of the surface keratin mainly by breakdown of cystine cross-linkages. Resins may act (1) by polymerizing on the surface of the fibre and strengthening the cuticle (2) by penetrating into the fibre before polymerizing and decreasing the contractile tendency of the cortex. Experiments in stress-strain characteristics of resin treated fibres show alterations in their elastic behaviour.[20]

Phillips has pointed out that if 5% of untreated wool is mixed with 95% of a fully chlorinated wool the blend will felt. This emphasizes the need for careful control of chlorination processes to ensure adequate and uniform treatment of the wool before the process can be a success.

Chlorinated wool takes up dyes more rapidly than untreated wool. Chlorinated wool, being available in quantity, is therefore being used to produce tone-in-tone and cross-dyeing effects. When acid and chrome dyes are used in the presence of retarding agents, such as Tanninol W.R. and Lissatan A.C., which are employed in reserving wool in union dyeing, the rate at which the untreated wool dyes is reduced to a much greater degree than the rate of dyeing of the chlorinated wool.[21, 22] When the two kinds of wool are dyed together, this gives rise to a large difference in shade which is fairly resistant to boiling.

General

The effect of different mechanical and chemical treatments on the structure of the wool fibre have been studied by means of the electron microscope.[23] The wool fibres were subjected to a number of chemical, physical and mechanical treatments. Trypsin and concentrated sulphuric acid both cause " mild " fibrous breakdown of the keratin without attack of the peptide and disulphide linkings. Alkalis affect the disulphide bond but with less fibre disorientation and a more uniform attack, in contrast with the highly localized action of acids. The nature of the trypsin sensitive part of the keratin is obscure.

Keratin has been dissolved in sodium sulphide at p_H 11.[24] On standing, these solutions show a very slow, reproducible decrease in viscosity, indicating a slow degradation process, which has been followed also by means of ultracentrifuge and diffusion experiments. The products are polydisperse. Immediately after dissolution, they have an average molecular weight of the order of 10,000. The molecules are highly asymmetrical, having an axial ratio about 1 : 20, which indicates that they consist of single peptide chains. It is assumed that the decrease in viscosity is due to cleavage of peptide bonds in the protein.

Wool de-amidated with cetylsulphonic acid (0·05 M., 65°, 6½ days) is partially dispersed if stirred in dilute alkali (p_H *c.*11) leaving a suspension of the persistent residues of scales and cortical cells. When the clear alkaline supernatant liquor is acidified to p_H 4–5, a protein-like material is precipitated and this is soluble in either dilute acid or alkali.[25] The amino acid analysis shows that the general tendency is for amino acids of high molecular weight to be concentrated in the soluble component, while the resistant component is particularly rich in cystine and proline.

The amounts of HCl and KOH combined by wool in presence of 0·25 M–1·0 M–formaldehyde over the p_H range 3·0–13·3 are determined and compared with the results obtained in absence of formaldehyde. The effects of formaldehyde on the dissociation curve of wool are mainly consistent with current views on the combination of formaldehyde with the amino-groups of lysine. There are indications that the guanidino-groups of arginine also combine with formaldehyde, at least in absence of salt. Owing to the pronounced basicity of the guanidino-groups, the maximum base-binding capacity of wool has not yet been determined.[26]

Scouring

Recommendations for conserving alkali in raw wool scouring and in neutralizing after carbonizing are made by Gillam.[27] In the recommended scour the basic assumption is that very little alkali is actually used in the bowls by chemical reaction, but is lost by carry-over to later bowls, giving alkaline solutions, which can be made satisfactory scours by additions of soap and salt solutions. The alkali conservation methods recommended are partial substitution of alkali by salt in the second bowl and addition of salt to the third bowl, and substitution of part of the soda ash in the bulk solution used to supply the bowls with an equivalent weight of salt. Economy in neutralization after carbonizing can only be effected by water washing.

Dyeing

It is difficult to reduce the affinity of wool for acid dyes by means of compounds which react simply to form condensation products with the basic side chains. Lipson and Speakman[28] have obtained a successful " resist " against acid dyes by the formation of an acid polymer within the fibre. The formation of 20% of polymethacrylic acid within the fibres of a wool fabric was found to give a good " resist " and to have remarkably little effect on the handle. It is likely that the use of more strongly acid monomers will achieve equally satisfactory " resists " with much smaller deposits of polymer.

Examination of wool treated with chromic acid solution for different periods of time show that all the chromium left on the wool is in hexavalent form.[29] The data suggests that trivalent chromium does not interfere with the combination of the basic side-chains of wool with chromic acid. Wool was chromed with 0·0025 M-potassium dichromate and it was found that the rate of chromium absorption is most rapid at the beginning. The absorption appears to be governed by a simple diffusion law and this could be true if a film of absorbed chromium existed on the outside of the fibre from which it diffused into the fibre.

Even with short chroming times, not all the chromium is extractable with buffer solution, which suggests that the chromium is combined in a more stable manner than a simple acid base combination. The hydrolysis of disulphide linkages is favoured by rise in p_H and is known to occur in water at 55°, the reactions taking the following course:

$$R{-}CH_2{-}S{-}S{-}CH_2{-}R + H_2O = R{-}CH_2{-}SH + R{-}CH_2{-}S{-}OH$$

$$R{-}CH_2{-}S{-}OH = R{-}CHO + H_2S$$

If such reactions occur in the chroming bath, then the reduction of chromium could be easily explained and might be lessened by the use of ammonium salts to stabilize the p_H of the bath.

When chroming was done in the presence of ammonium sulphate the chromium absorbed more rapidly than in the absence of sulphate and less trivalent chromium was formed. All fibres show an increased resistance to stretch after chroming.

The relationship between dyestuffs constitution and the dyeing properties of damaged wool was discussed by Townend,[30] who drew attention to the physical differences between the various cells in wool as well as the main differences of chemical reactivity. The most common effect is the loosening of surface scale structure. This action, which ultimately leads to complete descaling, may be associated with superficial attack of the cortex itself or with more obscure structural changes. As a result the fibre is more readily penetrated by chemicals in later operations. In addition, some treatments may have a specific effect on free basic groups or introduce new acid groups, resulting in lowered reactivity to acids.

In spite of the complexity of the situation, the technical dyeing properties of those chemically treated wools are closely related to the simpler features of acid dyestuffs constitution, namely, the number and nature of the acid or acid-forming auxochromes.

Factors affecting the absorption of infra-red radiation by textiles have been investigated.[31] The spectrum intensity falls rapidly in moving from the long- to the short-wave end of the visible spectrum; dyes which have the greatest effective absorption are those which absorb in the red and near infra-red. Yellows, oranges, reds, and violets all have absorption coefficients of zero or approaching zero in the red; this is also true of many blues, greens and blacks. There are exceptions, *e.g.*, Chlorazol Black ZVS and SDS, and Fast Blue FFKS, etc., which show marked absorption in the red. Fabrics absorb considerably less energy when dry than when wet. Low temperature radiation is much more strongly absorbed than high temperature radiation for both wet and dry fabrics.

Spinning

Progress in worsted spinning research has been reviewed by Martindale[32] and developments in worsted and woollen yarn manufacture by Townend.[33]

A machine was designed to measure the irregularity of worsted rovings. Yarn levelness is measured by passing the yarn between a light source and a photocell. Factors influencing the count to which a top can be spun are discussed.

The general trends in the manufacture of woollen and worsted yarns are in the direction of increased speed of production, flexibility of design, simplification, and elimination of operations. Greater efficiency of drying is obtained by passing the wool through a continuous drier on an endless lattice, the speed of which is variable. The flow is countercurrent to the stock being dried.

The electronic control of cloth drying machines has been described by Chamberlain.[34]

Protective value of clothing

Peirce and Rees[35] discuss the utilitarian and physiological aspects of clothing under normal and tropical conditions. They describe the physiology of the temperature control of the body.

For maximum heat insulation there is an optimum density of fibrous materials which should be about 0·03–0·06g./c.c. (about 3lb. per cu. ft.). Fabrics with a cellular structure have been found to be very efficient for heat insulation. The most efficient type of structure for heat insulation is not a woven fabric but a fleece, that is, a lap of well-opened fibres spread between two layers of thin muslin. The effect of air currents on thermal insulation is indicated. Various fibre fleeces, in decreasing order of thermally effective specific volume (ratio of equivalent air thickness to weight per unit area), form the series: kapok, resin treated cotton, resin treated viscose, wool, cotton, viscose, glass and acetate rayon; the value for a raised wool blanket is much less than that for a wool fleece.

Factors concerned in the assessment of the thermal protective value of clothing fabrics are discussed. A convenient unit for the measurement of the thermal resistance of a fabric is the " tog ", *i.e.*, the resistance that will maintain a temperature difference of 0·1°C. with a flux of 1 watt per square metre. Extremely light and extremely thick clothing have tog values of the order of 1 and 10 respectively. It is assumed that the normal metabolism for a resting subject corresponds to a heat flux of about 50 kg. cal. per sq. m. per hr. The apparatus for thermal transmission tests described previously is modified for use on thick fabrics and fleeces, and the results of its application to a wide range of fabrics are described and discussed.

The physical properties of knitted fabrics have been studied by Fletcher.[36] The strongest fabrics were nylon and silk and the most resilient, wool and silk. Wool had the greatest and nylon the least moisture regain. Cotton, wool and silk fabrics were comparable in resistance to abrasion, linen was considerably inferior and nylon the best of all. Nylon and cotton fabrics were less permeable to air than were the linen, silk, wool and spun rayon fabrics.

The methods of assessing the efficiency of raising woollen textile fabrics has been studied by Whewell, Selim and Wood.[37] The mechanical and chemical factors are discussed. Factors involved in the raising of viscose and nylon pile fabrics are indicated.

Silk

Silk fibroin, pretreated with 5% soap solution, has been dispersed in lithium iodide solution or, even faster, in lithium thiocyanate.[38] At 20° the viscosity of the lithium iodide solution falls constantly, but that of the lithium thiocyanate solution is higher and remains very nearly constant. It indicates progressive degradation by lithium iodide and probable molecular dispersity in the thiocyanate. By varying the fibroin concentrations and the lithium thiocyanate concentration, the dispersion of the peptide chains is shown to be molecular. The duration of the pretreatment with 5% soap has a marked effect on the viscosity which falls with increasing time. Although it is established and confirmed experimentally that soap hydrolyses the shorter chains, the tenacity of the fibre was not affected by treatment for 180 minutes as compared with 15 minutes. From the extrapolated viscosity of fibroin in lithium thiocyanate solution, the conclusion is drawn that the molecular weight is 10,000–26,000, thus comparable with synthetic polyamides but far below cellulose. On the assumption that the fibroin particles in lithium thiocyanate are ellipsoids the axes are calculated from viscosity and streaming birefringence to be 460A. and 6A. respectively.

Silk fibroin has been iodinated and analysed by *X*-ray diffraction. Iodination was carried out by treatment with 0·1 N-solution of iodine in potassium iodide, using secondary phosphate as buffer for three hours at 37°, excess iodine being removed with sulphurous acid. The tyrosine is thought to have been converted to di-iodotyrosine. An *X*-ray picture of iodinated silk shows the first order (spacing d=7A.) which is missing from *X*-ray pictures of ordinary silk. The tyrosine content is calculated at 10·5%, while chemical analysis of *Bombyx mori* fibroin shows 14%.[39] The authors explain the difference by stating that *X*-ray analysis takes in only the crystalline, but chemical analysis may include amorphous as well as crystalline material. The deductions are stated to be tentative, but the figure of 10·5 is surprisingly near the figure of 10·6 for the tyrosine content of fibroin given by Howitt,[40] particularly in view of the limits of accuracy which can be expected by this *X*-ray analysis.

Those interested in the subject of silk are indebted to Dr. Howitt, who, with his collaborators, has added very fundamentally to our knowledge of fibroin, and has in 1947 published a *Bibliography of Silk*, which surveys comprehensively all that has been published with regard to the silk industry in its technological and scientific aspects.

Synthetic fibres

Nylon

Multi-ingredient polyamides have been prepared[41] by the condensation, under amide forming conditions, of various combinations and ratios of components comprising hexamethylene diammonium adipate, hexamethylenediammonium sebacate and ε-aminocaproic acid or ε-caprolactam.

An examination of the elasticities of nylon 66 (polymer of hexamethyleneadipamide), nylon 6 (polymer of ε-aminocaprolactam) and natural silk,[42] shows that the elongation is higher in the case of the nylon than for silk, and likewise that the instantaneous recovery of the nylons is about 99% of total recovery compared with 94% for silk.

The effect of moisture on nylon yarns and fabrics has been described and data given for the moisture regain of various textiles at 65% relative humidity and 25°.[43] Nylon textiles do not exhibit moisture hysteresis. Nylon is one of the less hygroscopic textiles and this property of drying readily can have practical advantages. Even after 16 hours soaking nylon samples became " air-dry " in three hours when placed in a standard atmosphere. The wet strength of nylon is 85–90% of the dry strength. Loasby and Puls give correction factors for test results on denier, tenacity and extensibility under conditions departing from the standard 65% R.H. and 25°.

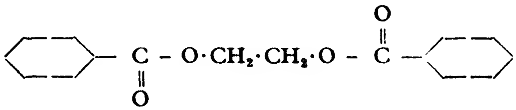
From the standpoint of the dyer, the dispersed acetate colours seem to offer a simple and effective method of colouring nylon.[44] Careful control of the conditions is essential. Koestler[45] describes the dyeing of polyamides, polyurethanes and polyvinyl chloride-acetate fibres. To avoid crimping, polyamide fibres must be steamed under tension before dyeing at 10–15° above the dyebath temperature. The absorption of acetate dyes is independent of the constitution of the fibre, very level dyeing being obtained, together with good wet fastness, but in some cases only medium light fastness. However, no single class of dyestuffs ever meets all the demands of any particular fibre. Azoic colours will probably be best for hose. When a fabric with mixed fibres is to be dyed, the acetate dyes are ruled out because of a lack of fastness as well as the limitation in available shades. Acid and direct colours can be used to meet all but the highest fastness standards. The absorption of acid dyes, on the contrary, depends on the number of free amino-groups in the fibre, and careful control of the acid content of the dyebath is necessary for level dyeing. Most acid dyes are tightly bound on the fibre, and good moisture and light fastness can be obtained. Similar considerations apply to substantive dyes. Sulphur and vat dyes are not usually very satisfactory.

The problem of dyeing nylon is only partially solved, and awaits new advances in dye and dyeing techniques before nylon can be dyed as easily as the older synthetic fibres.

A limited commercial production of crimped nylon staple fibre started in U.S.A. in 1947.

Terylene

A logical extension of the work of Carothers (of nylon fame) has been made by J. R. Whinfield, and has resulted in the discovery of " Terylene". " Terylene " is a new fibre-forming polymer derived from terephthalic acid and ethylene glycol.[46] The polymeric polymethylene phthalates, first described by Carothers, are devoid of crystallinity. The corresponding *iso*phthalates and terephthalates were unknown until Whinfield prepared polymeric ethylene terephthalate, the repeating unit of which may be represented thus:



This product is conveniently obtained by direct esterification of the glycol or by catalysed ester interchange between ethylene glycol and dimethyl terephthalate at 160–200°, with complete exclusion of oxygen and in the presence of a small amount of catalyst, such as magnesium or sodium methoxide. The low-molecular weight product on heating in nitrogen at 290–300° increased in average molecular weight.

Polymeric ethylene terephthalate (or " Terylene ") as obtained by the solidification of the viscous reaction mass is a hard, porcellaneous substance melting slightly above 250°. The higher polymeric polymethylene terephthalates show diminishing melting points with increasing length of the polymethylene chain; trimethylene terephthalate melted at 221° and decamethylene terephthalate at 123°.

The reaction melt described above displays random crystalline orientation. Fibres are obtained by extrusion from the melt and subsequent cold drawing, as in the manufacture of nylon. The fibres thus made have been shown to be highly oriented.[47, 48]

The ester linkages should be more stable to heat and light than the amide linkages of polyamides and fibroin. Experiments bear this out, for

" Terylene " is found to be remarkably stable and does not deteriorate on continued exposure to sunlight. Unexpectedly, " Terylene " resists hydrolysis even under severe conditions, probably because of the high degree of orientation and the close molecular packing, which renders access of hydrolytic agents difficult. Undrawn " Terylene " is readily dyed by dyestuffs commonly used for cellulose acetate rayon, but after cold drawing the dyeing affinity of the fibres is much reduced and dyeing presents a fundamental problem.

" Terylene " can be ironed, laundered and steam pressed in the normal way. Like nylon it can be heat-set and possesses good resilience and high ratio of wet to dry strength. It will withstand the effect of micro-organisms and bacteria and is resistant to chemicals like acids, organic solvents and bleaching agents. Resistance to heat and light is high. " Terylene " possesses a high elastic modulus that should allow easy weaving and knitting. Moisture absorption is low and the fibre does not swell in water.[49]

Acrylonitrile polymers

Another new fibre forming material is acrylonitrile polymer. The acrylonitrile is dissolved in dimethyl formamide and dry or wet spun.[50] This polymer has a crystalline structure and can be oriented to yield fibres of high strength and good resistance to heat, light and chemicals. Some principles in the production of acrylonitrile fibres are indicated and a number of uses for the new fibre are predicted.[51] Acrylonitrile can be copolymerized with other compounds to form fibres. Two such copolymers are Vinyon N, based on a copolymerization of vinyl chloride and acrylonitrile, and G.E. fibre, from the copolymerization of acrylonitrile and itaconic esters and also acrylic esters.

Regenerated protein fibres

As in the case of the manufacture of rayons, regenerated protein fibres are made from polymers provided by nature. The earlier fibres of this type were all made from casein, but animal proteins, from hide, have been used to make the fibre " Marena " and, from mammalian tissue, to make " Carnofil." B.I.O.S. reports also tell us that fish muscle protein has been considered in Germany but the work does not seem to have gone beyond the laboratory stage. There is no reason why the raw material should be of animal origin, and in recent years the emphasis in research has been shifting towards vegetable proteins, particularly the easily accessible seed proteins, of which large quantities are harvested throughout the world. These are grown primarily for the oil which they contain and which is a valuable human foodstuff. Before the war the residual cake after oil extraction was available in quantity. The increased population of the world, the loss of pasture land, the changeover in some countries from feeding animals on ranch pastures to feeding them on concentrated feed cakes and many other perplexing features of post-war life have reduced, for the present, this accessible source of raw material.

When the seed meal is required as a raw material for fibre production it is advisable to remove the oil at temperatures not exceeding 60°. The protein can then be dissolved from the oil-free meal with aqueous saline solutions or dilute alkaline solutions. From saline solutions the protein can be precipitated by dilution or by lowering the temperature; from alkaline solutions it is precipitated at the isoelectric point by the addition of acid.

The protein is then dissolved to form a viscous spinning solution. The solvent may be aqueous urea, detergents such as alkyl benzene sulphonate, or alkalis like ammonia or dilute caustic soda. The composition of the solvent and the concentration of the protein have to be carefully adjusted to obtain a satisfactory spinning solution.[52] The solution is matured for a period of approximately 24 hours. After maturing, the solution is extruded through a spinneret into an acid coagulating bath, generally a concentrated solution of sodium sulphate containing sulphuric acid. Some experimenters have used a dry spinning process in which an alkaline solution of protein is extruded through a spinneret into a chamber against the advancing current of warm air. Partial alignment of the molecules is attained through stretching during the spinning operation.

The most important stage of manufacture is the tanning or hardening of the fibre. Modern techniques use vigorous formaldehyde tanning, chrome tanning, deamination and acetylation.[53] Numerous patent processes include the use of chromium and aluminium salts, and an improvement of 30–50% in the wet strength of casein fibres by treatment with heavy metals has been described.[54]

Regenerated protein fibres produced at present are not outstandingly strong, and in this respect resemble the early rayons. Senti[55] examines the structure of natural protein fibres as well as protein synthetic fibres to find which aspects of these structures contribute importantly to their macroscopic physical properties. In the globular proteins the polypeptide chains are folded or coiled, and must be unfolded and arranged with the prevailing direction of their long axis along the fibre axis. This is illustrated by a comparison with natural silk, a fibre with high strength and a moderate degree of extensibility. The tensile strength can be accounted for by the crystallinity of the fibre which is conceived to be composed of crystalline regions interspersed with amorphous regions. The latter explain the extensibility. The strength of the fibres will increase as the degree of orientation of the molecules in the fibre direction increases. Compared with other protein fibres, natural or synthetic, silk is highest in the scale of crystallinity.

From the viewpoint of composition, that is, the bulkiness and polar nature of a high proportion of the side chains, protein synthetic fibres would be expected to resemble wool more than silk and this is borne out in practice. Experiments with ovalbumin fibres demonstrate the increased strength which accompanies increased stretching. Elongation passes through a maximum in an ovalbumin fibre stretched 100% and decreases with further stretching. Above 35% stretch the flexibility of the ovalbumin fibre decreases.

Coloured regenerated protein filaments are spun from alkaline solutions of casein, soyabean, peanut, and other proteins containing an after-chrome dye, and the dye is developed in a chromium salt bath after insolubilizing the protein by means of acidified formaldehyde.[56]

In America the word " Azlon " has been adopted to cover regenerated protein fibres, and conforms with the accepted conventions of rayon for regenerated cellulose fibres and nylon for polyamide fibres.

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CELLULOSE TEXTILE CHEMISTRY

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THE physical properties of a textile fibre are, of course, derived ultimately from those of the individual molecules and the way they are built up to form the fibre structure. Much is known about the cellulose molecules, but far less about their arrangement within the fibre. One speaks of " highly oriented " fibres when referring to those in which the crystallites lie in a more or less orderly fashion about the fibre axis, but the term is used only qualitatively. Degree of crystallinity is also hard to define, and although it is recognized that the cellulose at the surface of fibres is associated differently from that within, little more than this has been deduced. It would seem that one cannot expect much progress here until new techniques have been devised from the closer examination of partially degraded fibres. In the meantime, the theories advanced to explain the superiority of the native over the regenerated cellulose fibres are of interest.[1] K. Hess and E. Steurer[2] have shown that in a vibratory mill cellulose undergoes degradation to the point where the *X*-ray diffraction pattern disappears with only a small change in its viscosity in cuprammonium. Earlier work from the Kaiser Wilhelm Institute has shown that the pattern is destroyed long before significant amounts of sub-microscopic material, as revealed by the electron miscroscope, have been formed.

Threads of cellulose hydrate spun without stretching and dried are practically isotropic in character and possess a high degree of elasticity. This material has been used[3] in an *X*-ray study to determine whether or not stretching has any effect upon crystallinity. Within the limits of experimental error there was no indication that cellulose, like rubber, becomes more crystalline on stretching.

These papers, owing to war conditions, have only recently become available, as have many papers written by the physicists under P. H. Hermans at the Institute of Cellulose Research at Utrecht. Fortunately, this work has been excellently summarized up to 1944 in a monograph[4] which also contains much new work, particularly in the section in which quantitative relationships between double refraction and orientation are established.

Differences in the reactivity of cellulose from different origins have been investigated by A. Marschall and H. Stauch,[5] using an 80:20 mixture of formic acid (85%) and zinc chloride. Cellulose hydrate fibres are rapidly dissolved by this solvent, whilst native fibres, even when chemically modified to give a corresponding mean degree of polymerization, are only partially dissolved, although the sodium hydroxide, potassium thiocyanate, and sodium zincate solubilities are all considerably increased. Native fibre mechanically degraded in a vibratory mill may dissolve completely in the new solvent, but the reactivity towards homogeneous acetylation was not improved by such treatment. The cellulose recovered from solution was, however, much more reactive. To verify the hypothesis that the reactivity of different grades of cellulose is related to the degree of cross-linking of the molecules, G. Centola[6] treated a cellulose sample of optimum solubility and reactivity with small amounts of formaldehyde to give products containing up to 0·10% of combined formaldehyde. On subsequent acetylation and xanthation, the treated products gave solutions which, containing much swollen and undissolved fibre, were inferior to those obtained from the original cellulose.

Several years ago Linderström-Lang devised a density gradient tube for use in a study of the volume changes occurring during peptide hydrolysis. This ingenious technique has now been applied to fibre research,[7] and may be employed successfully to follow fluctuations of density across and along rayon yarns, and for determining the density of residual cotton cellulose after different periods of digestion with Nickerson's hydrochloric acid/ferric chloride reagent.

Work in the field of molecular weight determination has been confined largely to the interpretation of sedimentation and diffusion data, although two short reviews, suitable for the non-specialist reader, of the physico-chemical studies made on cellulose and nitrocellulose at the Institute of Physical Chemistry, Upsala, have been written by T. Svedberg[8] and I. Jullander.[9] They deal not only with the difficulties encountered in the extrapolation of sedimentation constants to zero concentration, but also with the determination of molecular weight distribution from the combined results of osmotic and sedimentation experiments. In interpreting sedimentation data it is generally assumed that the frictional coefficient of a thread-like molecule in solution is independent of the centrifugal field. This assumption has now been verified on the basis of the Kuhn and Kuhn model of randomly-coiled thread molecules.[10] Under the action of the field the molecules tend to orient themselves in the direction of flow, thus decreasing frictional resistance, and they also have a tendency to extend, which has the opposite effect. The resultant change in the frictional coefficient is smaller than it would be if either orientation or stretching alone were to occur.

The chain length uniformity of partially degraded cotton and ramie cellulose, which is greater than one would expect if the chains were randomly broken, has led to G. V. Schulz and E. Husemann[11] to conclude that there are present easily cleavable bonds spaced at regular intervals of approximately 500 glucose units along the cellulose chains. The lengths of the fibre fragments, determined with the aid of the electron microscope, were predominantly in the range of 2000-2500A., whilst cellulosic rayon fibres showed no such periodicity. L. A. Hiller and E. Pacsu[12] also hold the view that there are two types of bond in the cellulose chain. From observations of the viscosity changes which occur during the acid attack of bleached cotton cellulose dissolved in 85% phosphoric acid they conclude that the large initial fall in viscosity is due to the rupture of semi-acetal linkages and hydrogen bonds, and not to the breaking of the 1:4 glycosidic linkages. This contention is supported by the results of end-group analysis by the acid-permanganate method, which indicate that the rate of aldehyde group formation and therefore of the rupture of the 1:4 linkages is extremely slow in strong mineral acid solution. E. L. Hirst and his colleagues at Manchester University[13] have commented on Pacsu's general theory of polysaccharide structure as it affects starch, and point out that the theory requires the formation of three molecules of formic acid per end-group in periodate oxidation, whereas it has been established that they yield only one molecule per end-group. Also the bonds broken during starch hydrolysis have kinetically the stability of glycosidic links, and it is not necessary to postulate an additional type of bonding.

A team of cellulose chemists, led by W. O. Kenyon, at the Kodak Research Laboratories, has published a series of papers devoted to nitrogen peroxide oxycellulose.[14] They have studied the behaviour of these oxycelluloses (celluronic acids as they are termed) in the uronic acid estimation, and found that the carbon dioxide evolution values of non-uronic acid substances are only a fraction of those recorded for the nitrogen peroxide oxycelluloses. This provides strong evidence of their uronic structure. The CO_2 evolution data indicate that the oxycellulose is composed essentially of β-D-glucuronic acid and unchanged D-glucose units. The calcium acetate method for carboxyl analysis did not produce theoretical results for the celluronic acids nor for alginic acid; the uronic acid method, on the other hand, gave results which were high, due to further oxidation of the celluronic acid by residual nitrate groups. A third analytical method—potentimetric titration of the celluronic acid suspended in N-sodium bromide—gave results substantially in agreement with those obtained by the calcium acetate method. The same team has investigated the mechanism of the oxidation with nitrogen peroxide in carbon tetrachloride solution.[15] Initially nitration of cellulose occurs, but, even in the presence of added nitric acid, the nitrogen peroxide appears to restrict the nitration reaction to a nitrogen content equivalent to that for a cellulose mononitrate. Oxidative-denitration of the preliminary nitrate in which the primary hydroxyl group is esterified then occurs. As an outcome of this work a whole series of mixed solvents for cellulose has been discovered.[16] These consist of nitrogen peroxide and an organic substance containing an electronegative group, this substance being, of course, unreactive towards nitrogen peroxide. Nitroparaffins, sulphones, nitriles, aryl sulphonates, ketones, and esters were all effective as the second component of the solvent.

The carboxyl groups in cellulose are known to exert a pronounced effect upon certain physical properties. Their effect upon the electrical insulation resistance of paper has been determined.[17] When the carboxyl groups are present in the unneutralized state the electrical resistance of the paper is at a minimum; it is at its highest value when the acidic groups have been neutralized by base-exchange reactions with the salts of bivalent metals. A comprehensive study of the conduction of electricity by sheet cellulose impregnated with metallic salts has been made by J. B. O'Sullivan,[18] of the Shirley Institute. For a given salt content the conductivity is an exponential function of the conditioning humidity over a wide range, and the mobility of various inorganic ions is, like the conductivity, a function of the moisture content of the film.

An interesting direct application of pure cellulose research is contained in a patent[19] covering the manufacture of high-grade cellulose film (for use in electric condensers) by the action of *Acetobacter xylinum* on a nutrient solution. The film may be withdrawn continuously from the bath and, after suitable washing treatments, dried and reeled.

It is possible to determine the solvation of dissolved compounds from the compressibility of their solutions, which is derived, in turn, from the rate of propagation of ultrasonic waves through the liquid. This method has been applied[20] to determine the solvation of nitrocellulose, cellulose acetate, and ethyl cellulose in acetone. The solvation of these high polymers per polar group or molecular unit was found to be similar to that for non-electrolytes of low molecular weight.

The mechanism of nitrocellulose formation continues to claim much attention, for, apart from its obvious industrial importance, the kinetics of a heterogeneous reaction of this type are of interest in studying the macromolecular structure of cellulose itself. The theory has been advanced[21] that the planar structure and high dipole moment of nitric acid favour its penetration into the crystalline regions, whereas bulky molecules, such as that of sulphuric acid, are only capable of penetrating the disordered areas. During nitration of hydroxyl groups within the crystallites the concentration of nitric acid within the micelles builds up to 70%. This theory has been supported by analysis of the nitrating acid retained by the product after centrifuging and by the results of nitration experiments on cotton linters, where the reaction is more accurately represented by assuming two consecutive reactions with different velocity constants.[22]

Structural studies of nitrocellulose have led to the differentiation of gelatinizing agents.[23] Some, like ketones and esters, modify the *X*-ray diagram on absorption and are solvents; others, such as those containing the nitrate group, do not affect the diffraction pattern. Camphor occupies an intermediate position in that it belongs to the first group when its action is catalysed. In a further paper Thérèse Petitpas[24] has reported modification of the *X*-ray diagram of trinitroramie which occurs during the absorption of camphor from the vapour phase. When approximately one molecule of camphor had been absorbed per glucose unit a rapid transition to the diagram of a new crystalline substance was observed. This diagram was identical with that for Hess's camphor-nitrocellulose I, which was obtained in hexane-camphor solution at 80°, or at room temperature in the presence of traces of acetone.

The esterification of cellulose with triphenylmethyl chloride (tritylation) and *p*-toluenesulphonyl chloride (tosylation) in pyridine has been followed systematically by determining the rate of esterification and the position of the substituent groups in the glucose unit.[25] Initially the primary hydroxyl group was esterified at 58 times the average rate for the substitution of the secondary hydroxyl groups. This relative rate decreases rapidly however, and finally the reaction enters a stage in which there is an apparent loss of trityl in the C_6 position while substitution is still occurring in other positions. No difficulty was experienced in the reaction between tosyl chloride and cellulose in obtaining a degree of substitution corresponding to two tosyl groups per glucose residue, which suggests that no steric hindrance effect is involved in the esterification of the secondary hydroxyl groups, as was formerly held to be the case from the work of Sakurada.

It has been shown[26] that, during the heterogeneous acetylation of cellulose with acetic anhydride in benzene solution, catalysis by perchloric acid takes the form of intermediate compound formation with the cellulose. The compound then slowly breaks down as acetyl groups are introduced, and finally the product contains a small number of perchlorate ester groups.

Manufacturing methods for the production of lower fatty acid esters of cellulose,[27] cellulose acetate propionates and butyrates in which high ester content and high viscosity are both obtained[28] have been protected. A further patent covers the production of highly-substituted acetone-soluble cellulose acetate.[29] Here acetone-insoluble fibrous cellulose acetate (acetic acid yield 58·5%) is dissolved in a fatty acid or chlorinated hydrocarbon, isolated by precipitation with water or by evaporation according to the type of solvent employed, suspended in acetone and cooled to less than –20°. It is claimed that the ester will then dissolve. The use of an impelling anhydride such as chloracetic anhydride in conjunction with a sulphuric acid catalyst in the manufacture of cellulose esters containing high alkyl groups, *e.g.*, dodecyl or stearyl, is the subject of an Eastman Kodak patent.[30] Contaminating fatty acid is removed from the product by washing with acetic acid or acetone in which the ester is insoluble. A procedure for the stabilization of esters generally has also been covered.[31]

Full experimental details for the preparation of cellulose acetate 2-aminoethyl and 2-cyanoethyl ethers, which are less soluble than similarly substituted esters and are dyed by acid colours, are given in a paper by T. S. Gardner.[32]

Bast fibres

The affinity of jute fibres for basic dyes has been shown to result from the presence of carboxyl groups in the holocellulose fraction.[33] Carboxyl contents, determined by the silver absorption method of Sookne and Harris, were proportional to the methylene blue absorption at p_H 7 for raw, defatted, alkali-treated, and lignin-free jute; approximately one mol. of dye was absorbed per acid equivalent. Treatment of raw jute with 1% sodium hydroxide solution at room temperature increased the apparent carboxyl content substantially, and it is possible that ester groups have been saponified in the process. Since lignin-free jute has a higher acid value than alkali-treated jute, any ester groups which are present may be associated with the lignin. Other workers[34] have also established that the lignin is not responsible for the basic dye absorption.

The discoloration of bleached bast fibres which occurs during light exposure is a disadvantage severely limiting the usefulness of these fibres. P. L. D. Peill[35] has found that the discoloration may be prevented by esterification and etherification treatments, which he tentatively suggests may prevent quinone formation by blocking reactive phenolic groups in the lignin. Similar effects have been observed by H. J. Callow,[36] who suggests that acetylation has a secondary function of causing the production of bleaching agents during irradiation. It is interesting to note in this connexion that peroxide formation has been observed in acetate rayon irradiated by light from a mercury vapour lamp.[37] Reactions of this kind are likely to lead to tendering unless, of course, the presence of readily oxidizable material in the bast fibres protects the cellulose from degradation.

The claim has been made in a British Celanese patent[38] that the tensile strength of linen is increased by esterification with a high molecular weight fatty acid and a lower fatty anhydride. As a result of this type of treatment it is claimed that the dry strength is improved by one-third and the wet strength by one-sixth.

Rayons

German processes for the extraction of high α-content cellulose (93%) from sulphite and sulphate pulps of coniferous woods[39] and a British method for the production of cellulose from woody matter and straw have been described.[40] A technical paper discusses previously published methods for the determination of α-cellulose and the alkali-solubility of cellulose pulps, and concludes that gravimetric methods are preferable to volumetric ones; determination of solubility/alkali-concentration curves for a number of pulps showed their form (and the proportion of pentosans and hexosans extracted) varies widely with the nature of the cellulose, and it is inferred that alkali extraction of cellulose supplies only arbitrary information unless analysis over the whole range of alkali concentration is carried out.[41] Treatment of pulp with Cl_2 and aq.Na_2SO_3 until completely delignified, followed by washing, drying, and weighing the residual fibres, constitutes a standardized method for the determination of cellulose in wood-pulp.[42] Several minor improvements in the determination of β- and γ-cellulose in wood have been detailed.[43]

It has been shown that CS_2 reacts with alkali cellulose only after solution in alkali and the reaction velocities and stages of equilibrium have been determined for various ratios of cellulose to alkali; the reaction velocity decreases when the volume of alkali is sufficient to suspend the fibres and is increased by emulsifying the CS_2 in the alkali, but it is independent of the degree of polymerization or the type of cellulose used.[44] Ageing has been studied by following the decrease in D.P. kinetically; degradation products are assumed to retard the ageing process, and reduction of D.P. attains a limiting value. The heat of activation for a number of cellulosic materials was found constant at approximately 13,340 cal. During ageing the carboxyl content changes, and finally approximates to one carboxyl group per molecule, but replacement of ageing by other means of degradation is unsatisfactory; mild " superoxidation " during ageing furnishes somewhat more than one carboxyl group per molecule, but appears to improve the filtering properties of the viscose.[45] Ripening, to the same D.P., by atmospheric oxygen and by H_2O_2, followed by viscosimetric, osmotic, and fractionation characterization, indicated peroxide was some six times faster in action, but there appeared to be no essential differences in the products.[46] The presence of cellulose xanthate reduces the precipitation of dispersed cellulose, the protective power appears to be independent of the time of ageing of the alkali cellulose from which the xanthate is made, and of the sulphur/cellulose ratio of the xanthate.[47]

Microscopic examination of viscose shows the presence of small particles (due to secondary reactions during sulphurization, to undissolved fibres, and to impurities) which affect filtration.[48] Another article claims filter-clogging is due to undissolved particles and to the formation of cellulosic aggregates; the latter break down under high rates of shear such as occur in pressure filtration.[49] Accessory substances (pentosans, hexosans, etc.) introduced by substitution of wood for cotton may exert an injurious effect upon fibre properties.[50]

Incorporation of 2–5% resorcinol-formaldehyde condensate[51, 52] or up to 2% casein[53, 54] in viscose dope enhances adhesion between regenerated cellulose and rubber. The adhesion, on vulcanizing rubber to rayon tyre cords, is doubled, and becomes comparable with that to cotton; soaking rayon in ammoniacal casein solutions is much less effective. Tyre cords that have been acetylated to 10–30% acetyl content show much improved heat resistance, acetylated cotton will withstand high temperatures for a much longer time than grey cotton before tendering to half strength.[55]

General developments in rayon and industrial uses of high-tenacity yarns (*e.g.*, by the rubber industry) have been summarized in a lecture.[56] The fine-structure of viscose rayon has been examined by quantitative *X*-ray diffraction methods and distinctions between axial and lateral ordering are made. Lateral ordering can vary independently of orientation and can be increased by aqueous annealing, although the degree obtained appears to be limited by the structure originally set up. The composition of the coagulating bath has a considerable influence; tenacity and elasticity are not uniquely related to orientation, and, for constant orientation, elongation at break increases with lateral disorder. In addition, since yarns of essentially the same axial and lateral order can show different properties, an undefined variable is indicated.[57] Crystallinity is largely independent of the crystallinity of the original cellulose or of tension variations occurring in spinning, but is mainly determined by the amount of swelling on coagulation. A photomicrographic method which reveals the orientation of crystalline regions after etching affords a new technique for investigating micellar structure.[58]

Properties of cotton and staple fibre have been compared experimentally; the degradation of staple in washing and on swelling in alkali and the variables that influence spinning are discussed; in oxidation and hydrolysis, as might be expected, the structure and surface of staple are of importance and protection of the surface is considered; physical properties of wool and staple fibre are also compared.[59] Periodic action of a jet of gas or liquid, causing localized weakening of freshly spun filaments, allows them to be broken into staple lengths on stretching.[60]

An apparatus for measuring axial swelling and recovery in 1-metre lengths of low-twist rayons[61] revealed that, if the threads are free from strain, length changes are reversible on repeated wetting and drying, but with strained rayons successive dry lengths diminish and approach a constant value. Axial swelling is inversely related to the degree of orientation.

The production of durable three-dimensional crimp in filaments formed from the union (just prior to their entering the spinning bath) of streams of different kinds of viscose, or by the use of septum-divided spinnerets permitting viscoses of different characteristics to be extruded side by side, has been the subject of several patents.[62, 63] The viscoses may be obtained from wood and cotton, or from differences in CS_2 content; the composite filaments are coagulated, stretched up to or beyond the elastic limit of one component, allowed to relax, and finally set in the crimped state which they then possess. An entirely different method for obtaining permanent crimp consists of passing threads through a machine, or knitting them into fabric, impregnating and subsequently baking with a thermosetting resin, and (in the second instance) resolving the fabric into its constituents.[64]

Continuous after-treatment of freshly spun viscose has been effected by passing newly-formed filaments in a generally helical path, at high speed, over a series of thread-storage and thread-advancing squirrel-cage-like devices, the thread being finally delivered dried in the form of a wound package.[65] Freeze-drying of wound cakes has been successfully applied,[66] and high-frequency currents, induced longitudinally in fibres, have been used to dry wet filaments with free shrinkage.[67] The use of sulphuric acid solutions of cellulose for filament spinning has also been patented,[68] and oxidation of cellulose by periodic acid or NO_2, prior to solution in sodium zincate and spinning into an acid coagulating bath, is the theme of a process for oxycellulose rayon production.[69]

In rayons from cellulose derivatives the ascendency of acetate staple is to be remarked; blended with rayon it imparts crease-resistance and improves the handle of mixed yarn fabrics.[70] German production of cellulose acetate from beechwood pulp (98% cellulose), pretreated with glacial AcOH, then acetylated with either Ac_2O, AcOH and $ZnCl_2$, or AcOH, CH_2Cl_2 and H_2SO_4, is given in various C.I.O.S. reports;[71, 72] the acetylated material was hydrolysed, for example, by AcOH, $ZnCl_2$ and HCl, until acetone-soluble, then precipitated by flooding. A British patent specifies the use of ice when hydrolysing the tri-ester to prevent undue local heating and irregularity of product.[73] Esterification with an organic acid in the presence of an inorganic one, followed by continuous addition of water during ripening, until the ester is of suitable acyl content, is the subject of another patent.[74] The use of formaldehyde reduces loss of strength in cellulose regenerated from ordinary fibrous esters.[75]

The rate of saponification of cellulose acetate in fibrous form and in solution has been studied; soap-phenol delustering reduces saponification rate in fibres, but all acetate fibres differing in heterogeneous saponification rate behave identically in solution, where the rate is higher and follows a second order law. Some of the saponified acetates are water-soluble. A method for reducing the acetic acid yield from 53–15% homogeneously is recorded.[76] Dyed cross-sections of filaments show that saponification varies from a diffused effect to a sharp line of demarcation (when surface saponification is carried out); the effects of time, temperature, and concentration for various alkaline agents have been studied in this way.[77]

When cellulose acetate is spun from acetone solution the use of infra-red rays focussed by suitably shaped reflectors (which can be made the side of the spinning chamber) assists a current of gas to effect solvent removal;[78] when wet-spun from AcOH solution the filaments can be coagulated in a bath of an ammonium salt and afterwards stretched to increase their tenacity.[79] Crimped acetate staple, resilient and wool-like, has been produced by swelling in a solvent, dipping in hot water, and drying.[80]

Esters prepared from mixed mono- and dibasic derivatives, *e.g.*, cellulose adipo-laurates, or butyro-sebacates, possess less plasticity but greater elasticity than the commoner ones.[81] Alkali- or water-soluble derivatives can be produced direct by addition of acrylonitrile to viscose solutions; the alkali present hydrolyses the cyano-ethyl derivatives to give a product, having homogeneously distributed carboxy ether groups, which can be spun into special-purpose filaments.[82] Cellulose ethers (such as ethyl cellulose) are considerably improved in thermal stability by the addition of about 1% quinol;[83] neutralizing the solvent-swollen material with acids is claimed to have the same effect.[84]

Three methods for determining the degree of substitution of sodium carboxymethyl cellulose have been examined. They consist respectively of: titration of the free acid produced on treatment with aqueous methanolic HCl; direct conductimetric titration of the salt in alkaline solution; H_2SO_4-hydrolysis of the $-CH_2COOH$ groups to glycollic acid and determination of the latter with 2:7 dihydroxynaphthalene. The three methods give comparable results when the degree of substitution ranges from 0·2 to 1·3.[85] Nomographs and equations for rapidly relating the percentage composition of cellulose esters to the theoretical number of ester groups per anhydroglucose unit have been published.[86]

Employment of calcium alginate filaments for scaffolding purposes in fabric construction and their subsequent removal by scouring has been detailed,[87] and acetylation of alginic acid yarn to give a somewhat unstable product, swellable but insoluble in water, alcohol, etc., but soluble in aqueous acetone and in dilute calcium acetate solution, has been recorded.[88]

Scouring and bleaching

Although many papers have been published on this subject during the year there is little progress to report. Recent developments in the continuous processing of textiles are given in a review by R. G. Fargher and F. W. Thomas,[89] which serves to put into perspective modern trends in plant design and chemical processing technique.

The view is now generally held that cotton fabrics only become wettable when fatty impurities have been removed and the surface layers of the fibre broken down under the action of alkali at high temperatures or during mercerization. A claim has now been made[90] that wettability may be increased during desizing by enzyme action with the aid of a product which contains, in addition to an amylase, a phosphatide such as lecithin.

The scouring efficiency of soap has been compared with that of synthetic detergents under conditions simulating those used in mill practice in the woollen industry.[91] Whilst the synthetic detergents as a class showed excellent results for oil removal, their suspending power for dirt was poorer than soap. Their performance in this direction was improved by adjusting the solution to approximately p_H 11 by the addition of sodium carbonate. The inclusion of sodium sulphate in solutions of cetyl trimethyl ammonium bromide has been found to reduce the concentration required for the maximum lowering of the surface tension from 0·015% to 0·0025%, whilst this salt is also effective in reducing the rate of acid hydrolysis of aliphatic alcohol sulphates.[92, 93]

An attempt has been made to determine the balance between the oxygen lost by decomposition and that consumed by cotton and its impurities during hydrogen peroxide bleaching,[94] whilst A. Klein[95] has compared the degree of whiteness and permanence of the sodium chlorite bleach with that obtained by the use of sodium hypochlorite and hydrogen peroxide. Plant requirements for ozone bleaching have also been described.[96]

Dyeing

The application of scientific methods to the dyeing process is gradually bringing about the transition of an art to a science. Progress along these lines is hampered more by variabilities and uncertainties connected with the fibres upon which the dyers have to work than upon the dyestuffs themselves, which are now well characterized. Differences in the dyeing properties of 21 types of commercial viscose rayon yarns have been recorded by J. Boulton and J. Wardle.[97] The rate of diffusion of the direct dyes tended to decrease with fineness of the filament, and not all the rayons absorbed the same amounts of dye at equilibrium. " Durafil " presents a special problem owing to its high degree of dichroism, appearing to be dyed a lighter shade than coarser filaments dyed equivalently. From a qualitative examination of all the dyed yarns for dichroic behaviour it was observed that the degree of orientation falls with increasing filament denier. On account of their anomalous dyeing properties only limited assistance can be gained in the dyeing of highly oriented rayons from the nomogram devised by F. Fothergill.[98] The wider problem of the relationship of dye concentration to intensities of reflection of polarized and non-polarized light from dyed fibres has been studied by J. M. Preston and P. C. Tsien,[99] using a series of rayons stretch-spun to different extents and therefore possessing different degrees of orientation. A team of American workers, using a " dyeometer " linked with a recording photo-electric spectrophotometer, has determined the effect upon the dyeing properties of rayons, of the age of viscose before spinning, filament size, skin structure, and many other factors influencing the physical properties of regenerated cellulose, with results similar to those already reported.[100]

The rate-accelerating effect of anionic surface-active agents on the dyeing of cotton with direct dyes has also received attention.[101] They become less effective in increasing the amount of dye sorption with increase in the dyebath temperature. Controlled oxidation of cellulose with dilute solutions of periodic acid has been patented as a means of increasing dye-receptivity,[102] whilst a British Celanese patent[103] covers the use of thiocyanates to achieve a similar result with cellulose derivative rayons. Lower alcohols are incorporated in the dye liquor to assist with dye penetration.

Shade changes which occur during the hypochlorite bleaching of fabrics containing yarns dyed with colours of low fastness to chlorine is a familiar problem to dyers. This can be overcome by impregnation of the fabric before bleaching with small amounts of melamine-formaldehyde resin.[104] The chloramine derivatives formed by reaction of the resin with sodium hypochlorite may be removed by sodium bisulphite. This would seem to avoid the danger of degradation which is associated with the bleaching of fabrics containing urea and melamine-formaldehyde resins.

It is well known that certain vat dyes falling mainly in the yellow and orange range bring about accelerated photochemical degradation of cellulose. G. E. Egerton,[105] of the Shirley Institute, has determined the influence of many variables on the extent of the degradation suffered by cotton from this cause. Whilst generally the tendering is more severe when the cotton yarns (irrespective of whether they have been dyed or not) are irradiated in a moist atmosphere, certain inactive blue and green dyes appear to exert a protective action under these conditions. In another paper from these laboratories, D. A. Clibbens and A. H. Little[106] have reported experiments in which the influence of many vat and sulphur colours in accelerating the hypochlorite oxidation of cotton, particularly under acid or neutral conditions, has been studied. The claim has been made in a Swiss patent[107] that tendering induced by active vat dyes may be substantially reduced by after-treatment of the dyeings with a reaction product of formaldehyde and a compound, like dicyanodiamide or melamine, containing a $-\mathrm{N}{:}\underset{|}{\mathrm{C}}-\mathrm{NH}$-group.

The difficulty of obtaining thorough penetration with vat dyes arises in its most acute form in package dyeing. In the Abbot-Cox system the pigment is gradually exhausted from the liquor by the controlled addition of electrolytes. Dyes of good levelling properties are essential and, owing to variations in the behaviour of the leuco-compounds towards the dispersing agent, the optimum conditions for each dye must be maintained. These have been outlined in a paper in which the general application of the process is also considered.[108]

Undoubtedly the most important development of recent years in the field of vat dyeing is the discovery by the chemists at I. G. Farbenindustrie A.-G. that the poor penetrating properties of these dyes, due to the high substantivity of the sodium leuco-compounds, may be overcome to a remarkable degree by employing a dispersion of the "vat-acid" in place of a pigment dispersion. As the free acid has only slight substantivity it is possible with the use of suitable dispersing agents to obtain much improved penetration both in piece and package dyeing. Details of this technique, which may be applied successfully to many but not all vat colours, have been given,[109] whilst a committee of the American Association of Textile Chemists and Colorists has reported favourably on the process after several full-scale trials.[110]

In the continuous vat dyeing of piece goods by the pigment-pad method one of the major sources of trouble, particularly with heavy shades, is accumulation of colour in the developing bath. Several devices have been patented for avoiding this difficulty, and the latest, the Williams Unit, has been fully described by the inventor.[111] The liquor ratio in this machine is kept small and the fabric passes through a series of narrow channels surrounded by a steam jacket.

Improved penetration of dyes into viscose rayon without the use of swelling agents, it has been claimed,[112] may be obtained by creating vibrations of the order of 1000–500,000 cycles per sec. in the dye liquor.

Printing

Difficulties are sometimes encountered in the printing of viscose staple fibre fabrics with leuco-ester salts of vat dyes owing to the low affinity of this type of material. The claim has been made[113] that these can be overcome by the use of a chlorate oxidizing agent in the presence of a catalyst, preferably a ferrocyanide. This causes the oxidation of the leuco-compound to occur more slowly than when ammonium vanadate is used. A British Celanese patent is concerned with the composition of pastes suitable for printing cellulose acetate without resort to a preliminary saponification process. Inorganic thiocyanates are used to swell the fibre and assist penetration of acid dyes.[114]

The failure of attempts to develop acetate print styles in America is attributed[115] to the difficulty of discharging acetate rayon satisfactorily in dark shades, and that direct and acid colours applied by the urea method are fast only to dry-cleaning.

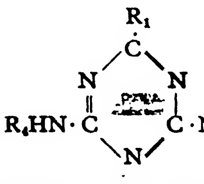
Imperial Chemical Industries patents[116] protect the use in discharge printing of soluble salts of 4:4′-di(benzoylamino) stilbene-2:2′-disulphonic acid or benzoyl substituted derivatives. The fabric may be pre-treated with this derivative (which is related in chemical structure to one of the fluorescent whitening agents) or it may be applied in the discharge printing paste. An American firm has patented the use of sodium chlorite under slightly acid conditions as the discharging agent for fabrics dyed with sulphur, direct, developed, azoic, or vat dyestuffs.[117]

The photographic production of silk gauze printing screens is the subject of another recent patent.[118]

Finishing

Summaries covering recent finishing processes and developments in machinery in Europe[119, 120] and in America[121, 122, 123] have been given. Specialized methods for applying plastic materials include a vacuum impregnation technique,[124] vapour-phase polymerization of vinyl monomers (recovered from acrylic scrap) within catalyst-saturated fibres,[125] and the use of polymer film supported on temporary backing sheets which are removed after hot-pressing with cloth, felt, etc.[126, 127, 128] Poly*iso*cyanates and -*iso*thiocyanates continue in development as finishing agents;[129] they modify the properties of textiles containing -OH or -NH groups, probably by cross-linkage,[130] and impart high resilience and good wet and dry strength to regenerated cellulose.[131] Crossed fabrics bonded by means of *iso*cyanate-modified polyesters or -amides possess exceptional impermeability to hydrogen, but retain sufficient flexibility for balloon use.[132] The adhesion of vinyl copolymers is improved by use of primer coatings containing traces of unsaturated maleic resins.[133] Thermosetting vinyls (contact resins) have been much used for fabric laminates, but await development as finishes; an Electrochemical Society preprint describes their characteristics.[134]

Modifications of aldehyde and condensation resin techniques have received attention: pretreatment of cellulosic textiles with animal and vegetable stiffening agents, which are insolubilized on subsequent formaldehyde processing, assists in stiffening them.[135] Impregnation of textiles with a soluble quaternary ammonium salt of an ether of an insoluble alkylol urea (*e.g.*, butyl derivative),[136] or of a melamine analogue,[137] followed by heating, decomposes the salt and sets the resin in the fibre. Melamine resins, condensed under acid conditions to an early hydrophobe stage, possess cationic properties and will deposit on cellulosic fibres.[138] By addition of alkyd resins to amino-condensates thermal and chemical resistance is claimed.[139] A number of guanamine derivatives.



(where R_{1-4} represent hydrocarbon groups or hydrogen, totalling not less than 7C atoms) which will condense with formaldehyde, have been introduced for use in conjunction with the commoner acid-curing thermosetting amino-resins. Wash-fast, water-proof, crease-resistant finishes, etc., are claimed.[140]

In the rubberizing of rayon tyre-cords coating with adhesive agents is much less effective than incorporation of them in the initial viscose dope, and, as this process can hardly be termed finishing, has been dealt with under viscose additives in the section on regenerated cellulose. A general review of surface-active compounds, their nature, action, and textile uses, is of interest;[141] employment of cationic surface-active agents to induce substantivity is common in several patented compositions, aqueous dispersions of a variety of vinyl resins being exhausted in this way on to stockings to improve their wear, etc.[142] Silicone resins have found no fresh applications to textiles, but their general properties have been reviewed in various articles.[143, 144]

Fabrics containing cellulose ester (acetate) fibres can be waterproofed by wax and an aluminium salt after treatment with an aqueous oxidizing agent, *e.g.*, dilute $KMnO_4$, followed by decolorizing in $NaHSO_3$ solution.[145] From analysis of the products of the decomposition of Velan on cotton it has been concluded that the methylolstearamide formed may partially dimerize and also some formaldehyde may be lost; hydrolysing with 5% H_2SO_4 removes formaldehyde (steam distillation of which forms a basis for estimating the Velan in fabrics) and all other products, except where primary linkage to cellulose occurs and this may amount to 2%.[146] Methods for the preparation of behenamidomethylpyridinium chloride ($C_{21}H_{43}CONH.CH_2Py.Cl$), the docosyl ($C_{22}H_{45}$-) analogue and related structures have been patented;[147] outstanding water-repellence and greater resistance to dry cleaning than that offered by the C_{17} compound is claimed. Reaction, in the presence of an acid condensing agent, of C_{8-22} methylolamides (*e.g.*, methylolstearamide) with various ether-forming agents (*e.g.*, glycol) produces waterproofing and other finishing compounds.[148] Another wash-resistant finish employs aqueous dispersions of C^{8-28} bisalkylolimides of aromatic nuclei (*e.g.*, *NN'*-distearoylbenzidine).[149]

Extensive evaluation of proofed fabrics,[150, 151, 152] the use of a rain room, and submission of American Navy Department canvases to tests of increasing severity[151] have been described. A spray-penetration test simulating severe conditions[151] and criteria for wettability and penetration tests have been summarized.[153] The Bundesmann water-repellency test for textiles is to be made the basis for a standard specification.[154] The construction and performance of fabrics becoming waterproofed by swelling have been described.[155, 156]

Articles dealing with the fundamental causes of dimensional instability in cellulose divide means for its rectification into mechanical, resin-deposition, and chemically-reactive processes.[157, 158, 159, 160, 161] The practical process (Definising) for alkali swelling, followed by successive washings and compression between squeeze rollers, with controlled drying, has been described and illustrated.[162, 163] Mechanical processes are more satisfactory with cotton than with rayon, for which baking with glyoxal and an acidic catalyst (Sanforsetting) is preferable to the use of formaldehyde.[161, 164, 165] When formaldehyde is used and $AlCl_3$ supplies the necessary acid concentration a complex which reacts directly with the fibre is thought to be formed, the metal (or salt) becoming bound to the cellulose, which suffers only slight degradation. Methods for determining the formaldehyde-, Al-, and Cl-content of staple rayon are given.[166] Shrink resistance is also conferred by melamine-formaldehyde ethers on resinification,[161, 169] and urea-acrolein resins were manufactured in Germany for crease-proofing purposes;[167] inhibition of the absorption of direct dyes by these resins has been studied and compared with their stabilizing effect; where shrinkage is $<1\frac{1}{2}\%$ good correlation exists.[168]

Combat by Service Departments (especially in the tropics) of fungal and microbiological deterioration in cellulosic textiles necessitated identification of the various organisms, study of their life cycles, and the precise nature of their attack upon textiles, together with measures for controlling it.[170, 171, 172] The measures include isolation of the cellulose (by protective coatings), the use of toxicants (such as fungicides), or modification of the fibre surface by chemical reaction.[173, 174, 175]

Mildew on cotton equipment in the S. Pacific Ocean was prevented by dichlorodihydroxydiphenylmethane,[176] which is, in addition, a mothicide; for this latter purpose silicofluorides of lower alkylolamines have also been proposed.[177] The properties of DDT have been reviewed: 20% aqueous emulsions containing a cation-active dispersing agent can be exhausted on to textiles; although largely removed by washing, retention of 0·1–0·2% is satisfactory.[178] Methods for determining the insecticides hexachloro*cyclo*hexane and 1:2:3:4–tetrahydro–2–naphthol[179] in impregnated fabrics have been given.

The rot-proofing efficacy (by soil burial tests) of metallic naphthenates on cotton duck and cellulosic cordage, after aerial weathering, has been studied in Canada; wax reduces loss of Cu on weathering, Hg does not assist weathering but reduces Cu-loss on soil burial, mixed naphthenates are more effective on soil burial than single ones, while tertiary mixtures (of equimolecular composition) were even better. Only about 0·2% metal is required.[180, 181] Naphthenates, $HgCl_2$, 8-quinolinol, etc., usually provide fungal-, bacterial-, and insect-resistance, but mildew-resistance imparted by milder methods (*e.g.*, admixtures of $CuSO_4$, AlOAc, etc.) may not prevent insect (termite) attack.[182, 183]

Chaetomium globosum and *Spirochaeta cytophaga*, grown on mineral agar, bring about progressive physical and chemical degradation of cotton duck, the *Chaetomium* being the more active; changes in the cellulose Cu-no. reveal different paths of attack by the two organisms, but both appear indifferent to the presence or removal of evolved CO_2.[184] The use of ultra-violet rays with cotton fibres can halve the subsequent growth-rate of mildew upon them, but irradiation-intensity has a proportionally deleterious effect (catalysed by the presence of Fe or Mn salts) upon tenacity.[185]

The chemistry and bacteriology of perspiration has been summarized, and it was concluded that odour in fabrics is best treated with wash-fast germicides of low toxicity.[186]

Combustion of textiles is retarded by deposition of refractory matter or by chemical modification, fire- or flame-proofing being distinguished from smoulder- or after-glow reduction.[187, 188] Chemical flame-proofing of cellulose is best effected by surface treatment with phosphoric acid;[187] physical protection has been effected by ammonium phosphate and urea,[188] by guanidine- or urea-phosphates,[189, 190] thiourea,[191] dicyandiamide-formaldehyde condensates prepared in the presence of $NH_4H_2PO_4$[192] and by deposition of Fe_2O_3 or Sb_2O_3 within the fibre.[189, 193, 194, 195] Zinc oxide, stannic phosphate, and chlorinated waxes reduce smouldering.[189, 194] American requirements for a fire-resistance test have been described.[196]

Coating methods are mentioned at the commencement of this section; some more specific treatments include the use of solutions of regenerated cellulose for stiffening and to impart transparent finishes to fabrics; the solvent is sodium zincate[197] or stannate, and is assisted by urea and related materials,[198] the solute can be rayon mill scrap. Solutions of cellulose in sodium zincate may be prepared at room temperature by initial use of concentrated zincate followed by dilution with ice-water or dilute zincate solution.[199] Water-insoluble alkylated amino-resins, applied in butanol solution, followed by drying and subsequent baking, will also produce organdie finishes and local pattern effects.[200] Amino-resins have also been used to retain the filler in permanent chintzes.[201] Linen-like finishes imparted to fabric by a carefully prepared series of hydroxyethyl celluloses have been studied;[202] a Russian article discusses the preparation, use, and advantages of cellulose ether sizes.[203] Applications for mixed or higher esters of cellulose are receiving attention: a hydrophilic thin film of cellulose acetobutyrate or acetopropionate upon fabric coated with cellulose nitrate prevents staining by foodstuffs, etc.,[204] and melt-coating with CAB mixtures has been studied.[205] Moisture-proof melt-coatings of ethyl cellulose[206] and of polyvinylidene chloride latex[207] have also been proposed. To prevent pressure-sensitive adhesives from diffusing into woven fabric backing, an intermediate film consisting of poly*iso*butene, filler, and a resin compatible with the adhesive is used.[208]

Cellulose (and other) fibres or sheets have been rendered abrasion-resistant by coating with acid polysilicic acid esters.[209] Rayons are softened by treatment with an acidic aqueous dispersion of a compound made by reacting a hydroxyalkyl diamine (*e.g.*, $OH(CH_2)_2NH(CH_2)_2NH_2$) with an –OH containing glyceride (*e.g.*, coconut oil).[210] An antistatic coating for cellulose acetate employs the products from unsaturated natural oils (*e.g.*, neatsfoot, cod-liver, olive, etc.) which have been oxidized by blowing, phosphated or phosphited, and finally neutralized.[211]

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PULP AND PAPER

By E. L. HILL, B.Sc., A.R.C.S.

Ministry of Supply

DESPITE the setbacks of the coal shortage during the spring, and the economic crisis later in the year, paper production for 1947 compares favourably with that for 1946. Nevertheless, owing to shortage of raw materials, particularly wood pulp, the industry continues to operate much below its capacity. Esparto imports reached a higher figure than for any year since before the war, and the greater availability of this material helped to compensate for the fact that, owing to the severities of the winter and the abnormal heat and droughts of the summer, there was a shortage of straw for paper-making. The maintenance of waste paper recovery on an adequate scale also continues to be a matter of concern, more especially to the board mills.

A feature of the year has been the publication of a series of reports dealing with investigations of the German pulp and paper industry. These reports vary considerably in length and technical interest, but special mention should be made of J. N. McGovern's[1] " Manufacture of Pulp and Paper and Related Products from Wood in Western Germany ", which gives an excellent account of German pulping and bleaching procedures and of the processes used for sulphite waste utilization. One field, in which large-scale developments had taken place, is in the fermentation of waste liquors from the sulphite cooking of beechwood to yield fodder yeast. Details of the techniques used by German sulphite mills for the production of fodder yeast are given in reports by H. J. Bunker[2, 3] and by J. P. Saeman, E. G. Locke and G. K. Dickerman.[4] Another German process meriting attention is the nitric acid pulping method employed by I. G. Farbenindustrie for production of high alpha pulp from beechwood (*v.* reports by A. M. Malcolm[5] and by D. B. Wicker, L. H. Smith, J. B. Quig and J. I. Schilthuis[6]). The process, which is used to produce about 40 m. tons of pulp per day, consists essentially in treating the chips, at atmospheric pressure, first with 15% nitric acid at 40–45°, then with 4% nitric acid at 95°, and finally with various washing and dilute alkali extraction stages, making a cooking cycle totalling 21 hours. It appears doubtful whether, under normal economic conditions, the process could compete with established pulping methods. For accounts of the German paper-making industry, reference should be made to the reports of H. L. Cremer, T. Frankel and W. Rough,[7] and of W. A. Wiltshire, W. J. Carter and A. J. C. Aikman.[8]

In general, apart from the developments mentioned, and various other points of minor technological interest, the conclusion reached by most investigators was that the German pulp and paper industry was not very advanced and had little to reveal that was worth application elsewhere.

Raw materials

An interesting new process, which may have applications in the collection of pulp-wood, is described by A. R. White.[9] Prior to felling, a 2in. wide strip of bark, together with sapwood to a depth of about half an inch, are removed from the tree and the exposed area is treated with ammonium sulphamate. The results of this treatment, which causes the rapid death of the tree, are that (*a*) the tree gives off moisture—not less than 25% of its total weight being lost before cutting or transportation takes place, (*b*) shrinkage and seasoning of the wood are accelerated and (*c*) the adhesion of the bark is so weakened that it becomes detached during normal handling and transport. The method promises to provide a means of delivering peeled wood to the mill in a denser, drier and more fully seasoned condition.

Rising pulpwood prices, and the increasing scarcity of the preferred types of coniferous woods in U.S.A., are reflected in the number of papers devoted to the utilization of lumber and other wood wastes, and to the possibilities of various hardwoods for pulp and paper manufacture.

As regards the use of wood waste, E. L. Keller and J. N. McGovern[10] have experimented on the sulphite pulping of Eastern hemlock sawdust and have found that, whereas, as was to be expected, pulps from sawdust are weak, dirty and poor in yield, pulps can be produced from a mixture of 75% sawdust and 25% chips which are usable where cleanliness and strength are not critical, *e.g.*, for paper-board and mill wraps. Mention must be made of two investigations on the value of logging waste. M. W. Bray and J. S. Martin[11] describe sulphate pulping trials on logging and mill waste from the four major West Coast species, *viz.*, Douglas fir, Western hemlock, Pacific silver fir and Western red cedar, as a result of which it is established that, in general, there would be no difficulty in producing good quality kraft or bleachable sulphate pulps from these wastes. Douglas fir pulp is outstanding in tearing strength but mediocre in other properties, whilst Western red cedar possesses high strength properties with the exception of tearing strength. Suitable mixtures of wastes should, therefore, yield pulps with excellently balanced physical properties. Other possible outlets for Western mill wastes have been examined by S. L. Schwartz, J. C. Pew and E. R. Schafer,[12] who have given the results of their trials on the suitability of such materials for the manufacture of insulating board and hard-board. Of various treatments for softening the material prior to disintegration, steaming (taking 30 minutes to reach 180° and maintaining that temperature for 15 minutes) is the most advantageous method, although precautions against corrosion may be necessary in view of the acidity developed during this treatment. Boards of acceptable quality can be made from Western hemlock and white fir wastes, but only inferior boards could be produced from Douglas fir wastes, although it is possible that better results could be obtained by other methods of processing.

Turning to investigations on hardwoods, the potentialities of aspen, a predominant species in certain areas of U.S.A., are now receiving more attention. This wood has for many years been pulped commercially on a limited scale, but its utilization has hitherto been restricted by the poor strength characteristics of the resulting pulps. A. Hyttinen, G. E. Mackin and E. R. Schafer[13] have studied the technology of the grinding of aspen for the production of mechanical pulp. When aspen and spruce are ground under the same conditions, aspen consumes less energy, grinds at a higher rate, and yields a pulp which has higher freeness, but which is much weaker, than spruce ground-wood pulp. In order to produce pulp equal in strength to that from spruce, aspen would require much greater energy consumption. Trials with experimental aspen groundwood pulps as components of the furnish of book paper indicate that such pulps can be satisfactorily utilized without any appreciable change in operating conditions. The papers produced are, in general, denser and of lower porosity and opacity than when spruce groundwood is employed, and in most runs were of lower strength. J. N. McGovern[14] has considered the semi-chemical pulping of aspen and reports that, by using a neutral sulphite semi-chemical process, followed by disk refining and two stage bleaching, it is possible to obtain a high yield (58%) of pulp with much improved strength characteristics. Trials, both on experimental and on mill machines, suggest that this pulp could be used in partial replacement of softwood sulphite pulp in the manufacture of coated groundwood book paper, provided that the total of aspen groundwood and bleached aspen semi-chemical pulp does not exceed 50% of the furnish.

The suitability of yellow birch (*Betula lutea*, Michaux) for the manufacture of glassine paper has been the subject of trials by J. A. Feola and C. E. Libby,[15] who report that sulphite cooking gives good yields of pulp which hydrates readily. As might be expected, the strength characteristics of glassine from this source are lower than for glassine produced from Mitscherlich spruce pulp. Yet another investigation into the potentialities of hardwoods has been undertaken by C. W. Tasker and C. E. Libby,[16] who have examined the refining treatment necessary for the production of viscose grade pulp from sugar maple (*Acer saccharum*, Marshall) by the sulphate process. As is usual with hardwoods, the pentosan content of sugar maple sulphate pulp is high (16–18%) and cannot readily be reduced by changes in digestion variables. Pulps with reduced pentosan content (3–6%) can be produced by an acid hydrolysis-alkaline extraction refining process, the optimum conditions for which are, treatment for 2 hours at 90° with HCl (20% on pulp weight) at 5% consistency, followed by extraction for 2 hours at 0° with caustic soda (100% on pulp weight) at 10% consistency.

As is well known, the manufacture of cigarette papers from linseed (seed flax) fibre is a development of the last few years, which has rendered North America largely independent of imports for this type of paper. The encouragement now being given to linseed cultivation in the United Kingdom makes this development of increased interest to British paper-makers. Mill practice in the manufacture of cigarette and other fine papers from linseed straw is described by H. S. Spencer.[17] The tow is extracted from the straw by scutching at a centre convenient to the growing area and the baled fibre despatched to the mills. Pulping is carried out by means of a modified kraft process, preferably in spherical boilers. Two stage bleaching is employed, with chlorination for the first stage. Yields vary considerably according to the cleanliness of the tow, but may reach 60% for exceptionally clean raw material.

Among new raw materials, the report by L. G. S. Hebbs and E. L. Hill[18] on the papermaking value of Yawa fibre deserves mention. This material is obtained from the flowering stem of *Vigna sinensis* var. *textilis*, a variety of the common cow-pea grown in West Africa. Yawa fibre contains 59·1% of Cross and Bevan cellulose (moisture-free basis) and has an average fibre length of approximately 4mm. The conditions necessary for pulping the material by the soda cooking process are rather more severe than are required for the digestion of new Manila fibre and the yield (52 to 66%, according to cooking treatment) is somewhat lower. Yawa pulps approached Manila standards for tearing and folding strength and trials in three mills confirmed that, for many applications, Yawa fibre can satisfactorily replace Manila. Although technically of undoubted value, the exploitation of this material must depend on the availability of adequate supplies and on the development of a cheap, mechanical method of extracting the fibre from the plant stems.

Brazilian Caroa fibre has been examined by R. C. Sproull[19] as a substitute for Manila fibre for the manufacture of insulation paper. Despite its much lower strength characteristics, no difficulties occur in using Caroa paper as a turn insulator. It ages satisfactorily in chlorinated diphenyl at 125° and, in its electrical properties, is comparable to Manila insulating paper.

Alkaline process

Various modifications to the normal alkaline boil have been proposed. Thus, experiments have been carried out by M. W. Bray and B. Singer[20] on the substitution of sodium sulphite and sodium thiosulphate for sodium sulphide in the sulphate pulping of spruce. When either of these chemicals is used in conjunction with caustic soda, the resulting pulps are less strong than those resulting from normal kraft cooking; but when they are used to substitute only half of the sodium sulphide present in kraft cooking liquors, and are added in such quantity that the original reducing power of the solution is maintained, pulps much superior in strength to kraft pulps are produced. In view of this result the authors suggest that spent liquors from the neutral sulphite semi-chemical process could be used in diluting strong white liquors for kraft pulping.

D. M. Sutherland,[21] for example, advocates the continuous, disk refining of kraft pulp, direct from the blow pits, whilst it is still alkaline and hot (175°). Data are given showing that by this method harder cooked pulps may be used and higher pulp yields obtained at lower cost. For a pulp with a chlorine number of 15–16, the yield amounts to 62–63% (moisture-free basis); such pulps have good strength at high freeness.

During the course of a normal kraft cook, the rate of pulping reactions slackens as the digestion liquor becomes exhausted. S. L. Schwartz and M. W. Bray[22] have experimented with a modified method of sulphate cooking which depends on maintaining a continuous flow of fresh, preheated liquor through the digester. By this technique, cooking time can be substantially reduced and the resulting pulps are more easily bleached, and are higher in α-cellulose and lower in pentosans than ordinarily cooked sulphate pulps.

Improvements in black liquor evaporator engineering have been reviewed by R. E. Bergstrom and J. R. Lientz,[23] who discuss development in design, such as the use of longer tubes and advances arising from the use of corrosion resistant materials in construction. The design and operation of modern, continuous re-causticizing plant have been discussed by R. F. Clemens,[24] who states that the efficiency of the plant should be above 99% for soda recovery and of the order of 90–95% in lime recovery. A part of this lime loss occurs, not in the re-causticizing system, but as stack losses during re-burning. The reduction of these stack losses has been the subject of investigations by C. C. Porter, F. W. Bishop and J. G. Liskow,[25] who recommend the installation of type N Roto-clone, an equipment in which the dust-laden gases are passed through a continuous sheet of water. By the use of this installation, new lime consumption is said to have fallen from 156 to 15lb. per ton of pulp produced.

Increasing attention is being paid to the utilization of the by-products from sulphate pulping. The recovery of turpentine from digester relief gases during the cooking of pines is practised by many mills; turpentine from this source now accounts for about 23% of the total turpentine production of U.S.A. W. P. Lawrence,[26] in a summary of the replies recovered from 24 mills in response to a TAPPI questionnaire, gives details of the equipment and techniques used by American mills practising turpentine recovery.

The composition and potential uses of Canadian tall oils are discussed by G. N. B. Burch, A. C. Shaw and R. V. V. Nicholls,[27] who report that, on the average, Canadian tall oils appear to be characterized by low acid and saponification numbers and high iodine values. The Canadian materials also appear to be particularly rich in phytosterols.

W. P. Thielens and R. R. Fuller[28] have designed a collector for separating sulphate soap. Despite the fact that the yield is lower than if the soap is removed after the black liquor has been evaporated, it is recommended that the collection should take place during evaporation when the liquor has been concentrated to 20–25% total solids, since the capacity and operation of the last effects of the evaporation are thereby improved and the soap-free liquor is more easily handled. This conclusion is confirmed by A. Pollak and P. R. Wiley,[29] who give data for the fuel value and soda content of commercial tall oil skimmings. The effect of temperature and sodium chloride concentration on the salting out of tall oil soap have been studied by O. Harva,[30] who finds a multiple salting-out process effectively removes most of the resinous and tarry matter. The utilization of tall oil in the paint industry is dealt with by M. Hess,[31] whilst C. J. Vander Valk and H. Burrell[32] suggest that polypentaerythritol-modified tall oil has characteristics which should render it of value in printing ink formulations. B.P. 586,091 (H. O. V. Bergstrom, G. B. Heijmer and K. G. Trobeck) covers the use of a tall oil distillate for the impregnation of fibre-board.

Present outlets for tall oil are reviewed in a well documented paper by L. Byman,[33] who discusses the applications in relation to the composition and properties of the commercial material and of the products which can be produced by fractionating into its constituents and by manufacturing derivatives.

The prospect of an entirely new and important outlet for lignin from sulphate pulping black liquors is opened up by the work of J. J. Keilen and A. Pollak[34] on the use of this material as a reinforcing agent for synthetic and natural rubber. The fact that it is soluble in aqueous alkalis, in which respect it is unique among rubber reinforcing agents, affords the possibility of co-precipitating the lignin with the rubber when the latex is coagulated. This co-precipation technique enables milling time to be considerably reduced. Only minor adjustments to accelerators are required when curing lignin co-precipitates. The abrasion resistance of lignin-reinforced GRS vulcanizates is intermediate between the values for carbon blacks and inorganic pigments; other strength properties are comparable with those obtainable with carbon blacks—and at higher loadings are, in some respects, superior. Lignin also possesses the advantages of low specific gravity and light colour.

Sulphite process

The most important development in the sulphite pulping field is the erection of a mill, due to commence production in 1947, employing the magnesium bisulphite cooking process. This plant, the Longview mill of the Weyerhaeuser Timber Co., is the first commercial installation to operate the Tomlinson-Babcock and Wilcox process for the recovery of the cooking chemicals by the burning of the concentrated waste liquors to yield magnesium oxide and sulphur dioxide, from which the cooking liquor is reconstituted. The energy requirements of the mill are to be supplied by the combustion of the organic material in the waste liquors. If this process proves technically and economically successful, it will constitute a most important advance in the development of the sulphite process since, not only does it provide for recovery of chemicals and economy in fuel, but it also largely eliminates stream pollution.

R. S. Hatch[35] has compared the merits of the various bases which can be employed in the sulphite process, and has discussed the economics of recovering the chemicals used.

Although reference is frequently made to the value of sulphite waste liquor as a tanning material and the commercial use of this liquor in the leather industry, usually as accelerator to other tanning agents, is well known, fundamental knowledge on the subject is very incomplete. The U.S. Quartermaster General has now sponsored a long-term research involving a systematic study of the factors affecting the development of tanning material from sulphite waste. The first results of this investigation are given in a paper by M. A. Buchanan, R. M. Lollar and D. D. Niemeyer,[36] who have examined the properties of the liquors resulting from the pulping of aspen and spruce under conditions varying in severity from Mitscherlich to rayon cooks. The liquor from the spruce rayon cook gave the best result, but none of the liquors was very satisfactory as a tanning material and, indeed, those from the cooking of aspen were almost devoid of tanning properties.

E. O. Ericsson[37] has published details of the process employed on a commercial scale in U.S.A. for the production of alcohol from sulphite waste. Sulphur dioxide is removed by steam stripping and used in making up the cooking acid; 95% of the fermentable sugars are converted in 12 to 20 hours to give a yield of about 20 gallons of alcohol per ton of pulp. The economic prospects of an expansion of the production of sulphite alcohol by Pacific Coast Mills has been considered by R. D. Tousley.[38] The group of large mills in the State of Washington are potentially capable of producing about 15,000,000 gallons of alcohol per annum, but it is predicted that U.S.A. will soon revert to the position of having excess industrial alcohol capacity and West Coast producers would be at a disadvantage in being remote from the large consuming industries. Experiments based on German methods of producing fodder yeast (*Torula utilis*) from sulphite waste are described by E. E. Harris, M. L. Hannan and R. R. Marquardt.[39] By employing a continuous fermentation process, up to 79% of the reducing material present in the liquor can be fermented, but it is pointed out that in designing full scale plant special measures must be taken to deal with the tendency for excessive foaming to occur.

Other chemical pulping processes

The use of neutral sodium sulphite for the pulping of straw is not new, but the relatively high cost of this chemical, combined with the difficulty of evolving any simple recovery system, have hampered commercial developments. The prospect that supplies of a technical grade of sodium sulphite may be available, in U.S.A., at a reasonable price, has led S. I. Aronovsky, A. J. Ernst and H. M. Sutcliffe[40] to re-examine the merits of this chemical as a pulping agent for the production of straw-board. As a result of experimental cooks, in which sodium sulphite was used both alone and in various combinations with lime, it was found that cooking with 2% sodium sulphite plus 2% lime (calculated on moisture-free straw) gives the best results and yields exceptionally free pulp, with better strength characteristics and lower density than pulp from lime-caustic cooking. The authors consider that this pulping reagent is likely to have commercial applications.

Mechanical pulping

W. H. de Montmorency[41] has reported on the progress of experiments on longitudinal grinding. Compared with normal transverse grinding, longitudinal grinding involves a considerable drop in production rate and an increase in power costs. Longitudinal grinding also results in a reduction in freeness, some increase in tensile and bursting strength, and a reduction in tearing strength. The most notable effect on sheet properties is, however, the 10 to 20 fold increase in air resistance. In general, the advantages to be gained from present techniques for longitudinal grinding are not considered to outweigh its very serious disadvantages.

Bleaching

The multi-stage bleaching of sulphite and sulphate pulps has been the subject of study by O. S. Sprout and T. W. Toovey,[42] who have investigated the conditions affecting the optimum extent to which the chlorination stage should be carried. In bleaching procedures involving two chlorination stages, the reaction rate in the second chlorination is unduly prolonged, and wastage of unconsumed chemical occurs. A scheme is, therefore, proposed whereby the last chlorination is terminated after 5 minutes, and the liquor, containing excess chlorine, recycled to the first chlorination stage. No worthwhile benefit ensues from the insertion of an alkali extraction between the first and second chlorinations. The effect of secondary factors, such as souring, flash chlorination and washing, in sulphite bleaching has been dealt with by V. Oleskevich.[43]

The use of chlorine dioxide as a finishing bleaching agent, to produce the ultimate degree of brightness without loss of strength, continues to receive attention. For the final bleaching of Southern pine kraft pulp, already bleached by conventional methods to a G.E. brightness of 60–70, W. P. Lawrence[44] prefers to activate chlorite with hypochlorite, rather than with acid, as mill corrosion problems are thereby avoided. The p_H and the ratio of hypochlorite to chlorite must be adjusted so that the two reagents are consumed at approximately the same rate. G. P. Vincent[45] claims that a mixture of chlorine and chlorine dioxide is at least as effective as chlorine dioxide alone. Even when the chlorine content of the mixed gases is as much as 72% by weight, high brightness is obtained without any substantial loss in strength.

The bleaching of neutral sulphite semi-chemical pulps from 8 species of North American hardwoods has been studied by F. A. Simmonds and R. M. Kingsbury.[46] It is possible to obtain pulps of quite different characteristics according to the bleaching method employed. When single-stage bleaching with either hypochlorite or sodium peroxide is employed, very little delignification occurs and high yields (92–99% on the unbleached pulp) are obtained. Bleaching with 10% of chlorine as hypochlorite gives, in general, a slightly lower yield of pulps which are brighter, although of lower brightness stability, than those obtained using 2–3% of sodium peroxide. The maximum brightness attainable is about 75; strength is usually slightly improved. Multi-stage bleaching (chlorination, hypochlorite), on the other hand, produces pulps which are quite different in character, being fully bleached, lower in lignin content and of much improved strength. These bleached pulps, which are obtained in yields of from 55 to 85% on the wood, show rapid development of strength and grease-proofness on beating.

W. E. Stobo and J. K. Russell[47] consider that the sodium peroxide bleaching of groundwood pulps is industrially feasible, but emphasize the considerable difference in the response of pulps from different species of wood to this bleaching agent. Thus, whilst balsam fir and spruce pulps usually bleach satisfactorily, pulps from various pines scarcely show any improvement. Accurate control of p_H is essential, consistency should be as high as is convenient and temperature maintained between 35–40°. A brightness of at least 70 G.E. should be attainable.

Paper making

Beating.—W. Boyd Campbell[48] has briefly discussed the fundamental considerations involved in stock preparation. Strength development on beating is attributed to fibrillation; the slow drainage of beaten pulp is due to the friction presented to the passage of water over the increased external surface; and the increase in sheet density arises from the increased capillary forces acting on the smaller units produced by fibrillation. Finally, the theory is advanced that the bonding of contacting cellulose surfaces on drying is to be ascribed to crystallizing forces. It is postulated that all cellulose surfaces in water are covered with a layer of cellulose in partial solution and such surfaces unite on the evaporation of the water by crystallizing action.

A new beating technique has been described by F. North and H. Samuels,[49] who have experimented with the two-stage milling of pulps in a Werner-Pfleiderer type mixer. In the first stage the pulp is milled at 25% consistency, followed by milling for a further short period at 20% consistency in the presence of a viscous solution, preferably 10% on the weight of the pulp of gum ghatti.

Sizing.—The use of sulphuric acid for the p_H adjustment of hard waters is familiar to the paper industry. D. Price and D. D. Cameron[50] advocate that sulphuric acid should also be used for adjusting pulp slurries to $p_H 5$ and further recommend the precipitation of rosin size with alum-acid blends in preference to alum alone. Not only an economy in alum consumption but better sizing is claimed to result from this procedure. In a further paper by D. Price,[51] it is demonstrated that alumina has a detrimental influence on rosin sizing, as measured by the news ink test. Although not a normal constituent of the size precipitate, alumina may be present if alkali is introduced into the system. The advantage of using sulphuric acid for p_H adjustment is ascribed partly to the avoidance of the precipitate of alumina.

The possibilities of silicone resins (methyl silicone resin and oil types) as beater sizes have been examined by C. J. Bergendahl and C. E. Libby.[52] Satisfactory sizing can be achieved with very small percentages of silicones, but hard or impure water impairs the effectiveness of these materials. According to E. F. Horsey,[53] 5% beater additions of sodium carboxymethylcellulose followed by precipitation with alum improves both dry and wet tensile strength, increases air resistance and decreases opacity. Surface applications, *e.g.*, at the calender stacks, increase oil resistance and improve surface properties generally.

Drying.—The theoretical principles involved in the mechanical removal of water on the paper machine have been surveyed by W. Boyd Campbell,[54] who points out that more information is needed concerning the specific surface of pulp and its compressibility phenomena in order to provide a basis for the mathematical treatment of the subject. J. E. Sapp and W. F. Gillespie[55] have investigated the influence of tension during drying on paper strength and have found that, for hand sheets dried under uni-directional tension, the bursting strength of an unbleached kraft paper is a linear function of the extent of stretching. Tensile strength in the direction of tension passes through a maximum slightly higher than the tensile strength of the unstretched sheet and then diminishes. The properties of hand sheets dried under tension resemble those of machine-made paper more closely than do the properties of hand sheets made in the usual way.

Slime control.—The progress of the work being undertaken on slime control by the Institute of Paper Chemistry has been reported by J. W. Appling, J. F. McCoy and B. F. Shema.[56] Laboratory tests, with three typical organisms, were carried out, using four slime control agents, two of which (Lignasan and Merfenel A.) were based on organic mercurials, another (Dowicide G) on pentachlorophenol and the last on a quaternary ammonium detergent. The toxicity of these materials is shown to vary very considerably, according to the particular organism under test and the p_H conditions. Experience in the use of these agents during mill trials is described. C. Brown and H. A. Harrison[57] find phenyl mercury acetate effective for slime control and have standardized on a dosage of 1 oz. per 5 tons of paper.

High wet strength paper.—W. A. Wiltshire[58] has published data showing the influence of factors such as the type of stock employed, beating, sizing and loading on the production of high wet strength paper by the use of urea formaldehyde and melamine-formaldehyde resins. Detailed studies on the use of melamine formaldehyde resin for the manufacture of high wet strength paper have also been carried out by B. Steenberg.[59] This author shows that for the retention of the resin, which he regards as a rapid and irreversible reaction, to be a maximum it is necessary that both the stock and the resin concentrations should be as high as possible. Retention is also improved by beating and by using as high a p_H as is practicable. The presence of electrolytes in concentrations below the level at which they would cause flocculation of the resin also improves retention. It is, therefore, recommended that, before undertaking manufacture of melamine high wet strength paper, experiments should be undertaken to determine the influences of the mill water and the water extract of the pulp as well as the behaviour of the pulp itself.

D. J. Salley and A. F. Blockman[60] provide evidence, based on comparison of zero span and one inch length tensile strength determinations and sheet adhesion tests, to support the view that the wet strength effects, resulting from the beater addition of melamine-formaldehyde colloid resin, are due to its functioning as a water resistant fibre bonding agent. The treatment appears to produce only a relatively minor increase in ultimate fibre strength.

The repulping of melamine-formaldehyde treated paper, which is liable to be so resistant that there is a danger that any method sufficiently drastic to be effective will cause either chemical or mechanical damage to the pulp, has been investigated by D. D. Niemeyer and L. V. Forman.[61] Repulping with alum, at a temperature near boiling point, in a beater fitted with jets for the introduction of pressure steam between the roll and the back-fall, is recommended. By this method, completely defibred stock, of high freeness and good physical properties, can be produced from paper containing a high percentage of melamine-formaldehyde resin.

Analysis and testing methods

Raw materials.—TAPPI Tentative methods have been published for the determination of the specific gravity and the moisture content of pulpwood (T 18m–47)[62] and for the estimation of the cellulose content of wood (T 17m–46).[63]

Pulps.—The method used in the preparation of pulp samples for analysis may have an important effect on the values obtained. According to B. L. Browning,[64] differences as great as 2·7% in the alpha cellulose determination and 1·4 for copper number result from variations in the method of reducing the sample to a finely divided state. A mild treatment, such as hand tearing, is recommended. P. F. Cundy and M. M. Beck[65] have commented on the effect of the presence of the lignin in unbleached pulps on the alpha cellulose determination. The correction of the result, by the estimation of the lignin in the cellulose, is time-consuming and of doubtful accuracy. The initial delignification of the pulp with sodium chlorite is proposed. The lower results obtained by this procedure are attributed to the removal of hemicellulose materials which are otherwise protected by the lignin.

TAPPI suggested method T.230 sm-46[66] covers the determination of the cupriethylenediamine disperse viscosity of pulp. This method is much more rapid and more convenient than the cuprammonium method T.206m.

The drainage characteristics of groundwood pulps have been studied by S. A. Collicut.[67] A method of evaluating the unbeaten strength of unbleached chemical wood pulp described by N. S. Grant, O. A. Mason and H. F. Donnelly[68] has been found of value in assessing the strength of chemical pulps which are used in the mill with little or no refining. The pulps are treated in a British Standard disintegrator at 35°, a Canadian freeness of 600 being taken as the standard for the evaluation of the strength of the unbeaten pulp.

R. de Montigny and P. Zborowski[69] have carried out work on the relationship between pulp properties and their index of fibre length.[70] Whereas, for a given pulp, bulk and tearing strength are linear functions of the fibre length index, bursting strength and tensile strength are more complex properties in which slowness as well as fibre length is involved.

Paper testing.—A study of the stress-strain relationships of paper, and in particular creep and permanent set phenomena, has been carried out by B. Steenberg.[71] In a further paper, in collaboration with B. Ivarsson,[72] mathematical theories relating to the interaction of elastic and viscous proproperties are considered, and the extension of Eyring and Halsey's work to cover paper is discussed.

A TAPPI method (T.478 sm–46)[73] for the determination of the erasing quality of paper is now available. The method involves the mechanical abrasion of the specimen, under controlled conditions, with No. 180 silicon carbide cloth. The thickness of the paper is accurately determined, a design is ruled on it with standard ink and the number of strokes required to erase the design determined. The test paper is then re-ruled and the procedure continued until the paper is abraded through. The ease of erasure, *i.e.*, average number of strokes for the first, second, etc., erasure, average loss of thickness per erasure, tendency to fuzz and tendency to feather on re-ruling are reported.

Water vapour permeability continues to be a subject of considerable interest, and F. A. Paine[74] has reviewed the literature dealing with the permeability of organic membranes to gases and vapours. Factors affecting the measurement of water vapour permeability at low temperatures have been discussed, and methods for its determination described, by W. H. Aiken[75] and by S. W. Pierce and J. F. Helms.[76] The main source of variability in the determination of water vapour permeability at high temperatures and humidities, by TAPPI method T.464–45, has been traced by M. S. Renner[77] to variations in the conditions, *e.g.*, temperature in the laboratory housing the humidity cabinet.

V. V. Vallandigham[78] advocates the measurement of the oil absorption of paper by a photo-electric method as a useful means of assessing printing characteristics. The measurement of printing smoothness has been reviewed by S. M. Chapman[79] who describes a new apparatus for its determination which gives highly reproducible results correlating fairly well with printing tests carried out on a proof press. J. H. Bardsley and J. Monin[80] recommend the Carlsson printability test as a convenient method for evaluating newsprint.

For the evaluation of the fungicidal properties of treated paper and paperboard, B. F. Shema[81] proposes that *Chaetomium globosum* or *Aspergillus niger* should be used as the test organism, according to a prescribed procedure.

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PLASTICS

By MEMBERS OF THE PLASTICS GROUP

INTRODUCTION

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ONE of the serious difficulties facing the reviewer of high polymers, is that of devising a rational classification. Hitherto in these reports the headings " Thermoplastics ", " Thermosetting Plastics " and " Cellulosic Plastics ", have been adopted, but these have not proved entirely satisfactory. For example, doubly unsaturated materials such as diallyl phthalate logically should be included as thermosetting materials, whereas common sense suggests they are more nearly allied to the vinyl resins included as thermoplastics. Furthermore, certain plastics based on natural products other than cellulose were not easy to fit into the scheme. With the idea of reducing such anomalies the sectional titles have now been altered to " Polymerization Products ", " Polycondensation Products ", and " Plastics from Natural Polymers ". It is believed that such a classification will be more informative than the previous ones used, although it is realized that other systems have equal claims to consideration.

The amount of work on Plastics continues to grow so rapidly that it becomes increasingly necessary each year to make a selection which in some cases may be considered invidious. This year the policy has been continued of concentrating rather on important scientific and technical advances than on applications, numerous though the latter are.

The number of polymerization products made on an industrial scale is now so considerable, that it has only been possible to deal with investigations on the better known materials. Newly announced polymers, as yet only partially developed on a commercial scale, have of necessity been largely excluded. Polycondensation products have been dominated by the work on phenolic resins carried out by the schools of Zinke, Hultzsch, and von Euler during the past ten years or so. The review of this field is therefore largely concerned with these investigations, which have not hitherto received the detailed attention they deserve in these reports. Attention may however be directed to the growth of interest in melamine resins, polyesters and polyamides, polyurethanes (in Germany), and silicones, all of which possess a potential significance possibly out of all proportion to the space it has been possible to devote to them. In the natural polymer section cellulose derivatives continue to occupy by far the most important part, only protein products being thought worthy of inclusion in addition. The application to plastics of cellulose derived from wood pulp, particularly in Germany, may be considered of much interest in this section.

Perhaps the outstanding feature of plastics development is the rapidly growing realization of the importance of fundamental research. Such work is found desirable, not only in the planning and evaluation of new polymers, but also for a proper understanding of older materials. The development of new high softening dielectrics, such as polytetrafluorethylene, and the detailed examination of phenolic resins, provide excellent examples.

POLYMERIZATION PRODUCTS

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Polyethylene

The period under review has seen the appearance of a number of patents dealing with processes and process details for the production of polyethylene. Processes described include systems in which water is also present, with[1] or without[2] an organic solvent. Catalysts for the polymerization include oxygen, organic peroxides, and per-salts.[2] Dispersing agents are not required in the aqueous phase, their absence giving a product of better quality[3]. The amount of oxygen present in the ethylene monomer is kept within defined limits, otherwise inhibition of reaction occurs in the polymerization catalysed by a peroxy-compound.[4]

Carbon monoxide[5] should be kept less than 20 p.p.m. in the ethylene, to avoid rise in power factor of the polymer. Presence in the monomer of olefines other than ethylene (*e.g.*, propylene), and of saturated hydrocarbons, tends towards lowering of the molecular weight of the polyethylene.[6] Irregularities of yield and molecular weight are caused by hydrogen present in the ethylene more than 0·2% by volume,[7] and acetylene, which acts as a polymerization inhibitor, should be kept less than 0·1% in the monomer.[8] On the other hand, ethers containing up to 10 carbon atoms, preferably diethyl ether, may be present with advantage in the ethylene, as they produce an increased rate of polymerization.[9]

Amongst new or special catalysts for ethylene polymerization may be mentioned amine oxides,[10] N-halo compounds,[11] metallorganic compounds,[12] dialkyl peroxides.[13]

Polyethylene is soluble in the gas phase of the reaction mixture and du Pont[14] operate the polymerization process, exemplified as carried out continuously in a tubular reactor, so that all the polymerization product remains in solution in the gaseous reaction mixture, under the conditions of pressure and temperature obtaining in the polymerization zone. By addition of benzene to the reaction mixture, solubility of the polymer in the gas phase is increased and higher conversion of ethylene to polymer per pass permitted.

Where oxygen is used as catalyst, it is conveniently dispensed to the reaction system by dissolving it under pressure in the water phase before injecting the latter into the reactor. Where a tubular continuous reactor is used, this injection may occur at various points along the length of the reactor to give better control of the process.[15]

The use of a tubular reactor is the main claim in a patent by du Pont;[16] besides ethylene and catalyst, the system may include water and organic solvents, to promote agitation and scouring of the interior of the reactor. More specifically, water and benzene or chlorobenzene are the liquids employed,[17] and the mechanical properties of product thus prepared are improved if the water phase is treated with alkali to give a p_H of 11–14.[18]

Tough, soluble polyethylenes result from the polymerization of ethylene in presence of anhydrous benzene, employing a dialkyl peroxide catalyst, and either batch or continuous reaction.[19] The benzene should be free of thiophene and alkyl benzenes. The improved properties of the polymer are believed to be due to reduced chain branching.

A review of the history and development of manufacture of polyethylene[20] has appeared. On the process side it is concerned more with the production of waxy and macromolecular products by I.G., details of which have been made available by post-war investigations in Germany. Published details of American and British manufacturing procedures are few. Whilst the original British procedure involved the use of ethylene made from alcohol, American manufacturers are reported to be employing ethylene derived from fractionation of coke oven gas, or cracking of petroleum. The presence of 0·1–0·3% of acetylene in the ethylene used by the Germans (which was made in some cases by reducing acetylene) was stated to have had no noteworthy effect on the polymerization.

The effect of carbon monoxide present as impurity in ethylene on the power factor of polyethylene is discussed by W. Jackson and J. S. A. Forsyth.[21] Carbon monoxide is always present and copolymerizes with the ethylene. The presence of enolizable groupings—$CH_2.CO.CH_2$— in the polymer is suggested as a reason for the marked effect of carbon monoxide in raising the power factor.

The electrical breakdown value of polythene has been measured by W. G. Oakes,[22] with reference to thickness of the dielectric and temperature of measurement. A linear relationship was found between B.D.V. and thickness at 20°. Discrepancy was found between observed and calculated B.D.V.s when temperature varied (theoretically $F \propto {}^1/_T$). It is suggested that the discrepancy may be connected with changes in the crystalline phase of the polymer.

Polyethylene is being developed for uses other than the original submarine cable and high frequency dielectric applications. Its use as a wrapping film is discussed by J. W. Shackleton.[23] The film is chemically inert, odourless and tasteless, and of low density; although flexible to below −50°, it is not limp. Absence of exudable plasticizers excludes one form of contamination of wrapped materials. Tear resistance is good, and the material is not notch sensitive. Water absorption is negligible; water vapour transmission is very low and is not altered appreciably by sealing or creasing. Contact of the film with water scarcely affects the water vapour transmission. The film is a candidate for such uses as the storage of foodstuffs where retention of flavour and moisture are required. The flexibility at low temperatures makes the material of interest for wrapping foodstuffs for deep-freeze storage.

Sealing of polyethylene film cannot be carried out electronically because of the low electrical loss of the polymer, but a variety of heat sealing techniques can be used. The polymer has been extruded as wide, thin walled (0·0015–0·010in.) tubing,[24] which requires sealing only at the ends when used for packaging.

Techniques of compression and injection moulding polyethylene are discussed by J. W. Shackleton.[23] The large volume change at the crystallization point when cooling down calls for a special moulding cycle. The polymer becomes relatively fluid above its melting point, and flows easily, whilst it is highly stable at extrusion temperatures.

Polystyrene

The technically important synthesis of monomeric styrene consists in ethylating benzene in presence of aluminium chloride, and dehydrogenating the ethylbenzene to styrene. The first stage of the synthesis has been examined by A. W. Francis and E. E. Reid.[25]

Concluding that ethylation rates of benzene by ethylene in presence of aluminium chloride are the same for successive ethyl introductions, the low yields of monoethyl benzene obtained when working under normal conditions (low temperature and pressure) are attributed to reaction occurring in the small catalyst phase, in which the concentration of benzene is low. By using elevated temperature (and pressure) the catalyst phase expands throughout the system, giving more favourable conditions for production of monoethylbenzene. The yields of this are increased considerably and speed of operation is much greater. Panizo[26] finds the ratio of ethyl to polyethylbenzenes is affected by the amount of aluminium chloride present and reaches a maximum (3·1) with 5–6% of chloride, corresponding to the limit of solubility of the intermediate active product.

H. H. Smith[27] describes with flow diagrams the process, from ethylene to styrene via ethylbenzene, employed at the Los Angeles styrene plant.

Parallel to work on the reduction of crotonaldehyde to butadiene, Quattlebaum, Toussaint and Dunn[28] obtain styrene by deoxidation of acetophenone with ethanol.

On account of the small difference in boiling point between styrene and ethylbenzene, and the necessity for minimizing impurities in styrene to be used for plastics, the separation of the two materials, always present together in dehydrogenated ethylbenzene, calls for elaborate rectification plant. L. Berg, J. M. Harrison and C. W. Montgomery[29] have investigated the possibility of finding substances which will form azeotropes with either or both components of the above mixture, which azeotropes will widen the boiling point difference between the constituents and make fractional distillation easier. Azeotropes of such properties have been found. Their use, and regeneration of ethylbenzene for recycling, are investigated and discussed.

The thermodynamic properties of styrene monomer are given by K. S. Pitzer, L. Guttman, E. F. Westrum.[30] The heat of polymerization of styrene, *o*- and *p*-chlorostyrenes and 2:5-dichlorostyrene have been measured by L. K. J. Tong and W. O. Kenyon;[31] the heats of polymerization show an approximately linear variation with catalyst concentration, which is put down to existence of a side reaction with the peroxide catalyst (*e.g.*, oxidation of monomer).

The oxygen-produced induction period in the emulsion polymerization of styrene has been studied by I. M. Kolthoff and W. J. Dale.[32] The induction is explained by reaction of styrene molecules, activated by the persulphate catalyst, with oxygen to form peroxides. The induction period for a given amount of oxygen is inversely proportional to the persulphate concentration and no normal polymerization occurs until all oxygen has disappeared. Induction periods in styrene polymerization, caused by addition of quinones, are terminated when the quinone present has reacted with the benzoyl peroxide catalyst to give non-inhibiting products.[33]

R. S. Spencer and J. L. Williams[34] have examined the viscosities, in concentrated solution in toluene or *iso*propylbenzene, of a series of five technical polystyrenes giving a representative range of molecular weights. The data show reasonably good fit with Martin's equation

$$\frac{\eta_{sp}}{c} = [\eta]_{\mathrm{exp}} \, (K^1 \, [\eta] \, c) \qquad \begin{array}{ll} (\eta_{sp} & = \text{specific viscosity,} \\ {[\eta]} & = \text{intrinsic viscosity,} \\ c & = \text{concentration)} \end{array}$$

up to 20% concentration. For higher concentrations, the data can be represented adequately by Flory's relationship in which the logarithm of the viscosity varies linearly with square root of the weight fraction of polymer in the solution.

A process for doubly orienting extruded polystyrene sheet is described by Plax Corporation.[35] Rigid, doubly oriented polystyrene sheet is highly flexible compared with the brittle oriented sheet; its application in the production of cheap rigid transparent boxes made by a pressing process is outlined.[36] Thickness of the material can vary from 0·01 to 0·1 inches. The dimensional stability of the polystyrene makes close fitting tolerances possible.

Halogenated polystyrenes

The physical properties of polydichlorostyrene, and some applications, are reported on by L. E. Russell, J. D. MacMahon, and G. P. Vincent.[37] The outstanding feature of the resin is its high heat-distortion temperature.

Seven fluorinated styrenes have been synthesized, polymerized and copolymerized with other ethenoid compounds by G. B. Bachman and Miss L. L. Lewis.[38]

Polyvinyl chloride

Production of vinyl chloride by reaction of acetylene and hydrogen chloride on a catalyst of active carbon containing mercuric chloride has been modified[39] by suspending the catalyst in an inert liquid and bubbling the reagents through the mixture. The suspending liquid assists removal of the rapidly generated and large heat of reaction, eliminating the hot spots, obtained in a solid bed catalyst, which lead to volatilization and reduction of the catalyst.

A combination of the known process for production of vinyl chloride, by pyrolysis of ethylene dichloride, with use of the hydrogen chloride split off to react with acetylene over a mercury chloride—silica gel catalyst is patented by Bataafsche Petroleum Maatschappij.[40]

Vinyl chloride, pure, or containing traces of oxygen, can be heated for prolonged periods of time up to 100° without significant polymerization;[41] catalyst (benzoyl peroxide) is necessary to initiate this. Substituted styrenes, on the other hand, will give macromolecular polymers by purely thermal activation.

The association of polyvinyl chloride molecules in dilute solution has been studied by P. Doty, H. Wagner and S. Singer.[42] The apparent number-average molecular weight of fractionated polyvinyl chloride[43] obtained from osmotic pressure measurements, is independent of temperature over the range examined for the solvents *cyclo*hexanone and butanone; a high value is obtained at room temperature in dioxan, but this decreases above 40°. Weight-average molecular weights found from light scattering measurements on the solution in dioxan showed a much larger decrease between 28° and 63°. These results indicate a very broad, perhaps discontinuous distribution, instead of the simple continuous distribution expected for a fraction, also that the high molecular weight components break up into a low molecular weight species on heating. Sedimentation experiments confirm breaking up of the large molecules in dioxan solution on heating; for butanone solution, on the other hand, the same method confirms lack of change of distribution on heating. In dioxan, therefore, it is concluded that some of the molecules are associated into clusters which break up on heating and reform (slowly) on cooling. Light scattering dissymmetry measurements on dioxan solution indicate that the average molecule or cluster size does not greatly diminish on heating, and that the cluster and individual molecules are of about the same size. From the measured depolarization of scattered light in dioxan solution it is concluded that the clusters are more closely packed homogeneous particles than are the individual molecules.

R. F. Boyer[44] has examined the light transmission of coloured heat-degraded resins formed by loss of hydrogen chloride from vinyl-vinylidene chloride copolymers and finds fair agreement of the practical results with those calculated for polyenes distributed on a probability basis throughout the macromolecules present. Copolymerization with (non-reactive) monomer leads to much reduction of formation of long conjugated systems, due to the effect of the second component in breaking up such runs of double bonds.

Factors controlling loss of plasticizer from polyvinyl chloride compositions have been investigated by P. A. Small,[45] who has measured relative vapour pressures of a series of plasticizers, together with rates of their loss from compositions in an air stream and in high vacuum. The results show that where the rate of loss was low, diffusion in the gas phase controlled the rate, and the vapour pressures of the plasticizers were the determining factor. The relationships between gas- and solid-phase diffusion rates, plasticizer molecular weights and temperature are discussed.

Two papers by X. Thiesse[46] describe experiments on the incorporation of plasticizers into polyvinyl chloride by hot rolling of the plasticizer-polymer premix. It is found that elongation and tear strength of the moulded products reach a maximum as rolling time increases, this time depending only on rolling temperature and polymer molecular weight. The value of the maximum depends on rolling temperature, nature and proportion of plasticizer and polymer molecular weight.

The use of nitrile rubber (acrylonitrile-butadiene copolymer) as a non-migratory plasticizer for polyvinyl chloride is dealt with by M. S. Moulton[47] and Pittenger & Cohan.[48] The polymers are blended during manufacture and the product contains the polymers dispersed through the mass as particles of colloid dimensions. The material is supplied in sheet form, which gives a smooth band on a cold mill. For thermoplastic-type processing, heat-treatment at around 150° is necessary to give plasticization of this product. Calendering can be carried out at the moderate temperatures used for rubbers. On account of its nitrile rubber content, the material can be vulcanized. Advantages and disadvantages are stated.

Coloration of polyvinyl chloride with synthetic dyestuffs has been investigated by F. Gournay.[49] Chemical constitution of the dyestuff influences its affinity for polyvinyl chloride. Nitro-, most azoxy-, polyazo-, hydrazone, quinoline and sulphur dyes have poor affinity, whilst monoazo-, hydroxyquinone, and diphenylmethane dyes have fair to good; the best colouring agents are aminoquinones (anthraquinone derivatives), diphenylmethane derivatives (especially chlorine derivatives), phthaleins and quinoneimides.

Two reports have appeared[50] giving further information on the manufacture, properties and application of the Luvitherm film developed by I.G. This film is prepared by calendering hot-milled unplasticized polyvinyl chloride, sintering the weak film produced at high temperature (250°) to knit it together and seal up pores, and thereafter stretching at 110°, either very slightly for unoriented packaging film, highly (250%) in one direction for Magnetophon tape or wire insulation, or in two directions for high tenacity film (experimental only). Properties of this film—high strength, flexibility, stiffness, low water vapour and oil permeability, low cold crack—are very interesting. Non-employment of solvents, and the cheapness of the polymer used are attractions. The unstretched or doubly stretched film would appear to have special interest in the wrapping and packaging fields.

Polyvinyl fluoride

Preparation of vinyl fluoride, and its polymerization are described by A. E. Newkirk.[51] The monomer was prepared by addition of hydrogen fluoride to acetylene on a catalyst of mercuric and barium chlorides on active carbon. It could be polymerized by ultraviolet irradiation or by heating with peroxide catalysts, best in a solvent. The polymer has a high softening point (around 170°) and density (1·3). At elevated temperatures decomposition occurs with darkening of the polymer and evolution of hydrogen fluoride. The polymer is highly crystalline. Copolymers have been made with a number of other ethenoid monomers.

Polymerization of vinyl fluoride in presence of water and a peroxide catalyst is patented by du Pont.[52] The same firm claims the use of di*cyclo*hexylamine[53] or glyceryl monolaurate[54] as thermal stabilizer for polyvinyl fluoride.

Polytetrafluoroethylene

The monomer can be obtained[55] by non-catalytic pyrolysis of chlorodifluoromethane, in 80–90% yields. Other products of the pyrolysis have been identified.

Pyrolysis of polytetrafluoroethylene[56] leads exclusively to formation of simple substances C_2F_4 to C_4F_8. Reduction of pressure favours formation of C_2F_4, and at 5 mm. it is practically the sole product of the pyrolysis.

Polymethacrylic esters

A new process for methacrylic esters has been developed by A. Brothman and Associates.[57] Acetone is condensed with acetylene to give dimethyl hexinediol $(CH_3)_2C(OH)C\colon C(OH)C(CH_3)_2$, which is oxidized to hydroxy*iso*butyric acid (2 mol.). This on esterification and dehydration yields methacrylic ester.

Details have been given of the processes used by Röhm & Haas, of Darmstadt, for monomeric and polymeric methyl methacrylate.[58] Monomer was made by the cyanhydrin process. Polymerization techniques included casting between plate glass for sheet polymer. Granular polymer was made in aqueous dispersion of monomer, stabilized with either fine magnesium carbonate or dispersed methacrylic acid-methyl methacrylate copolymer. Some solution polymerization was also used for production of lacquer resins.

The polymerization of methyl methacrylate in aqueous emulsion has been studied by J. H. Baxendale, M. G. Evans, and J. H. Kilham.[59] Conclusions reached are: the rate of polymerization in the initial stages of the reaction is that which would be expected for polymerization occurring in the aqueous phase; from the rapid rate of disappearance of monomer from the non-aqueous phase—much greater than required by the polymerization which is proceeding—it is concluded that colloidal particles of polymer which have been formed are swollen by monomer, and the chief locus of chain growth is in this new phase. Termination is by union of two growing polymer chains; the rate of this decreases as polymerization proceeds due to the increasing viscosity of the system in which the chains grow. The increase in molecular weight of polymer produced in later stages, which would be expected from the above, has been confirmed.

Problems met with in the extrusion of methacrylates are dealt with by J. Bailey.[60] Formation of bubbles in the extruded material is a tendency of methacrylates. This may be due to evolution of dissolved gas or monomer from the hot and soft plastic as it leaves the die, or to vacuum pockets produced by shrinkage of the hot interior on cooling off. Methods of dealing with this are discussed. Extrusion in the normal manner results in distortion of the section by " puffing-up ", an effect due apparently to flow orientation and hot relaxation of the extruded methacrylate or styrene polymer. This effect leads to the need for use of dies of distorted cross section to compensate for it. The effect can also be circumvented by extrusion into moulds, or by continuous extrusion through long, lubricated dies. Defects in extruded plastics are dealt with, and the necessity for annealing emphasized.

Crosslinked polymers

Dialkyl phenylphosphonate,[61] introduced as a crosslinking resin monomer, forms copolymers of possible technical interest; the copolymer with methyl methacrylate may be adjusted in composition so as to have the same refractive index as glass. Glass cloth laminates produced with this have a high degree of transparency. Another advantage claimed for the copolymer is very good flame resistance.

The effect of copolymerizing methyl methacrylate with unsaturated (allyl, vinyl) methacrylates is described by B. N. Rutovskii and A. M. Shur.[62] Solubility is lowered, heat and scratch resistance increased.

A casting resin based on styrene, dichlorostyrene, divinyl benzene and fillers has been developed by the Bureau of Standards for high frequency electrical applications.[63] The shrinkage on polymerization is low, and heat stability good because of the cross linking.

The low pressure laminating industry is assessed economically in a symposium[64] in which resins, manufacturing methods and costs, properties and applications, are considered. The resins include crosslinking polyesters Continuous laminating is an application of outstanding interest.

Polymerization catalysis

There are indications that the use of organic peroxides, now general for monomer-phase polymerization of ethenoid compounds, may be attended by undesired secondary effects, especially on subsequent thermal processing. Crosslinking of polyethyl acrylate on heating with benzoyl peroxide has been reported,[65] whilst the thermal instability and unsatisfactory calendering and stretching behaviour of granular polymerized vinyl chloride may be due to the presence of residual benzoyl peroxide catalyst in the polymer.[66] It is thus of interest to note the appearance of information on polymerization systems in which the catalyst produces by its decomposition radicals unlikely to give rise to oxidative crosslinking or degradation of the polymer molecules, such as might be the case with the organic peroxides.

Harris, Marshall and Jarrett[67] have used benzyl hyponitrite to catalyse polymerization of methyl methacrylate. This catalyst is considered to break up into nitrogen, and benzyloxy radicals ($C_6H_5CH_2O$-) which are responsible for initiation of the polymerization process. The ester is effective at 30°, and the rate of polymerization at this temperature is about thirty times as great as with an equal concentration of benzoyl peroxide.

Substituted triazenes,[68] aliphatic diazocompounds,[69] and aromatic diazocompounds[70] are also applicable to polymerization of ethenoid compounds; their use is exemplified in the emulsion polymerization of butadiene—acrylonitrile mixtures. Their effect is apparently due to the free radicals formed on their decomposition.[71]

Aliphatic azo compounds of specified type are employed for the polymerization of ethenoid compounds, in an application[72] in which it is stated that, whereas organic peroxide catalysts destroy most dyestuffs dissolved in the monomer to produce a dyed polymer, the specified azo catalysts do not exert such effect. These catalysts are applicable to photopolymerization as well as thermally induced polymerization.[73]

Highly concentrated (*e.g.*, 90%) hydrogen peroxide has a much higher solubility in organic compounds generally than has water;[74] the polymerization-catalysing properties of hydrogen peroxide can be employed in homogeneous liquid-phase polymerizations by using the concentrated material. J. Delmonte,[75] in a series of comparative polymerizations of cross-linking polyesters with various catalysts, found 90% hydrogen peroxide the most rapid acting of those tried.

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POLYCONDENSATION PRODUCTS

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Phenolic plastics

The dominant feature of the phenolic resin manufacturing industry during 1947 has been the shortage of phenol. A great deal of work has been devoted to alleviating this shortage by partial substitution by cresol, lignin,[35] or in other ways. A general review of phenolic plastics has been published.[1]

Condensation and curing

Some important studies of the kinetics of the initial portion of the phenol-formaldehyde reaction have been made.[2] The initial reaction rate in the presence of acids was found to be proportional to the apparent hydrogen ion concentration as measured by the p_H. This suggests that hydrogen ions are the effective catalysts. The reaction was followed by measuring the rate of disappearance of formaldehyde, and also the rate of formation of water by using the Karl Fischer reagent. It may be noted that phenols cannot be estimated in the presence of phenol alcohols by bromination, since the hydroxymethyl groups of phenol alcohols are displaced to a varying degree by bromine.[3] At 80–100° under acid conditions the phenol-formaldehyde reaction is bimolecular, but in the acid reaction at 30° and the alkaline reaction at 40°, the formaldehyde disappearance is unimolecular indicating dialcohol formation, which is supported by the comparatively small amount of water formed under alkaline conditions. The initial formaldehyde addition with an alkaline catalyst is roughly twice as fast as the subsequent condensation to dihydroxydiphenylmethanes, while in acid conditions the condensation is probably more than five times as fast. A method of determining methylol groups by oxidation with iodine[4] should be of value for future kinetic studies.

Some thermochemical measurements on the phenol-formaldehyde reaction[2] have shown that the heat evolved during the reaction of the initial 30% formaldehyde is about twice as much under acid as under alkaline conditions. The heats evolved per mol. of formaldehyde reacted and of water evolved are 4·1 and 16·9 kilocalories respectively, indicating the much greater exothermicity of the condensation than that of the formaldehyde addition.

During the recent war, a considerable amount of work was done in Germany and in Sweden on the chemistry of the hardening of phenolic resols,[*5, 6, 7] that is, resins having reactive methylol groups in the molecule and therefore able to condense to resites without the addition of hardening agents. Although some of this work has been already reviewed,[8] most of it has not been mentioned in these reports, so a brief account is now given. A fuller review by the present author was published during 1947.[9]

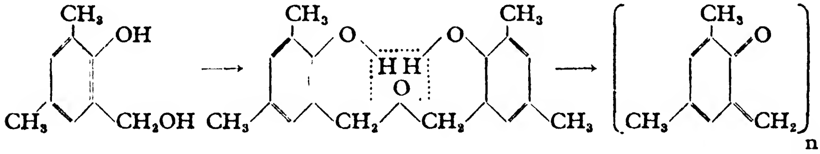
[*] "Resol" is preferred to "Resole" since the former fits in with the international "ol" termination for alcohols.

Hardening was studied by heating pure samples of various phenol mono- and dimethylols, mainly those of *o*- or *p*- substituted phenols. When devoid of reactive positions these give dimethylene ether-linked (-CH_2-O-CH_2-) polycondensates at temperatures of 110 to 180°, as was shown first by treatment of the products with cold hydrobromic acid when high yields of di(bromomethyl) phenols are obtained.[5, 6] Various dimethylene ether intermediates have now been isolated as pure compounds from the resinous products of heating phenol alcohols, even when these have free reactive positions as in *p*-cresol monomethylol[6k] and saligenin.[5h]

The ether-linked structures become unstable at temperatures around 180°, when complex secondary breakdown reactions occur. These reactions have been studied by a quantitative determination of the amounts of water and formaldehyde evolved on hardening at various temperatures.[5a, b, f, k, 6b, m, n, o] Dialcohols without free reactive positions usually lose one mol. of water per mol. at 150°, and then, for example, 0·6 mol. more water and 0·2 mol. of formaldehyde at about 200°.

The high temperature secondary stage of hardening of resols is accompanied by a number of changes in physical properties. The colour changes from yellow to dark brown[7a] and the resin gradually becomes insoluble, and while partially soluble the hydrobromic acid reaction shows that only the soluble portion contains ether links.[5a, 6m]

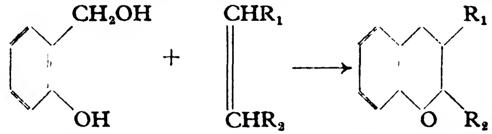
The liberation of less than one molecule of formaldehyde per ether link during this hardening at 200° was at first attributed to cross-linking reactions by some of the formaldehyde,[5f, 10] but it appears more probable that breakdown involves the phenolic hydroxyl groups and leads to polymeric quinone-methides.[6h, o, 7a]



Several dimers and trimers of quinone-methides have been isolated from the products of the hardening of various phenolmethylols.[5k, n, 7b, c, d] They may be formed directly without the intervention of ether-linked structures.[6o] The *o*-quinone-methides tend to polymerize directly to stable polymers either by 1 : 2 polymerization of the vinylidene group or by 1 : 4 polymerization through the oxygen atoms as well, and the products are extremely inert to acids and bases, give no colour with ferric chloride, and cannot be acetylated or methylated.[6h] The *p*-quinone-methides, however, tend to dimerize to dihydroxy-stilbenes which undergo simultaneous oxidation and reduction to dihydroxydiphenylethanes and to stilbene-quinones which may then polymerize further.[6k, n] Some mono- and di-aldehydophenols and various alkylphenols are also formed[5f, h, i, 6o, 7h, 10] perhaps by rupture of primary ether chains or perhaps from quinone-methides.

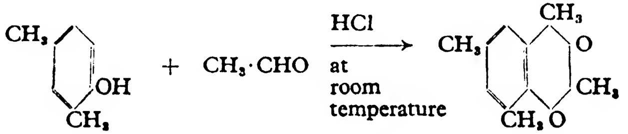
As a summary of this work, a typical phenol alcohol without reactive positions such as *p*-cresol dimethylol may be considered. At 140° it gives a resin containing methylol groups and both methylene (-CH_2-) and dimethylene ether (-CH_2-O-CH_2-) bridges and having a molecular weight of about 5,000. The methylene bridges are quite stable, but the ether links are only stable up to about 160° and at 170–230° considerable quinone-methide formation occurs, with, particularly above 200°, polymerization to inert resins, and some formation of aldehydophenols, diphenylethanes and stilbene-quinones.[5n, o, 6j, n, 7f]

This work on the hardening of resols has indicated the importance of the phenolic hydroxyl groups in that they take part in the formation of quinone-methides. Other reactions involving the phenolic hydroxyl groups which may have some importance in resin hardening are the Hultzsch reaction of *o*-phenol alcohols with unsaturated substances to form chromans.[11]



and the formation of benzodioxans from phenols and aldehydes[5j, m, 6p, r]

e.g.,



The benzodioxans break down on strong heating giving vinylphenols and, presumably by the Hultzsch reaction, chroman derivatives.[6p, r]

Further evidence that the phenolic hydroxyl groups are involved in the high temperature secondary hardening reactions is provided by the fact that the *p*-toluenesulphonic esters (through the phenolic hydroxyls) of phenoldimethylols without free reactive positions harden to resins containing only ether linked chains even at 200°.[5b, f] The formation of thermoset resins from phenols with a substituent in the *o*- or *p*- positions has recently been cited[12] as evidence for cross-linking reactions taking place through the hydroxyl group, but the dominance of *o*- and *p*- reactions has also been stressed,[13] even if other reactions occur under extreme conditions.

The infra-red absorption spectra of phenolic resins should be of value in correlating structure and physical properties. Some recent studies of phenols and derived resins are of particular interest in the 3μ. region. The normal sharp band of the hydroxyl group at 3615cm.$^{-1}$ is displaced to 3100–3400cm.$^{-1}$ when hydrogen bonding occurs. The experimental results indicate different degrees of hydrogen bonding in different novolaks and resols. In contrast with the phenols, the resins continue to show the hydrogen bond absorption found in the solid state when examined in carbon tetrachloride solution, suggesting that the majority of the hydrogen bonds may be intramolecular. This result accords with the inactivity of the resins towards diazomethane, and it is possible that during curing the intramolecular bonds are opened and replaced by intermolecular association. Such a change might cause a considerable increase of melting point and hardness apart from that caused by any new primary bond cross-links. It has been noted that in hardened phenolic resins only a comparatively limited amount of cross-linking can be present, because of the limited freedom of rotation of the primary methylene-bridged chains.[15]

The change of the electrical conductivity during the cure of phenol and resorcinol resols provides a valuable means of comparing different curing conditions,[16] as had been previously noted.[17] The property appears to be sensitive to the internal molecular rearrangements of resite formation with the accompanying decrease in the mobility of included ions. Phenol formaldehyde casting resins were cured at 80° and 90°, when complete cure took 15–20 days, compared with the 3–5 days used commercially. This shorter cure may give less brittle products but the castings will continue to cure slowly at room temperature over a period of months and the accompanying contraction may be the cause of crazing. The minimum molar formaldehyde to phenol ratio for complete cure is 1·2.

The dielectric properties of phenolic resins have been studied over a wide range of frequency.[18] When novolaks are cured with hexamine the dielectric constant and the power factor at low frequencies increase probably because of retained ammonia. At above 10^5 cycles per second the power factor decreases owing to reduced possibilities of dipole orientation. The freedom of the phenolic hydroxyl groups to oscillate in the electric field may be reduced by introducing alkyl groups in the *p*-position of the phenol or into the aldehyde, or the hydroxyl groups may be benzylated. All these modifications decrease the power factor and dielectric constant, but these improved electrical properties are obtained at the cost of reduced rates of cure and hardness, and a compromise must be adopted in practice between electrical properties and moulding characteristics.

Manufacture and processing

The processes involved in resol manufacture have been examined,[19] and for obtaining a product of a predictable polycondensate condition it is recommended that the same property, such as specific gravity, viscosity or refractive index, be used both for determining when to stop the reaction and when to stop the vacuum evaporation.

An important technical development in the moulding of phenolic plastics is preheating with live steam.[20] This method is simpler and cheaper than high frequency preheating and is much quicker than air-oven preheating. It also gives more rapid cure because the absorbed water acts as a plasticizer and improves the flow properties. The process is being adopted by a number of moulders and is of particular value for transfer moulding because of the good flow properties.

Nylon fabric has been found to be a valuable filler for phenolic moulding materials, giving mouldings with excellent chemical resistance.[21]

Testing

An interesting paper on the relation between impact and flexural tests[22] for phenolic and other moulded plastics, and indeed for all materials, presents a theoretical treatment indicating that rupture under dynamic stress-strain conditions results from the same basic considerations as those governing static or flexural failure. Impact strength is evaluated in terms of stress rather than energy using a high speed electronic technique, and impact loading is thus shown to be a special case of static loading with almost identical stress-strain conditions. Consequently, a static flexural test may be used to evaluate the energy required for fracture and the notch sensitivity, and is in fact sufficient to predict service characteristics of essentially brittle materials under both static and impact loading.

Applications

In using phenolic resins as cold-setting wood adhesives, the fairly high acidity necessary for hardening is a disadvantage.[23] Considerable use is now being made of resorcinol-formaldehyde resins as wood adhesives since these will harden at a neutral p_H.[24] The effect of p_H on the setting of such resins has been examined[25] and it is found that the *m*-dihydroxy structure is essential for obtaining products which will harden at room temperature at p_H 7, while conductivity measurements show that more complete cross-linking occurs on curing at p_H 7 than at a lower p_H.[16b] These resorcinol-formaldehyde resins are also used for bonding leather and plastics. For stable laminating varnishes the absence of free formaldehyde is important.[26] Wood flour, walnut shell flour and various proteinaceous materials may with advantage be used as fillers and extenders.[27]

Very strong bonding between dissimilar surfaces has been achieved by using a combination of a phenol formaldehyde resin and a polyvinyl acetal.[28] This combination gives stronger bonding than either component alone. The same type of product may also be used as a wire enamel.[29]

Ion exchange resins are now being put to a wide range of uses, some of which have been recently reviewed.[30] Another important new use developed by the U.S.A. Atomic Energy Project is for the separation of the rare earths.[31] Selective elution with ammonium tartrate or citrate at a controlled p_H is used and several rare earths have now been separated in kilogram quantities. The method is now being used for separating valuable radioactive isotopes from among the fission products produced in the uranium pile. Other new uses[32] include the estimation of trace elements in plant material,[33] and the use of acid regenerated cation exchange resins in place of mineral acids as catalysts for organic reactions.[34] For this latter purpose the resin can be removed by filtration without neutralization, can be used repeatedly without reactivation, and can be used in the presence of acid-sensitive materials.

Lignin and cashew nut shell oil resins

The various natural complex phenolic raw materials, such as lignin and cashew nut shell oil continue to receive attention in the patent literature, but only occupy a small place in industrial production. The present shortage of phenol may however encourage the development of these products. Thus a lignin phenol-formaldehyde resin was produced in Germany during the war,[35] and a lignin paper laminate " Arborite " is now being produced in Canada using lignin obtained from alkaline pulp mills and incorporated with the paper during the beating stage of paper manufacture.[36]

Furan resins

In addition to phenol-furfural resins, furan resins have been produced commercially during the last few years in America.[37] These are derived from furan raw materials without using any phenolic substance. Resins made by the acid condensation of furfuryl alcohol with formaldehyde or furfuraldehyde have been described in the patent literature.[38] These resins have good chemical resistance and are used for corrosion resistant coatings, and as binders for abrasive particles.

Amino-plastics

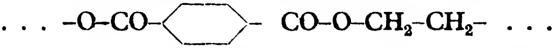
Little work has been done recently in this field which includes both amine- and amide- aldehyde resins. The kinetics of the initial reaction between urea and formaldehyde in aqueous solutions have been studied.[39] The free formaldehyde was determined by the acid liberated on reaction with hydroxylamine hydrochloride. At the fairly high concentrations used and at p_H around 6 and between 30 and 60°, the reaction is mainly of the slow bimolecular type, with monomethylol urea as the sole product.

The direct manufacture of melamine from urea by heating under pressure with ammonia has been described.[40] Melamine- and urea-formaldehyde adhesives have been reviewed,[41] with emphasis on the advantages of incorporating melamine or resorcinol with urea to improve the water resistance. Urea and melamine resins are used for improving the wet strength of papers,[42] but for making resin-impregnated compressed wood the U.S. Forest Products Laboratory have concluded that urea resins have no advantage over phenolic resins while they have a number of disadvantages.[43] Urea formaldehyde resins modified with ethylene glycol have been used for embedding and preserving biological specimens in Germany.[44] A new use for a urea formaldehyde polycondensate, " Uraform ", is as a slow acting nitrogen fertilizer particularly for soil-less culture.[45] A urea to formaldehyde ratio of about 1·3 is used and the product is sufficiently insoluble not to leach out easily.

Polyesters

Simple unmodified polyesters are of small importance to the plastics industry if judged by the quantities manufactured, but they continue to be extensively used for scientific studies of the relations of structure and properties. An example of this is an important paper[46] on the gelation and thermosetting of linear polyesters by heating with free radical producing agents such as benzoyl peroxide.

As regards the production of linear polyesters of commercial value, the development of " Terylene " is a notable advance.[47] This polyester is made by ester interchange between methyl terephthalate and ethylene glycol, to give the microcrystalline polyethylene terephthalate or " Terylene " melting at about 250°



A similar product can be made by the self esterification of *p*-hydroxymethyl benzoic acid. Terylene appears to be of primary value as a fibre forming polymer, but like nylon it may be of use for monofils, films and mouldings.

Solutions of unsaturated polyesters in monomers, such as vinyl acetate or styrene, polymerize to infusible resins on heating with a catalyst and are used for low-pressure laminating[48] since no volatile by-products are evolved on setting. Electrical conductivity studies of these resins show that curing continues for several days after it is apparently complete.[16b]

Saturated alkyd resins containing free hydroxyl groups such as those from adipic and phthalic acids reacted with glycerol, trimethylolpropane or hexanetriol may be cross-linked by mixing with di*iso*cyanates. Lacquers, coatings, adhesives and laminating resins of this type were manufactured in Germany during the war.[56, 58]

Polyamides

A number of papers on the chemistry of polyamides or nylons have been published.[49] The polyamides were purified by dissolving in cresol and precipitating with alcohol. Their molecular weights were determined by end-group titration with dilute acids and alkalis. With equimolar proportions of hexamethylenediamine and adipic acid, terminal amino groups predominate owing to decarboxylation of the adipic acid during the reaction, but the molecular weight is a maximum and falls off rapidly with departure from equimolarity. A comparable fall off in molecular weight occurs on heating preformed polyamides for 4 hours at 240° in cresol solutions with adipic, or stearic acids or with hexamethylenediamine.

The hydrolytic degradation of polyamides with subsequent repolymerization provides a useful method of recovering scrap nylon.[50]

In Germany, in addition to the hexamethylenediamine adipate type of nylon, considerable quantities of poly-ε-aminocaprolactam were made from phenol through *cyclo*hexanone oxime, which was rearranged to caprolactam with sulphuric acid.[51] A possible alternative to phenol as basic raw material for nylon is furfural, derived from pentosan-containing vegetable raw materials,[52] and converted through tetrahydrofuran, 1:4-dichlorobutane and adiponitrile to adipic acid and hexamethylenediamine.[53] The latter part of this synthesis has been operated commercially in Germany, using tetrahydrofuran made from acetylene and formaldehyde.[54]

The use of nylon in the plastics moulding industry may be by direct injection moulding or as a filler in phenolic compression moulding materials.[21] The former use requires some modification of the injection-moulding nozzle because of the low viscosity of the melt at temperatures just above its rather sharp melting point.[55]

Polyurethanes

Closely related to nylon are the polyurethanes which were developed in Germany during the war.[56] These are typically made by the interaction of organic di*iso*cyanates and dialcohols, and contain the linkage -NH-CO-O- as compared with the -NH-CO- of the polyamides. The reaction is somewhat intermediate between those of polymerization and polycondensation and has some of the advantages of both, such as the production of hetero-chains and the absence of low molecular products. The *iso*cyanates are made[56, 57] by treating diamines with phosgene, but it should be noted that either the diamine or the dialcohol may be reacted with phosgene followed by reaction with the other component

$$\text{-R-NH}_2 \xrightarrow{\text{COCl}_2} \text{-R-N-CO} \xrightarrow{\text{-R}'\text{-OH}} \text{-R-NH-CO-O-R}'\text{-}$$

$$\text{R}'\text{-OH} \xrightarrow{\text{COCl}_2} \text{-R}'\text{-O-CO-Cl} \xrightarrow{\text{-R-NH}_2} \text{-R-NH-CO-O-R}'\text{-}$$

The di*iso*cyanate manufacture is carried out in chlorobenzene in the absence of water. The polyurethane is formed simply by adding the di*iso*cyanate to the molten dialcohol or to a solution of it in chlorobenzene. The reactants used are principally hexamethylene diamine derived from phenol, mixed 2:4 and 2:6 toluene diamines derived from dinitrotoluene, and 1:4 butanediol made from acetylene and formaldehyde.

Polyurethane resins resemble nylon with somewhat better water and acid resistance and smaller contraction on cooling making them valuable for injection moulding, but they are stiffer and have lower melting points. They may be extruded as bristles for which purpose their stiffness and low water absorption are advantageous. Other products include toothbrushes, dentures, foamed insulating boards and artificial leathers.

Di*iso*cyanates will react with most compounds containing hydroxy or amino groups, and will therefore cross-link hydroxyl-containing polymeric materials, such as alkyd resins with free hydroxyl groups, polyvinyl alcohol, including partially hydrolysed polyvinyl acetate, phenolic resins and cellulose derivatives, but not cellulose itself. This reaction permits di*iso*cyanates to be used as curing agents for alkyd resin lacquers, films and adhesives and as tanning agents for leather. The adhesives may be used in ethyl acetate solution with urea as hardener at temperatures as low as 0°, and very strong bonds to wood, metal or plastic surfaces are obtained.[58]

Silicones

Extensive academic studies on these materials continue to be carried out, including comparisons of cyclic and linear polymers,[59] and the derivation of intrinsic viscosity molecular weight relationships.[60]

Full reviews of the silicone polymers or organopolysiloxanes have been published.[61] The polymers are made by the hydrolysis of alkyl or aryl chlorosilanes, which are obtained either by reaction of silicon tetrachloride with Grignard reagents or unsaturated hydrocarbons under pressure, or by direct treatment of silicon copper alloys with alkyl or aryl halides. The polymers may be oils, elastomers or rubbers according to the degree of polymerization and the amount of cross-linking. For cross-linked polymers the alkyl to silicon molar ratio must be less than two. As this ratio is raised from one, the methyl silicone polymers change from hard brittle resins to flexible and more durable resins, their density and refractive index fall, and the curing temperature is raised. With higher alkyl groups the resins become progressively softer, more flexible, slower curing and more easily oxidized, so that an ethyl silicone is similar to a methyl silicone, which has a higher proportion of alkyl groups. The mixed aryl alkyl silicones are tough resins suitable for insulating and protective coatings. Besides many varnish and coating uses silicone resins are being used as mould release agents and for bonding glass fabric laminates. Most of these applications depend on the great heat resistance of silicones, but another use as water repellent surface films depends on their very high contact angle to liquid water and their low solubility in water. For waterproofing, the silicone may either be applied as a lacquer or a surface containing hydroxyl groups may be exposed for a few minutes to the vapours of mixed methyl chlorosilanes, or better, to acetoxyalkylsilanes,[62] since this avoids the harmful liberation of hydrochloric acid.

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PLASTICS FROM NATURAL POLYMERS

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The opening paragraphs of last year's report on " Cellulosic Plastics "[1] might be repeated here, for circumstances have not changed in such a manner as to permit notable advances to be made during the period now under review. The effort to secure an early improvement of British export trade has been necessarily focussed upon short-term policy, since facilities for introducing new processes and products have been restricted in spite of the evident desirability of ultimately providing materials which will compete with the new products of overseas manufacture. P. S. Adamson,[2] in a paper delivered in February, 1946, has reviewed recent developments in cellulosic plastics and indicates what might be looked for if plant and materials could be made generally available.

Census of Production figures for this country are still not available, so that United States statistics must again form the basis of an assessment of the activity in the industry. The Bureau of Census data[3] reveal a continuous fall in the production of cellulosic plastics from nearly 13 million lb. in January to about 5 million lb. in July, and a slight recovery through August to 6·3 million lb. in September, the latter figure being little more than half the average monthly figure for 1946, although, except in July, the total production of all plastics and synthetic resins has been running above the average for 1946. Simultaneously, the output of cellulosic plastics in relation to total plastics production has fallen from 16% to 9%, and in relation to total production of thermoplastic materials from 34% to 21%. These figures emphasize the need for greater freedom for the British industry to implement its plans for development in the technology of production and utilization of cellulosic plastics if these materials are to withstand the competition of the increasing variety of plastic materials now being developed abroad.

Cellulosic plastics

Information on the production methods employed for cellulose derivatives in German plants appears in a number of the reports made by Allied investigating missions.[4] The general principles of these methods are well known, but the details disclosed are of importance to the development of the industry. Circumstances in Germany have led to the exploration of raw materials other than cotton, and there has been considerable success in the employment of wood pulps. Both hard and soft woods have yielded useful esters for plastics and for textile purposes, by solution esterification using sulphuric acid catalyst in acetic acid[4a] and in methylene chloride[4b] and using zinc chloride catalyst in acetic acid,[4c] and by fibrous acetylation using perchloric acid catalyst in benzene,[4d] but the general opinion of the German technicians appears to be that cotton linters are preferable to the best of wood pulps. Wood has also been employed as the source of cellulose for ethyl and benzyl cellulose production.[4e] The information given in these reports, though in large measure now published for the first time, hardly represents recent progress and it is therefore not now more full discussed.

Several publications relate to the activation of cellulose for esterification and other purposes. A 4 : 1 mixture of 85% formic acid and zinc chloride is said to exert a specific action on celluloses, and the connexion between the reactivity of cellulose and its structure has been investigated.[5] Although cellulose hydrate is fairly rapidly dissolved in the mixture, native and moderately degraded celluloses are hardly dissolved unless the actual structure of the native fibres is attacked as by mineral acids in acetic acid; mechanically deformed (milled) native fibres may dissolve completely. Homogeneous acetylation is not materially facilitated by milling, but chemical treatment does assist it, though not, it is suggested, simply owing to dissolution of pentosans since the effect is also observable with linters, which are free from pentosans. G. Centola[6] has reacted cellulose with formaldehyde to obtain products containing 0·10% of combined formaldehyde. The cross-linkages so formed result in inferior products after acetylation, mercerization and xanthation; indeed, the formaldehyde-treated cellulose strongly resembles wood cellulose of poor reactivity. The reactivity of cellulose, as determined by its dye-receptivity, is increased by partial oxidation with 0·12–0·15 M-periodic acid at room temperature for more than 24 hours.[7]

An investigation by Mlle. G. Petitpas[8] into the mechanism of catalysis by perchloric acid in the acetylation of cellulose using acetic anhydride in benzene solution reveals that the catalyst initially forms an addition compound with the cellulose, but is gradually displaced from this as acetylation proceeds. In the absence of acetic anhydride, most of the perchloric acid itself forms an ester with the cellulose.

The importance of high acetyl-value cellulose acetate as regards flexibility at low temperature and resistance to plastic flow at elevated temperature is illustrated in a Patent specification[9] which claims sheets, films, and other articles made from such a plastic base with 1–2·5 parts of plasticizer for each part of the acetate, without the addition of a resin.

Following the announcement of cellulose propionate plastic by the Celanese Plastics Corporation towards the end of 1945,[10] cellulose acetate propionate plastic has now been made available by the Tennessee Eastman Corporation.[11] It is reported to possess higher impact strength and dimensional stability but lower resistance to organic solvents than the same Company's cellulose acetate plastic and less odour and slightly higher solvent resistance than its cellulose acetate butyrate plastic.

The developing interest in higher fatty acid esters of cellulose is responsible for a number of patents in this field. C. J. Malm[12] claims to reduce the degradation of cellulose in producing acetate propionates and acetate butyrates containing at least 25% of the higher acyl radical by destroying the moisture content of pre-treated cellulose by reaction with propionic or butyric anhydride in the presence of 0·2–2% of sulphuric acid, and then esterifying at a temperature not exceeding 33° under the influence of additional sulphuric acid. Mixed fatty tri-esters of cellulose may be stabilized,[13] combined sulphuric acid being removed, by treating the reaction mixture containing the ester (*e.g.*, cellulose acetate butyrate of butyryl content 15–19%) with aqueous lower fatty acid to hydrolyse the anhydride, without precipitating the ester, in the presence of sufficient of an alkaline alkali-metal salt to neutralize only part of the sulphuric acid catalyst, and then maintaining a temperature of not less than 48° but not high enough to cause degradation. A property of acetate propionates and acetate butyrates of cellulose is brought out by a proposal[14] to apply them with about 30% of their weight of solvent plasticizer (*e.g.*, toluenesulphonamide) as an additional thin coating on light-coloured fabrics pre-coated with cellulose nitrate; by this means the products are protected against permanent staining by foodstuffs, cosmetics, etc.

A useful collection of equations, nomographs and charts for inter-converting data on weight percentages and numbers of acyl and hydroxyl radicles in cellulose acetate propionate and acetate butyrate has appeared.[15]

Cellulosic 2-aminoethyl and 2-cyanoethyl ethers have been produced[16] by reacting cellulose acetate or acetate propionate with ethyleneimine, and cellulose or cellulose acetate with acrylonitrile. Films of cellulose acetate cyanoethyl ethers may be cast from low viscosity solutions or moulded from highly swollen gels.

J. Chédin[17] has determined the rates of nitration of cellulose between 0 and 40° in two baths of different concentrations, and finds the results most accurately represented by assuming that there are two consecutive reactions having different velocity coefficients. He proposes a reaction mechanism involving first, the rapid nitration of hydroxyl groups at the surface or in the disordered regions of the fibres, probably controlled by diffusion of nitric acid through the bath to the surface, and then the nitration of hydroxyl groups within the crystalline micelles, brought about by penetration of nitric acid and water molecules into the micelle and apparently continuing until the nitric acid concentration within the micelle falls to 70%.

Three papers on the resistance of cellulose derivatives to oxidation were contributed to the meeting of the American Chemical Society in the autumn of 1947, but of these only abstracts[18] are available at the time of writing. Thermal degradation of ethylcellulose at 69–90° is due to atmospheric oxidation and is determined by the rate of formation of peroxides, whose decomposition leads to loss of ethoxyl radicles and reduction in viscosity. The induction period is shortened by the presence of chain reaction initiators, and lengthened by typical antioxidants. The resistance of ethyl cellulose to the action of ultra-violet light is related to its ease of oxidation, and apparently the same antioxidants inhibit the ultra-violet catalysed oxidation. Oxidation of cellulose acetate by pure oxygen at 160° shows an induction period, which is roughly correlated with the standard heat-stability tests, and after that period becomes quite rapid. Initially, the number of chain breaks is proportional to the amount of absorbed oxygen, but subsequently the rate of chain-breaking falls off sharply. Traces of acetone in cellulose acetate films cause a small but rapid initial oxidation, and as little as 0·001% of free sulphuric acid reduces the induction period and catalyses the oxidation. The observation that oxidation of secondary cellulose acetates yields products in which the combined acetic acid approaches that of the triacetate leads the authors to deduce a course for the reaction, though its nature is not stated in the material published so far. A general discussion of the factors affecting the degradation of cellulose acetate and acetate butyrate in coatings has been published by W. S. Penn.[19] Factors affecting the weathering of ethyl cellulose compositions have been analysed;[20] water-insensitive plasticizers capable of screening ultra-violet light and a little phenolic antioxidant result in very good stability.

C. J. Malm and C. L. Crane[21] claim to stabilize cellulose ethers by converting them to a smooth plastic mass with methyl ethyl ketone containing sufficient water to prevent solution and then adding acid and mixing until a constant p_H value of about 7 is obtained. The properties and methods of manufacture of cellulose ethers, including ethyl, benzyl, methyl, hydroxyethyl and carboxymethyl ethers, have been reviewed by S. Sönnerskog,[22] who also discusses possible improvements in the manufacturing processes.

Ethyl cellulose compositions for protecting metal articles are described by H. C. Phillips, P. F. Robb, and the Hercules Powder Co.[23] Fully esterified cellulose acetate butyrate[24] has found application as a melt-coating base for paper when the butyryl content is about 50% and the intrinsic viscosity about 0·9 in acetone, and the effect of plasticizers and waxes on the physical characteristics of the coated product is discussed.

Solvents and plasticizers

As usual, a large number of substances have been suggested for use as plasticizers, among which are esters of 3-acetyl-3-alkylpentane-1 : 5-dicarboxylic acids,[25] and 4-*tert.*-butylphenoxyalkyl esters of lower fatty acids.[26] Aryl morpholidophosphates[27] are said to promote fire-resistance while conferring good flow characteristics. Activity of the I.G. Farbenindustrie research groups in this field is evidenced in captured documents; mention may be made of the imides of di- or polycarboxylic acids in which the hydrogen atom of the imido group is replaced by the residue of an esterified mono- or polycarboxylic acid (*e.g.*, phthalimidoacetic ester and succinimidoacetic *iso*butyl ester),[28] and the cyclic acetals of tetrahydrofurfural with polyhydric alcohols.[29] The employment of dimers and trimers of α-methyl-*p*-methylstyrene as plasticizers for ethylcellulose is stated[30] to lead to compositions possessing particular merit where high dielectric strength and low power loss are essential.

High molecular weight saturated or unsaturated linear polyesters plasticize certain cellulose acetate butyrates, greatly reducing brittleness without unduly softening the cellulose ester;[31] the compositions may be rendered infusible and insoluble by cross-linking, *e.g.*, by heating in the presence of benzoyl peroxide or other agent generating free radicles.

Allied to work reported last year,[32] P. Clement[33] has examined various ternary systems of dry cellulose acetate, chlorinated hydrocarbon gelatinizing agent and triphenyl phosphate at 20°, and finds that gel formation corresponds to a chemical action of the chlorinated solvent on the acetyl groups. He reports that preferential absorption of the solvents occurs and that in the presence of mixed alcohols a chlorinated hydrocarbon-alcohol complex is probably formed.

A comparison of the physical properties of 49 plasticizers and of their mixtures with nitrocellulose[34] reveals no general correlation between the viscosity of the plasticizer and the rheological and elastic properties of plasticized films. Recommendations are made concerning plasticizers giving good flexibility at low temperatures, high tensile strength at high elongation, and good elongation at the yield point. The greatest solvent power for nitrocellulose, as shown by resistance to blush, is possessed by di-2-ethylhexyl phenylphosphonate and the least by pentaerythritol tetra-acetate. A discussion of suitable solvents and plasticizers for use with various cellulose derivatives is given by Y. Talvitie and E. Makinen.[35]

Methods for the identification of plasticizers have been amplified by the observation[36] that various polar plasticizers may be characterized by the curves of their dielectric loss factor and dielectric constant against temperature at high radio frequencies. Such curves may be determined with less than 0·3 ml. of the substance over a 100° range within an hour, and the method may be employed for routine testing of identity and purity, usually by merely covering a range of about 10° around the loss factor peak. The paper includes data showing variations among data for different plasticizers and describes the experimental technique and details of the apparatus involved. A modified Zeisel method has been described by P. W. Morgan[37] for determining ethylene glycol and its ethers and esters, including polyethylene ethers, and hydroxyethyl cellulose, making use of their property of yielding ethyl iodide and ethylene on boiling with hydriodic acid. The iodide is absorbed in alcoholic silver nitrate and the ethylene in bromine-acetic acid mixture.

Ultra-violet light absorption may be used to determine certain inhibitors present in polymer compositions.[38] The absorption of phenyl-β-naphthylamine, for example, shows up strongly in the near ultra-violet against the background absorption of polymer solutions in chlorinated hydrocarbons and the concentration may be calculated, from readings on a spectrophotometer, by means of an equation derived in the paper.

Protein plastics

Protein plastics have been reviewed by S. H. Pinner,[39] who considers their production and general properties with special reference to attempts to counteract the high water absorption of casein plastics and the undue length of the formalizing treatment. A patented waterproofing treatment for casein-formaldehyde plastics[40] involves the action at the boil or (more slowly) at a lower temperature of a solution of a quinone or of tannic acid in a moderate swelling agent for the plastic, *e.g.*, water or a lower alcohol. The treatment at the boil appears to be effective only if continued for several hours. Another treatment[41] calls for coating or depositing synthetic resins such as phenol-formaldehyde, polystyrene or polyvinyl ester resins by formation *in situ* on preformed casein-formaldehyde plastics. Interesting thermoplastic materials are reported[42] as obtained by acylating proteins with higher fatty acid chlorides, *e.g.*, palmityl and oleyl chlorides. Increasing degrees of acylation reduce the water absorption and improve the effect of 6–12% of water on the plastic flow, but decrease the tensile and flexural strengths. The best overall combination of properties results from a moderate degree of acylation followed by a short treatment with formaldehyde, though formaldehyde-hardening is unnecessary with palmitylzein. Acylated caseins cannot be safely used at above 130° but they have a greater degree of plastic flow at that temperature than some commercial thermoplastics at the higher temperatures at which they are normally worked.

Another protein-base plastic material, described by O. Huppert,[43] is produced by boiling prolamines, particularly zein, with an aqueous solution of an α-thiocyano-acid to produce a thermoplastic powder which, after mixing with 0·01% of formaldehyde at room temperature, can be moulded and then cured.

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RESINS, DRYING OILS, VARNISHES AND PAINTS

BY MEMBERS OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

NATURAL AND SYNTHETIC RESINS

BY E. A. BEVAN, B.Sc., F.R.I.C.
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Messrs. Beck, Koller and Company (England) Limited

No startling discoveries have been made in this field during the period under review. I.C.I. Ltd. have claimed the use of aryl glycide ethers[1] in styrene compounds and of a small proportion of formaldehyde[2] in the preparation of polyvinyl chloride. For similar purposes Wingfoot Corporation in the U.S.A. has claimed the use of zirconium or thorium salts[3] and nitrates, nitrites, or sulphides.[4] R. E. Reeves and J. E. Giddens[5] have suggested the stabilization of cellulose nitrate by simple treatment with dilute aqueous ammonia.

The recently published work of W. Reppe[6] on the employment of acetylene under high pressures in various new syntheses may possibly throw new light on the manufacture of materials for the synthetic resin industry.

Amongst new uses suggested for synthetic resins is the estimation of trace elements in analytical work.[7] Various synthetic resins have been tried out by the American National Bureau of Standards for sealing metal castings.[8] Of these, the best two proved to be a phenolic resin and a styrene polymer, the former being superior in respect to resistance to high temperatures and pressures, and the latter in respect to resistance to thermal shock and petroleum products.

Natural resins

D. A. Sutton[9] has described the preliminary work of himself and his colleagues on the chemical constitution of Congo copal.

The use of shellac in the preparation of oil-varnishes continues to be the subject of much work. B. S. Gidvani and N. R. Kamath have now found[10] that whereas only 60% of the hydroxyl groups of shellac are esterified when it is heated alone with linseed fatty acids, if the heating is carried out in the presence of quinoline complete esterification can be effected. The employment of shellac naphthenate as a plasticizer for alcoholic varnishes and lacquers has been claimed by H. H. Bassford.[11]

The polymerization of rosin by various methods has been described during the past few years. C. A. Braidwood and A. G. Hovey[12] now claim a much-improved process involving the use of fluorosulphonic acid as the catalyst. A rosin ester having a high melting point and low saponification value has been described,[13] in the preparation of which rosin is first converted into an alcohol by reaction with paraformaldehyde, this alcohol then being esterified by means of acetic acid. Another interesting series of resins of the rosin ester type, capable of producing flexible coatings, has been claimed by the Hercules Powder Co.[14] These are adducts derived from the interaction of monohydric alcohol esters of rosin and glycol maleate type esters. Tall oil has become more widely known and used on account of the shortages of vegetable drying oils of recent years. This has been employed not only in its simple esterified form and in conventional varnish formulations, but also in alkyd resins. B. Widegren[15] has shown that when the pentaerythritol esters of tall oil are used as the bases of varnishes, those derived from the tall oils with high rosin contents give poor water-resistance, and those with low rosin contents exhibit slow drying and poor weathering.

Alkyd resins

Owing to the shortage of phthalic anhydride brought about by the inadequacy of naphthalene supplies, some work has been carried out in the U.S.A. with a view to producing phthalic anhydride from petroleum.[16] Processes for the manufacture of aliphatic dicarboxylic acids have been claimed by British Celanese Ltd.[17] by the electrolysis of cyclic oxides, and by Du Pont de Nemours & Co.[18] from olefinic or hydroxyl monobasic acids by heating with carbon monoxide and water under pressure. Another new series of dicarboxylic acids of particular interest has been produced by H. A. Bruson[19] by the reaction of ketones with acrylonitrile. Of other polycarboxylic acids, the use of the adduct of *cyclo*pentadiene and fumaric acid in alkyds has been claimed by the I.C.I. Ltd.[20]

With regard to the polyhydric alcoholic reactant in alkyd resin production, Shell Development Co. have claimed[21] the use of polyallyl and polymethallyl alcohols made by the oxy-polymerization of the monomers. A terpenic alcohol has been made by J. P. Bains[22] by reacting pinene with formaldehyde under pressure.

Numerous modifications have been suggested, one of the most interesting of which is that of H. J. Wright and R. N. Du Puis.[23] This involves the replacement of some of the ester linkages in the alkyd with amidic linkages by the use of glyceryl monoamine. Other modifications claimed include the incorporation of organic silicols[23] and hydroxyacetic acid.[24] The former is said to result in high resistance to acids, alkalis, and heat-treatment, and the latter to effect fast drying. Modification by co-polymerization still offers numerous possibilities. Pittsburgh Plate Glass Co.[25] have co-polymerized drying-oil modified alkyd resins with *cyclo*pentadiene, and American Cyanamid Co.[26] claim the use of triallyl phosphate as the co-polymerizing agent.

Alkyd resins of the linear type have attracted a great deal of attention, in particular those from glycols and *para*-dicarboxylic aromatic acids, for use in filament manufacture.[27] In such linear polyesters cross-linking must be avoided, and it has been claimed[28] that this can be done by the inclusion of a small amount of an ester of a compound containing trivalent phosphorus. A linear alkyd having exceptionally good plasticizing properties in polyvinyl esters and made to a high molecular weight from sebacic acid and 1:2-propylene glycol has been claimed by Resinous Products and Chemicals Co.[29]

Phenol-formaldehyde resins

C. E. Little and K. W. Pepper,[30] in investigating the influence of p_H on the setting of phenolic resins, have shown that whilst most phenols yield resins setting by hydrogen ion catalysis, those from 1:3-polyhydric phenols will set under neutral conditions and are presumably catalysed by hydroxyl ions. 3:5-Xylenol has been suggested as a curing accelerator for phenolic resins.[31] Resorcinol-formaldehyde resins, on account of their cold-setting properties, are still the subject of a large number of patents. G. E. Little has described the preparation of stable resins of this type by a two-stage process, employing a very low formaldehyde ratio in the first stage,[32] and states that these resins are most stable at a p_H of about 3.[30] Another patent[33] claims the use of anhydrous methyl alcohol as a stabilizer.

Bakelite Corporation[34] have prepared a styrene-modified oil-soluble phenolic resin by co-polymerization.

An iodometric method for the determination of methylol groups in phenol-formaldehyde resins has been described by H. S. Lilley and D. W. J. Osmond.[35]

Amino resins

Improvement in the toughness and flexibility of urea-formaldehyde resins is claimed by A. A. Drummond and J. W. Dorling[36] by incorporating some succinamide in the reaction mixture. Confirmation of the belief that in the preparation of urea-formaldehyde-butanol resins the butanol reacts with the methylol urea polymers to form relatively heat-stable ethers has been made by B. M. Shaw,[37] who has determined the butoxyl contents of cured films.

In the past melamine has been produced mainly from dicyandiamide, but Du Pont de Nemours & Co.[82] now claim a process whereby urea, ammonium cyanate, or ammonium carbamate are heated with ammonia under pressure.

A process has been described by the I.C.I. Ltd.[38] for the manufacture of varnish resins by the interaction of etherified melamine-formaldehyde resins with phenol-formaldehyde resole condensation products in which two *ortho* and *para* positions are unsubstituted by the formaldehyde.

Polyamides

The number of patents taken out relating to polyamides still continues to be very high. I.C.I. Ltd.[39] have vulcanized polyamides of an unsaturated character with sulphur. Du Pont de Nemours & Co. have claimed processes for the preparation of polyamides suitable for use as surface coatings whereby linear polyamides are reacted with formaldehyde.[40] These products have also been alkoxylated with alcohols.[41]

Methods for the determination of the molecular weight of various types of nylons have been described by J. E. Waltz and G. B. Taylor.[42] Other work relating to the molecular weight of polyamides has been carried out by V. V. Korschak and V. V. Golubev,[43] who have investigated the diminution effect of an excess of any of the reactants upon the molecular weight.

Other polyamide type resins have been made by heating monoarylamino-carboxylic acids or their amides,[44] and by the polymerization of *N*-carboxy-*a*-amino acids.[45]

Ethenoid resins

It is in this field that by far the greatest part of recent research work has been concentrated. The production of coloured ethenoid resins by polymerizing in the presence of coloured chelate compounds of certain metals has been claimed by J. W. Coates and J. W. C. Crawford.[46]

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DRYING OILS, DRIERS, AND VARNISHES

By J. H. GREAVES, B.Sc., A.R.I.C.

Younghusband, Barnes and Company Limited

In the period under review special attention may be drawn to reasonably direct methods for conjugating double bonds, to theories dealing with polymerization and formation of hydroperoxides and, from the Reports on German Industry, to the preparation of alkyd-like coating materials by reacting diglycerides from linseed oil with di*iso*cyanates.

For many reasons, not the least being the expansion of the linseed crushing industry in the Argentine,[1] investigations into cultivation of drying oils in the British Empire,[2, 3, 4] and especially linseed in Britain,[5] continues with sustained vigour. In the Empire, progress, although marked,[3] has been perhaps less rapid[2] than may have been hoped, while in this country there is as yet insufficient experience to judge soundly between the view that the English summer is normally insufficient for the necessary ripening of the seed and the view which is confident concerning indigenous linseed oil.

Tall oil.[6]—In Germany[7] distilled tall oil has been produced by continuous vacuum steam distillation in a vertical tower, a residue being drawn from the bottom. This oil[8] was used chiefly for varnishes of the alkyd type, esters being formed with a mixture of whatever polyhydric alcohols happened to be available. Experiments[9] on varnishes prepared from a modified phenolic resin with pentaerythritol esters of tall oils of varying resin content have shown that a low resin content impairs drying and gives poor weathering results while high resin content impairs water resistance.

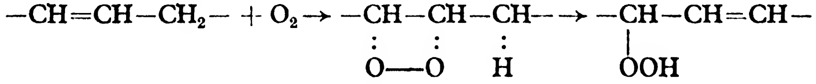
Other oils.—Stillingia oil,[10] similar to linseed oil as regards constituent fatty acids, although botanically related with tung oil, is noteworthy because of appreciable quantities now being imported for the first time. Although plants of the genus *Impatiens*[8] give a fast drying oil, it is likely that collection would provide insuperable difficulties, as the seed capsules burst prematurely and distribute the seed. The shrub *Tetracarpidium conophorum*[4] gives a drying oil of iodine value 200–205, the linolenic acid content being 64–68%. The seed tissues are rich in lipase, causing rapid formation of free fatty acids *in situ*, but it is possible, and necessary, to destroy the enzyme by heating at 100° for some hours.

Modification of oils.—It has been known for some time that during hydrogenation of triglyceride oils using a nickel catalyst, there is a tendency for some double bonds to change their position in the fatty acid chain, but the production of much conjugation (estimated by ultra-violet spectrophotometry)[11] from isolated double bonds by such means is a new departure. By heating linseed oil at 180° for 3 hours with a specially prepared nickel catalyst supported on a closely specified carbon as much as 30% conjugation[12] can be produced. These conjugated oils body more rapidly,[13] but some varnishes made from them provided films which were on the whole no improvement. Other methods for producing conjugation are by heating with magnesium silicate[14] and iodides.[15] Although such processes appear to be more economical and practicable than the alkali method, it is unlikely that artificially conjugated oils[16] will quickly be manufactured in quantity while tung oil, naturally conjugated, is readily available at a price not much greater than that of linseed oil. Alkali and water resistance of oils is claimed to be improved[17] by heating with resorcinol and other polyhydroxyphenols.

The addition reaction of alcohols with *iso*cyanates to form urethanes has been used in Germany to provide modified drying oils stated to have exceptionally good properties. A typical preparation[18] is to heat linseed diglycerides with 15% chlorophenylene di*iso*cyanate in toluene solution at 150° for half an hour. Among the claims[8] for these urethane oils are quick dry to tack-free films hardening through rapidly, and high resistance to water, dilute acid and alkali. In this country one sample has been judged[8] to equal a good quality medium oil length alkyd.

Oxidation and polymerization

The *a*-methylene hydroperoxide theory of Farmer[19] has given rise to interesting consequences. Hilditch and the Liverpool school[20] have suggested that the hydroperoxide may be produced by a mechanism initiated by a molecule of oxygen reacting at a double bond, whereupon the following changes take place:—



$$-\mathrm{CH}{=}\mathrm{CH}{-}\mathrm{CH_2}- + \mathrm{O_2} \rightarrow -\underset{\overset{\vdots}{\mathrm{O}}}{\mathrm{CH}}-\underset{\overset{\vdots}{\mathrm{O}}}{\mathrm{CH}}-\underset{\overset{\vdots}{\mathrm{H}}}{\mathrm{CH}}- \rightarrow -\underset{\overset{|}{\mathrm{OOH}}}{\mathrm{CH}}-\mathrm{CH}{=}\mathrm{CH}-$$

It is seen that the formation of the hydroperoxide involves the movement of a double bond one position along the carbon chain. This theory therefore readily and elegantly explains the production of conjugation during oxidation of esters of linoleic and linolenic acids. Investigations[21] into the kinetics of the oxidation of ethyl linoleate by oxygen have established the reaction mechanism; in the early stages the only product is ethyl linoleate hydroperoxide, which then undergoes thermal decomposition to start the chain reaction. The oxygen content[22] of a sardine oil has been found to fluctuate markedly when blown with air at 105°, in contrast with the steady rise associated with linseed oil. This behaviour may be connected with formation of highly reactive molecules from poly-unsaturated acids.

A general theory[23] has been proposed to account quantitatively for heat polymerization and gelation (or non-gelation) of non-conjugated vegetable oils, with particular reference to linseed, soya-bean and olive oils. This is based on polyfunctionality considerations, with special attention to the distribution of linolenic, linoleic and oleic acids in the triglycerides, rotational hindrance, relative accessibility of the α and β positions in the glyceryl radical and the influence of *cis-trans* isomerism. When an oil is bodied[24] at a constant temperature it has been shown that the equation connecting the viscosity η_1, at a time t_1, to the viscosity η_2 at time t_2 is $\log \eta_2 - \log \eta_1 = K\ (t_2 - t_1)$ where K is a constant dependent on the oil and temperature. The effect of sulphur dioxide on the polymerization of linseed oil is merely to increase K. A note[25] on modern theories of polymerization, both brief and general in nature, draws attention to the most important recent work.

During technical polymerization of drying oils, when quantities up to several tons may be maintained at a temperature of 300° for some hours, disposal of the fume is most important. A method[26] has been described where the fume is introduced tangentially into a cylinder in which it is wetted with water droplets sprayed from a central manifold. A simpler means[27] of wetting the fume appears to be that where the fume is drawn along by and with a jet of water directed into a Venturi tube.

Miscellaneous

Tall oil has been found to provide drier metal soaps[28] which compare reasonably well with naphthenates. Octoates[29] and hydroxynaphthenates[30] have also been described.

Two causes of blooming of varnish films, namely craters (formed by water droplets when the film is still soft), and a crystalline deposition, have been shown to be inadequate to cover all phenomena and two additional types,[31] " syneresis " bloom, due to displacement of oil by water in the gel structure, and " wrinkle " bloom, due to swelling by water, have been postulated.

During water estimations with the Dean and Stark apparatus trouble is often encountered because drops of water adhere to parts of the glass. This can be remedied[32] by rendering the surfaces water-repellant by treatment with a silicone. In an iodometric determination of peroxide the necessity for exclusion of oxygen[33] has been emphasized, and acetic anhydride[34] has been suggested as the solvent for the oil.

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SOLVENTS

By H. L. HOWARD, B.Sc., A.R.C.S., M.I.Chem.E., F.R.I.C.

THE flood of American patents on the production of aromatic hydrocarbons from petroleum appears to have abated, but the economic position continues to develop and, according to J. M. Weiss,[1] the day of industrial aromatics based solely on coal carbonization is fast drawing to a close. Toluene will probably remain in fair supply, but the prices of benzene and naphthalene are expected to rise, as the supply is not likely to meet the increasing demand, due largely to the increasing requirements for the production of phthalic anhydride and other synthetics.

Synthetic diterpenes.—From a review of the literature, G. Swann[2] comes to the conclusion that the dimerization of terpenes by means of acid results in a single linkage between the two terpene nuclei, and that it is unlikely that these substances possess the condensed nuclear structure commonly found in the natural diterpenes. The possibility of utilizing this means of synthesising products related to the sterols is therefore precluded. It is possible that enhanced drying properties may be obtained in some cases by dehydrogenation, and that hydrogenation would yield colourless non-polar solvents of low volatility.

Solvent power.—According to E. H. McArdle[3] the reduction in the viscosity of a solution by the addition of solvent is proportional to the number of molecules present and not to the volume of thinner added. Deviation from this relationship is held to indicate a change in the character of the dispersion and may be taken as a measure of the dispersion power of different thinners. R. B. Pollack[4] compares hydrocarbons from petroleum and coal tar, and discusses the effect of constitution on solvent power. The known high solvent power of tetrahydrofuran is the basis of a claim for the use of this solvent in cellulose lacquers by W. Reppe, O. Hecht and F. Oschartz.[5]

Nitro-compounds.—The systematic development of new nitro-compounds in connexion with explosives may continue to yield solvents of considerable utility. A. E. W. Smith, C. W. Scaife and H. Baldock, with Imperial Chemical Industries,[6] claim the production of dinitroparaffins admixed with nitroalkyl alcohols and their esters by reaction of olefines with nitrogen peroxide in ether solution. New nitro-ethers are claimed by A. Lambert and Imperial Chemical Industries[7] from nitro-olefines and alcohols, while nitro-thioethers are produced under analogous conditions employing thio-alcohols, according to R. L. Heath, A. Lambert and Imperial Chemical Industries.[8] Nitro-ethers, nitro-thioethers or nitroparaffins in turn, when reacted with the appropriate nitro-olefines, yield the corresponding substituted dinitroparaffins, according to A. Lambert, H. A. Piggott and Imperial Chemical Industries.[9] A. McLean and Imperial Chemical Industries[10] claim the production of nitro-derivatives of polyhydric alcohols by reacting nitroparaffins with paraformaldehyde in the presence of alkali using glygerol as solvent.

Analysis.—A simple method for analysis of naphthalene-tetralin-decalin mixtures, resulting from the hydrogenation of naphthalene, is described by W. J. Cerveny, J. A. Hinkley, Jnr. and B. B. Corson.[11] The heat of nitration of the mixture depends only on the decalin content, and the amount of naphthalene is found from the cloud point of the mixture, tetralin being obtained by difference. An accuracy of about 1% is claimed. For the determination of allyl groups in polyallyl ethers and esters, H. M. Boyd and J. R. Roach[12] find the rapid Wijs method (4 minutes) satisfactory and give comparative figures for other halogen addition procedures. In general, the Kaufmann bromide addition method yields results about 10% low.

D. O. Hoffman and M. L. Wolfrom[13] describe apparatus suitable for the micro-determination of methoxy and ethoxy groups in acetals and volatile alcohols. The method is based on a modification of the Viebock and Schwappach method[14] and yields results comparable in accuracy with those obtainable for less volatile substances. Using the Cox vapour pressure chart (which permits the complete vapour pressure curve to be obtained from determinations at two pressures only), H. S. Nutting and L. H. Horsey[15] describe a graphical method of predicting the effect of pressure on azeotropic systems, and in a subsequent paper[16] by L. H. Horsley, plots are given for 45 systems for which the data is available. Nomographs for converting distillation temperatures and pressures of low boiling hydrocarbons to boiling point at atmospheric pressure are described by F. M. Nelson, F. R. Brookes and V. Zahn.[17]

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CELLULOSE ESTER AND ETHER LACQUERS

By H. L. HOWARD, B.Sc., A.R.C.S., M.I.Chem.E., F.R.I.C.

ATTENTION continues to be directed towards obtaining higher solid content in cellulose lacquers, whereby the number of coats required is reduced and a substantial saving in volatile solvent effected. The " melt-coating " technique, in which solvent is eliminated altogether (see Report 1946, p. 420), is the subject of further investigations by C. J. Malm, M. Salo and H. F. Vivian,[1] who find that cellulose esters containing increasing amounts of higher acyl groups show progressive improvement in the required properties. Cellulose acetate is unsuitable, temperatures in excess of 200° being necessary for application. Complete replacement of the acetate by propionate just fails to meet the requirements, whereas mixed acetate-butyrates containing over 35% butyrate are satisfactory. The optimum is considered to be reached at about 47% butyrate, with a hydroxyl content below 0·1 group per anhydroglucose unit. Compatibility with plasticizers is satisfactory, and the potential commercial uses for such materials are discussed. They are of value in the surfacing of papers, and compositions incorporating resins show promise in the manufacture of laminates from cloth, wool and metal webs. Ternary diagrams relating the desirable properties of resins used in cellulose nitrate lacquers for the surfacing of papers are provided by L. G. Little and C. D. Ender.[2]

Methods for the stabilization of mixed cellulose esters by means of magnesium carbonate incorporated into a dough of cellulose ester-water pulp, to which acetone or other water miscible solvent is added, are the subject of a patent by C. J. Malm and C. L. Crane.[3] An interesting observation on the stabilization of cellulose nitrate is reported by R. E. Reeves and J. E. Giddens.[4] It is well known that long beating or boiling with dilute alkali is necessary, and a variety of bases, *e.g.*, metallic hydroxides, carbonates, etc., as well as alkyl amines have from time to time been proposed and used. Cold dilute ammonia, however, produces an almost instantaneous effect, and the fact that it differs so materially from other bases in this respect appears to have escaped prior mention in the literature. Explanation of its action is the subject of a subsequent paper by the same authors,[5] who find that stabilization takes place most rapidly at high p_H, under conditions where the undissociated ammonia content is high. Apparently, the residual acidity is held in the fibres as an acid sulphate of cellulose, which the ions of ammonium and other bases are unable to penetrate sufficiently to effect neutralization. Methods for the preparation of cellulose esters containing longer fatty acid chains (stearyl, decoyl) are claimed by G. D. Hiatt and C. L. Crane.[6]

Formulations for brushing cellulose lacquers possessing non-lifting characteristics and good brushability are put forward by J. J. Coughlan and R. F. Wint,[7] in which cellosolve acetate (35%) is the main solvent and turpentine or Amasco F. (45%) the chief diluent. Suitable viscosity is stated to be 160/175 centipoises to prevent brush-drag with drying times of about 90 min. The Philadelphia Paint and Varnish Production Club,[8] reporting on the incorporation of Perbunan 76–65A in cellulose lacquers, reach the conclusion that, although such materials could be employed, they are without significant advantage either in clear or pigmented finishes.

Plasticizers.—The Chicago Paint and Varnish Production Club[9] report that exceptional acidity is developed by pentaerythritol esters and di-*n*-amyl carbonate exhibits high volatile loss. Tributyl citrate and di-(2-ethylhexyl)-sebacate incorporated in clear films applied over white panels and exposed in the fadeometer did not discolour in 216 hours' exposure. Various plasticizers did not notably affect ultra-violet transmission down to a wavelength of 360μ., but at 290μ. there was considerable variation. P. A. Small,[10] investigating the conditions in which plasticizer loss occurs in vinyl chloride plastics, considers that, under conditions where service life is reasonably long, the controlling factor is the rate of diffusion in the gas phase, which in turn is dependent on the vapour pressure of the plasticizer. However, at high temperatures or reduced pressure, it is quite possible for the rate of diffusion in the solid phase to become the controlling factor, in which case the viscosity of the plasticizer will become dominant. With low plasticizer content (below 20%) these latter conditions may operate at relatively low gas velocities. Under such conditions it is possible for the surface layers to be seriously depleted of plasticizer in a relatively short time. M. A. Elliott, A. R. Jones and L. B. Lockhart[11] draw attention to the characteristic curves exhibited for dielectric loss factor and dielectric constant by plasticizers of the polar type when plotted against temperature at high radio frequencies, and suggest that such technique can be employed for routine tests in the identification of plasticizers. The action of triphenyl phosphate on cellulose acetate in the presence of gelatinizing agents, such as chlorinated hydrocarbons, is considered by P. Clement[12] to be due to the preferential adsorption of the chlorinated hydrocarbon, and that, in the presence of alcohols, a chlorinated hydrocarbon-alcohol complex is formed.

An approach to the evaluation of plasticizers, whereby the properties of the polymer-plasticizer complex may be correlated with significant properties of the plasticizer itself is suggested by H. Jones and E. Chadwick.[13] Employing the concept of a liquid-liquid mixture and selecting co-ordinates such that linear relationship substantially obtains, they are able to relate viscosity with the physical and mechanical and sometimes with the electrical properties of the compositions. It is pointed out by W. P. Moeller and N. Taylor[14] that, in the case of ethylcellulose plastics, adsorbed moisture behaves as a plasticizer. They suggest that, by addition of water as a third component in the system, the manner in which the plasticizer is held might be investigated. The effect produced is the same irrespective of whether the plasticizer is of the solvent or non-solvent type, which would favour a mechanism of the polymer chain spacing type[15] rather than the polar attachment hypothesis.[16] As, however, solvency tests are carried out at high temperature, whereas the properties of the plastic are generally determined at room temperature, due consideration must be given to the possibility that plasticizers of the solvent type may in fact behave as non-solvents at the lower temperature.

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PIGMENTS AND PAINTS

By L. J. BROOKS, A.R.I.C.

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DURING the year under review a series of notable conferences have made important contributions to the progress of pure and applied chemistry. Besides the Centenary of the Chemical Society and the XIth International Congress, these include: The First International Technical Congress of the Paint and Allied Industries in Paris, the Silver Anniversary Convention of the Federation of Paint and Varnish Production Clubs held at Atlantic City, and the Buxton Conference of the Oil and Colour Chemists' Association, on paint performance and specification.

The year also concludes the final reports of the B.I.O.S., C.I.O.S., and F.I.A.T. It seems clear that there were few striking developments in the German paint industry. Nevertheless, the pressure of economic necessity demanded a degree of exhaustive invention in the search for substitutes and alternatives. This tendency, to a greater or lesser extent, has affected the progress of the industry as a whole over the past few years, sometimes accelerating but often retarding and distorting its logical development.

There are no outstanding developments reported in the technical or patent literature of pigments, although numerous claims of a character affecting the details of well-established processes continue to appear. Those affecting the details of titanium production are particularly abundant. The addition of small quantities of the refractory oxides, or the salts of silicon, zirconium or thorium, to the hydrous pulp, followed by careful calcination at 920° is claimed[1] to produce a rutile pigment of greater tinting strength and brightness, and smaller particle size.

There is considerable interest in various methods of preparing synthetic iron oxide. Two methods[2] given are said to produce good yellow iron oxide from the partial oxidation and hydrolysis of ferrous sulphate in the presence of sodium carbonate. The utilization of various iron oxides formed as by-products during the reduction of nitrobenzene to aniline with iron filings has also provoked some study.

J. Riskin[3] has made a fundamental investigation of the composition and properties of the oxides produced by this method in the presence of various electrolytes which, it seems, largely determine the character of the oxide produced. Details of the German production of yellow and red iron oxides by the reduction of nitrobenzene are reported by H. R. Bolt and others,[4] who also describe the production of a high quality red pigment, " Vulcan Rot ", formed by the calcination of a finely divided brown oxide produced by the combustion of iron pentacarbonyl.

Continued and active attention is being given to the general problem of corrosion and to pigments for which a definite functional activity in preventing corrosion is claimed. These include the chromates, red lead, ferrous ammonium phosphate, metallic zinc, compounds of silicon, silicon carbide and aluminium, and the interesting product, lead cyanamide. Barium potassium chromate in ordinary paint media is said[5] to give good protection against the corrosion of iron, steel and light metal alloys.

The interest in zinc yellow developed as an alternative to red lead in war-time primers continues.[6] Several patents claim improvements in manufacture.[7]

The use of zinc yellow in marine primers is not, however, without its disadvantages and, in defence of red lead, an extensive study of marine primers has been carried out by the Red Lead Technical Committee of the Lead Industries Association.[8] From a considerable number of formulations, several have been selected as fast-drying coatings for priming ships' bottoms and topsides. Suitable pigmentations included red lead as the predominant ingredient, together with zinc chromate, zinc oxide, iron oxide, and a proportion of micaceous pigment and/or magnesium silicate, in vehicles containing varnishes cooked to a low viscosity. In general, short oil vehicles were best for total immersion, and long-oil alkyds were said to give outstanding results above the light load line.

The effectiveness of ferrous ammonium phosphate as an anti-corrosive pigment is claimed in a recent patent[9] where methods of preparing and using it are described. The same company[10] advocates the use of a black anti-corrosive pigment produced by alkaline earth fusion of a chromite ore in an oxidizing atmosphere; the resulting mass is subsequently finely ground.

Developments in the use of " Silcar " and " Silgar " (silicon carbide and silicon/aluminium respectively) are reported by H. O. Farr, Jr.[11] These are said to produce remarkable toughness and chemical resistance in chlorinated rubber media, and as such were used as anti-corrosive paints in the German navy. The same observer notes the experimental investigations into the use of lead cyanamide as an anti-corrosive pigment. A method of preparing a purified form of this interesting pigment is described by G. Guainazzi.[12]

While the general utility of certain metallic pigments, notably zinc, in operating as cathodic protectors of steel is well known, J. E. O. Mayne[13] places this empirical information on a fundamental basis, by performing a series of careful conductivity experiments using aluminium, magnesium, zinc, tin and lead powders in paint media. Of these, only the first three are sufficiently electronegative with respect to iron, and of this group only zinc powder is considered to possess the necessary inter-film conductivity to maintain electrical contact with the steel.

J. C. Hudson[14] describes the general problem of the corrosion of steel and its prevention, and an important paper by F. Fancutt and J. C. Hudson[15] summarizes the work of the Marine Corrosion Sub-committee on the protection of ship's bottoms and the formulation of successful anti-corrosive compositions.

The idea of adequate preparation of a surface prior to the application of a system of paint coatings, is crystallised in important contributions by F. Fancutt[16] on the effects of different methods of pre-treating iron and steel and a notable report by J. C. Hudson and T. A. Banfield[17,18] on exposure tests on iron and steel panels protected by metallic coatings.

A further contribution to an important study of water absorption and blistering is presented,[19] in which it is shown that, in addition to the absorption of water by a paint system due to a solute concentration gradient set up across the face of the coating, there is superimposed upon this effect one due to an electrical potential gradient giving rise to electro-endosmosis, whenever there is electrical activity in the neighbourhood of the paint, as in corrosion of the metal surface. This second complicating influence largely determines the transport of fluid through the film. It seems clear from the experimental evidence, and contrary to general belief, that the water absorption of a paint film is by no means necessarily a function of the water solubility of the pigments. Significant relations are given between moisture permeability and pigment volume concentration. In association with moisture permeability factors or impedence for the different pigments these relations have obvious practical significance in formulation.

Anti-fouling investigations have been largely overshadowed by the activity due to the related marine problem of anti-corrosion, but there are one or two items of interest. A. L. Alexander and B. L. Benemelis,[20] in an investigation stimulated by the shortage of high grade cuprous oxide, have determined the critical safety limit at which it is possible to use metallic copper flake and copper powder in anti-fouling compositions on steel without promoting accelerated corrosion and inactivation of the anti-fouling properties; the data shows that this critical value of pigmentation in a rosin-Me-abietate-Pliolite medium is of the order of 25/30%. The numerous and complex practical factors involved in the assessment of the performance of anti-fouling paints in actual service are described[21] by H. Barnes, M. W. H. Bishop and K. A. Pyefinch in a study of dry-docking reports. The problem of stabilizing freshly precipitated cuprous oxide is claimed in a recent patent[22] to be overcome simply by treating the filtered material with a weak solution of dextrin and drying.

There are several papers dealing directly or indirectly with the significance of binder and pigment relations in determining the properties of paint. W. G. Armstrong and W. H. Madson,[23] for example, have applied these relations to the more economical use of titanium dioxide in stoving enamels. In another paper[24] the same investigators carry their study of binder and pigment relations still further, and draw attention to the particular significance of oil absorption values in comparative studies of undercoat formulations, which they contend should include, not merely the pigment volume relation, but a new quantity described as the " saturation value ". This is defined as a function of the volume of the pigments, the volume of vehicle and the volume of vehicle required to saturate the pigments.

The familiar problem of the loss of leafing suffered by ready mixed aluminium paint in storage has been investigated by R. I. Wray,[25] It is contended that with proper control aluminium paints stable up to 18 months may be prepared.

S. Wertham[26] continues the observations made last year[27] on an extensive study of some 400 paints and over 1200 test panels, and reports favourably on the general behaviour of heavily bodied linseed oil formulations as compared with raw linseed oil, although the gloss and gloss retention were slightly poorer.

The Oil and Colour Chemists' Association in conference at Buxton, England, in May, 1947, made a series of important contributions to the study of paint performance and its assessment by maker and user.[28-35] They are briefly as follows.

The general dilemma created by the user's demand for rigidity in specification and the maker's appeal for flexibility is judicially examined[28] by H. A. Newnham, with special reference to the testing of decorators' finishes. The severe effects of high temperature and humidity on paints exposed in the tropics are described by H. B. Footner and G. Murray.[29] The systematic and thorough painting schedules demanded by railway companies are comprehensively reviewed by F. G. Dunkley and D. P. Earp,[30] who define the main criteria upon which selection is based. The general nature of laboratory performance testing of paints as required by Government departments are described[31] by H. Hollis. The special requirements of automobile paints are covered[32] by E. W. Plowman and H. J. Mason, and those of aircraft finishes are considered[34] by R. J. Ledwith. An important contribution by the Admiralty representatives,[35] C. D. Lawrence and G. E. Gale on the assessment of ships' paints for use in the Royal Navy concluded the conference.

Analysis

A micro-chemical method of identifying chromium in mineral pigments is described[36] by S. Augusti, a positive reaction for chromates being shown by a purple to red coloration on treating the test solution with a 1% solution of strychnine in sulphuric acid.

The insolubility of metallic lead in either ammonium acetate or $HClO_4$ in the presence of hydrazine hydrate is the basis of a method developed by R. Salmoni[37] for the determination of the free lead content of red lead and other lead compounds.

A simple colorimetric method of determining red lead is described,[38] by M. H. Swann, which depends on the hydrolysis of a glacial acetic acid solution of the pigment to a yellow or red suspension of PbO_2, on dilution with alcohol and water.

A. Steigmann[39] describes more selective uses for salinogenic and chelate forming dyes as analytical reagents which may be used for detecting cerium, calcium, magnesium and, under certain conditions, copper, nickel and cobalt.

A method is given for differentiating mixtures of carbon black and aniline black,[40] in which the aniline black may be removed as a brown oxidation product by treatment of the mixture with nitric acid.

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RUBBER

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THE flow of information mentioned in last year's report concerning the methods of polymerization or copolymerization of materials used for the manufacture of synthetic rubbers has continued. This is particularly so in respect of work designed to produce an improved type of general purpose synthetic (GR-S), and emphasizes the importance attached to the production of a synthetic material more closely resembling natural rubber in its general utility and convenience in processing.

In the U.S. there has been considerable diversity of opinion as to the amount of general purpose synthetic rubber which should continue to be produced in the Government-owned plants, the latest estimates varying between 150,000 tons and 350,000 tons per year. As the total consumption of raw material is estimated to be of the order of 1,200,000 tons, this would mean in any case a greatly increased usage of natural rubber by American manufacturers.

Although there has been an increased absorption of synthetic latices, largely in conjunction with an appreciable percentage of natural rubber latex, there have been very marked indications of a preference by American manufacturers for the complete use of natural latex for many products, particularly those made from foamed latex. There is, therefore, a general shortage at the moment in the supply of natural rubber latex relative to the demand. The output of natural rubber from the Eastern plantations, particularly Malaya, has continued at a high rate, and the fluctuations in price during the year have been largely caused by the current market estimate of the trend of output from manufacturers in relation to the amount of synthetic material produced either through economic demand or for political reasons.

Latex

Among the many questions to which, owing to insufficient data, it is still not possible to give definite answers may be mentioned the mechanism of creaming, the phenomenon of sensitization and the nature of the rubber globule in the latex. The view previously expressed that the particle size of latex coming from the tree is much smaller than the size usually found after agglomeration has occurred[1] has been criticized by H. P. Stevens.[2] It has been found that particles tend to form a string of beads as a preliminary to coagulation, but these comma-like particles are present only in a very small proportion. Particles from the leaves have been found to have a particle size of about 0·5 to 1·0 micron, but these cannot reach the rest of the tree because of the membrane at the base of the petiole.

Work on the creaming of latex has resulted in a number of suggested creaming agents, including an ammoniacal solution of aluminium cellulose glycollate,[3] aqueous extracts of half-ripe seeds of the Avenga palm,[4] and pectin derivatives.[5] Flocculation of natural and synthetic dispersions can be brought about by the controlled addition of certain organic sulphonic acids or their salts together with an organic polyamine. The flocs are separated from the serum by filtration, and may be redispersed by adding an alkali.[6]

Factors involved in the preservation and storage of latex, mentioned in last year's report, have been further elaborated by J. McGavack.[7] The simple addition of ammonia is sufficient to destroy bacteria where infection is slight, sodium pentachlorophenol, trichloronitromethane, chloropicrin, etc., being used in cases of more severe infection. The changes resulting from bacterial activity in *Hevea* latex have also been studied[8] and an attempt made to correlate the yield of rubber, saponification number, acid number, and the non-volatile acid content of the non-rubber ether-soluble substances during the natural coagulation of latex. The reduction of the protein content of latex has been the subject of a number of patents concerned with the addition of alkali to prevent coagulation during heating.[9, 10, 11, 12] General questions in handling on a commercial scale have been discussed by J. H. Pidford.[13]

Among the more interesting developments in latex compounding may be mentioned the use of Pliolite latex 190, a highly stable water dispersion of a high styrene copolymer resin, which imparts reinforcement, reduced water absorption, and increased tensile strength when added to latex.[14]

The addition of fluosilicates to reduce local coagulation has been resorted to in the production of foamed latex for sponge manufacture. A sufficient quantity of an alkali fluoride is added to repress the hydrolysis of the fluosilicate.[15]

In the Kaysam process for the production of moulded articles the coagulation of the latex is attributed to the addition of zinc oxide, it being necessary to add a so-called " sensitizing " salt to be removed later by a difficult and tedious washing process. As a result of war-time experience it was found that latex which had been kept a long time gave satisfactory results without the sensitizer, and a method has been evolved to reproduce this desirable " ageing " effect in fresh latex by heating under pressure in the presence of ammonia. A similar result has been observed on the addition of a small percentage of trypsin, but in this case the latex rapidly coagulated when cold in the presence of zinc oxide unless the degradation of the proteins was arrested at the right time by inactivating the trypsin by heating.[16]

The production of latex dipped articles with good tensile strength, elongation, and ageing characteristics is claimed for a process in which a former is immersed in a coagulant containing metallic activators of vulcanization and an aliphatic amine sufficient to impart a p_H of 1·5–7·8 to the coagulant. The former is then dried and dipped in compounded latex containing little or no vulcanization activator.[17]

The development of the use of rayon cord for tyres, mentioned in last year's report, continues to stimulate interest in the application of latex to this field. The adhesion of rayon to latex has been found to be a function of solids pick-up which in turn depends on the wetting-out properties of the rayon, the characteristics of the latex bath and the operation of the dipping machine.[18] Of special interest is the increase in concentration of the dipping bath caused by rayon. The magnitude of this increase depends on the finishing agent used in the rayon, and, unless it is controlled, a variation in solids will occur which affects adhesion, square yard weight to the calender, drying rate, and cost. The relation between adhesion, dip deposit, and tyre life has been investigated by R. T. Murphy and L. M. Baker,[19] who conclude that tyre flex life is improved by lower dip pick-up even though cord adhesion values are reduced.

In view of its unusual properties and extended application neoprene latex must now be regarded as a new and basic material rather than as a substitute for the natural rubber product, and investigations into its characteristics and potentialities continue to be reported in the literature. The control of p_H value has been discussed by H. K. Livingston and R. H. Walsh,[20] who point out that excess alkali in commercial types of neoprene latex cannot be satisfactorily controlled by either concentrated or dilute acids of ionization constant greater than 5×10^{-6}. Amino acids of acidic ionization constants as high as 10^{-2} to 10^{-5} do not cause coagulation, even in concentrated solution. Glycine is the preferred p_H regulator, and its use in froth sponge manufacture overcomes variations in gelation properties. In examining the stability of synthetic rubber dispersions the phenomena of low-temperature thickening of neoprene latex have also been investigated,[21] and an attempt has been made to correlate them with the phase changes that occur in aqueous rosin soap systems resembling those used in making neoprene latex. The instability of neoprene latices shown by the abrupt thickening at low temperatures is concluded to be, not evidence of incipient coagulation, but the result of phase transition in the dispersing phase. An investigation of the coagulation of neoprene latices by freezing[22] shows that neoprene and butadiene copolymer latices coagulate more rapidly than natural latex, and it is suggested that such coagulation probably results from the formation of ice crystals, but may be prevented or delayed by a dispersing agent. Latex rapidly frozen at −60° or −186° coagulates if warmed slowly, but not if the thawing is rapid. This suggests that the latex is in a metastable condition at very low temperatures. The instability of synthetic rubber dispersions at sub-zero temperatures makes operable an efficient, continuous process for isolating dry polymers.[23, 24]

A process analogous to the creaming of natural rubber latex can be carried out with neoprene by the addition of certain hydrophilic colloids in solution.[25] The neoprene latex separates spontaneously into two layers on standing, the lower layer containing the greater concentration of neoprene. Separation can also be carried out by electro-decantation or by cooling, and in each case an increase in viscosity occurs before the separation. This is in agreement with the theory that there is a critical range of viscosity where the increase in creaming, resulting in clustering, is greater than the decrease resulting from frictional drag.

The preparation of a synthetic latex by the emulsion polymerization of styrene and isoprene with the use of organic salts for coagulation has been described in a paper by W. Heller.[26] Latex with positively charged polymer particles was prepared which could be used for the coagulation of ordinary synthetic latex, and a series of measurements carried out on the relation between polymer concentration and the electrolyte concentration necessary to coagulate completely, within a fixed period of time, latex with negatively charged particles.

Exceptionally stable concentrates have been obtained from Type III GR-S latex involving gelation by the use of an electrolyte (sodium chloride), cooling and processing to yield a fluid and rapidly filterable mass. The small quantity of electrolyte in such concentrates results in gel points below room temperature.[27] Further work on Type III GR-S includes a method of vulcanization using zinc ethylphenyldithiocarbamate as accelerator. The latex shows no tendency to coagulate, and vulcanization is effected in air at 60–80° in short periods.[28]

Buna latices have been investigated by the ultra-centrifuge and the electron microscope,[29] and, in a paper by S. H. Maron and C. Moore,[30] comparisons have been made between the German Buna in " Stockpunkt " concentration and GR-S rubbers. GR-S latices cannot be concentrated by analogous means without pre-treatment due to the fact that they do not contain the high quantities of electrolytes shown by the Buna latices.

Raw rubber

A critical review of present developments and suggestions for future improvements in plantation rubber have been made by D. F. Twiss,[31] who points out that the aim should be to improve the qualities in which natural rubber excels synthetics rather than to introduce the properties of synthetic elastomers. The non-rubber portion of latex, which influences the processing qualities of the rubber, may be controlled by suitable treatment of the latex, and copolymerization in the latex stage has possibilities in this connexion. The attempt to develop a type of rubber more suitable than smoked sheet for large-scale operations, together with the possibilities of obtaining an improved hydrocarbon, have also been discussed.[32, 33]

The field of investigation of the physical and chemical properties of the rubber hydrocarbons is so wide and varied that only a few lines of research can be touched upon in this report. The phenomenon of elasticity has been studied by examining stretched material under the ultramicroscope.[34] When the rubber is stretched liquid droplets are squeezed out, and can be seen collected in the form of small droplets on the stretched fibrous molecules, whilst balata shows droplet formation only when heated to temperatures at which it becomes elastic. This difference between the behaviour of rubber and balata is put forward as the first visible evidence of how the configuration of a molecule can affect some physical properties of a substance.

The existence of a relation-time spectrum for high molecular weight substances has been discussed in a series of papers by W. Kuhn and others,[35, 36, 37, 38] and on the basis of flow-curves of rubber-like materials a quantitative expression for such a spectrum has been derived and studied in connexion with dynamic viscosity and elasticity.

Attempts have also been made to explain, on a molecular basis, the deviations from ideal behaviour of rubber when stretched, by the use of thermodynamical equations for isothermal deformations.[39] The stress optical properties of rubber have been examined under conditions of homogeneous stretching,[40] and ultramicroscopic observations have also been used in an attempt to establish visual proof of the phenomena of plastic flow and recovery in vulcanized rubber.[41]

Chemical derivatives

The partial or complete saturation of the double bends of the rubber molecule, in order to obtain materials of superior ageing and general resistance properties, continues to receive attention. An alkylated rubber is described[42] with an iodine number of 32, which, while retaining most of the desirable properties of rubber, is resistant to oxygen and halogen gases.

Further work has been done on the production of water soluble amino derivatives of rubber which are said to be useful as rubber tougheners,[43] on the reaction of rubber with maleic anhydride and similar unsaturated compounds,[44] and on the modification of rubber by means of *iso*cyanate compounds to give materials of increased oil and gas resistance.[45]

The study of the action of chlorine and metallic halides on monomers and polymers in the emulsion stage has been discussed in some detail,[46] and comparisons are made of the various products, while improvements in the preparation of chlorinated rubber, including a method for production of homogeneous derivatives in which all the chlorine is present by substitution have been described.[47]

The search for effective means of stabilizing chlorinated rubber has led to a treatment with chlorine in the presence of water,[48] and a method of drying in nickel apparatus.[49] A number of patents dealing with the stabilization of rubber hydrochloride are also to be noted in this connexion.[50, 51, 52]

Cyclized rubber preparation and the effects of oxidation (improving adhesion) and over-milling (improving solution clarity) form the subject of an American patent; the properties of the film are also dependent on the cyclizing agent employed.[53] Agents for promoting the stability of cyclized rubber have been described,[54, 55, 56] and the use of this material, treated with 1·5%, or more, of di*iso*cyanate compounds to give products useful in paints, adhesives, and moulding compounds is also to be noted.[57]

Consideration of a method of rendering natural rubber more resistant to solvents, to a degree of the same order as that characterized by some synthetics, while retaining substantially the rubber-like qualities, is given by J. Le Bras and P. Compagnon;[58] products based on partially hydrochlorinated rubber and on a copolymer of natural rubber with acrylic nitrile are the most promising. A rubber hydrochloride of 25–28% chlorine content may, with suitable compounding, be processed in the ordinary way, to yield vulcanizates with good mechanical properties.[59]

Synthetic rubber-like materials

Improvements in the production of raw materials for manufacture into synthetic elastomers have received attention; a yield of 60% butadiene and acetaldehyde is obtained by catalytic heat treatment of ethanol.[60] Acceleration of synthetic rubber production is claimed by the conversion of acetaldehyde and alcohol to high purity (98%) butadiene over a catalyst of silica gel treated with tantalum oxide,[61] and a new polymerization catalyst in cumene hydroperoxide is said to cut production time, give a better product, and be safer and cheaper than other peroxides.[62] An account of the manufacture of acrylonitrile in Germany is contained in a B.I.O.S. report published last year (1947).[63]

GR-S continues to hold its place as the leading general purpose synthetic rubber in the U.S., and the literature on the subject shows no signs of abated interest in this material. F. H. Cotton puts in a plea for a small quota of GR-S to be imported into the U.K. in order that the skill acquired in processing this material in British factories should not be lost because of economic difficulties.[64] This writer discusses the future of GR-S, and forsees a healthy rivalry between natural rubber and this synthetic. C. S. Fuller[65] discusses the production of the best possible butadiene/styrene rubbers and the concomitant problems, and reference is made to some hitherto unpublished work. The various types of available GR-S polymers are tabulated and classified into seven groups by J. L. Brady,[66] with notes on types and uses of special grades, and a summary of R.A.B.R.M. Research Memoranda by R. Elliott and R. G. Newton gives a large amount of useful information regarding compounding, processing, testing, and properties of GR-S, and is further amplified by a second summary covering the physical and chemical properties of the vulcanized elastomer.[67]

Improvements in the properties of GR-S are said to result from the incorporation of a small amount (0·5%) of a cross-linking agent at the polymerization stage, better processing qualities, and improved physical properties resulting,[68, 69] while tack of the polymer is improved, with better ply adhesion, when rosin soap, instead of fatty acid soap, is used in the polymerization.[70] Other improvements in GR-S include the enhancing of insulating properties[71, 72] by reducing the amount of water soluble salt in the product, and low moisture absorption by means of a modified coagulation technique.[73] Continuous preparation of GR-S has been successfully carried out on a laboratory scale in one, three, and five stage systems,[74] and it is claimed that a polymer of good quality should be obtainable on a large scale in this way. An interesting modification is the replacement of butadiene by isoprene to obtain a GR-S type more closely related chemically to natural rubber,[75] and the effect of impurities (nineteen) on the polymerization of GR-S has been examined, the results stressing the importance of using freshly distilled butadiene.[76, 77] A gutta-percha-like material was obtained from a mixture of dimethylbutadiene and acrylonitrile,[78] in an investigation of the copolymerization of butadiene and its dimethyl homologue with styrene and acrylonitrile.

Sulphur containing elastomers of olefinic polysulphide types are obtained by treating olefinic compounds with sulphur chloride and reacting the product with sodium polysulphide;[79] an interesting polymer is obtained by interpolymerization of thiophen and vinyl acetate,[80] while solutions and aqueous dispersions of olefin polysulphides, with properties and applications of latex and film, have been discussed.[81]

Fluorine containing rubber-like polymers have been described,[82, 83] high resistance to oils with good resilience properties at low temperatures being claimed. The silicone rubbers continue to attract some attention, the published work including a history of silicon organic compounds, with comments on the properties of the polymer in general,[84, 85] a discussion of the materials with special reference to insulations,[86] and a report of a series of tests in which silastics are exposed to conditions which cause deterioration in organic rubbers.[87]

A new rubber, "Lactoprene EV,"[88] made by copolymerization of ethyl acrylate and chloroethylvinyl ether, has been put on pilot plant production. Possible uses are in specialized applications where oil and high temperatures are encountered, or where purity of colour is desired, but the product is inferior to GR-S in some respects. Plasticization of the material is discussed by W. C. Mast and C. H. Fisher, with a study of the resulting effects on certain physical properties.[89]

The use of certain synthetic elastomers to replace the more conventional plasticizers for polyvinyl chloride has been attended with some success.[90, 91] Geon Polyblend is such a material, with improved resistance to solvent extraction, easy processing, and good colour possibilities.

Among the newer specialized elastomers is a material of low iodine number (as low as 3·7) with good resistance to oxidizing agencies,[92] a butadiene copolymer highly resistant to oil and freezing,[93] a poly*iso*cyanate modified polyester amide highly resistant to oils (3% vol. increase after one week in gasoline at 25°),[94] while the preparation of rubber-like polymers by condensation reaction and the factors influencing the properties of these materials have also been discussed.[95]

Compounding materials and methods

Carbon black is still by far the most used and effective reinforcing agent. An account of the production in Great Britain,[96] its manufacture from gas works residues in Germany, Czechoslovakia, and Poland,[97] and a recent investigation of the carbon black industry in Germany[98] show how production has increased outside the U.S.A. In a review of carbon black types, properties, and uses, reference is made to a combustion product, ethyl silicate, which may be used as a non-black reinforcing agent to replace carbon black.[99]

G. L. Brown[100] has compared easy, medium, and hard processing channel blacks in a GR-S tread stock, and this reference is one of the few dealing with channel blacks, probably due to the transition in the industry from the channel to the furnace process.[101] The furnace process is stated to give higher yields, the resulting blacks offering a wider range of characteristics in compounded rubber.[102] A number of the publications deal with the increase of furnace black consumption, and give critical comparisons of the two types of black.[103, 104, 105, 106] An interesting new furnace process for the production of a superior carbon black, known as Statex K, is given,[107] and the product is said to equal, or surpass, channel black in road wear tests in both synthetic and natural rubber tyres.

Pliolite S-3,[108] a new styrene/diene copolymer, is chiefly of interest in possessing, in mixtures with rubber, unique balata-like properties. Other Pliolite copolymer resins, Pliolite S-5 and S-6, which are butadiene-styrene copolymers containing a high proportion of styrene, have been reviewed.[109, 110]

T. Patrin and S. Pilat have made determinations of the absorption of carbon tetrachloride vapour, the heat of wetting by carbon tetrachloride, the oil number (quantity of linseed oil absorbed), and the temperature of spontaneous combustion of several carbon blacks. The values of carbon tetrachloride absorption were found indicative of the origin of the carbon black.[111] Surface activity as revealed by surface heat absorption measurements on carbon black has been found to parallel the rubber reinforcing properties of the blacks studied.[112] Another important physico-chemical study[113] has shown that the p_H of a slurry of carbon black boiled with distilled water is a characteristic quantity of the black. A more fundamental property of the black was its titration curve. A straight line relationship was found, together with a positive correlation between the slope of the curves and the oxygen content of the black, providing the particle size remained constant.

Amongst the many antioxidants mentioned in the patents are: amino derivatives, such as a mixture of N-N′-diphenylbenzidine derivatives, and secondary amines which inhibit deterioration of vulcanized rubber at elevated temperatures;[114] esters, amides, and salts of N-arylaminoaryloxyacetic acids;[115, 116] N-(*p*-hydroxyaryl)pyrroles;[117] and a secondary aromatic amine with a terpene thiol or terpene mercaptide of a metal in Group IIb of the Periodic Table.[118] It has been found that the effectiveness of secondary aromatic amines was increased by the addition of a phthalocyanin or a metal complex thereof.[119] What may be considered as a new class of antioxidants are the organic esters of phosphorous acid[120] which are non-discolouring. J. Le Bras and R. Hildenbrand[121] report that a mixture of an antioxidant and a deactivating agent reduces the rate of oxidation of a vulcanizate, more than does the former alone.

An evaluation of nine softeners in GR-S tyre treads showed that the best were unsaturated petroleum softeners and coal tar, with medium hard asphalt giving the poorest results.[122] A satisfactory solid substitute for pine tar and coal tar derivatives is prepared from pine tar and coal tar bitumen with a resin-like high boiling petroleum containing vanadium pentoxide.[123] Paint driers (or siccatives), resinates, oleates, tungstates of lead, manganese, etc., are tack producing agents for butadiene synthetics, and a mixture of drier and degrading agent (phenylhydrazine) with GR-S, heated to 100°, results in a sticky mass which can also be used for this purpose.[124] Tackifiers for natural and synthetic rubbers are obtained by condensing high molecular weight crotonaldehyde type of autocondensation products of ketones with an aldehyde. Tack increasing agents consist of materials which are good solvents for the ketone resin and are swelling agents or weak solvents for the rubber.[125] A U.S. patent claims to have caused tack to be developed by addition of a copolymerization product of a di-olefine (37–65%), a 2-aryl-1-alkene (1–3%), and an unsaturated ketone (20–60%) to a non-tacky rubber-like polymer.[126]

As in previous years, many plasticizers are mentioned in the literature. For nitrile-type synthetics, such as GR-A, Buna N, etc., ricinoleate esters are used as low-temperature plasticizers.[127] Water insoluble naphthenic acid amides and anilides,[128] alkyl-NN-dialkylcarbamates,[129] and trichloropropionates are also used for this purpose.[130] Certain *o-o′*-diacylaminodiphenyl disulphides are effective for the hot mastication of GR-S and natural rubber.[131] To this list of plasticizers may be added: *o*-nitrodiphenyl (plasticizer ONB),[132] the reaction product of an aldehyde and a primary aromatic amine or a thiophenol,[133] terpenes through which air or oxygen has been blown,[134] and "Red Oil," which is a red resinous distillate recovered above the anthracene oils in the distillation of coal tar.[135]

G. H. Piper and J. R. Scott have investigated the factors operative in plasticization of rubber and synthetics.[136]

The restrictions on the export of carbon black from the U.S.A. has led to the development of a new reinforcing agent, lignin. Sources of lignin are straw and the sulphate wood pulp process. In general, it is an agent for obtaining specific properties, and is not a substitute. Its advantages are its light weight and the fact that the straw variety does not tint the mix.[137] A process has been described whereby lignin is mixed with either natural or synthetic rubber latex and is then coagulated with the rubber, the material being thereafter processed in the normal manner.[138, 139]

A new active filler is Franclay B, the chief component of which is the aluminium silicate known as halloysite.[140] Other significant fillers are: the product formed by reacting sodium silicate with a calcium or magnesium salt solution in the presence of crystallization-impeding agents (*e.g.*, glue, casein, etc.),[141] and pure wood cellulose flock.[142] A paper by F. S. Rostler and H. I. du Pont[143] deals with a method of simultaneous incorporation of fillers and plasticizers in the form of premixed preparations.

The effect of small proportions of ethylene glycol in a natural stock with two loadings of Silene E.F. has been reported.[144] There is a tendency for the glycol to accelerate the rate of vulcanization, to increase stiffness, hardness, and resistance to tear.

The physico-chemical aspects of reinforcement have been studied by G. Antonoff.[145] A close analogy was found to exist between the behaviour of pigments (chiefly carbon blacks) in some oils and rubbers.

In the blending of natural rubber with GR-S it has been suggested that the maximum physical properties are not being obtained because of lack of knowledge of the best compounding technique, and in order to increase the effectiveness of such blends more attention should be paid to the solubility of accelerators in the two rubbers.[146] A comparison of the effect produced on the physical properties of a GR-S 100 E.P. channel black 50 mixture, after vulcanization, by substitution of increasing proportions of GR-S by Hevea smoked sheet and guayule has been made.[147]

Various miscellaneous rubber compositions are of interest. A suitable electrical insulating material has been made from a low protein or deproteinized rubber with (preferably) 20–50% cyclized rubber.[148] Indanol esters (5–30%) have been compounded with natural rubber to produce uniform compounds remarkably free from bleeding, blooming, leafing, and lamination.[149] Combinations of Buna N or neoprene-type synthetic rubbers with Durez 12687 (a phenolic resin) containing hexamethylene tetramine as curing agent give products in which many of the valuable properties of both the resin and rubber are retained.[150]

Vulcanization and accelerators

Among the further work that has been done on the theory of vulcanization, E. H. Farmer and F. W. Shipley[151] have discussed the various types of sulphurization of unsaturated organic compounds in relation to the vulcanization of rubber. The chemistry of the reactions of hydrogen sulphide with olefines gives support to the theory that in the reaction of sulphur with polyisoprenes the radical chain mechanism proceeds only as far as the thiol, and subsequent addition is of the polar type.[152] Additional studies on the reaction of methyl iodide with sulphur compounds have been carried out, and experiments on the hot acetone-*iso*pentane extraction of vulcanizates give no support to the idea that polysulphides decompose on hot extraction to give extractable free sulphur.[153] A contribution by A. M. Zolotareva[154] studies power loss and deformability of sodium butadiene at various stages of its vulcanization to elucidate the state of sulphur in partly and fully vulcanized rubber. Heating was required to make the uncombined sulphur a plasticizer. The change in properties of rubber through maximum or minimum values during vulcanization[155] have been considered due to the interaction of rubber with the vulcanizing agents and the sulphur molecule. An equation for tensile strength in terms of combined sulphur and oxygen is included in this reference.

Work on the non-sulphur type of vulcanizing agent has been extended. J. C. Arnold[156] claims that quinone dioxime esters of aromatic or substituted aromatic acids give better results than quinone dioxime or quinoneimine compounds. A chromatographic resolution of the quinone oximes has been carried out.[157] Related to this is vulcanization by means of compounds which, during vulcanization, can assume a methylene-quinoneimine or a methylenequinone configuration.[158]

Cross linking has been effected by bifunctional mercaptans $M(SH)_2$ where M represents a hydrocarbon or other divalent radical. Natural rubber and GR-S have been subjected to vulcanization of this type.[159] An investigation of the tack-producing and vulcanizing qualities of some twenty-five alkylphenol sulphides has been carried out. The monosulphides are mild vulcanizing agents, the disulphides being much stronger, apparently due to their containing labile sulphur.[160] Another sulphide class of vulcanizing agent that has been used with synthetic rubbers is the xanthogen sulphide type together with an accelerator of the arylene-thiazole class,[161] giving superior elastic properties to those obtained with free sulphur. For Buna-N type rubbers, sulphur is caused to react with a partially unsaturated hydrocarbon oil, etc., the boiling point being not greater than 160° and not less than 40% soluble in concentrated, or fuming, sulphuric acid.[162]

GR-S gives heat resistant vulcanizates by vulcanizing with *m*-dinitrobenzene and litharge.[163] The use of 10%–20% of an aldolnaphthylamine is reported to impart the property of "reversion" to GR-S during vulcanization.[164] Adding a small proportion of thiuram disulphide retards the vulcanization of GR-S by a chlorinated quinone and prevents scorching.[165] Important new types of non-sulphur vulcanizing agents for GR-S, which are halogen compounds, include chlorinated aryl methyl compounds and halogenated aliphatic hydrocarbons containing one $-CCl_3$ group attached to a strong polar group. A note on the mechanism of vulcanization has been given.[166]

No new type of compound has been reported for use for vulcanizing Butyl rubber. *Meta*-and *para*-dinitrobenzenes have been mentioned as activators,[167] and a quinone dioxime with a small amount of an aryl polycarboxylic acid or anhydride has been suggested for curing Butyl rubber.[168]

Anhydrous halides of boron or a bivalent or multivalent metal, plus a nitrogenous organic base (not hydrazine compounds), are non-scorching vulcanizing compounds for chloroprene.[169]

Many of the accelerators mentioned in the literature are based on the well-known types. Dealing with the thiuram disulphide class, the general compounding characteristics of tetramethyl and tetraethyl thiuram disulphide,[170] the use of a mixture of tetrabutyl thiuram monosulphide, tetrabutyl-thiourea and urea,[171] and the preparation of tetrahydro*iso*quinoline thiuram disulphide[172] are given. The reaction product of an alkylenimine with ammonium dithiocarbamate,[173] the preparation of heavy metal salts of dithiocarbamic acids,[174] and the reaction product of a secondary aliphatic amine, carbon disulphide, formaldehyde, and an aromatic amine,[175] which are claimed as low-temperature accelerators for natural rubber and GR-S, are typical dithiocarbamate derivatives. N-disubstituted sulphenamides[176] and bis(arylsulphen)amides,[177] of which the latter give useful scorch and curing properties, also a diarylguanidine thiazole formaldehyde complex[178] and reaction products of two amino-thiazolines with zinc salts of heterocyclic nitrogen containing mercaptans[179] may be included.

In the resinous accelerator class, the reaction products of zinc chloride, formaldehyde, mercaptobenzthiazole and a monoarylguanidine are strong accelerators for natural and synthetic rubber.[180, 181]

Some interesting new activators and accelerators are mentioned. The preparation of a rather different type of accelerator, the dithiofuroates, stated to be useful for natural rubber and GR-S, is to be noted.[182] Aldehyde condensation products with amidine thiocyanates are used as activators for certain accelerators of the thiazole type.[183] 0·1–2% of a 3:3:3′:3′-tetra-alkyl-1:1′-*spiro*di-indan-5:5′:6:6′-tetrol is described as a useful accelerator for neoprene in latex products where fast cure and high modulus are desired, although it causes scorching in mill stocks.[184] This latter compound is a good example of the complexity of some accelerators.

Finally, mention may be made of a review by C. Philipp[185] of the rubber vulcanization accelerators on the basis of British, U.S., French, and Belgian patents.

Vulcanized rubber

Interest continues to be shown in materials alternative to cotton, such as: rayon, nylon, woven glass, and wire cord.[186] In a paper on this subject G. S. Dolby points out that the stimulus given to cotton research by the pressure of competition from rayon is likely to result in a healthy rivalry between the two.[187] Nylon combined with rayon in passenger car tyres has been discussed and some advantages of this method of construction pointed out.[188]

In a discussion on fabrics for mechanical rubber goods L. Larrick has stated that out of a total of approximately 120 vegetable, animal, and mineral fibres four only occupy a dominant position, and no synthetic has yet appeared combining the best properties of the natural fibres.[189] A combination of nylon and Ustex yarn in a new type construction is said to give a conveyor belt of 250–400% increase in strength,[190] with great improvement in load-carrying capacity, and, with consequent reduction in weight, saving in power and installation costs also results. Concentric layers of glass fabric have also been used in the manufacture of rubber hose.[191]

The influence of molecular structure on the elasticity and tensile strength of rubber is discussed by G. Gee; the tensile strength appears to be related to the degree of crystallization, and the increase in strength on vulcanization is explained on this basis.[192] A further step in the investigation of the interaction between liquid and rubber has been reported by the same author.[193, 194] F. S. Rostler and his collaborators have published parts III, IV, and V of their work on the swelling of rubber, dealing respectively with the action of hydrocarbon solvents, the effect of carbon blacks on the swelling of vulcanized GR-S, and the comparative swelling of vulcanized natural and synthetic rubber; the latter article contains 21 references.[195, 196, 197]

The photoelastic properties of rubber, including double refraction and crystallization in stretched vulcanized rubber, is discussed by L. R. G. Treloar,[198] and other papers, essentially of theoretical interest, include heat conductivity of rubbers at low temperatures,[199] thermoelastic properties of rubber in which small changes in volume (causing changes in internal energy and entropy) due to deformation are considered, and departure from ideal behaviour thus explained,[200] and the variation of specific heat with extension, with a note on the heat of crystallization.[201]

Adhesion and bonding

A review of the various bonding processes for rubber to metal developed in Great Britain and the U.S.A. since 1939 has been presented,[202] with a detailed description of the Canite process,[203] which consists of a layer of chlorinated rubber and one of a reaction product of acrylonitrile on natural rubber. C. M. Blow[204, 205] has discussed the bonding of rubber to metal by the brass plating technique, and the bonding of rubber to metal with Ty-Ply in regard to present technical developments is the subject of an informative report.[206]

Rubber cements containing over 100% channel black are described in a U.S. patent,[207] excellent bonds of rubber, neoprene, and GR-S are thereby said to result without brass plating; details of the bonding of Perbunan to metal by means of chlorinated rubber are given in a Board of Trade report,[208] and a cyclized substituted pentadiene polymer is claimed as an adhesive for rubber to metal bonding.[209]

Textiles are said to adhere tenaciously to rubber by means of a poly*iso*cyanate-treated isoprene polymer, effective at elevated temperatures and in the presence of water.[210] An adhesive for rubber to nylon comprises a protein, a synthetic latex, and a phenol,[211] and improved adhesion of rubber to fibrous materials is said to result by incorporation of an aryl sulphide.[212] An adhesive requiring only moderate heat for setting is made by adding a solution of a rubber to a phenol formaldehyde condensation.[213]

Synthetic and reclaim rubber dispersions as adhesives in the shoe industry have been discussed,[214] and the attachment of rubber soles to leather shoes by means of polyvinyl chloride/acetate copolymer and nitro-cellulose adhesives[215] has been described. Fluosilicic acid is used to prepare magnesium for bonding to rubber,[216] rubber to carbon joints are prepared from chlorinated rubber,[217] and this material is also used in bonding rubber, after halogenation, to metal and glass.[218]

Reclaim

There has been little of outstanding importance to report during the year on rubber reclaim. Patents have been taken out covering regeneration processes involving the use of organic acid materials with mercaptan-type compounds,[219] oxidoplasticization materials with kerosene or xylene as softening agents,[220] organic solvents,[221] alkylolamine,[222] and aromatic compounds with at least one hydroxyl group directly attached to a polycyclic nucleus.[223] A further patent relates to a method in which waste rubber, preheated to 174°, is masticated in a Banbury mixer with exposure to air for 30 minutes or less, the addition of 0·5% phenylhydrazine enabling the time to be reduced.[224] Finally, mention may be made of a non-staining reclaimed rubber prepared by treating solid devulcanized rubber with carbon tetrachloride and an alcohol.[225]

The influence of temperature, antioxidant, and defibring agents on the basic reactions occurring during the reclaiming process has been examined,[226] and the familiar differences between alkali and metallic chloride reclaims shown to have their counterpart in the respective analytical data obtained from each reclaim.

Interest in synthetic rubber reclaims has for some time centred mainly on neoprene, and the problem of the hardening of the material, which results from heat treatment and precludes the use of the conventional digestor, has been dealt with by W. G. Kirby and L. E. Steinle.[227]

Certain highly alkylated phenol sulphides are recommended as producing reclaims from GR-S and other synthetic elastomers with properties comparable to those of natural rubber reclaims; it is probable that the predominant chemical reaction taking place during the reclaiming process is one of oxidative degradation or chain scission.[228] Among other materials involved in reclaiming processes forming the subject of patents may be mentioned organic amides,[229] aryl amides,[230] and alkylolamines.[231]

Analysis and testing

The microchemical analysis of rubber has been studied, and considerable saving in time without sacrifice of accuracy is claimed,[232] while the application of the chromatographic technique with reference to identification of accelerators has been described.[233] Details of spot tests for rubber chemicals with appropriate data have also been given.[234]

The direct estimation of GR-I (Butyl rubber) has been examined, and a method involving a controlled nitric acid oxidation is recommended.[235] The bromine numbers of certain rubbers have been measured, and an indirect relationship found between this value and plasticity.[236] The rates of dissolution of vulcanized rubbers in *p*-dichlorobenzene and nitrobenzene have been measured, and the application of the results to rubber analysis indicated.[237] A dielectric identity and purity test for plasticizers has been proposed,[238] and the application of infra-red spectroscopy in qualitative and quantitative analysis described.[239]

A symposium on Rubber Testing of the D.11 Committee A.S.T.M. at a meeting of the Society in June, 1947, attempts to cover the progress made on physical and chemical testing methods of rubbers, making available work done by the government and industry during the war, when secrecy was maintained.[240] A B.I.O.S. report contains an account of interviews with

O. Bayer and H. Roelig, of the I.G. Farbenindustrie, with information, *inter alia,* on the measurement of physical properties as carried out in the I.G. laboratories,[241] and a C.I.O.S. report includes information on specifications of testing methods for the German Navy.[242]

The laboratory testing of cut growth has been studied by W. L. Holt and E. O. Knox,[243] with comments on the results of studies of various vulcanizers. The precision of tests for tear resistance has been examined,[244] and a further paper on methods of measuring tear resistance has been presented.[245]

A summary of the conclusions of the Birmingham Conference of 1945 on the physical and chemical breakdown of rubber is contained in a Ministry of Supply publication,[246] and data obtained in the I.C.I. laboratory at Blackley are analysed in some detail.

The effect of metallic poisons, especially manganese, on the ageing of vulcanized natural rubber has been examined, and the results indicate that the non-metallic radical exerts considerable influence on the rate of ageing.[247] Copper, when rendered inert by certain chemical combinations, in this case the phthalocyanine complex—Monastral Fast Blue B.S.—has no harmful effect on the ageing of rubber,[248] and neoprene is reported to be suitable for direct application to copper for insulation without the need for tinning.[249]

The correlation of laboratory and service tests, a point of great importance, forms the subject of an investigation in which the opinions of representative technologists are summarized,[250] while A.S.T.M. test results[251] have shown disagreement with road tests on GR-S capping compounds, and to a less extent with natural rubber, due to a lubricating effect on the test machine. A preliminary extraction treatment is recommended to overcome this, and excellent correlation is claimed as a result. Variations in physical test figures obtained from different laboratories show a need for further work in this direction,[252] and the reproducibility of test figures in the same laboratory, from day to day, has been examined by J. R. Scott and his co-workers.[253]

The evaluation of relatively small amounts of new diene-type polymers has been studied,[254] and the development and standardization of tests for evaluating the processability of rubber have been discussed by R. H. Taylor, J. H. Fielding, and M. Mooney.[255] A paper on the statistical analysis of plasticity measurements has been published, in which different methods of measuring plasticity are compared,[256] and the rheology of processing quality of raw rubber, with eighteen references, has been discussed by M. Mooney.[257]

Hysteresis and its measurement, with comments on the interpretation and value of the results, has been discussed.[258]

The pendulum and falling weight impact testing machines have been critically examined and compared,[259] and the buffing of samples for the preparation of dumb-bell specimens has been studied from the point of view of achieving greater accuracy.[260] It is concluded that tensile tests should be made within definite time limits (12-18 hours) as any increase in this period causes a distinct fall in tensile strength. In a series of papers by J. R. Scott and others, work has been reported on the determination of resistance to abrasion, and some interesting comment is given on the influence of calender grain.[261] Results indicate that vulcanizates containing anisotropic fillers wear much more rapidly on a surface parallel to the plane of the calendered sheet ("flat surface") than on a surface at right angles to it ("edge surface"). Grain effects and methods of milling or calendering have considerable influence on abrasion resistance properties. Variations of conditions of test, with the consideration of consistency[262] and the uniformity of results[263] have also been dealt with. Abrasion results are not seriously affected by moderate changes in temperature, but consistent differences have been found through such causes as variability in abrasion paper, variation in the rate of abrasion, etc. A method of measuring resistivity in conductive rubbers has been described[264] which eliminates the high electrode contact resistance of other methods. It consists essentially of measuring the potential drop along a portion of a sample while a current is being passed through, and the results may be used to give an indication of the relative value of compounds as conductors in actual service.

J. R. Scott and his co-workers have also examined the measurement of the hardness of vulcanite types of rubber by the ball indentation test[265] and the effects of French chalk, paraffin wax bloom, the condition of the surface and thickness of the sample are discussed. The conclusion is drawn[266] that the Herbert pendulum is not satisfactory for measuring hardness, although it is of potential value in measuring resilience and, possibly, some other properties of the rubber not measurable by any other instrument. Experiments with an unloaded ebonite with approximately 30·8% combined sulphur have given some indication[267] of an appreciable temperature coefficient for the results of cross-breaking strength tests. The effect within the normal range of room temperatures is too small to affect seriously the result of the measurements, although materials with a lower combined sulphur content may be more influenced on account of their greater plastic yield. The influence of the rubber-sulphur ratio and the vulcanization time on the properties of hard rubber has been investigated[268] in relation to swelling, water absorption, and ageing characteristics, and the action of hydrocarbon oils on hard rubbers has been examined.[269] It is stated that vulcanite-type compounds with more than 25% sulphur are affected very little by exposure to oils up to 100°.

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LEATHER

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THE published works on protein analysis continue to illustrate the variety of techniques which are available. An electrodialysis method has been employed by McPherson[1] for separating the amino acids produced by hydrolysis: the analyses of 15 proteins, including collagen, are given. Another paper[2] describes the separation of the mixed amino acids into five groups by adsorption analysis: (i) aromatic (ring compounds, such as tryptophane), (ii) basic (such as arginine and lysine), (iii) acid (*e.g.*, aspartic and glutamic), (iv) those giving stable combination with formaldehyde (*e.g.*, glycine and cystein), and (v) neutral, aliphatic, or cyclic (*e.g.*, alanine and proline).

Glutamic and aspartic acids have been found to be separable by elutriation through an acidic alumina column followed by removal by different alkalis.[3] Another worker[4] claims to differentiate most of the monoamino carboxylic acids by observation of the Raman spectra of chloro-derivatives produced by the action of hydrochloric and nitric acids on the protein hydrolysate.

Various techniques have been reviewed in papers presented to the New York Academy of Science under the headings of: (i) chromatographic and ion exchange methods,[5] (ii) microbiological,[6] making use of bacteria whose nutritional requirements result in specific attack on the respective amino acids, (iii) enzymic methods[7] based on the use of enzymes of specific action.

Partition chromatography on silica gel has been described by Tristram[8] with details of the necessary conditions of preparation of the silica. The protein is hydrolysed, extracted, and the amino acids acetylated before the partition examination. " Synthetic " mixtures using up to seven amino acids were taken to test the method, and more than 95% recovery of the acids was obtained, but collagen is not among the several proteins examined.

It is stated[9] that application of the electron microscope reveals a consistent repeat distance of 640 A. in collagen, with six unequal sub-periods within this interval, and further, that no hitherto proposed structural model for collagen accounts for these phenomena.

The possibility that the components of a tissue, while identical from the histological point of view, may have different chemistry has been discussed by Bate-Smith.[10] He deals mainly with the staining reactions of the important protein fibres of skin, and declares that the identity of collagen with reticulin is still an open question.

A collection of information on the factors which affect the growth of animal skin, and its consequent quality from the point of view of leather production, was presented in a paper[11] to the Association of Applied Biologists; it includes consideration of the influences of breed, nutrition, age, sex, environment, and certain artificially imposed factors.

Introductory speculations have been made by Ames[12] on the nature of the cross-bonds of collagen which are broken in the degradation to gelatin by acid or alkaline treatment. The gelatins have been examined by formol titration, by magnesium sulphate precipitation, and by treatment at 85° under different p_H conditions, which gives varying loss of gel strength and viscosity according to p_H. From the differentiation of the properties and reactions of the gelatins, the author postulates that there are four types of cross-linkage between the collagen backbones, one of which is broken in producing gelatin, but a different one according to whether the acid or alkaline process has been used.

Preservation of skins

The suggestion has been made in a Russian paper[13] that the putrefactive degradation of animal skin might be followed, and assessed, by chemical tests designed to detect and estimate the products which characterize such breakdown of the protein. Among those are tyrosine, tryptophan, and cystine—for the estimation of which the Folin-Denis reagent is suggested—lactic acid, and aldehydes—detected by Schiff's reagent.

The intensification of reaction given by these and by some other reagents over a period of 20 days' degradation of skin samples is described, and the suggestion made that the technique is simple enough for use in tanneries.

Some advocacy has appeared,[14] in American publications particularly, of brine curing of skins as against the more usual salting; better uniformity, freedom from salt staining, and better cleanliness are claimed. A new form of curing for world shipment has been proposed in South America. In this " Accel " process the hides or skins are unhaired by normal methods, delimed, and then given a treatment which may be described, perhaps, as a " tawing " or reversible tannage, from which they may be dried out for transport. The claims are for lower weight, as against a salted skin, and for ease of wetting by the tanner, as against dried skins; this product has yet to prove itself technically satisfactory, however.

Work has been published by Pankhurst[15] on the changes which can occur in skins in sun drying and drying after salting. He points out that difficulty in " soaking-back," that is in rehydration, may be the result of wet heat damage to the protein, and that curing salts whose vapour pressure is such that a high humidity is produced against the fibres may be unsuitable when temperature of drying is high.

The relative merits of the newer insecticides continue to be thrashed out. In one report,[16] 1% on the skin weight of a 75% DDT and 0·1% of a 13% Gammexane preparation were both reported to give as effective control of hide beetles (Dermestidæ) as 1% sodium fluoride. Further, some woolskins infested with Dermestes beetles were treated with approximately 1% their weight of dusts containing 4% DDT, 0·4% and 1% Gammexane, respectively; only the last had given satisfactory control after two months' storage. Lastly, some Nigerian skins are reported to have been satisfactorily protected during shipment to England by a 1% application of a 2·5% Gammexane preparation. In a later report[17] a dusting preparation of Gammexane (containing ½% of isomer) applied at the rate of 2½% on the skin weights (therefore equivalent to 4oz. of active material per ton of skin) gave complete immunity in three months' storage in Africa under conditions favouring insect attack, and during shipment to England.

A DDT soap/solvent dispersion has been reported very effective against sheep-maggot fly,[18] but ineffective against ox warble.[19]

The possibility of using a DDT preparation by spray as alternative to the less easy, conventional dipping of the animals has been indicated:[20] the DDT only needs surface application to the fleece to provide toxicity against the blow-fly, whereas good penetration of the fleece and wetting of the skin is necessary with conventional larvicidal dips.

Claims are being made now[21] for the value as an insecticide of Velsicol 1068 (empirical formula $C_{10}H_6Cl_8$—an octachloro derivative of a reduced indene molecule). It has been declared more effective than DDT against certain beetle larvæ.

The general problem of mould and insect attack on leather has been summarized by Musgrave.[22] He includes notes on laboratory technique for testing fungicides and insecticides, and the further considerations which arise on translating control to the manufacturing stage.

Pretannage processes

Liming.—Board of Trade circulars,[23] concerned with promoting economy, have contained analyses of the wide variation in the consumption of lime and sodium sulphide by hide tanners. It is found, by dividing consumers into the two categories " Above average " and " Below average " and taking averages within the two groups, that about 11% and 6% of lime on the hide weight is used respectively. The sulphide quantity variation is less remarkable because there may be differences of technique which justify it—such as whether or not the hair is preserved, or the process is done rapidly in a drum or slowly in pits. Three degrees of consumption are shown by the analysis, (*a*) 0·11–1·01lb., (*b*) 1·15–1·92lb., (*c*) 2·5–5·71lb., expressed as crystalline sulphide per hide.

Bating.—Pickard[24] proposes to test bating materials (proteolytic enzymes) by using limed catfish skin as substrate; these skins contain a brown or black pigmentation which is loosened by the bate, and the progress of the action is marked by transference of the colour from the skin to the solution. This worker remarks that the conventional methods of testing bates—using gelatin or casein as substrates for assessing the proteolytic activity—are often given a quantitative interpretation which may not have any significance in the tannery: his proposed technique is only claimed to make qualitative assessments. A French paper[25] records the opinion that the testing of bating preparations involves, first, tests in the laboratory by the Loehlein-Volhard method, using casein—with possible modification of the usual p_H if the proteinases are not pancreatic, but of bacterial or mould origin—followed by works-scale trials to supplement the laboratory work. The deliming components in the bate—and activating agents if these are distinct—have to be determined by analysis, and the p_H maximum activity by trial. Results for one type of skin do not necessarily apply to other types, and the extent of liming which the skin has been given has its effect on the enzyme digestibility of the proteins.

Degreasing.—The principles involved in degreasing skins have been expounded by McLaren[26] and also by Pankhurst,[27] the former giving an account of some extensive experimental work.

Pankhurst makes reference to the several methods of pre-tannage degreasing—solvent, aqueous, and pressure—and stresses the necessity of releasing fats from their cells and the effect of acid pickling in that connexion, and also for splitting calcium soaps which may have been formed in the liming. He states that the surface-active agent which is used with paraffin degreasing should not be so efficient as to make the paraffin difficult to remove from the wet skins, and indicates the advantage, as such an accessory, of agents which are hydrolysable in acid, such as sulphated amyl oleate: the products of this hydrolysis are less effective and have lower affinity for the protein. McLaren claims that non-ionic agents make effective accessories for paraffin degreasing; water-in-oil type emulsions result, which are inverted when the paraffin-treated skins are washed with brine. He deals also with the possibility of cationic agents (inverted soaps, such as quaternary ammonium compounds) or non-ionic agents. Among the latter the alkylated phenol-ethylene oxide condensates are found particularly effective, and are the subject of a British patent.[28]

Tanning

General.—A paper by Balfe and Jordan Lloyd,[29] read to the XIth International Congress of Pure and Applied Chemistry, dealt with the tanning of collagen from the viewpoint, particularly, of its effect on the physical structure. It pointed out the various criteria of tannage—not all of which may necessarily be met in any particular leather—and went on to deal at greater length with the maintenance of the separated fibrous structure, which is one of the features of satisfactory leather. Tanning and the ancillary processes must preserve this structure and prevent its collapse during the drying of the leather. The mechanism of the different types of tannage is outlined, and the distinctive character of mineral tannage in this connexion is shown.

A Russian paper[30] reports work carried out with ox hide fibres to determine dimensional changes during tanning. Several different tannages were applied, and the length of fibres was found to alter very little, whereas width might increase by over 60%. It would be deduced from the results that leather volume increased with angle of weave only up to about 40°—which seems not in accordance with macro-scale tannage—and it is suggested that negligible increase of fibre length when tanned supports the conception of the tannin molecules becoming attached at right-angles to the polypeptide backbone.

Vegetable tanning.—Gustavson[31] has been concerned with investigation of the system vegetable-tanned protein/mineral acid, and the information which it can supply concerning the mode of combination of vegetable tannins with collagen. The possibilities of this combination include (1) co-ordination on non-ionic, peptide groups, (2) co-ordination with basic groups, and (3) electrovalent reactions with basic groups. He has studied the hydrochloric acid-combining power of leathers made by different tans at different p_H levels, and with and without subsequent washing to differentiate between " fixed " and " reversibly fixed " tannin. It was found that with some tans the fixation of acid by the washed leathers indicated 80–100% of the basic groups still free, but in other cases with more astringent tans the washing of the leather had little effect on the acid-fixing capacity, indicating tan fixation on the basic groups. That these groups may also react with tan electrovalently is also indicated by the tan-displacing ability of certain simple sulphonic acid syntans, reacting as simple acids without any co-ordinating tendency.

Page and Holland[32] report on the relative uptake of fixed tans and "combined water-solubles." (Page had earlier worked on the water extraction of leather, and distinguished between different degrees of extraction which he considered indicated different modes of combination: he now supposes that the "fixed tan" is attached to the basic groups, and the "combined water-solubles" co-ordinated to the peptide groups.) Working with wattle bark they find a decrease of fixed tan with increase of tan concentration, accompanied, however, up to a tan concentration of 4%, by an increase of the "combined water-solubles." The suggested explanations are (i) that the fixed tan and "water-solubles" compete for attachment to the peptide groups, or (ii) that there are steric limitations to penetration by both, reinforced by "case hardening"—the tanning of the surface to an extent which hinders subsequent diffusion into the skin.

The bearing on leather properties of the salts and acid content of tan liquors has been investigated by Benskin[33] in respect of mimosa tannage. Tensile strength was found to be little influenced by salt concentration, except in the hot-pitting, when p_H levels of below 3 may call for salts to be higher than 0·3N. if strength is not to be adversely affected. The elastic modulus of the wet leather (more popularly "wet firmness") is considerably influenced by the p_H/salt relationship, and the higher the salt the less the effect of hot-pitting in increasing the firmness, unless p_H is correspondingly lowered. Variations in salt and acid—even to extremes—have unimportant effects on leather thickness.

Humphreys[34] contested to some extent the orthodox views on the firmness effects of salt concentration, and suggested that not all salts, as estimated by the resin exchange methods, are non-tans, and that there may be, for example, compounds such as quebracho-sodium sulphonate fixed to the protein. This work, however, has been criticized by Benskin and Cheshire,[35] who assert that no fixation of sodium salts by collagen from sulphited quebracho takes place in the p_H range typical of heavy leather tannage, that this tannin does have its salt content removed by exchange resins in that p_H range, and that the salt level variation used by Humphreys was not sufficiently wide to refute the general contention of its effect on firmness.

Chrome tanning.—A historical review of the development since 1930 of theory as to the mode of combination of chromium with collagen has been given by Gustavson[36] showing the evolution of the bridging concept according to which the protein backbones are linked through the co-ordination of their carboxyl and amino groups with internal salt complexes of the chromium. The same author elsewhere[37] has made a convincing attack on the adsorption theory of chrome tanning.

The effects of formaldehyde pretreatment on subsequent chrome tanning and of chrome pretannage on subsequent formaldehyde tanning have been studied by Theis and Kleppinger.[38] Broadly, they found that formaldehyde pretreatment lowered chromium fixation, and that the chrome retannage resulted in the removal of some formaldehyde, but that chrome pretannage resulted in the subsequent fixation of more formaldehyde than would otherwise have occurred, in this case with higher shrinkage temperatures in the resulting leather. Having regard to the accepted view that chromium tannage involves the amino groups—and possibly the imino, too—and formaldehyde tannage involves the acid amide, imino and amino groups, according to the p_H of the reaction, it is deduced that the higher formaldehyde fixation referred to indicates association of the aldehyde with the chrome complexes also.

Analytical studies of chromium solutions have been made by various methods. Using ion exchange resins, Gustavson[39] found that typical tanning solutions contain cationic, anionic, and uncharged chromium complexes, the anionic and uncharged being favoured by high basicity and high neutral salt concentration, the latter particularly favouring uncharged complexes. Chromium chloride liquors of high basicity (70%) are said to show a predominance of uncharged complexes with a high degree of molecular aggregation. Adams[40] has given particulars of this analytical technique, and strikes a warning note on the shift of equilibrium which the ion removal may cause. Allowing for this, he states that sulphate chrome tanning liquors always contain some anionic chromium with basicity having little effect on the proportion; also that displacement of sulphate from the complex by oxalate or formate (" masking ") is slow at room temperatures and never attains complete conversion of all the chromium to anionic form.

Using formate-modified chrome tannage up to 3 molecules of sodium formate per 1 molecule Cr_2O_3, Theis[41] found advantage in speed of tanning without sacrificing smoothness of grain or fine break. Laboratory and pilot-scale tannages were carried out, and it is stressed that, to take advantage of the formate action, the p_H should be taken up to over 4·5. This author, with Thorstensen,[42] has investigated the formate-chromium solutions by exchange resin technique, and reached the conclusion that their specific action is due to the whole formic acid molecule entering the complex as distinct from only the masking anion as usual.

A continuation of his conductimetric method is reported by Shuttleworth,[43] with some conclusions as to the effect of masking by dibasic organic acids: the increasing chromium uptake which they effect may be connected with their ability to form bridges between two complexes.

An original method for supplying the phthalic acid for masked chrome tanning has been proposed in Russia:[44] naphthalene is sulphonated and used to reduce bichromate, whereby the phthalic acid and the trivalent chromic salt are simultaneously produced. Details of procedure are given. Patents[45, 46] have been taken for the reduction of bichromate by waste material from the paper industry—the lignin sulphonates—and also for a tanning process[47] which makes use of myrobalans-reduced chromic acid to give a combination vegetable/chrome leather of high resistance to hot oil.

Leather oils and oiling

Burton[48] has published another stage of his work on the analysis of sulphated oils such as are used in the fat-liquoring of leather, in this case dealing with the estimation of the carboxyl, sulphuric, and sulphonic acid groups, and the salts resulting from their neutralization with soda and/or ammonia.

A new scheme has been proposed,[49] too, for the analysis of petroleum sulphonates containing salts. This estimates mineral oil, sulphonic acids, and carboxylic acids and their salts, and makes use of solvent-extraction separations and adsorption in a column of clay.

The mechanism of sulphation of oils, particularly as regards the location of the sulpho-group, whether at double bonds or via hydroxyl groups, has been dealt with by Kroch and Tomlinson.[50] They refer to the effect on properties of the position of sulphation: reaction at the end of the long chain tends to give detergents, while reaction at the middle, with shorter chain anions in consequence, favours wetting and emulsifying. It is also pointed out that oils containing less sulpho-groups than one per molecule of oil can nevertheless form clear solutions in water by micellar dispersion.

The B.I.O.S. report on the German light leather industry[51] states that of the substitute materials imposed upon the industry by the war, or by political economic policy, the Derminol oils and fat-liquors were to be counted among those which might still be technically acceptable in a free trading economy. There is information on their composition and manufacture in another report:[52] they are essentially chlorinated hydrocarbons.

Some joint investigations have just been reported from America[53] into the technical results obtained with several of the sulphonyl chloride derivatives of hydrocarbons as used in Germany for substituting oil tannage in " chamois " or " wash leather " production. This work has been aimed mainly at producing such type of leather, and the conclusion is drawn that further research is justified by the world shortage of glyceride oils.

A report from the American Military Research programme[54] gives results obtained in an investigation of certain physical properties of chrome/vegetable retan leathers fat-liquored and stuffed with various oil combinations: among other things water repellance and water absorption were examined. The absorption was found to be no indication of repellance, and the effect of flexing on the speed of water penetration was noted. Potassium soap as against sulphated oil in fat-liquors was found to lower repellance, as did aromatic-base oils as against paraffinic mineral oils.

Physical properties

Mitton and Lewis[55] have contributed again to the subject of leather abrasion testing. From a study of the effect of atmospheric humidity they deduce (1) that at a humidity characteristic of the particular leather the action of the abrasive changes from a tearing—at low humidity—to a cutting —at higher—consequent on the swelling of the leather fibres at higher moisture content and the change in hardness, (2) that it is of no importance whether the leather specimens had been kept in higher or lower humidities than that to which they were conditioned for testing, and that preconditioning was unnecessary anyway, as adjustment of the leather to the humidity prevailing at the testing was so rapid, (3) that the difference between abrading along the direction of the run of the hair follicles and across them is so small as to be doubtful, and is certainly too small to be technically significant. Another paper[56] has investigated the effects of compression and the removal of water-solubles on abrasion resistance: the results in such cases have to be carefully interpreted to avoid misconceptions which may arise from the change in thickness as a result of the compression. The authors enumerate the following principal conclusions: (1) water-solubles content is not better than tanned protein for wear resistance, but of two leathers of equal thickness made from similar hide and tanning materials, that with the higher water-solubles may give slightly better result, (2) compression of English-type sole leather does not increase abrasion resistance on a weight basis, but would appear to do so in terms of thickness with time, (3) compression effects depend on the water-solubles content, and may not be translated to different leathers.

An American patent[57] claims to improve wearing properties of soles without detracting from natural porosity by impregnation with a solution of a synthetic resin, and there have been British patents[58, 59] relating to the filling of chrome upper leather during its manufacture with aqueous dispersions of resinous polymers. In one case an interpolymer of vinyl chloride is drummed into the pickled stock before tanning; and in another the use of several types of synthetic resin is claimed for the same purpose: improved fullness of the looser parts of the skins is alleged.

Maeser[60] has described mechanical devices designed for testing American army boot upper leathers for water penetration during flexing. A machine which tested whole boots under walking action indicated that passage of water occurred most rapidly through the vamps, as is generally found in actual wear. Aluminium stearate applied from a solvent gave pronounced water-proofing effect.

In investigation of vapour permeability of leather it is important to avoid stagnant layers against the surface, and Mitton[58] has stressed this in his description of two types of apparatus designed for water vapour permeability determinations. The diffusion was found to conform to Fick's law whether the partial pressures at the faces were varied by humidity change or by adjustment of temperature. The corollary of this is that permeability is greatly raised by rise of temperature. This study was extended to determinations of the production of perspiration by the feet under conditions of rest and exercise, and the conclusion was drawn that during moderate exercise the amount produced is greater than will allow of its moisture content to escape by vapour diffusion through the upper leather of a boot or shoe. An average value for perspiration production during rest is 6–7 mg. per sq. cm. per hr. over the whole foot.

The amount of adsorbed moisture in raw hide and different types of leather in equilibrium with different atmospheric humidities has been investigated by Kanagy.[62] Chrome leather and collagen show very similar figures, but vegetable leather, in general, gives lower contents except that sole leather may be more hygroscopic by reason of added salts and sugars. Using a thermodynamic treatment for the adsorption of gases in multimolecular layers, the difference between heats of adsorption and desorption are found. The low value for this difference for collagen, and leather in general, as against those values which characterize chemi-sorption suggests a substantially van der Waals type of adsorption. Up to 75% R.H. the water uptake is a function of the surface of the fibres only—which is calculated to be 298 sq. m. per g. for collagen and chrome-tanned leather, but less for vegetable leather. By extending his hypotheses to the oiling of leather, and then finding that the amount calculated to coat the fibres is substantially higher than the oil contents which can, in fact, be used, the author deduces that much less fibre surface area is available to the oils owing to the greater size of their molecules.

Analysis and miscellaneous

Several papers have been concerned with modifications to the Kjeldahl nitrogen determination. The suggestion is made[63] that the ammonium sulphate may be determined by standard soda titration in the presence of formaldehyde, instead of distilling the ammonia from excess alkali; also that potassium di-iodate[64] should be used to determine the liberated ammonia by iodometric titration.

The application of spectrophotometric analysis to commercial chrome liquors is made possible by the utilization of oxalate complexes according to Theis and co-workers.[65] The addition of excess oxalic acid to the solutions produces trioxalate-chromiate, which has strong spectral absorption with extinction values at 4,200A. and 5,600A., the latter being unaffected by iron contamination.

A chromed hide powder has been produced in France[66] which is claimed to keep satisfactorily and to obviate the need for chroming before use in the tan/non-tan determination on vegetable tannins. Considerable time is thereby saved as against the official method.

Possibilities of error in the determination of chromium by the perchloric acid oxidation method have been considered by Schuldiner and Clardy:[67] the most serious is said to be due to volatilization of chromyl chloride, and a modification of apparatus to trap this is suggested.

A volumetric determination of small amounts of chromium in sewage has been described:[68] it is presumably applicable to tannery effluent, and depends on acid permanganate oxidation to chromate, the removal of excess permanganate by hydrochloric acid, and then the colorimetric estimation of the chromate by diphenyl carbazide.

The troublesome effect of water drops remaining attached to the glass in the Dean and Stark procedure for water determinations may be obviated by lining the glass apparatus with a silicone resin.[69]

An alternative to the well-known potassium hydrogen phthalate as a standard buffer has been proposed:[70] the corresponding tartrate is claimed to be stable to storage and to be very little affected by CO_2. Its p_H value is 3·57.

The action of iron in catalyzing oxidational rotting of leather is recognized in a British patent[71] which claims to introduce oxalates of alkaline earths for the purpose of sequestering the iron as a complex anion. A paper by the South African Research Institute[72] suggests other oxalates and certain fluorides for the same purpose, and states that anti-oxidants also afford some protection.

A procedure for sterilizing leather without causing any chemical or physical damage was worked out in America.[73] It is based on heat treatment at 250°F. after thorough drying.

The "bloom" formed by pyrogallol tannins is stated[74] to be the result of an enzyme characteristic of the tans. With some tannins, for example valonia, this deposit is essentially ellagic acid, with others, for example myrobalans and algarobella, both ellagic and chebulinic acids. If the enzyme is removed from the liquors by adsorption on to clay, bloom does not form: the activity of the enzyme is maximum at p_H 5 and ceases below 2·2. Solubilities and colour reactions for these two bloom components are given.

In preventing mould growth on tan liquors by the use of β-naphthol it appears that there is possibility of its absorption by the hides or skins,[75] and that proportions which are effective in the absence of skin may not be so in tanyard practice.

There have been published during 1947 two volumes, of the three intended, of "Progress in Leather Science, 1920–1945." These have been written by members of the staff of the British Leather Manufacturers' Research Association, and present a review of current knowledge in the science and practice of leather manufacture.

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PEST CONTROL IN AGRICULTURE

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IMPORTANT advances have been made during the past few decades in the chemical protection of crops from insect attack. In this work, the chemist and the biologist have played complementary parts; the chemist in perfecting suitable spray materials and the biologist, from his study of the habits and life cycles of the pests, in ensuring that the insecticides are applied when they will be most effective. As a result, the grower for some time has had at his disposal many types of sprays; tar oils, petroleum oils, dinitro-*o*-cresol-petroleum and thiocyanate-petroleum preparations have proved to be valuable winter ovicides, while nicotine, derris (or lonchocarpus) root, lead arsenate, calomel and a number of other materials have been used for particular purposes in spring or summer.

In the search for additional insecticides (in some cases to meet shortages due to war) many compounds, particularly synthetics, have been tested. Among outstanding discoveries in recent years are those of DDT and benzene hexachloride; other compounds likely to be of value have been recognized. Specificity of action, a feature of many insecticidal principles, has been observed; thus DDT, which is now known to be effective against a wide range of agricultural and horticultural pests, has little action on red spider mites, apple sawfly and some aphides. A vast amount of work has been necessary to determine the degree of usefulness of the newer compounds, and the steady carrying out of this work has been a notable feature of the period under review. In assessing the materials a number of considerations have to be borne in mind; while being effective economically against pests they must be without serious detriment to beneficial insects, they must be capable of use in different formulations, they must not damage foliage or leave poisonous residues when used at effective strengths, or be unduly poisonous in the concentrated form to operators. It is not surprising that in spite of the fact that much progress has been made, an insecticide fulfilling all these conditions has not yet been found.

DDT

The preparation, properties and methods of estimating DDT (1 : 1 : 1-trichloro-2 : 2-di-*p*-chlorophenylethane) were fully covered in the last Report. A one-step method has been described[1] for the synthesis of DDT from chloral hydrate, chlorobenzene and chlorosulphonic acid. The method is superior to the original method in yield, simplicity, ease of control of conditions and reproducibility of results. A. L. Flenner[2] has reported that impurities present in technical DDT inhibit catalytic dehydrochlorination; if purified, the addition of inhibitors may be necessary. A. H. McIntosh[3] has discussed the relationship between crystal size and shape and the toxicity of DDT suspensions, while N. Woodruff and N. Turner[4] have considered the effect of the particle size of DDT diluents in water suspension. The most commonly used method of determining DDT is conversion by alkali into the ethylene derivative with titration of the one equivalent of chloride liberated; R. L. Wain and A. E. Martin[5] have found that when the *p*-*p*′-isomer is boiled with N. alcoholic alkali, it loses slightly more than 1 g.-ion of chlorine per molecule. That the reaction was not a simple dehydrohalogenation was shown by the isolation of di-(*p*-chlorophenyl)acetic acid. They suggest a milder alkali or heat treatment to obtain a more accurate estimation. J. B. LaClair[6] has described a method based on dehydrochlorination in ethyl alcohol or kerosene solution for the determination of DDT in dusts and oil solutions; possible sources of error are indicated and discussed. F. R. Bradbury, D. J. Higgons and J. P. Stoneman[7] give details of a colorimetric method for the estimation of DDT, utilizing the reaction with hydroquinone and concentrated sulphuric acid at 100° to give a wine red colour, while estimation of the isomers in technical DDT has been carried out by the determination of the setting point of the mixture of the corresponding dichlorobenzophenones.[8] Useful reviews of methods of estimating DDT in insecticide preparations have appeared,[9] while other work[10] has been concerned with the question of assessing DDT in residues on crops.

The fate of DDT in the animal body has also received attention. It has been observed that when DDT was ingested in foods it accumulated in the body fat and appeared in the milk of animals.[11] A. W. Lindquist, E. F. Knipling, H. A. Jones, and A. H. Madden[12] have shown that the blood of rabbits fed on DDT and the pyrethrins was toxic to bed bugs feeding on the rabbits. The need for further information on the question of the conservation and effect of DDT in animal tissues has resulted in methods for the analysis of such materials.[13] C. J. Tressler[14] has investigated the recovery of DDT from canned foods and its stability during processing. Interest has been taken in other insecticidal members of the DDT group, notably in 1 : 1-dichloro-2 : 2-di-*p*-chlorophenylethane (DDD)[15] and in the *p*-*p*′-methoxy analogue[16, 78] of DDT, both being less toxic to warm-blooded animals than DDT. H. V. Claborn[17] has described a method for the determination of DDT in the presence of DDD. No theory to explain the mode of action of DDT has yet been generally accepted. M. D. Proverbs and F. O. Morrison[18] in an investigation of the insecticidal activities of DDT and related organic compounds show the effect on toxicity of the removal or substitution of the Cl of the phenyl groups. H. Martin[19] has referred to the parallelism between dehydrochlorination and insecticidal activity in DDT analogues, but P. Müller[20] and also E. A. Prill, M. E. Synerholm and A. Hartzell[21] have found that activity varied according to structure but was not necessarily correlated with the ease of loss of HCl in alkaline solution. H. Hurst[19] has attributed the action of DDT to the indirect blocking of the cytochrome oxidase and succinic dehydrogenase systems by the storage of the insecticide in the phospholipoids of the cell membranes. J. H. Welsh and H. T. Gordon[22] discuss the mode of action of certain insecticides, including DDT and the pyrethrins, on arthropod nerve tissue.

There is no doubt that DDT is a valuable agricultural and horticultural insecticide although its full merit is still under investigation. It may be used as dusts, containing 2 to 5% DDT intimately mixed with inert materials, or as sprays made from wettable powders suspended in water, emulsions, or oil solutions. Concentrations of DDT of the order of 0·05 to 0·1% are normally required in the diluted spray material. It is effective against a variety of pests, and has provided a control of some insects which earlier could only be kept in check with difficulty. An outstanding case is the apple blossom weevil, where work on the biology of the pest was followed by recommendations for its control.[23] DDT has been widely used against caterpillars on Brassicæ, the dusts or sprays giving excellent control, although egg-laying by the adult insects was not prevented.[24, 25] Further work has shown that among other important pests in this country excellent control may be obtained of the bean and pea weevil,[25] strawberry rhynchites,[26] carrot fly,[27] flea beetles,[28] pea moth[29] and leatherjackets.[30] Tomato moth caterpillars under glass have been found[31] to be particularly susceptible, sprays containing as little as 0·02% DDT being effective. C. Potter, F. Tattersfield, and (Mrs.) E. M. Gillham[32] have compared the contact poison action of DDT with nicotine, derris and the pyrethrins, and have shown[33] that the effect of DDT on aphides is markedly influenced by the medium in which it is applied. F. F. Smith[34] has found that aphides rendered moribund by DDT can produce normal offspring, with rebuilding of the infestation. DDT has only a moderately toxic action on wasps, its effect being rather slow.[25] An outstanding development has been seen in North America, where remarkable increases in the yield of potatoes have been obtained by the use of DDT combined with certain fungicides.[35] A valuable account of the uses of DDT in agriculture and horticulture in this country has been given by C. T. Gimingham and R. A. E. Galley.[36]

Recent work in Ceylon, with a survey of the world literature, has shown that DDT is harmless to operators applying it for insecticidal purposes.[37] The persistence of DDT residues is of value in conferring upon plants a longer period of protection against pests, but at present little is known of the possible cumulative effect in man of small amounts of DDT ingested regularly in food over long periods. Until further information is obtained, excessive residues on crops should be avoided; in this connexion the U.S. authorities have imposed a tolerance of 7 p.p.m. on the DDT residue permissible on apples and pears.

Considerable attention has been given to the possible effects of DDT on beneficial insects. *Aphelinus mali*, a parasite of woolly aphis, has been found[38] to be more easily destroyed by DDT than is its host, so that the use of DDT has sometimes resulted in a marked increase of woolly aphis. Ladybirds and their larvæ, predators of aphides, are readily killed by a spray containing 0·1% DDT.[25] In various parts of the world it has been found[39] that the use of DDT against the codling moth of apple has tended to result in a marked increase in red spider, normally kept in check by numerous predators. For this reason, the use of DDT against codling moth in this country has been discouraged, and until further information is obtained and the risks have been clarified, a safe ruling would be not to apply DDT in orchards at any time during the summer later than the green cluster stage[40] of fruit development, before which few beneficial insects are likely to be encountered.

Much concern has been expressed at the possibility of DDT killing bees. Recent investigations,[41] however, have shown that earlier fears have not been substantiated. While further information is undoubtedly required the use of DDT is now generally considered to be much less hazardous than that, for example, of lead arsenate. As with other materials, DDT should be applied with discrimination, and use upon open blossoms in particular should be avoided. A recent report[42] gives data on the potential danger to honey bees of many insecticides, including some of the more recently discovered materials. DDT has been found to have no effect upon bacteria or fungi although it may slightly retard yeast fermentation.[43] It has been shown[44] not to affect certain biological processes in the soil and its possible effect upon tidewater aquatic animals[45] and upon fish, bird and wild life[46] in general has also received attention.

Benzene hexachloride

L. Ramsey and W. Patterson[47] have described the separation and purification of some of the constituents of commercial benzene hexachloride (1 : 2 : 3 : 4 : 5 : 6-hexachloro*cyclo*hexane). The material contained 65-70% of the α-isomer, 5% of β-isomer, 10–12% of γ-isomer, 6% of δ-isomer, 4% of ε-isomer, 4% of heptachloro*cyclo*hexane and 0·6% of octachloro*cyclo*hexane. The isolation and properties of the newly-found ε-isomer have been described by K. C. Kauer, R. B. DuVall and F. N. Alquist.[48] The earlier recognition that the γ-isomer was the chief insecticidal principle of benzene hexachloride has been further substantiated by the work of R. L. Metcalf,[49] who determined the relative toxicities of the isomeric hexachloro*cyclo*hexanes and related materials to greenhouse thrips; toxicity to thsi insect was shown to be entirely due to the γ-isomer, additions of the α-,β-,δ-,ε-isomers, either singly or in combination, having little effect. Hexabromo*cyclo*hexane and 1 : 2 : 4-trichlorobenzene, which is formed from the α-, γ- and δ-isomers by the action of alcoholic alkali,[50] were found to be non-toxic to this insect. B. Melander[51] has found the insecticidal activity of the isomers of benzene hexachloride to increase with increasing dipole moment, and concludes that these properties are closely related. A cryoscopic method for the determination of the γ-isomer content has been referred to by C. V. Bowen and M. A. Pogorelskin,[52] and a method for the determination of small amounts of benzene hexachloride, based upon dehydrochlorination with monoethanolamine, has been published by B. H. Howard.[53] A review of the chemistry of benzene hexachloride is given by H. L. Haller and C. V. Bowen.[54]

As with DDT, much work has been carried out to determine the value of benzene hexachloride against plant pests. Of special interest is the discovery of its paralysing or repellent effect on the wireworm, a serious pest of which no satisfactory control by chemical means has hitherto been found in spite of extensive investigations. H. R. Jameson, F. J. D. Thomas, and R. C. Woodward[55] have shown, following earlier reports,[56] that two to five fold increases of grain may be obtained on heavily infested land by the application of a few pounds of crude benzene hexachloride per acre. Further work is in hand, preliminary reports confirming the value of the treatment. H. C. F. Newton, J. E. Satchell, and M. W. Shaw[57] have obtained excellent control of carrot fly by means of a 2% benzene hexachloride dust, and H. W. Miles, D. J. Finney, and F. J. Anscombe[28] have shown the value of the material against flea beetles. An interesting example of the complementary nature of DDT and benzene hexachloride is shown in the case of pear psylla, resistant to DDT but capable of control by benzene hexachloride.[58] F. J. D. Thomas[59] has successfully used benzene hexachloride to control crickets, and

R. B. Dawson and J. R. Escritt[60] to control leatherjackets. An account of the use of DDT and benzene hexachloride in agriculture has been given by H. Shaw.[61]

One of the most important developments of the use of the material abroad is in the control of locusts. O. B. Lean[62] describes the effect of benzene hexachloride in a poison bait against the hoppers, in which as little as a fraction of an ounce of the γ-isomer per acre has proved effective, while from Australia J. Loughlin[63] reports the successful spraying of the hatching grounds from aircraft. Benzene hexachloride has also been shown to control other plant pests, notably grasshoppers,[64] certain cotton insects,[65] and pests of tobacco soils.[66]

As with DDT, care has to be taken when using benzene hexachloride to prevent the killing of beneficial insects; honey bees are known to be very susceptible to its action. Reference has been made[67] to the risk of certain crops, *e.g.*, potatoes, acquiring an unpleasant taint following the use of benzene hexachloride in pest control; as with other insecticides, the material should be used judiciously and excessive applications avoided.

The toxicity of benzene hexachloride to mammals has been found to be of a relatively low order,[68,69] while its deposits on foliage are less persistent than those of DDT. Further observations have been made on the occurrence of benzene hexachloride in the blood of animals after it has been taken in food. P. C. C. Garnham[70] found the blood of rabbits fed with benzene hexachloride to be toxic to mosquitoes feeding on the rabbits. E. Hixson and M. H. Muma[71] have observed the tainting of poultry flesh after the administration of food containing benzene hexachloride, while F. Barlow[72] reports that benzene hexachloride persists in the blood of cattle after oral ingestion, the blood being toxic for a considerable time to tsetse flies feeding on the cattle.

Other chlorinated compounds

Further reports have appeared in the U.S.A. on the usefulness in agriculture of chlordane ($C_{10}H_6Cl_8$, 1 : 2 : 4 : 5 : 6 : 7-hexachloro-4 : 7-dichloromethylene -3a : 4 : 7 : 7a-tetrahydroindane) and a chlorinated camphene. Little work with these materials, however, has so far been carried out against agricultural pests in this country. In U.S.A., J. W. Brooks and L. D. Anderson[73] have compared chlordane with DDT and benzene hexachloride in work on several pests of vegetable crops, while L. A. Stearns *et al.*[74] have investigated the effect upon vegetable pests of the chlorinated camphene. E. E. Ivy and his co-workers[75] have carried out further comparisons of both materials with DDT, benzene hexachloride and other insecticides in the control of certain cotton insects. Chlordane is known to be highly effective for the control of grasshoppers, with good residual effect.[76] It has been found to have a toxicity to white rats of the same order as that of DDT[77] and to have little action on honey bees.[42] F. C. Bishopp[78] has reviewed recent investigations with chlordane, benzene hexachloride and other materials.

Organic phosphorus compounds

Several alkyl phosphates have recently been found to have marked effect particularly on aphides and red spider mites, and research on this new class of insecticides is likely to be actively pursued. Among the most interesting at present are hexaethyl tetraphosphate $P(O)[OP(O)(OC_2H_5)_2]_3$, tetraethyl pyrophosphate $(C_2H_5O)_2P(O)OP(O)(OC_2H_5)_2$, the diethyl ester of *p*-nitrophenoxythiophosphoric acid $NO_2C_6H_4OP(S)(OC_2H_5)_2$ (E605), and the tetraethyl ester of thiopyrophosphoric acid $(C_2H_5O)_2$ $P(S)OP(S)$ $(OC_2H_5)_2$, investigated by Schrader[79] during the recent war.

The compounds vary in their toxicity to warm blooded animals and in their stability when diluted with water or added to alkaline materials for spray purposes. S. A. Hall and M. Jacobson[80] consider that hexaethyl tetraphosphate hydrolyses in water to a mixture of diethyl and monoethyl orthophosphoric acids, and tetraethyl pyrophosphate to diethyl orthophosphoric acid, the products of hydrolysis being devoid of insecticidal action. Research has been directed towards finding a compound which while not unduly toxic in the concentrated form to operators will be compatible with alkaline sprays such as lime sulphur, and will be stable in water for a period sufficiently long to give good insect control without leaving dangerous residues on crops. Unlike hexaethyl tetraphosphate, the diethyl ester of *p*-nitrophenoxythiophosphoric acid is not readily hydrolysed and is stable to lime. The tetraethyl ester of thiopyrophosphoric acid also is lime stable.[79] G. F. Ludvik and G. C. Decker[81] in an examination of the toxicity to aphides of a wide range of organic phosphorus compounds, found eight, including hexaethyl tetraphosphate and tetraethyl pyrophosphate to be superior to nicotine. Among the most promising were tetrapropyl pyrophosphate and *sym*-tetrapropyl phenyl triphosphate which also may have commercial possibilities. J. W. Hansen[82] by distillation has separated commercial " hexaethyl tetraphosphate " into several inactive and one active fractions. Analysis has shown that the active fraction probably consists of tetraethyl peroxydiphosphate. This was found to occur in commercial preparations to the extent of 10–20% and to have 5–10 times the toxicity of the original material to rats, mice, and insects. Hansen suggests that the mechanism of toxic action may well be an interference with an enzyme system similar to adenosine triphosphate. K. P. Dubois and G. H. Mangun[83] and also T. Koppanyi, A. G. Karczmar, and T. O. King[84] have shown hexaethyl tetraphosphate and tetraethyl pyrophosphate to be powerful inhibitors of cholinesterase activity. The physiological effects of the alkyl polyphosphates have been further investigated by A. S. V. Burgen *et al.*[85] T. E. Bronson and S. A. Hall[86] describe the preparation and properties of hexaethyl tetraphosphate and report good control of aphides on cabbage and peas, by sprays and dusts, without foliage damage. A digest of information on hexaethyl tetraphosphate is given by R. C. Roark,[87] while J. S. Harris[88] has reviewed the present position with regard to tetraethyl pyrophosphate.

The discovery by Schrader that certain compounds, notably bis (dimethylamino)phosphoryl fluoride and tetramethylaminopyrophosphoric acid, when sprayed round the roots or on to the leaves of plants are absorbed and give protection against suctorial insects, has stimulated interest in the so-called " systemic insecticides." This effect has been investigated before, notably with selenium compounds.[89] D. C. Kiplinger and G. Fuller[90] have found that sodium selenate applied to soil reduced the infestation of red spider on chrysanthemums growing in the soil. The selenium content of the lower leaves rose to the high value of 330 p.p.m.; vegetables showed varying abilities to absorb and accumulate selenium. Until non-poisonous compounds which markedly show this property are found the method has limited application but may prove of value in pest control of ornamentals.

Azobenzene

Azobenzene ($C_6H_5N : NC_6H_5$) has given promising results in the control of red spider mites, particularly in glasshouses. W. E. Blauvelt[91] successfully fumigated rose houses by vaporizing a paste of the material on steam pipes, all stages of the mites, including the eggs, being killed. R. C. Haring[92] found dusts containing azobenzene to be effective against several economically important pests although a number of species, including some aphides, were observed to be highly resistant. In this country G. L. Hey[93] has investigated the value of sprays containing 0·1% azobenzene; red spider mites, certain caterpillars and wasps were readily killed, but no control was obtained of black fly on beans or of mealy plum aphis. The material damaged the foliage of some varieties of apple and further trials are needed before definite recommendations can be made. W. H. Read[94] has further examined the use of azobenzene under glass by fumigation and vaporization and has confirmed the high promise of red spider control on certain glasshouse crops. The question of the toxicity to man of azobenzene has been reviewed by Blauvelt.[95]

Plant products

Many plant products have been shown to possess insecticidal properties, although none has so far exceeded the toxicity of high-grade *Derris* or *Lonchocarpus* root, pyrethrum flowers or nicotine. *Derris ferruginia* has been found to contain rotenone and the active constituents of *D. scandens* and *D. robusta* have been examined.[96] M. A. Jones, W. A. Gersdorff, and E. R. McGovran[97] have shown derris to be more toxic than lonchocarpus of the same rotenone content, while M. A. Jones[98] has given a confirmatory modification of the test for rotenone-type compounds. Among the most promising of the new materials now recognised is sabadilla (seeds of *Schoenocaulon* spp.), which has given good control of lygus bugs on cotton and other pests.[99] The insecticidal constituents of *Pachyrrhizus erosus* have been investigated by R. Hansberry, R. T. Clausen and L. B. Norton[100], and by T. M. Meijer,[101] while *P. tuberosus* has been shown to have an appreciable effect upon the mealy cabbage aphis.[102] An insecticide based upon *Ryania speciosa* has been found to be effective against the oriental fruit moth,[103] while C. H. Brett[104] has reported on the insecticidal and repellent properties of the indigo bush (*Amorpha fruticosa*). S. H. Harper, C. Potter and (Mrs.) E. M. Gillham[105] have investigated the insecticidal properties of *Annona* species, while M. Jacobson and H. L. Haller[106] have shown the active principle of *Eugenia haitiensis* to be 1 : 8-cineol. Other plants shown to be insecticidal include *Mundulea suberosa*,[107] *Diospyros maritima*,[108] *Milletia pachycarpa*,[109] *Rhododendron molle*;[109] and *Mammea americana*.[110] The botanical source of the insecticidal amide N-*iso*butyl-2 : 6 : 8-decatrienoamide has been shown[111] to be *Heliopsis longipes* and not *Erigeron affinis* as earlier reported.[112]

Work has been continued on the pyrethrins and cinerins, the active principles of insecticidal pyrethrum flowers, with contributions from S. B. Soloway and F. B. LaForge[113] on the structure of dihydrocinerolone, and from H. J. Dauben and E. Wenkert[114] on tetrahydropyrethrolone. Pyrethrum flowers are evaluated at present on their contents of "pyrethrins I and II," which include the cinerins, and interest has arisen concerning the relative toxicities of the component active principles now recognized. F. B. LaForge and W. F. Barthel[115] in a preliminary report of work by W. A. Gersdorff show that, to houseflies, pyrethrin I was 1·5 times as toxic as cinerin I and pyrethrin II was 1·3 times as toxic as cinerin II; pyrethrin I and cinerin I being some 4 times as toxic as pyrethrin II and cinerin II respectively. G. T. Bray *et al.*[116] have confirmed the revised factor in the mercury reduction method of Wilcoxon and Holaday[117]; and the analysis of oil concentrates[118] and dilute oil solutions[119] has received attention. A new account of H. A. Seil's method of analysis has been published,[120] while K. A. Lord and C. G. Johnson[121] have confirmed earlier work[122] that the insecticidal principles are not responsible for the dermatitis-producing property of the flowers. H. Wachs[123] has reported further work on the preparation of synergistic compounds for use with pyrethrum.

Miscellaneous

Among many compounds tested, E. H. Siegler and S. I. Gertler[124] have found the phenyl and *p*-chlorophenyl esters of benzenesulphonic acid, N-*p*-tolylglycinonitrile, *o*-hydroxy-*α*-(1-piperidyl)-*α*-tolunitrile, and 1-*iso*valeryl-2-phenylhydrazine to be at least as toxic to codling moth larvæ as lead arsenate. S. H. Bennett, H. G. H. Kearns and H. Martin,[125] in an investigation of the ovicidal properties of certain thiocyanates have shown dodecyl thiocyanate at 0·4% to be effective against the eggs of the green apple aphis, apple sucker, and the fruit tree red spider mite. Various thioethers including some containing the 3 : 4-methylenedioxyphenyl group have been found by E. A. Prill, A. Hartzell, and J. M. Arthur[126] to be toxic to a number of agricultural pests. Attempts have been made to counter the increase of red spider mite following the use of DDT. W. S. Hough[127] has indicated the beneficial action of 2 : 4-dinitro-6-*cyclo*hexylphenol, while R. M. Greenslade and E. G. Goscombe[128] have reported that in South Africa, the increase in a *Bryobia* red spider mite was checked by the addition of the di*cyclo*hexylamine salt of this compound. J. E. Dewey[129] found that the use with DDT of 2′-hydroxy-2 : 4 : 4 : 7 : 4′-pentamethylflavan offered some promise, but that its performance was erratic. C. R. Cutright and R. Sutton,[130] after tests with various adjuvants, conclude that a summer acaricide having ovicidal and residual properties is especially needed, while experiments in Ontario[131] suggest that the tendency of red spider to increase may be overcome by using a summer petroleum oil in combination with DDT or by alternating DDT with lead arsenate sprays. The use of phenyl mercury chloride with lead arsenate for the joint control of leaf-eating caterpillars and apple scab has been described by H. Shaw and M. H. Moore.[132]

Considerable interest has been taken in soil insecticides, particularly in relation to the difficult problem of controlling nematodes. A mixture of 1 : 2-dichloropropane and 1 : 3-dichloropropylene has been shown to be promising for the control of potato eelworm[133] and eelworms infesting tomato roots.[134] A satisfactory control of wireworms has been obtained using this mixture and also ethylene dibromide, giving increased yields of lettuce and beans.[135] Other soil insecticides which have been investigated include methyl bromide, benzene hexachloride, DDT, chlordane, and ethylene dichloride; recent developments have been reviewed by W. H. Lange.[136] T. Goodey[137] has shown that the stem eelworm infesting onion seed may be controlled by fumigation with methyl bromide, while C. Ellenby[138] has investigated the effect of allyl *iso*thiocyanate in preventing the hatching of the cysts of the potato eelworm.

As a result of the recent advances we are now within sight of controlling a number of our most difficult agricultural pests. Many of the compounds are still in the experimental stage and further information is needed; as more and more become available, only those that are most suitable are likely to survive. With the object of giving guidance to growers in the purchase of insecticides, a scheme has recently been instituted in Great Britain by which official approval may be granted to proprietary products designed for the control of pests and diseases of growing crops.[139]

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AGRICULTURE AND HORTICULTURE

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A SELECTION of a limited number of topics for review in the Report has again been made in preference to an attempt to review the whole range of the chemical literature of the application of our subject to the entire industry of agriculture and horticulture. In making this selection due regard to that made in previous years has been paid.

The remarkable developments of recent years made with synthetic insecticides and their successful application to control of pests in the field has been largely responsible for the inclusion of a special chapter dealing with insecticides and fungicides; a natural sequence to the preliminary introduction made in the 1946 Reports. The continued interest displayed in fertilizers, their application to, and reactions with the soil, and their influence on the uptake by plants of nutrients, demands some consideration of such matters, but it is pointed out that both major and minor plant nutrients were dealt with at considerable length last year so that this year an attempt is only made to indicate the lines along which progress is being made rather than to attempt to review that progress with stated crops or chosen elements. As plant nutrition has received such recent attention the opportunity is now taken to focus attention upon animal feeding stuffs, as in the war years considerable experience was gained of such use of farm products—pressed into service in the emergency—that usually are not so utilized. Continued advances have been made in the study of the organic matter in soils and from such materials have been extracted compounds that play an important part in the formation and maintenance of the "crumb"-like structure of soil particles. Similarly the products of bacterial activity have been shown to bind soil particles together. A prominent feature of the year's publications has been the large number of papers concerned with the use of selective weed killers, and these are now brought together; but the consideration of other uses of these active organic substances, as that of regulating the fall of fruit from the trees, for example, must be deferred as the limitation of space dictates.

Soil particles

Aggregates and organic matter

Factors influencing the formation and the stability of soil particles or aggregates have received further attention in the period under review, including the parts played by water or ice, by organic substances derived from addition of organic manures or by bacterial action, by aeration and by mechanical operations. Thus Gardner[1] observed that freezing, causing pressure on the soil particles, by compaction and dehydration, resulted in a flake-like structure that was stable in soils with high calcium, but not in soils of high sodium content. He observed that freezing and thawing failed to render impermeable soils of a sodium nature permeable, as did the replacement of the sodium by calcium, but after treatment of these soils with calcium chloride the subsequent freezing proved effective. In tests made by McHenry[2] the stability of mixtures of puddled clay and sand increased with the number of cycles of wetting and drying as they tended to reach a maximum at twenty cycles, after which segregation of the ingredients took place. The greatest degree of stability of the aggregates of the four soils from Iowa occurred near the moisture equivalent. Water stability followed treatment of the clay with univalent ions; bivalent and trivalent ions proved less effective. With bentonite a reduction of exchange capacity was accompanied by a decreased stability. The addition of organic matter derived from lucerne and maize gave two maxima for water stability of the aggregates, believed to be associated with the products of decomposition and the metabolic activity of bacteria but no identification of these products held responsible was attempted. Peterson[3] compared the capacity of kaolinite with that of montmorillonite to form water stable aggregates when mixed with sand and repeatedly wetted and dried, the latter was fairly high, the former low. He also found that the incorporation of organic matter, as ground lucerne, followed by incubation for a month before wetting and drying did not increase aggregation in his tests with kaolinite and montmorillonite. Peterson stated that the clay must dry from the gel condition, rather than from the flocculated, if it is to form water stable aggregates; greater stability occurred if the cations adsorbed on the clay were less hydrated. Under field conditions Alderfer[4] recorded the seasonal variation in the degree of aggregation of silt loams. The percentage of water stable aggregates reached its maximum in autumn and winter, and fell to a minimum in the hot dry summer months of July and August. Whilst the soil moisture content was related to the size distribution of the aggregates the effect was modified in summer by alternate wetting and drying and in winter by freezing and thawing. At the soil surface the percentage of large aggregates was low, but mulching of the surface with organic matter increased the aggregation in the surface layers but was without effect in the next few inches of soil. Stephenson and Schuster[5] found the growth of sunflowers highly satisfactory in soil taken from below a straw mulch, surpassing that made in other samples where nutrient deficiences were corrected; they observed a large proportion of aggregates of more than 1mm. in this layer of surface soil which was also rich in acids, soluble potash and humus.

Peele[6] reports that the mucus produced by bacteria, especially by the nodule bacteria from pea roots, produced water-stable aggregates when incorporated with soil or quartz particles. The direct addition of sucrose to soil containing bacteria and fungi greatly increased the aggregation; without the presence of the organisms there was no response, but of the organisms tried, a fungal culture was more effective than the bacterial in this respect. Martin[7] tested six polysaccharides isolated from bacterial filtrates in regard to their effect on soil aggregation, three fructosans and three dextrans. All gave positive results indicating high but varying efficiency in this respect exceeding the efficiency of " lignin." On the other hand, to two sterile calcareous soils, culture filtrates were added by Hubbell and Chapman[8] without effect in forming aggregates; the roots of a grass also produced no effect, but when living bacteria, fungi, and actinomyces were present they produced distinctive types of aggregates which in the soil were readily bound together by the roots of plants to give more elaborate structures. These considerations are related to soil aeration.

Webley[9] has described his technique for the study of the availability of oxygen to soil micro-organisms; a washed suspension of bacterial cells with an excess of oxidizable substance was added to air dried soil. The oxygen taken up was considered to be a function of the soil aeration. Quastel and Webley[10] observed the effect of the addition to the soil of alginic acid and other forms of organic matter on the aeration of the soil as assessed by the technique mentioned. The added sodium alginate improved the crumb stability and the water holding capacity; 0·1g. of sodium alginate added to 100g. of soil brought about changes equivalent to an increase of 11% of the water holding power, yet the relatively insoluble calcium salt caused very little effect. A combination of the alginate with a soil constituent was suggested. Cellulose acetate, methyl cellulose, and carboxymethyl cellulose also improved the water/air relationship; finely divided wheat straw increased the water holding capacity. The removal of these substances brought about a reversal of the effects. From the addition of dung arose effects considered to be due to polyuronides and polysaccharides. Extracts from fertile soils and from peat also improved the water/air relationship as assessed by this method.

Forsyth[11] has fractionated the fulvic acid portion of the organic matter of soils, obtained by precipitation by dilute acids after extraction by solution in cold alkali; this was accomplished by adsorption on carbon and successive elution with 90% ether, water and aqueous caustic soda. From four soils rich in organic matter, Forsyth obtained a polysaccharide containing in its structure uronic acid groups and a glucoside group. (The nitrogen of the fulvic acid was partly in acidic complexes and partly in degradation products). In a further paper Forsyth[12] dealt with the humic complex, its extraction, oxidation, and reduction, and its characteristic nitro-, chloro-, and bromo-compounds. Carboxylic, phenolic, methoxyl, acetyl, quinone, and tautomeric carbonyl groupings are considered to be present. Purification took place by freezing and thawing, and by hydrolysis of precipitated substances. Yields of 43% of crude humic acid were obtained from peat, and smaller yields from the organic matter of composts, 6·5%. Fractionation of the humic precipitates was carried out, by water, anhydrous and alcoholic bases. Pyridine under reduced pressure left the carbohydrate fraction, the alcoholic base was a solvent for lignin, and acid hydrolysis (2% HCl) removed the carbohydrates. The use of equal volumes of alcohol and benzene gave a 25% yield from heather of humic acid; the non-humic acid material was thought to be merely adsorbed as a contaminant and not to be an integral part of the molecule. The number of reactive groups and their nature was shown to depend on the length of time and other conditions under which the humus was formed.

Whilst the preceding papers concern the aggregation of soil particles into crumbs, the dispersion of soil colloids has also come under investigation. Wiklander and Hallgreen[13] determined the amounts of clay washed out of soil by leaching with varying concentrations of chlorides, from soils saturated in turn, with sodium, potassium, magnesium, calcium, or barium. Dispersion increased with decreasing concentration of the chlorides, and was greater in the case of sodium than barium soils. The organic colloidal fraction of the soils was dispersed in higher concentrations of salts, and more readily leached away than the mineral fraction. Thus structural aggregation may readily be destroyed.

Fertilizers: major nutrients

Nitrogen

Reviewing data collected from short duration experiments (usually of one year) made between 1896–1940, Cowie[14] found that a mean response of 2·4cwt. grain and 4·8cwt. straw resulted from a single application of nitrogenous fertilizer equivalent to 1cwt. per acre of $(NH_4)_2SO_4$ to wheat; with two applications the increase averaged 4·6cwt. and 9·9cwt. respectively. Only small, insignificant responses arose from added phosphates, and in only 40% of these cases was the gain of any economic value, whereas in 87% of the trials the response to the second cwt. of sulphate of ammonia proved remunerative under the rainfall conditions experienced. On semi-arid soils the relative effects of manure, sulphate of ammonia, and straw ploughed in (with sulphate of ammonia added), on the yield of wheat and the nitrogen content of the crop have been examined by Smith *et al.*[15] who reported that yields and bushel weights of grain were not greatly affected, but the yield of straw and its nitrogen content was thereby increased. Even under the semi-arid conditions the addition of the sulphate of ammonia failed to maintain a higher nitrogen content in the soil but the organic matter was naturally effective in this respect.

Volk and Tidmore[16] observed the effect of different sources of nitrogen on soil reaction, and the yields of cotton and maize. Yields from crops assisted by the acid forming types of fertilizer or manure were lower than from non-acidic, excluding cyanamide which gave low results. Correction of soil acidity overcame the effect and made the yields equal. Cropping for 13 years continuously without addition of lime lowered the soil p_H only 0·2 unit. The use of a mixture of 3 : 1 parts of nitrate of soda and sulphate of ammonia caused no p_H change.

In the analysis of another long series of observations made in the period 1872–1940 with mangolds at Rothamsted and elsewhere, Watson and Russell[17] found that the ratio of roots to tops was increased by nitrogenous fertilizers except sulphate of ammonia used with potash or sodium salts. Leaf yields were almost entirely dependent upon the nitrogen supplied, potash having a greater effect on the root growth, as did the sodium supplied. During the war years Crowther[18] showed that the actual yields of sugar from sugar beet were increased economically by the addition of sodium, as salt, so that for these plants it well may be considered as a major nutrient, not entirely effectively relaced by additional potassium.

Whilst Murneek[19] has discussed the use and effect of the various nitrogenous fertilizers in horticultural practice with especial reference to apples grown under American conditions, a more detailed study of the effect upon the tree has been made with peaches by Lott[20] who recorded an increased number of floral as well as vegetative buds after the application of sodium nitrate. This leads to increased yields of good sized and high quality fruits. Wander[21] showed that the total nitrogen in the apple leaf was correlated with the behaviour of the tree; very high nitrogen content was associated with poor crops and with the development of poorly coloured fruits.

The competition for nitrogen between crop plant and weed has been studied by Mann and Barnes,[22] using barley against the prevalent weeds, spurrey and mayweed. With limited supplies of nitrogen the barley obtained some 75% of the nitrogen available, the weeds the rest, even when the number of weeds exceeded the number of barley plants. The yield of the barley was depressed some 45% by mayweed in the presence of high nitrogen, and by spurrey some 12%—an effect considered to be entirely due to competition for nitrogen and root space, involving water uptake no doubt.

Another aspect of work with fertilizers is that shown in relation to disease, Glynne *et al.*,[23] report the effect on wheat receiving different amounts of nitrogen of the fungus causing " eye spot " (*Cercosporella herpotrichoides*); with high levels of nitrogen the fungus killed 11% and induced a straggling condition in 31% of the plants thereby reducing the yield of straw by 8% and the grain by 16%. With low levels of nitrogen the fungus caused greater damage, killing 23% and causing 86% to straggle; on the yield this gave a depression of 23% of the straw and 44% of the grain. Whilst all inoculated plants were diseased the higher levels of nitrogen permitted free tillering or branching of plants, so that the less severely injured shoots replaced those badly effected by the disease. In such cases the farmer states that the crop " grows away from the disease "; thus it is not always true that a high soil or plant content of nitrogen " encourages disease."

Phosphorus: soil fixation

Marquis[24] has pointed out the necessity for a vigorous policy in France for enriching the soil depleted of phosphorus in the war years, which was accompanied by the decline in yield of field crops, that of sugar beet having fallen to only 40% of the pre-war level. The growth of oats and rye in Kansas soils, where the replaceable bases were of great importance, was not limited by the phosphorus content of the soil, but the amount of growth was related to the phosphorus in the chemisorbed and readily soluble fractions in acidic solutions, provided these fractions of the phosphates were themselves related to the amounts of the replaceable bases (Wynd and Noggle).[25] The nature of the adsorbed phosphates was examined by Kurtz *et al.*[26] by leaching with water, aqueous sodium fluoride, and acidified solutions of that salt. They found a progressive adsorption with the elapse of time, a decrease in the water soluble fraction, an increase in that soluble in acid. Adsorbed phosphate was removed by sodium fluoride, other ions were used to disperse the adsorbed phosphate of which some were effective in varying degree. These workers regard fixation as adsorption rather than precipitation. Davis[27] added small quantities of phosphoric acid to soil suspended in lime water followed by treatment with carbon dioxide. The PO_4 was not, he thought, adsorbed by the colloids as an anion at p_H below 5, except in the absence of calcium; with further additions Davis considered that the calcium salts, $Ca(H_2PO_4)_2$ or $CaHPO_4$, formed were adsorbed in ionic form; this process of adsorption was associated with base exchange inversely related to the lime present. In a later paper Davis[28] reports his extraction tests; less phosphate was recovered after addition of the acid than from soil receiving equivalent amounts of the calcium salt $Ca\,(H_2PO_4)_2$. The difference was most marked when carbonated water was used for extraction. Ghani and Islam[29] incubated soil at optimum water content with various phosphatic fertilizers; during a period of contact of two weeks the proportion fixed after any given time decreased with larger quantities of phosphates present, but the quantity of fixed phosphate was related to the proportion of iron and aluminium phosphates recoverable from the soils. In suspensions of soil in water fixation took place rapidly for a short time, but after six hours proceeded more slowly.

Wynd and Noggle[25] in a further report state that the amount of phosphate present in the surface soil chemisorbed, when accompanied by adequate nitrogen, was closely related to the protein content of the leaves of cereals, but the amount of readily acid-soluble phosphate showed no relation to the yield or percentage protein in the leaves. The carotene content was reported to be related to the chemisorbed and readily acid-soluble fraction of the phosphate present, and claims were also made that the vitamin-*C* content was related to this fraction, and that with replaceable bases present final yield was related to this fraction. The argument would seem to preclude the uptake of phosphate from relatively and comparatively more insoluble sources.

Fudge and Fraps[30] find that prairie grasses fail to supply adequate protein and phosphates to grazing stock; phosphatic fertilizers tended to rectify this, young grass showing a closer correlation between the soil conditions and the chemical constitution of the leaves than did the older and more fibrous grass. Hinkle[31] obtained with lucerne good responses from superphosphates but not from ammonium phosphates. Greaves and Pittman[32] observed that the later cuts of lucerne were richer than earlier ones in both sulphur and phosphate content; despite the richness of the soil in phosphate this crop responded to additional phosphates by increased yields and by a higher phosphate content of the produce. Yet Lawton[33] under the conditions of his test made on the Michigan soils reported that phosphatic fertilizers depressed the growth of lucerne, although on the poorer soils potash and minor elements gave responses. The continuous use of ammonium phosphate in Burma for rice has been proved by Rhind and Tin[34] to give satisfactory responses only for a few years, and is later followed by decreased crops.

With tomato soils Owen and Rees[35] obtained comparable analytical results from extractions made by acetic and citric acids; with soils rich in calcium carbonate, as most of such greenhouse soils were, the loss of phosphates from the soil was very low but they recommend the addition of water soluble phosphates to these soils for propagation purposes.

There thus remain many points to be cleared up in regard to phosphatic manures and fertilizers, and the fixation and release of the phosphate; but for protein formation in plants, normally rich in protein, these substances are now being used more. A new line of approach is afforded by the use of radioactive isotopes. Spinks and Barber[36] have followed the seasonal uptake of phosphates using P^{32} as ammonium phosphate, applied to wheat; by late July some 25% of the added phosphate had been taken up. Comar and Neller[37] using a series of Florida soils in tests for phosphate fixation found that these samples were placed in the same ranking when assessed by chemical analysis of equilibrium solutions, using radioactive and inactive isotopes. They also determined the uptake of radioactive phosphate by oats grown for a short period of three weeks. Time and further work will surely provide many more details of the fate and nature of adsorbed phosphates in soils and of the uptake of this element by plants.

Potassium

Owen and Rees,[35] using 1% citric acid and 0·5N-acetic acid for potassium extraction from soils in addition to water extraction, obtained wide differences in their estimations; these were influenced by leaching, by previous manuring, by partial sterilization by steam, and by other factors. It was suggested that 0·06% potash (citric acid soluble) was sufficient in the soil for the satisfactory growth of tomatoes. Stewart and Volk[38] examined the relation between the potash present in soils and that taken up by plants during depletion over a ten year period by exhaustive cropping. Some two-thirds of the potash initially present in a non-exchangeable form was taken up, but the amount taken up was not closely related to the amount of exchangeable potash present. The ease of release of the non-exchangeable potash varied widely.

Whereas the nitrogen and potash taken up by *Perilla* was largely taken up during the early phases of growth the magnesium and phosphate was shown by Demidenko[39] to be taken up throughout the growing period at a more uniform rate. As yet we require much more information of this type for with the possible exception of the tomato, the times of uptake in regard to the phases of development, and the relative rates of uptake at these phases, are only imperfectly known for many cultivated plants.

Animal feeding stuffs

Restrictions on imported feeding stuffs accompanied by an increased demand for milk has resulted in the last ten years in the extended cultivation of kales. Fagan, Phillips and Davies[40, 41] provided analyses of the different varieties of kale grown in Wales; the dry matter varied from 12·5 to 15%, the crude protein from 19·6 to 27·8%—a very high figure—with phosphoric acid varying from 0·9 to 1·15% in samples tested in winter. By thinning the plants the yield of the marrow-stemmed variety, expressed chemically as protein, was increased by about 1cwt. of crude protein per acre. The protein content of the Hungry Gap and Rape kales, contrary to that of other sorts, increased as the season advanced. The silage made from kales was analysed; 14 to 19% of crude protein, 0·5 to 0·75% of phosphoric acid, and 1·5 to 2·2% of lime showed the food value of this product. Approximately 25–28lb. of the kale silage fed to dairy cattle, once they had acquired a taste for it, replaced some 30–35lb. of kale fed in the fields. Ferguson[42] provided similar data from other districts, and the earlier recommendations of Logan Wood[43] have been adequately confirmed. Two useful bulletins dealing with practical agricultural points concerning the production of kale and its ensilage have recently been published.[44, 45]

Bottcher[46] in a critical review of the ensilage process of grass and other fodders, comparing different methods, the A. I. V(irtanin) and ammonium phosphate ($NH_4H_2PO_4$ is used), states that the results cannot adequately and accurately be judged by chemical analysis alone, partly owing to difficulties in sampling. The estimations of ammonia, assessing the degree of rotting, showed the value of additions of ammonium phosphate. Haskell and Harvey[47] claim patent rights in the addition of mono- or di-ammonium phosphates and urea, for the making of ensilage using 0·2 to 2% of these substances. Using lucerne and timothy grass there was a loss of 28% as compared with only 7% by hay in the dry matter during the preparation. Of the original carotene content, that retained in hay was 40%, in A.I.V. silage 78%, using phosphoric acid 43%, molasses 22%, with no supplement 18%—according to the analyses of Camburn *et al.*[48] The comparative values of the digestible ether extracts of silage, of clover and timothy hay, of oats and barley, were very nearly equal at 8·6 to 8·7kg. cal. per g. Allowing for corrections due to loss of dry matter Ericksson[49] suggests a value for ensilage of 5kg. cal. of metabolizable energy per g. of the digestible ether extract, a rather lower value than previously put forward. This value was (at least with rabbits) independent of the crude fibre content which varied very widely.

With *Salsola pestifer*, the Russian thistle, using young plants with 16% protein, high carbohydrates and low fibre content, Donaldson and Goering[50] prepared good silage in small tests. Lindahl *et al.*[51] using cooked potatoes at a temperature of 60°F. found the loss of nutrients high. At lower temperatures the loss, due to putrefaction, was low, but the resulting product proved of little value in pig feeding, whereas that obtained at the higher temperature was palatable to the animals. Ensilage has been made from citrus pulp; Bondi and Meyer[52] supplied analytical data, and obtained information from digestibility trials made with sheep. Although protein was low the material was considered useful.

Amongst other tests those made by Briggs *et al.*[53, 54] to supplement the protein of prairie hay for young cattle, included the feeding of cotton seed meal, soyabean meal, and peanut meal. The apparent digestibility of 50·7% for peanut and 45% for the cotton seed meal was observed; but the utilization and storage of protein by the cattle was almost the same for the different feeding stuffs. The protein gave digestibility percentages of hay 43%, cotton seed 80%, peanuts 91%, and soyabeans 92%. A daily nitrogen uptake of some 8 or 9g. was estimated, but the peanut was not such an effective source of supply. As this crop assumes new importance in other parts of the world the increased significance of its protein feeding value for stock is not to be overlooked. Soyabeans, damaged by frosts, had quite a high feeding value, and gave high energy and protein figures in tests made with pigs by Fairbanks *et al.*[55] who used this material to supplement the ration along with corn, lucerne, bonemeal, limestone, and iodized salt. The value of damaged grain harvested under adverse conditions in a very wet season for feeding purposes has been pointed out by Crowther.[56]

The inadequacy of beet molasses, fed to young pigs at 40% of the feed, with useful other substances such as barley, tankage, or lucerne, was shown by the tests made by Rasmussen *et al.*,[57] for the animals developed a disease due to the beet molasses. Even 15% proved deleterious and was sometimes capable of causing fatal results; the addition of 5% of brewers' yeast, or the feeding of green lucerne, prevented the symptoms and corrected the diet. More mature pigs, of some 1cwt. or more, did not develop the disease and were able to utilize the beet residues satisfactorily and gained in weight thereby. Thus this material has a restricted use as have acorns, recently shown to be of limited value in feeding poultry (Temperton[58]). The residue from dressing flax seed has a reduced feeding value as the result of the weed seeds and immature linum seed present. The chaff might be superior to poor hay or oat straw, but inferior to high grade hay as shown by the analyses made by Common.[59] The apparent digestibility of the stems of peas and lima beans when fed to sheep was determined by Miller and Davis;[60] high crude protein figures were reported namely, 65 and 57%. Using the materials exclusively, the peas maintained the sheep with increasing live weights, but the lima beans failed to do so. In further reports (Davis *et al.*[61]) the by-products from cannery works were reviewed from the aspect of their lignin content. The pea stems were the richer at 16%, the lima beans contained 10% lignin. Phillips *et al.*[62] estimated the fractions of the fibre content, of which in the pea 55% and in the lima bean 61% was digestible. The pectic substances were completely digested. Fats were imperfectly dealt with by the animals. Bennett[63] has paid attention to the hemicelluloses of maize and rye straw; he reports that a pyranose structure was predominant with polyoses, polyuronides, and cellulosans present. Estimations were made of the molecular weights of the compounds, by reducing methods, by means of the ratio of uronic acid anhydride to anhydroxylase. The maize gave 81% anhydroxylase, 3·75% uronic acid anhydride, the rye 85·8 and 3·67% with traces of hexose. These figures have yet to be related to digestibility in ruminants and other livestock. But Woodman and Evans[64] have investigated the nutritive value of fodder cellulose from wheat straw, of which some three-quarters is crude fibre; sheep were used. As in paper making practices, hydrolysis by 5·9N-caustic soda for 7 hr. with 70lb. per sq. in. pressure was carried out followed by washing and drying at 100°C. A very high yield of true cellulose was obtained. With 800g. of hay, 600g. of cellulose was offered to the experimental animals daily. A coefficient of digestion of the total cellulose of 82%, and of the crude fibre 91%, was observed with sheep; with pigs, fermentation in the large intestine resulted in digestion almost as efficient as that of the sheep. Products of bacterial activity included the fatty acids—acetic, propionic, and butyric. For growing and fattening pigs the utilization of the fodder cellulose—80% of the crude fibre originally present—demanded fine grinding as a necessity. The fodder cellulose was evaluated thus: 25lb. was estimated to be equal to 17lb. of fine bran, or 8lb. of barley. The defects were the bulky nature of the material, the necessity of fine grinding, the low palatability necessitating other appetizing ingredients, the gas arising from fermentation in the intestines, the "negative" protein value; all these defects limit the quantity that can be used. Pigs make poorer use of cellulose; this material is of greater potential use to the ruminant.

Bartlett and Blaxter[65] have tested urea as a substitute for protein in the rations of a large dairy herd. Original protein deficiency was confirmed by the observed increments following an increase of some 5% in the protein content of the food supplied. This was also effective in raising the protein content of the milk. Supplying the same amount of additional nitrogen as urea gave no significant change in the milk production. When more than 3oz. urea was taken up daily the yield was depressed; data of body weight and butter fat ran parallel to the milk yields. Further attention is thus directed to the action of urease leading to the absorption of ammonia. This enzyme occurs in many leguminous fodders, and earlier in 1923 Kay[66] indicated the importance of its synthetic action.

A by-product arising from the production of penicillin, the dried fungal felt, containing about 42% protein, was tested by Woodman and Evans[67] as a possible nutrient for pigs and ruminants. No deleterious effects were reported. The material provided a fifth of the pigs' diet and half that of the sheep's. At higher rates of feeding signs of rickets developed, believed to be due to high phosphoric acid and low lime content. Used in moderation the material has some feeding value.

Whilst the utilization of such by-products may effect some economy and may be a necessity in war-time, the findings reported above must be considered in the light of Watson's[68] remarks about the efficiency of conversion of animal feeding stuffs into human food. He found that feeding below the maximum possible level at any stage of the growth of steers lowered the efficiency of food production; the maximum efficiency was approximately 8·6% on a calorific basis, or 10·5% on a protein basis. This can be readily impaired by attempted economy especially where steady growth of the animal is required.

Selective weedkillers

A very useful, but short, historical introduction to the subject of chemical weedkillers, covering the period 1896 to 1946, has been recently provided by Blackman.[69] The use of ferrous sulphate, copper sulphate, sulphuric acid, and other simple inorganic substances, was followed in 1932 by tests made by Trouffaut and Pastac[70] with nitrophenols, and nitrocresols. Long and Brenchley[71] have briefly reviewed the work carried out with these and other substances, such as cyanamide, and other fertilizers applied with a view to weed killing. Templeman[72] observed the killing of charlock by α-naphthaleneacetic acid and the degree of resistance offered by oats to this chemical. Slade, Templeman and Sexton,[73] drew attention to the differential effect of certain synthetic plant growth substances on plants; Nutman, Thornton and Quastel[74] reported inhibition of growth by means of 2 : 4-dichlorophenoxyacetic acid. Many substances have been tried out as weedkillers, since Templeman's observations, and amongst them the methylchlorophenoxyacetic acid has received a large number of tests.

The complexity of the relationship between plants and the toxic chemicals makes it very unwise to attempt to foretell the action of any substance on any weed without field tests; this state of affairs is well shown by the data from Blackman's [75, 76] tests reporting the action on many plants of the newer and other substances. Thus many investigations have been recently reported, of which Holmes[77] has reviewed those especially concerned with the annual weeds of cereal crops. Perhaps the most interesting point arising from these experiments is that the rate of application, proved sufficient, is as low as 2 or 3lb. per acre of the active substances.

Amongst earlier tests may be mentioned those of Hanmer and Tukey[78, 79, 80] using the dichloro- and trichlorophenoxy acetic acids as sprays at 1000 and 500 p.p.m. to kill bindweed. They later[81] reported that seedlings germinated in pretreated soil were readily killed or severely injured whilst grass proved resistant. A large number of trees and shrubs suffered severe injury to their leaves from application of sprays at 200 p.p.m. Mitchell and Marth[83, 84, 85] found that even very small quantities of 0·1mg. per lb. of soil might decrease the germination of mustard seed, but that grass seed was more tolerant. Thus the weed killers could be used for lawns. Van Overbeek and Gregory[86] using the dichloro compound as a spray at 750 p.p.m. found it effective in exterminating many weeds of sugar cane crops; but woody leguminous plants were more resistant and nut grass (*Cyperus rotundus*) required high concentrations for eradication (1500 p.p.m.); after the removal of competitors the more resistant weeds grew very well. Shafer[103] used the weed-killer with success in maize at an early stage of growth. The value of the phenoxyacetic acid weed killers is reduced by the fact that many vegetable crops are readily injured by the weed killer. Warren[87] found carrot, onion, beet, peas, all the cabbage tribe, and lima beans, very susceptible plants readily injured. Maize at certain stages of growth, when the tassels emerge,[103] proved resistant and weeds around may then be treated. The troublesome water weed, water hyacinth, has been effectively controlled by solutions at 1000 p.p.m. (see Hildebrand[90]). In New Zealand, Ward[91] reports the ragworts to be highly susceptible; Greenwood and Doak[92] found many weeds controlled, but the Californian Thistle required several applications to kill it. In Australia, Davies and Greenham[93] observed that the dichloro- and methylchlorophenoxy acids at rates equal to 1lb. per acre were effective in killing *Hydrocotyle tripartita* in golf and bowling greens without injury to the fine grasses of these lawns, but sodium dinitro-*o*-tolyloxide scorched both grass and weeds without any serious permanent effect on either.

Chondrilla juncea, a composite of probable introduction from northern latitudes, under Australian conditions proved resistant to naphthylacetic, methylphenoxyacetic, and naphthoxyacetic acids applied at 1000 p.p.m. In Greenham's[94] tests only a few leaves were killed; a heavy application of arsenic (7·5% As_2O_5) proved fatal. Similarly, Pridham[88, 89] has compared the arsenical weed killers, sodium chlorate and the selective growth substances in effect. Brown and Carter[95] show that the alligator weed (*Alternanthera philoxeroides*) can be checked amongst sugar cane by the dichlorophenoxy acid, the underground storage organs of *Caperonia castanefolia* were observed by Herbert and Mayeux[96] to be severely injured also. With other tropical weeds White and Villafane[97] report the control of nutgrass, waterweeds including *Eichornia crassipes*, *Nymphæa*, and *Victoria regia*. Poison ivy and other woody plants, although injured, proved more resistant in Grisby's tests.[98] Damage to a number of other shrubs has been reported (Tincker[99]), but the resistance of bracken has been found to be such that these weed killers cannot be used to clear this plant from hill country with a view to improving the grazing. *Equisetum* or mare's tail can be seriously checked by application of methylchlorophenoxyacetic acid at economic rates, though for eradication several applications are required. Using a wide range of vegetables Warren[104] made comparative tests with a number of herbicides; using sodium arsenate, ammonium sulphamate, trichlorophenoxyacetates, and pentachlorophenoxyacetates. Hopp and Linder[100] consider that high humidity promoted effectiveness, lower humidity and rapid drying decreased effectiveness; this led to attempts to use glycerine with the active substances to reduce the amount of the latter needed.

Crafts[101] tested some fifty nitro- and chloro-derivatives of benzene and phenol and of substituted phenols as weed killers; he found that toxicity increased from benzene to phenolic and to substituted phenolic compounds. Dinitro compounds were more effective than were chloro-nitro or nitrochloro compounds; *ortho*- more so than *meta*- or *para*-analogues. With dinitrophenols, those with aliphatic side chains were generally more toxic than cyclic or aromatic compounds. The most toxic of this series was 2 : 4-dinitro-6-*sec*.-butylphenol, but the concentrations suggested for use were comparatively high, at around 5% solutions.

Almost a thousand derivatives of phenoxyacetic, of benzoic, naphthoic, phthalic, sulphamic, carbamic, and other acids in addition to organic substances of dissimilar natures have been tested as growth regulators by the Chemical Warfare Service of the U.S.A.[102]

Amongst studies of the physiological effects of these compounds, such as the phenoxyacetic acids, may be mentioned those of Brown[82] who observed an increased respiration, a decreased translocation; a decline in the rate of photosynthesis was deduced. Mitchell[85] and Brown[82] reported the movement of the chemical slowly from leaf to stem; but more rapid movement took place downwards in the phloem and upwards in the wood following uptake from the soil. It was suggested that transportation from leaves was associated with movements of carbohydrates. The observations made to date do not assist us in understanding the reactions by means of which some plants resist and others closely related may succumb to these substances.

Templeman and Sexton[105] have studied the differential effects of these substances, using α-naphthalene acetic and aryloxyacetic acids on charlock and oats. The greater activity of β-naphthoxyacetic over the α- isomer was noted, chlorination was accompanied by greater activity with phenoxy acids, the introduction of methyl groups was also effective. The amides, nitriles, and esters of β-naphthoxyacetic acids were highly active. The effect of such compounds on enzyme actions is to be explored. In a further report, these authors compared the reaction of cereal and charlock to ethyl phenylcarbamate; tests were made with some thirty aryl carbamic esters, and thiocarbamates. These were prepared by the interaction of primary aromatic amines with chloroformic ester, and by the interaction of phenyl*iso*cyanate with the appropriate alcohol. *iso*Propyl phenylcarbamate was most active; followed by ethyl phenylcarbamate. These substances readily prevented germination of cereals, arrested early growth, and caused malformations of the shoots, and restricted the growth of the root system. Eleven active substances were reported. The very high degree of the activity of the leading substance was such that 1lb. per acre would be an effective rate of use, and at 5 p.p.m. immersion in aqueous solution would inhibit growth. At these levels of application there was no effect on sugar beet, potatoes, flax, mangolds, rape, or yellow charlock. This amounts to a reversal of the phenomenon seen with the methyl chlorophenoxyacetic acid, and some explanation is awaited. Lefevre[106] suggested that disorganization of nuclear division was the cause of the inhibition of growth with such substances as colchicine, and Templeman and Sexton are inclined to apply this to their results also. Ennis[107] recently stated that in his tests young oats withstood the effect of *iso*propyl phenylcarbamate when immersed in 500 p.p.m. for a period of ten minutes. He states that the oats and barley showed no ill effect, but application of 0·5g. per sq. yd. of the ester to soil proved highly deleterious, reducing the yield greatly.

The use of a number of other weed killers deserves brief mention. In Australia, commercial sodium dinitro-*o*-cresoxide has given good results when applied to the broad-leaved weeds amongst onion crops, using a 0·75% concentration. Cross[108] used a light grade of mineral oil effectively in killing small weeds amongst cranberries without injury to the crop. This has reawakened interest in the use of hydrocarbons generally and kerosene particularly. These have long been known to gardeners as useful for " spot treatment " of the rosettes of certain lawn weeds. Hardy[109] applied the kerosene as a fine mist to the weeds of carrot crops at the 3/4 leaf stage, using 70 gallons per acre. Effective weed control resulted without injury to the crop. Warren and Hanning[110] used a wider range of petroleum sprays, specifying by name the grades; they applied these at 50 or 100 gallons per acre. Early application to plants at the 2/3 leaf stage caused no injury, late application at a time when the crop measured some 8in. tall caused injury to the carrots. Undesirable flavours were caused by certain oils. Lachmann[111] found that a number of related crops of parsley, celery, dill, fennel, and others, were resistant to the oil (he used Stoddart solvent), at 125 gallons per acre, but the weeds were materially reduced; 5% anethole in kerosene, extracted from related crops, proved toxic to the weeds, but did not injure the carrots. He reports that with water emulsions the effects were reversed, injury to the crop ensued. Proprietary weed killers of American origin for killing dandelion, based on kerosene incorporating a toxic substance, have been tested in this country with quite good results. The value of all such tests is small as no exact specification of the oils are available. Blackman[75] states that the exact grade of oil is a necessary stipulation, for some oils may kill both crop and weed, other oils may only injure the crop; and yet others may be usefully selective in action. The real cause of this variability is not understood. Accurate specification is badly needed.

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STARCHES

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THE past year has been characterized by a relatively substantial contribution to the literature of starch technology from the continent of Europe, as well as from the United States. This, and the paucity of published information from Great Britain, is not unexpected. Much information has been released from Europe through Intelligence Reports and from previously occupied countries; whilst the result of war damage on starch production in Great Britain, coupled with a shortage of raw materials, has had its inevitable effect of some retardation in development work. Nevertheless, the increasing attention devoted to the preparation of starch modifications for special purposes has added greatly to our knowledge of its commercial utility, particularly in the textile industries. It is encouraging to learn that efforts are being made to put starch production in certain colonies on a more economic basis. Thus, arrowroot has been the subject of investigation at St. Vincent, West Indies, whilst Sir Norman Haworth's laboratory is active in examining starches from various sources on behalf of the Colonial Products Research Council.

Manufacture

Processes of manufacture of raw starch present interest, not merely on account of economic considerations, but also because of the variation of properties, especially physical, resulting from relatively slight modifications. Prior to the war there was much secrecy associated with processes adopted in European countries, and for this reason, the survey of the German Starch Industry, presented by British and Combined Intelligence Reports, is of much interest. J. Young and A. G. Tongue[1] provide information concerning the manufacture of starch from potatoes, rice, wheat and rye at the factories of Diamalt A.-G., the Deutsche Maizena Werke and Hoffman's Starke Fabrik. The full reports referred to will repay careful study.

The manufacture of starch from sweet potato is making great strides in America. A. A. Bourne and F. W. Thurber[2] describe the operation of a plant capable of producing annually more than 20,000 tons of starch for use in the textile, laundry and sizing industries, for the manufacture of adhesives and for use in food. According to A. K. Chaudhury[3] most grains of sweet potato starch are of size 4–6μ., but a small number are as big as 28μ. in diameter.

Maize starch, as usual, claims the attention of many investigators. N. F. Kennedy[4] furnishes a general description of its manufacture and uses. E. Szego,[5] in a historical review of starch products, gives statistical data on production of starch, with a general description of manufacture in the maize and potato starch industry, and other authors consider specialized aspects. Thus, R. E. Greenfield and G. N. Cornell[6] prevent loss of starch by using waste, instead of fresh water, for steeping. This enables soluble materials to be recovered for animal feeding stuffs. Corn Products Refining Co.[7] use starch-liquefying enzymes to produce a residue suitable, when mixed with a filler, for use as thin-boiling starch for paper coating.

A number of special processes in starch manufacture are worthy of record. O. H. Eble and M. J. Mason,[8] in a process for bleaching starch suitable for high grade paper sizing, refer particularly to the necessity of retaining the p_H at about 4 during the later part of the process, with the object of keeping low the N-content. Failure to do this usually results in a starch of poor colour. This point is also emphasized by E. Szego.[9]

R. L. Beukenkamp[10] makes thin boiling starch by mixing it dry with 20% or more of a soluble neutral salt or salt mixture, *e.g.*, NaCl, Na_2SO_4, alum, etc.

From Russia comes a process[11] for extracting starch from grain by means of sodium salicylate. The residue is washed with acetone to dissolve the salicylate, and the starch is then separated by adding acetone to the salicylate solution.

Starch products are especially liable, during processing and storage, to be attacked by bacteria and fungi. It may be rendered free of thermophilic bacteria by drying at 130–140°F. to a moisture content of 1–2% and by subsequently drying at 240–260°F. for 1–3 hours.[12]

Special and modified starches

Cold-water swelling starches

The preparation of modified and special starches for a wide variety of purposes continues to occupy much of the starch literature and a number of patents have been completed. The textile, paper sizing and adhesive industries have been enriched by several new processes for the production of cold-swelling (soluble) starches. G. P. Vincent[13] renders it soluble by treating it in suspension with acid and sodium chlorite. In order to prevent lumps when cold-swelling starch is added to water, an addition of lecithin to the starch is made.[14] Another process mixes starch with an aqueous solution of a cellulose derivative capable of swelling in cold water, and the whole is passed over heated surfaces at a temperature over 100°C., followed by grinding and screening.[15]

Pregelatinized waxy maize starch is prepared by H. H. Schopmeyer and G. R. Felton[16] by injecting steam into the starch at p_H 5·5–7·0, the resulting gelatinized product being dried on a combined flash drier and mill. The final product is claimed to have an adhesive strength five to six times that of similarly treated ordinary maize starch.

T. C. Chaudhury[17] describes a white starch, completely soluble in cold water at 28° made by drying the mature fruits of *Mirabilis jalapa* at 60–75°.

A form of starch soluble in organic solvents is prepared by treating starch with an allyl halide in the presence of concentrated alkali and an organic solvent.[18] The manufacture of cold-water-dispersible starches in Germany is dealt with in an Intelligence Report recently published.[19]

Non-swelling starch

Whilst much effort has been expended in the past in the production of these cold swelling starches, there is developing a demand for starches which will not swell in water. Such starches are specially useful for application to textiles and for special adhesive purposes (*e.g.*, for plywood). Processes for the production of such starches are becoming increasingly frequent. From W. A. Scholten's Chemische Fabrieken[20] emerges a method involving the treatment of a cold-water swelling starch with synthetic resins, such as urea or its derivatives, phenol or cresol. Such starch is resistant to washing. The same Company has another process,[21] making use of an aldehyde (*e.g.*, formaldehyde) or a substance producing an aldehyde by decomposition, with cold-swelling starch. The explanation of the action of the aldehyde is that it forms " bridges ", *e.g.*, methylene ether, between the starch molecules, the reaction being catalysed by mineral acids. The Perkins Glue Co.,[22] of U.S.A., describes a process, also based on the use of formaldehyde and acid, for the production of " insoluble " starch, particularly useful as a filling material for paints, adhesives, plastics, etc. F. A. Möller's[23] process again makes use of formaldehyde with a catalyst and results in the production by sudden heat of a gelatinous product which is pressed into thin lozenges and dried by heat.

Other processes designed to produce non-swelling starches are due to J. Lolkema and C. M. H. Kool,[24] who etherify or esterify cold-water soluble starches; and to J. W. Evans[25] by the use of an alkylolamine soap (*e.g.*, triethanolamine stearate). In both cases, the finished products are intended for coating paper and fabrics and for other sizing operations.

Stabilized starches

Some attention has been devoted to the production of stabilized starch, and partially hydrolysed starch pastes for easy use, particularly in adhesives and in the textile industries. S. N. Glarum and J. J. Thomas[26] have prepared a partially hydrolysed starch paste preserved against spoilage by bacteria, by a heating treatment followed by the addition of methylol urea and titanium oxide. The paste so prepared will keep for longer than 9 months. J. S. Pecker and E. A. Pecker's liquid starch preparation[27] is made by gelatinizing corn starch and adding pine oil or phosphorous acid as antiseptic. After the addition of blue and cooling, the gel produced is broken up into fine particles which do not coalesce.

L. O. Gill and J. W. McDonald's[28] viscous starch is prepared by treatment with dimethyl-urea, urea-formaldehyde polymer or melamine-formaldehyde monomer.

A pan-greasing preparation is described by B. F. Buchanan and A. L. Lloyd.[29] They mix gelatinized starch, containing water-insoluble protein, with 2 parts of molten fat. The mixture does not form aggregates nor does it set.

Starch ethers and esters

The ethers and esters of starch have been the object of investigation mainly owing to their moisture resistant properties and figure substantially in the patent literature. Starch acetate is produced by R. H. Treadway[30] by heating starch with acetic anhydride and acetic acid in the presence of perchloric acid. M. G. Groen[31] uses a mixture of ammonium acetate and acetamide at an elevated temperature with an acylating agent. Groen's product is a triester, white in colour, soluble in organic solvents, and usable with solutions of acetyl cellulose.

For the preparation of ethers and esters J. Lolkema[32] mixes starch, NaOH and dimethyl sulphate, followed by stirring at 40–50° and drying. To prepare esters, dimethyl sulphate is replaced by ethylene oxide. The same author, with F. A. Müller,[33] has made a starch product capable of producing starch ethers or esters in water, although it does not consist of them.

This is accomplished by mixing starch cold-water paste with sodium monochloroacetate and barium hydroxide. On heating with several times its weight of cold water, a ready-to-use starch ether is formed.

The starch ethers of A. L. Nichols and R. M. Hamilton[34] are prepared by pre-swelling starch with an equal part of formic acid, mixing with NaOH and adding allyl bromide and benzene. The whole is refluxed for 4 hours at 100° and purified by steam distillation. This preparation is claimed to be particularly moisture-resistant.

For an account of the significance of esters and ethers of starch, readers are referred to a paper by J. A. Radley.[35]

Dextrins and adhesives

The commercial production of adhesives in Great Britain continues to suffer from a shortage of raw materials, particularly of tapioca starch. The import from the Continent of Europe of potato starch, added to maize starch, has enabled better qualities of adhesives to be made available than in the war years. A valuable dissertation on starch adhesives is given by A. F. Gutman,[36] whilst K. Myrbäck,[37] giving a review of his own work concerning the enzymic hydrolysis of starch, describes the method of separation and characterization of the various dextrins produced from amylopectin by malt amylase.

A dry product particularly useful when applied to moist surfaces of paper, where it adheres without sticking to hot drying rolls, is the subject of a U.S. Patent.[38] It is prepared by heating dry converted starch or dextrin with an aldehyde. Another U.S. Patent[39] describes an adhesive suitable for plywood and fibre boxes made by treating maize starch with water, caustic soda, soap and the sulphate of copper (or Zn, Cr, As, Sn, Sb).

For the preparation of adhesives with a waxy appearance for use as dressing for textiles, in paper manufacture and for cigarette papers, starch is oxidized in alkaline solution[40] at 85° and mixed with Marseilles soap in water.

An examination to determine the maximum bonding capacity of mixtures of starch with urea and $Ca(OCl)_2$ is reported by R. L. Datta and N. N. Bose.[41]

An interesting report of dextrin manufacture in Germany appears in an Intelligence Report.[42] The dextrin is made mainly from potatoes and its production in several well-known German plants is described. It would appear that little research work on dextrin has been performed during the war in Germany, but it has been found that trivalent antimony compounds may be used instead of borax to give thickening. Useful dextrin formulæ are included in the report.

Analysis

The methods available for the estimation of starch, particularly in cereals and foods in general, are considered by many analysts to be unsatisfactory. Consequently, the efforts being made by L. H. Lampitt and his colleagues to investigate the factors concerned with the successful application of well-known methods of estimation should be of interest to a large number of chemists. They find[43] that in the hydrolysis of starch by hydrochloric acid, two reactions occur, namely a rapid hydrolysis to dextrose and a slower decomposition of the dextrose produced. It is necessary in employing this method to apply a correction factor for the dextrose subsequently destroyed, the correction being greater the longer the time of heating employed. In an earlier paper[44] they examine the method of determination of maltose and dextrose by the ferricyanide-carbonate reagent. The oxidation reaction of this reagent towards the sugars is decreased by the presence of sodium chloride and acetate such as would be present after hydrolysis of starch by HCl or by β-amylase in the presence of acetate buffer. Precautions in the use of the reagent are described, including the slow destructive effect on the oxidative capacity caused by storage both in daylight and in the dark, and the necessity of calibrating the reagent to allow for the influence of electrolytes.

A modification of the well-known A.O.A.C. method for the determination of starch is suggested by O. S. Rask,[45] who makes recommendations concerning the preliminary treatment with organic solvents, the standardization of the dispersion of the starch and the filtration of the acid suspension and reprecipitated starch through a specially prepared crucible.

J. Terrier[46] makes a comparison of starch determination (*a*) by difference, (*b*) by Ewer's polarimetric method, and (*c*) by a chromic method of von Fellenberg. Following this comparison the author proposes a method which involves the treatment of starch or flour with calcium chloride to peptize the starch, precipitation of dissolved protein, hydrolysis of the starch to glucose by acid, and the determination of glucose by iodine titration. This method, however, fails in the presence of glycogen and is not satisfactory with cooked starch. In a later paper[47] the same author gives the results of determination of starch by this method.

As changes in viscosity in starch suspensions on heating are of much importance in the physical testing of starch and for research work on starch products, the description of a recording viscometer by C. C. Kesler and W. G. Bechtel[48] is of interest. Variations in cooking procedures are prevented by automatic control of various factors such as the rate of heating, maximum temperature, rate of stirring and loss of water by evaporation. The viscosity is measured by the resistance of the starch paste to a propeller driven through it at constant speed. The curves recorded are characteristic for starches from different sources and are, in consequence, of use in identification.

Chemical properties

Several contributions of immediate industrial interest relating to the constitution and properties of starch have appeared during the year of this review. The term "susceptible" starch is freely used nowadays, and J. W. Dadswell and J. F. Gardner[49] estimate this as the proportion of granules stained by congo red; or as maltose produced by excess of β-amylase or excess of α-amylase acting on amylase-free flour. They show that the response of commercial wheat flours to α-amylase depends on this susceptible starch level, the greater the susceptible starch, the more maltose produced per unit of added α-amylase. In connexion with the action of α-amylase on starch, K. Myrbäck and B. Magnussen[50] conclude that it does not attack malto-triose since it does not produce more glucose after hydrolysis with hydrochloric acid.

On the question of the composition of the starch grain, M. I. Knyaginichev,[54] by dissolving the inner constituent with 30% aq. sodium salicylate, concludes that the outer, or membrane, constituent of starch is contained to the extent of 50% for wheat, rye, and barley, and 100% for rice and maize. The membrane portion gives the higher viscosity.

The different properties of amylose and amylopectin would appear to be becoming industrially important, in a manufacturing sense. E. Bois and G. Vallières[52] give a method for preparing crystalline amylose. A starch suspension (3–5%) is placed in oxygen-free 0·5 N-NaOH and kept at 37° until the solution is transparent. It is then dialysed against distilled water at 37°. On the dialysed solution a layer of butanol is placed at 37° and left for the alcohol to diffuse until saturation. Crystals of amylose form in needles in a helix, easily recognized microscopically. The crystals from corn and potato starch are identical.

W. N. Haworth and S. Peat[53] have patented a method for the separation of amylose and amylopectin, based on the addition to an ion-containing aqueous dispersion of starch of a group of phenols (thymol, cresol and others) to precipitate the amylose. In a report of the Colonial Products Research Council,[54] these authors express the opinion that many processes using starch would be improved and its industrial use extended if a separation into the constituents were effected.

The phosphorus content of starch is considered to have an influence on its properties, particularly on viscosity. D. R. Briggs and M. Hanig[55] correlate the buffer capacities of potato, wheat, and maize starches with the amount of phosphorus lost by dialysis. A. H. de Willegen[56] finds that, when washed and dried potato starch is kept from one to five years, phosphoric acid is liberated.

In view of the potential use as food of a number of new sources of starch, information concerning the composition of lesser known starchy grains and the properties of the starch are welcomed. H. N. Barham and colleagues[57] have supplied analyses of a number of different varieties of sorghum grains, together with information concerning the nature of the gels obtained from the extracted starch.

Physical properties

The physical examination of starches in order to determine their value for various industrial purposes continues to bring to light many useful facts.

I. A. Veselovsky[58] regards the percentage of large and small grains in potatoes to be a varietal characteristic. H. J. Cox and M. M. MacMasters[59] find that there is no correlation in the case of maize, tapioca and potato starches between the ability to stretch and the length and viscosity of the paste. The degree of stretching of maize starch is greatest in samples pasted for 30 minutes, and pretreatment with SO_2 or NaOH has no effect on the percentage of stretch.

W. G. Bechtel[60] emphasizes the importance of recording changes of viscosity of starch during cooking (*e.g.*, by the Corn Industries Viscometer) rather than dependence on a single viscosity test. Defatted maize starch differs in its viscosity curve from normal maize starch, the pastes breaking down at a greater rate than those from normal maize starch. Defatted samples are harder to suspend in cold water than commercial samples. The effect of defatting is also referred to by W. G. Schrenk and collaborators,[61] who find that defatting slows down the rate of maximum heat of hydration but does not change its magnitude. This observation was made during an investigation of the correlation between maximum viscosities on pasting and heat of hydration of starches.

R. S. Higginbotham,[62] for the examination of the consistency of starch pastes, uses an instrument composed of a glass tube fitted with a stirrer mounted in a thermostat. The stirrer is driven through a dynamometer and the torque is read from a quadrant balance.

In the paper dealing with the structure of starch, R. Haller,[63] by a study of the starch iodide complex formed between starch on the one hand, and iodine in water and KI respectively on the other, concludes that the peripheral membrane of natural starch contains cellulose as a framework.

Viscosity and swelling power of starches have been examined by R. H. Harris and E. Jesperson.[64] In the case of wheat, rice and barley starches, treatment during cooking with 0·001N. electrolyte decreases these properties whilst in that of potato starch they increase with the valency of the cation.

For the measurement of gel strength W. J. Hamer[65] describes a method which consists in suspending a disc in a gel from a balance arm and adding mercury to the other side so as to pull up the disc and fracture the gel.

By means of light transmission curves obtained by holding temperature constant during gelatinization, O. C. Beckord and R. M. Sandstedt[66] conclude that gelatinization occurs in steps, and that for some starches these steps occur at widely different temperatures. Some effects of environment on the swelling of cereal starches are considered by R. H. Harris and E. Jesperson.[67] The starches examined were millet, barley, wheat, rye and maize, and the changes in volume of the starch granules on heating with water were measured. Of the three methods adopted for this measurement, the most convenient is one which determines the loss of weight of the swollen granules on drying. It is found that treatment with 0·5% aq. NaOH at 5° increases swelling power, whilst addition of 0·01N–$Al_2(SO_4)_3$ decreases the swelling power of NaOH-treated starch. The $Al_2(SO_4)_3$ has no effect, however, on starch treated with water.

Saccharification of starch

Methods for the saccharification of starch have received much attention recently. A Dutch patent[68] claims a process in which the starch suspension is introduced into the boiling reaction-liquid without forming lumps. This is attained by admitting the suspension under the surface near to the steam supply and the stirring device. J. K. Dale and D. P. Langlois,[69] after acid conversion of a starch suspension, and following adjustment to p_H 4·6–5·0, carry out further conversion by the use of a purified enzyme preparation, *e.g.*, from *Aspergillus niger* and other moulds. From Russia[70] comes a patent process in which, after initial saccharification and cooling to 65–70°, a fresh quantity of starch is added without further water and saccharification is completed by the H_2SO_4 initially used. From the same source[71] is described a continuous saccharification process involving the passing of a starch-acid mixture through a succession of heat exchangers.

A. E. Williams[72] discusses hydrolysis under pressure and manufacture of crystalline glucose by hydrolysis of starch. Crystalline maltose syrup manufacture is described in a British patent.[73] Liquefied starch is submitted to the action of unrestricted barley malt amylase at 125–150°F. and p_H 5·0 for 48 hours. The liquid product is filtered, decolorized, filtered and evaporated under reduced pressure to a syrup containing 80% solids.

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SUGARS

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A SURVEY of the various journals devoted to sugar technology reveals a lively activity in most aspects of the industry. Research in the general field of carbohydrate chemistry is once more being intensively pursued, and several notable discoveries have been made. There is an ever-growing appreciation that precise structural knowledge on the complex sugars is fundamental to an understanding of most biological processes.

Following last year's reporter, Willett and Gray's estimates[1] of sugar crops of the world for 1946-1947 (in long tons) are compared with those for 1941-1942.

	1946-1947		1941-1942
Beet sugar	9,055,226	......	9,148,770
Cane sugar	19,062,975	......	19,262,747
	28,118,201	......	28,411,517

Thus last year's deficit of five million long tons has almost been made up, but there is still a big deficit in requirements which is not likely to be met by the 1947-1948 production. Despite the severe winter, the production[2] of beet sugar for 1946-1947 in this country reached at an opportune time the remarkable total of 556,731 tons. Controls on sugar in the U.S.A. were lifted in July, 1947.

New prospects on the medicinal and industrial application of sugar (sucrose) are being opened up in a remarkable way by the ever-expanding activities of the Sugar Research Foundation of New York and by the Colonial Products Research Council's sugar project in the University of Birmingham. The time is now appropriate, perhaps, to discuss some of the achievements gained from fundamental studies alongside the technological advances from the research groups in the established industry.

The work in progress subsidized by the Sugar Research Foundation, whose members now represent producers who supply more than 90% of all sugar requirements in North America, is ably summarized by a recent timely report[3] which lists no fewer than 52 projects allocated to distinguished leaders in universities and research stations, and supported to the extent of $704,000.

In the early days of rationing in the U.S.A. sugar was the victim of a very unfavourable press, so that a good deal of effort has been expended in proving the value of sugar as a food and in studying its physiological properties. The Foundation is rendering a fine service to the industry by publishing authoritative scientific and technological reports on sugar, some of which will be referred to later.

The Foundation's research projects are divided as follows: A. *Sugar as food,* e.g., sugar and vitamins,[4] sugar and hypoglycemia,[5] sugar and teeth,[6] sugar and fat,[7] fate of sugar in the body, etc. B. *Sugar as an ingredient of foods and beverages,* e.g., sugar in canned and frozen fruits,[8] in baking and confectionery, sugar sweetness,[9] etc. C. *Sugar in non-food industries,* e.g., metal, explosives, plastics,[10] adhesives,[11] pharmacy, horticulture,[12] etc. D. *Physical properties of sugar.* This includes crystallization (see below). E. *Sugar by-products,* e.g., molasses, bagasse, cane wax, etc. (see below). F. *Miscellaneous,* e.g., analytical methods and minor constituents of sugar. G. *Sugar derivatives and transformation products.* It is in this section that sugar is regarded as a potentially cheap raw material for the chemical industry.

The British effort, which is on a considerably smaller scale than the American, has been essentially concerned with this aspect and very substantial advances have been made.[13] The approach considered sucrose initially, and later cane or beet juice, as the immediate source of established raw materials, such as mannitol, sorbitol, furfurals, levulinic acid, lactic acid, etc. Methods for their production were studied, and they were converted into a variety of useful intermediates and finished products, *e.g.*, medicinals, etc., some of which are now ripe for technological development.

Cane sugar manufacture

An important report on the colour problem in sucrose manufacture has been written by F. W. Zerban.[14] Almost every aspect of the subject up to 1947 has been covered with full references. The major components of caramels from sucrose, fructose, and glucose appear to be mainly composed of anhydro sugars with sugar humins, hydroxymethyl furfural derivatives, etc. Melanoidins are condensation products of reducing sugars and furfural compounds with amino acids, and are formed by the Maillard reaction,[15] in which there is considerable interest among food chemists. Other colouring matters in sugar are polyphenol-iron compounds. Zerban discusses the production of these coloured products during evaporation, refining processes, and crystallization, etc.; he considers their detrimental effects on sucrose products, and outlines methods for minimizing colour increases. Several noteworthy papers[16, 17, 18] have appeared on clarification processes using bonechar, Percofil, bentonite, etc. Sugar bleaching using chlorine is discussed by H. S. Isbell.[19] An investigation[20] on unknown losses of sugar during storage leads to the finding that carbon is lost as carbon dioxide. In this connexion work on the drying of raw sugar may prove of some interest.[21] In the general field, comments on vacuum pan operation,[22] sugar boiling theory and practice,[23] and the lime treatment of sugar liquors will be found useful.[24]

A promising innovation is the use of tetraphosphoglucosate as an evaporator scale preventer,[25] but it may prove expensive.[26] Important fundamental work has been carried out by W. W. Binkley and M. L. Wolfrom,[27] who acetylate cane juice solids and separate the solids on a chromatogram of Magnesol-Celite and develop with benzene. Potassium permanganate is the streak reagent. D-Glucose and D-fructose were present in the juice in addition to sucrose.

Beet sugar manufacture

An investigation[28] appears to show that Bonelli's new process for extraction of sugar from beets, which involves reduction of the beets to a fine pulp, addition of small amounts only of lime, and expression of the juice by pressure at room temperature, etc., offers distinct advantages. A new filter (Niagra) for filtering thick juices has been described,[28, 29] while the general problem of the corrosion of filters has been discussed by H. Inglesert and

J. Anderson Storrow.[30] The scaling due to the formation of the calcium salts of decomposition products[31] can largely be prevented by addition of activated charcoal at p_H 7 during evaporation. An interesting point of view is put forward by E. Barbet,[32] who considers that it is uneconomical in certain agricultural areas to extract beet pulp exhaustively, and states that it may even be advantageous to produce low sugar beets. By careful analytical measurements of the development of acidity the stability of raw beet sugars during storage can be checked.[33]

The Swedish Sugar Corporation has discussed progress in a variety of processes.[34] On the microbiology of beet sugar manufacture there has appeared an interesting paper[35] in which the authors describe chiefly their chlorination experiences.

This work should be read alongside that of H. C. S. De Whalley and M. P. Scarr,[36] who deal with various aspects of sugar refining and discuss the elimination of injurious micro-organisms by use of heat, chemicals, etc.

Ion exchange methods

Judging from the very considerable activity in this field there would appear to be little doubt that ion exchange processes offer major technical improvements in the sugar industry. The economics of the methods are not yet entirely sound, but costs of new installations and materials will doubtless be cut down as the methods are more widely applied.

The heavy initial capital outlay is indicated by C. W. Fitzwilliam and R. D. E. Yearwood[37] in a notable paper, though this should be compared with the work of E. A. Haagensen, referred to in last year's Report. The production of direct consumption sugar[38] from cane juice involves an exchange method not superimposed on defecation methods, and gives a highly purified sugar solution containing sucrose with glucose and fructose. Other successful works[39, 40] have had as their object the replacement of defecative processes by a cheaper and less troublesome method. F. R. Riley and W. E. Sangborn[41] state that the methods have now matured, and in a useful paper explain the fundamental principles and describe a successful pilot plant which eliminates a raw sugar stage. Encouraging results on purification of beet juices are described by L. B. Porter.[42] Other detailed discussions are provided by F. N. Rawlings and his colleagues[43] and by P. Smit.[44]

Molasses

Important further fundamental work has been carried out by W. W. Binkley and M. L. Wolfrom[45] on the recovery of sucrose from molasses. The crude material is adsorbed on native clay and then developed with dilute aqueous alcohol. From beet molasses 93% of the sugar present was recovered, while the recovery from cane molasses was 74%.

Crystallization

The crystallization of sucrose from impure solutions has been discussed by S. E. Coalstad,[46] while two reviews[47, 48] of crystallization practice have recently been published. An account of a process for sugar recovery involving five stages for removal of the impurities that prevent crystallization has been given by A. M. Erickson and J. D. Ryan.[49] The work of

A. Van Hook[50] on the kinetics of sucrose crystallization is of high importance.

Centrifuges.—Some attention has been paid to special uses for centrifugal machines, a review on the practice of which since 1911 has been presented by S. G. Smart,[51] together with some indications on the possibilities of centrifugal clarification (see also F. W. Kopplin,[52] G. Anderson,[53] and S. Gordon[54]). Centrifugal purging and washing methods for sugar mixtures and the like are described by E. Roberts and G. E. Stevens.[55] These authors use centrifuges equipped with timing controls, and their washing treatments involve the use of super-heated steam to remove false grain and syrup. Considerable improvements are claimed for the methods, which are useful also for dextrose massecuite.

Analysis

A few investigations of note have appeared on problems connected with analytical methods. On the estimation of the sucrose content of molasses, G. R. Serbia[56] compares his experiences with those of others using well-known methods. The same author[57] discusses an ion exchange method for detecting the unfermentable reducing substances in molasses. Ion exchange resins are used to adsorb optically active unfermentable substances by F. W. Zerban and L. Sattler,[58] who call attention to a neglected source of error in the determination of true reducing sugars.

An electrometric method for the estimation of sucrose in reducing sugars is described by S. E. Coalstad.[59] Methods[60] have been described for the detection of the products, such as reducing sugars, 2:3-butylene glycol, acetoin, etc., of molasses and sugar fermentation.

A recovery formula for use in raw sugar factories has been provided by J. L. Clayton.[61] L. G. Davidson[62] describes a device for aiding the calculation of the percentage of sucrose from Schmitz tables, and claims that it facilitates calculations and reduces errors. A history of " normal weights, saccharimetry, and normal temperature " is reviewed, and new Schmitz tables are calculated for the international scale by R. Gonzalez Rivera.[63] A simple apparatus for determining the apparent specific gravity of refined sugar is described by S. P. Meade.[64]

By-products

Bagasse.—Attention is called to the comprehensive review by C. J. West[65] which brings the literature up to date on this subject. In an annotated bibliography with over 400 references this author reviews the analytical studies which show in bagasse the normal proportions of moisture, alcohol, fats, steroids, lignin, cellulose, proteins, ash, etc. Methods are described for its conversion into paper pulp, boards, plastics, chemicals, etc.

Cane Wax.—Two particularly useful investigations have been published on this topic. Writing on cane wax recovery, R. T. Balch and C. B. Broeg[66] state that 1000 tons of cane yield 8·75 tons of filter press cake. From this, by extraction with various solvents, there are obtained 1600lb. of wax, consisting of 1120lb. of hard wax and 480lb. of fatty acids. These can be further refined. The chemistry of cane wax has been studied by Ram Dev and J. C. Shrikhande,[67] who provide an interesting analysis of the various components present.

Sugar as a raw material of the chemical industry

On this subject attention must be drawn to the digest on patents on the reactions of sugars by A. Guttag,[68] which reveals some of the possible applications. The whole subject is now reviewed by L. F. Wiggins.[69]

From the work directed by Sir Norman Haworth and L. F. Wiggins on the utilization of sugar, almost 40 publications, mainly in the *Journal of the Chemical Society,* have already appeared on anhydrides of the polyhydric alcohols, carboxylic acids derived from sucrose, conversion of sucrose into heterocyclic compounds, etc.; 11 patents have been taken out on the more practical results. Some of the possible heterocyclics outlined in A. A. Morton's monograph on levulinic acid[70] have already been synthesized by L. F. Wiggins and his colleagues.

Miscellaneous

Another outlet for cane sugar as a raw material is to transform it into gum-like highly polymerized sugars, such as dextrans and levans, by means of bacteria. Numerous patents have been taken out on dextran derivatives, and with the development of deep culture methods these new type fermentations are likely to be of great importance in the future.

Traces of dextran in sucrose can be detected by immunological methods.[71]

Invertase is a commodity of growing industrial importance, and the monograph on invertase of C. Neuberg and J. S. Roberts[72] is timely, as is also that of B. S. Gould[73] on mould products derived from sucrose.

General carbohydrate chemistry

Attention is directed to recent reviews[74, 75, 76] which cover a wide field, for many schools of carbohydrate chemistry are now active again. Among the more outstanding advances are the investigations on streptomycin, which is now shown to be a complex carbohydrate derivative, a direct synthesis of cellobiose, a constitutional synthesis of chondrosamine (galactosamine), applications of chromatographic methods, degradative oxidation studies using lead tetra-acetate and periodic acid, and the elucidation of the structure of various plant gums and polysaccharides.

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FOODS

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LAST year's report on Foods opened with a reference[1] to an " economy of abundance " which was the objective of the F.A.O. of the United Nations. At the moment of writing the word economy has an austere and yet more austere meaning, and the word abundance might almost be dropped from the dictionaries so far as Europe is concerned. Britain has had to ration not only bread, but even potatoes; fats and bacon are more scarce than ever.

We read that in the U.S.S.R. rationing is abolished; but we also read quite heartrending stories of semi-starvation in some countries. The present time provides a unique opportunity for the study of nutrition and malnutrition in masses of people and for the practical observations of matters which previously had a more academic interest. No facts at variance with current basic nutritional principles have been observed.

M. Pyke[2] gives an informative survey of the effect of minimal diets on different classes of the population in Germany and in Austria. It appears that gingivitis, follicular keratosis, and oedema are among the unpleasant symptoms of malnutrition to be seen in Central Europe, and that but for the black market everywhere these things would be even more widespread. Pyke's data on loss in weight and diminished rate of growth in children are very interesting, but provide a sad commentary on the times in which we live. The subject of nutrition is of great interest now, so it is a pleasure to call attention to the publication this year by the Society of a survey of scientific data under the title of " The Nation's Food " edited by A. L. Bacharach and T. Rendle. This book contains many data particularly on eggs, potatoes, vegetables, cereals, meat, fish, and milk. There is also a new journal to be welcomed, *The British Journal of Nutrition,* of which Part I has now appeared, published by the Nutrition Society. As Mr. Sarson remarks,[3] a sound nutritionist must be not only a scientist, but also something of a cook and a good deal of a gourmet; perhaps he should also be something of a biochemist and a physiologist. Without being very expert in any of these subjects, all may read with interest and profit a series of papers on nutritive values which appeared in *Chemistry and Industry.*[4] These summarize the values of many familiar articles of diet in the light of recent knowledge, and reveal at the same time the many lacunæ which remain to be filled.

The value of meat extract lies in supplying accessory substances, including not only all or most of the members of the vitamin *B* complex, but also particular essential amino acids. The value of preserves and of honey is, of course, primarily that of the sugar they contain, but they are also important sources of vitamin *C*. Beer and wines contribute riboflavin, pantothenic acid, and other accessories besides phosphoric acid; spirits seem to do little more than supply some small quota of energy. Pickles and sauces have subtle qualities which will repay further study; it seems clear that, like the onion, they are of more value than appears on analysis in the conventional terms.

Prison inmates, being restricted to a rigid diet which they are quite unable to supplement, afford opportunities for study not only as to the adequacy of the diet supplied but also as to the effects of any deficiency. Pyke,[5] in an interesting study of this group, shows that the male English prisoner receives about 3,400 calories per day (compare this with the civilian ration now current in the British and American zone of Germany). The total quantity is adequate, but there is a shortage in the proportion of fat which makes for unpalatableness and, in the case of "open" Borstal boys, a degree of hunger which is described as voracious. There seems no evidence in any of the diets of serious shortage of vitamins except perhaps of *C*.

Studies in nutrition bring out clearly the need for critical examination of method, particularly in relation to vitamin assays. Not only do the methods themselves need careful study, but the results obtained must be examined statistically if valid conclusions are to be drawn. E. C. Wood[6] contributes useful notes on this subject and short cuts which enable the standard deviation to be readily calculated. To realize something of the difficulty besetting vitamin assay and the need for standardization on the international level a paper by N. T. Gridgeman[7] should be studied. It shows that the subject of vitamin *A* is truly in a chaotic condition; and it is to be hoped that the Third International Conference will produce a rational and acceptable plan. There is much to be said for the term vitamin *A* value advocated by Sherman as distinct from vitamin *A* content.

Studies in the *B* group of vitamins have been greatly clarified by the Analytical Methods Committee[8] of the Society of Public Analysts, who set out clearly the conditions necessary for the accurate assay of riboflavin by means of *Lactobacillus helveticus* (*L. casei* ϵ) and of nicotinic acid by *L. arabinosus* 17–5. Details of the basal media and of the technique are given together with precise conditions for the assays. There is and can be no doubt that these microbiological methods are to be preferred for most purposes; but they do require special media and careful preparative work. When isolated tests have to be made direct chemical methods are still useful. Thus M. L. Scott[9] and others have further studied the fluorimetric assay of riboflavin, and show how it can be applied to an extraction of the sample with acetone after acidifying with hydrochloric acid to p_{H} 4. Interfering substances can be removed by oxidation with permanganate and allowance made for the interference, if any, of stable pigments. E. M. James, F. W. Morris,[10] and F. Wokes show how the cyanogen bromide method can be used satisfactorily for the estimation of nicotinic acid; the yellow colour is measured by the Spekker absorptiometer after suitable procedures for the removal of interfering substances. Good agreement with microbiological methods is obtainable. Critical and comparative study of the microbiological assay is held up by the difficulty of obtaining nicotinic acid which is quite free from *iso*nicotinic acid;[11] the latter is unavailable to *L. arabinosus*, but gives the same colour with cyanogen bromide.

The Society was this year associated in the presentation of a Perkin medal to Dr. R. R. Williams, whose work on aneurin is so well known to us all. This provided the occasion for a stimulating survey of the rôle of synthetic vitamins in human nutrition.[12] Almost all the *B* vitamins are now known to act as co-enzymes, some of them to more than one enzyme system. Leading out from this comes the discovery of the anti-vitamins, and, in general, substances which may be described as near-vitamins are anti-vitamins, in much the same way as sulphanilamide is anti to *p*-aminobenzoic acid in effecting bacteriostasis. The enzyme function is impaired.

The enrichment of white bread and flour is to be regarded as a cheap insurance for almost the entire American people against deficiencies of the nutrients of the *B* group. In the Orient the incidence of beri-beri is so great that large-scale fortification of rice is planned, and, surprising as it may seem, it is cheaper to add synthetic vitamins than to conserve the natural vitamins in the grain by a process of parboiling. It is interesting to note that Williams thinks that in the long run the chemical factories will inevitably supplement the farm and help to avert Malthusian disaster to the human race. The effect of parboiling on the aneurin content of rice has been carefully studied by M. C. Kik,[13] who shows that boiling alone increases the B_1 content, but this is accompanied by excessive breakage during the milling. More prolonged boiling reduces the breakage during milling, but also slightly reduces the aneurin content.

Fruits and vegetables

To those who wish to survey the development of the dehydration of vegetables during the war can be commended a new book by T. N. Morris,* "The Dehydration of Food." It affords a very readable survey of both scientific and industrial developments to date. The widespread use of dehydrated potato in the form of potato mash powder has promoted interest in the study of this important food. It has long been known that potatoes contain about 50% of their nitrogen in the form of protein. This protein is a globulin long known as tuberin; it is now shown[14] that there are two quite distinct varieties of this globulin, to be called tuberin and tuberinin; these are present in the proportion of 7:3. The new protein is coagulable by heat, more hydrophilic, and of lower isoelectric point than tuberin. A method has also been described by which the oxidase activity of potatoes can readily be followed quantitatively;[15] it depends upon the formation of tyrophenazine by the condensation of *o*-phenylenediamine with the oxidized tyrosine (the "red body" described years ago by Raper). Tyrophenazine is soluble in acetone, and so can be extracted from the potato heated with *o*-phenylenediamine and measured colorimetrically. The effects of blanching and of cooking can be followed quantitatively.

The large-scale practice of dehydration has enabled a more thorough study to be made of the ascorbic acid content of raw, dehydrated, and cooked vegetables. W. Price-Davies[16] shows that there is no significant variation between standard and non-standard factories producing dehydrated cabbage. The mean ascorbic acid content is from 220 to 334mg. per 100g.; there are no significant inter-varietal differences; about 30% is retained in the reconstituted cooked product as compared with 50% in fresh-cooked cabbage. L. C. Baker and T. L. Parkinson[17] show that while individual tomatoes show wide variation in ascorbic acid content, the ripe fruit is richer than the unripe, and outdoor-grown tomatoes contain larger amounts than does hot-house fruit. Some contain quite notable quantities of dehydroascorbic acid, as much as 0·13 mg. per g. being found associated with 0·27 mg. of ascorbic acid. In cabbage and potatoes the average

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* Chapman and Hall Ltd., London, 1947.

retention of this acid is about 52 and 60% respectively in large-scale plants.[18] But it should be noted that the distribution of ascorbic acid in the cabbage is very uneven;[19] it varies not only according to season but even in different parts of the same cabbage, and in different heads grown from the same seed in one plot.

A. J. Cavell[20] contributes an interesting survey of Basra dates, describing the various stages of growth and development and the corresponding states of sugar content. Sucrose increases until it amounts to about half the total solids, then inversion begins, and by the time the fruit is ripe all the sucrose has been inverted. The presence of sucrose in a pack therefore connotes the presence of unripe fruit. Other studies which arise in connexion with fruits and canning include the carotenoids, flavones, and, that always truculent substance, pectin.

The carotenoids of dehydrated carrots after storage have been investigated by G. Machinney and W. E. Fratzke,[21] who show by chromatographic methods and by spectrophotometry that there is no major change in the *cis-trans* isomers on storage. Oxidation of ζ carotene proceeds no faster than that of the components; a fact which is rather surprising in view of the marked instability of this form of carotene on extraction. Flavones in citrus fruits can be most conveniently extracted and estimated[22] by means of ethylene glycol in alkaline solution. Naringin in grapefruit and hesperidin in other citrus fruits give a strong yellow colour which can be measured in a colorimeter. Most of the flavones are in the albedo layer, as is shown by the following examples:—

	Juice		Albedo	
Grapefruit	0·041	...	2·1	g. per 100 ml. or g.
Lemon	0·054	...	3·0	,, ,,
Orange	0·118	...	1·6	,, ,,

Studies in pectin are still hampered by an inadequate knowledge of the nature of the pectin molecule. The definition is thus a relative term, it represents a long chain of galacturonic acid units esterified to an unknown extent. So the pectin extracted from plant tissue is probably a mixture of chains of varying length, and the first need therefore is a method of purification whereby a single entity may be obtained. We may then find whether or not it is justifiable to speak of pectin as an entity or whether pectin in different plants or species is variable, and, given a pure substance, a constitutional study may begin. Attempts to purify pectin for these purposes shows[23] that dialysis followed by precipitation from aqueous solution by 70% alcohol gives a pectin of the highest pectin content when determined as calcium pectate. Dialysis is of particular value because it removes sugars, acids, and salts, whereas the alcohol removes organic compounds of presumably higher molecular weight. As dry grinding in a ball mill has been found to throw light on the composition of large molecules, purified pectin has been subjected to such grinding. It causes depolymerization of the molecules, and is evidenced by a fall in the viscosity of aqueous solutions and a parallel loss of gelling power, while the calcium pectate and saponification values are not significantly changed. Further studies in this direction may be aided by the contribution of H. Cheftel and J. Mocquard[24] to the examination of the rheological properties of pectin gels, for which purpose they describe a simple but ingenious instrument. It is shown that non-sugar pectin gels resemble gelatine gels, whereas when substantial proportions of sugar are present the properties of the gel are quite different. These rheological differences are thought to be the reason for the peculiar softness and freshness of pectin sugar gels to the palate as compared with the unfavourable properties of gelatine or agar gels.

Starch and flour

Despite the vast amount of work published on starch during the past 50 years we are still very much in the dark as to its true constitution and reactions. So the thorough studies initiated by Dr. Lampitt[25] and his colleagues are particularly valuable. The first paper of the series deals with the effect of inorganic salts on the determination of dextrose and maltose by the ferricyanide-carbonate reagent. This is necessary because the methods used for determining reducing values must be applicable to small quantities, and be of sufficient sensitivity to enable the reducing power of substances of relatively high molecular weight to be ascertained. It is found that the oxidative power of the reagent is decreased by sodium chloride or sodium acetate in quantities such as would be present after the hydrolysis of starch either by hydrochloric acid or by β-amylase in the presence of an acetate buffer. The oxidative power of the ferricyanide is also decreased by exposure to daylight. Steps being taken to eliminate these sources of error show that during the hydrolysis of starch by N-hydrochloric acid at 100° two reactions take place: first, rapid hydrolysis of starch to dextrose, then a much slower decomposition of dextrose by the hot acid. If then allowance be made for the dextrose destroyed, it is shown that quantitatively 90 parts of starch are converted into 100 parts of dextrose. The authors then proceed to the determination of the amylose-amylopectin ratio; this they find is best accomplished colorimetrically or by spectrophotometer by means of the colour of the starch-iodine complex. The use of a low starch-iodine ratio is necessary for accurate results and determination of the intensity of colour over the range 5700–6100 A. The proportions of amylose and amylopectin can be ascertained. Further developments promise to be interesting.

The dextrin content of flour is known to have bearing upon the stickiness of loaves, and observations on the dextrin content of loaves made with National flour containing added calcium carbonate, coupled with determinations of maltose and dextrin in the flour, indicate that the maltose and dextrin figures of yeast bread flour do not necessarily run parallel.[26] The border line for the dextrin figure of yeast bread flour is approximately 13; but the type of loaf and oven temperature are important factors. The addition of acid to p_H 5 has little effect, but if continued to p_H 4·65 it has a marked effect on the α-amylase activity, and tends to coagulate the gluten, with consequent production of a poor volume loaf.

A useful method for the determination of α- and β-amylase in flour has been described by E. G. Hoskam.[27] It is based on the observation of Hanes and Cattle[28] that the extinction coefficient of iodine-starch solution is proportional at all wavelengths to the concentration of starch. This is also true of erythrodextrin, so the concentration of erythrodextrin can be observed as well as that of starch; the former is the end point of the action of β-amylase, whereas the α-amylase does attack the erythrodextrin. By measuring the colours under appropriate conditions both the enzymes can therefore be determined.

There has always been difficulty in estimating the quantity of soyabean flour in cereal products. Many methods have been proposed, but little success achieved. A serological method is found to be satisfactory for this determination in cake mixtures and the like if the soya flour used in their manufacture is available as a control. In the absence of such advantage, serological methods, like the others, are at best only very approximate.[29] The method involves the use of specially prepared rabbit serum, so is not very easily available in most laboratories.

Careful study continues to be given to the nutrient content of different mill streams of high extraction flour. In 80% extraction in an English mill it is shown[30] that riboflavin, phosphorus, and iron follow the distribution of ash, whilst manganese is associated with the amount of germ. The browner flours seem to have increasing quantities of nutrients, but the baking qualities are less good. Study of the separate bran layers[31] shows that the nutritive value resides largely in the hyaline-aleurone fraction. This contains about 60% of the ash and minerals of the whole bran, and 90% of the protein. Wheat suspended in a Waring blendor and subsequently soaked in alcoholic sodium hydroxide solution has been separated in its various component layers and the total of 14·5% bran is shown to consist of 3·9% epidermis, 0·9% cross layer, 0·6% testa, and 9% hyaline-aleurone layer. Multiple bleaching systems for the treatment of flour may involve any two or three of the following gases: chlorine peroxide, nitrogen trichloride, hypochlorous acid, chlorine, and nitrogen peroxide; the greatest efficiency of bleaching is achieved by sequential treatment with any two of the five gases named; in order of preference chlorine and hypochlorous acid come first.[32]

Milk products

Factors affecting the bacterial flora and the keeping qualities of milk products have been very fully discussed by the Society of Applied Bacteriology in a series of papers published too late to be noticed in last year's review. It is a curious fact that farms of a poor type with simple equipment sometimes produce milk of better keeping quality than farms with more elaborate equipment.[33] This is found to be due to the fact that in the poor type farm the dominant flora are micrococci and Gram-negative alkali-producing bacilli having little effect on keeping quality, whereas in the more elaborate installations there is apt to be a predominance of streptococci and Gram-negative acid-producing organisms which adversely affect keeping quality. In order to test these properties most readily the resazurin and methylene blue tests are used, and it has been shown[34] that the reproducibility of these tests is better when the time taken is short as in summer milk than in winter when the time taken is longer. Study of the churns after washing show that heavily contaminated churns have high thermoduric counts, but only a minority of these organisms are thermophilic.[35] Thermoduric organisms are liable to arise from milking machines; common types are *M. lacticum* and *M. flavum*, both of which can survive 80–90° in milk for 10 minutes;[36] the original habitat of these organisms is unknown. Yet another type of organism to be found in raw and in commercially pasteurised milk are psychrophilic which grow at

3–5°. These are *Achromobacter, Alcaligines, Flavobacterium,* and *Pseudomonas* types.[37]

Continuing their studies on dried milk powder, J. A. Pearce and W. A. Bryce[38] show that the life of a whole milk powder is greatly enhanced and the quality somewhat improved by package in a vacuum or in an inert gas. The life of full cream milk powder increases from 3 to about 9 months.

DDT has been much in the air of recent years; it turns up everywhere. Cows are liable to ingest small doses of it in their diet, and in such case traces will appear in the milk. It may be extracted by repeated treatment with light petroleum, and determined either by nitration, or after refluxing with sodium and propanol, by estimation of the organic chlorine, which in pure milk is less than 0·2 ppm., whereas when DDT is present 1 to 12 p.p.m. of organic chlorine will be found.[39] The nitration method has been very thoroughly studied by P. A. Clifford[40] particularly in relation to DDT in milk and butter, and the procedure recommended, which is a modification of the well-known Schechter method,[41] enables the two main isomers to be distinguished.

There has long been wanted some more accurate or scientific method for the control of spoilage in fish and fish products. A useful step in this direction is made by G. J. Sigurdson,[42] who surveys the subject and deals with the appropriate analytical methods. With the herring the most reliable indications of quality are given by volatile acids and trimethylamine, but it is necessary to know the initial content as well as the actual figures; at a temperature of 0° these two constituents give a reliable indication, but at 10° there will be a more marked rise in the peroxide value of the fat and a slight degree of protein degradation, which is indicated by tyrosine, amino-nitrogen, and hydrogen sulphide; at temperatures of 20–25° there will be more marked protein degradation, but no oxidative rancidity.

There is an increasing use in some countries of quaternary ammonium compounds as preservative. They are, of course, prohibited in Britain by the Preservatives Regulations, the rigidity of which is a matter calling for serious consideration by those who administer the Food and Drugs Act. A preservative is any substance which is capable of inhibiting, retarding, or arresting the process of fermentation, acidification, or other decomposition of food—with certain named exceptions. This definition is so all-embracing that the use of any substance which has a beneficial effect is condemned before it is even tried or before its physiological properties are known. As these restrictions do not apply abroad it becomes necessary for the chemist to study the effect of the quaternary ammonium compounds and methods for their detection or estimation. Two such methods have appeared recently; the one is based on extraction by means of ethylene chloride,[43] and the other by the ferricyanide[44] reaction. In this connexion may be mentioned a method for the evaluation of the germicidal potency of quaternary ammonium compounds which eliminate bacteriostasis, details of which are given by R. Quisno, I. W. Gibby, and M. J. Foter.[45]

The use of antioxidants also would appear to be prohibited by definition by the Preservatives Regulations without any regard to the properties or amount of the antioxidant used and without any regard to the balance of advantage or disadvantage. This restriction does not, of course, apply in countries other than Britain. Rancidity in fats is due principally to the oxidation of unsaturated fatty acids, and is retarded by antioxidants in general. These substances, as is well known, usually have hydroxyl groups attached to a benzene nucleus, such as quinol, hydroquinone, catechol, and many other compounds. The use of these substances in bakery products, though dependent to some extent on the particular fat used, generally impart greater stability to biscuits and similar cereal products.[46]

Egg products

The changes occurring in the protein of egg on pasteurization or on drying are still subjects of much study.[47] The viscosity and rate of denaturation of liquid whole eggs progressively increase as the temperature rises: at about 56° to 66° denaturation takes place. The viscosity of the white drops rapidly at 62·5°, and is accompanied by turbidity, flocculation and coagulation of the protein; in the case of the yolk the increase in viscosity and rate of denaturation proceed up to 70°; at higher temperatures coagulation takes place. The lower temperature of denaturation of whole egg or of white than of the yolk is probably due to the smaller number of proteins in the yolk.

Pasteurization of liquid egg is effected by heating to 60° for a period of 30 minutes. This completely eliminates *Salmonella*, staphylococci, and coliform organisms, and reduces the total count by 98 to 99%, without affecting the quality of spray-dried powder prepared from the egg. But that this is not always achieved commercially is shown by M. D. Schneider,[48] who finds *Salmonella* organisms in 3·18% of high-grade egg powders, in 1·63% of samples in which both a pre-heater and multistage drier have been used, and in 18·27% of samples which have been spray dried without a pre-heater and multistage drier. This author names the types of *Salmonella* found. Properties upon which the quality of dried egg depend include the particle size as indicated by the surface area per g. and the nature and amount of the free fatty acids. The surface area may be from 0·1 to 0·8 sq. m. per g., and the areas of lyophilized powders is much greater than that of the spray-dried product.[49] When dried egg is extracted with ether the extract contains much kephalin; this may account for as much as 70% of the apparent acidity. So the true free fatty acid is best determined by extraction with acetone four times, then precipitation of the kephalin with a saturated solution of magnesium chloride in alcohol. The filtered solution is then evaporated and acidity titrated in light petroleum with dilute sodium ethoxide solution. Fatty acids can be bound by basic proteins in liquid egg, and, if so, are not easily extracted, but if the p_H of the emulsion is adjusted to 4 before drying and extracting, the acids are not so bound and can be extracted. The acids which develop in dry egg powder are not bound, and can be extracted by acetone as above.[50]

Rapid progress is being made in the study of the constitution of proteins occurring in food by the application of two of the newer types of method —partition chromatography and micro-biological assay. These methods are proving much more specific, more easy, and more accurate than the old type of chemical methods. For example, the mono-amino acids resulting from protein hydrolysis can be resolved with good success by the method developed by Tristram,[51] who uses a special technique in which the one liquid (water) phase is held on a silica gel carrier while the other liquid, which may be *n*-butanol, *n*-propanol, *cyclo*hexane, or chloroform, is used to extract the particular amino acid. The silica gel must be of a high degree of purity, and is "aged" by treatment with very dilute hydrochloric acid. Using such technique quite good quantitative separations are obtained for hydrolysates of insulin, edestin, casein, β-lactoglobulin, and certain other proteins. The determination of alanine, leucine, protein, valine, *iso*valine, *iso*leucine, and phenylalanine show a high degree of accuracy. As examples of the microbiological method may be mentioned the determination of valine, threonine and methionine which can both be assayed using the same basal medium but different test organisms. *L. arabinosus* is used for the valine, *S. faecalis* for the threonine and methionine.[52] A different basal medium and *Leuconostoc mesenteroides* P.60 is available for the determination of glycine;[53] and leucine can be similarly determined by means of *Neurospora* without hydrolysis of the foodstuff concerned.[54]

These are but examples of the many microbiological methods now put forward, and the multiplicity of these renders it the more necessary to understand the fundamental relationships involved in the computation of bioassays. The relationship between the dose and the response of micro-organisms is not linear, but it is often or usually possible to obtain a straight line over a reasonable range by plotting log dose against log response. From data so obtained it is possible to compute the standard error and to check the validity of the assay by simple statistical methods.[55] The importance of such study of the underlying principles cannot be exaggerated, and serves to eliminate unsound results and ill-founded claims for these methods. A very full discussion of the subject and its difficulties is to be found in the *Biochem. J.* 1947[56] contributed by a number of experienced workers.

A number of new colorimetric methods have also been devised which are available for special proteins, for example: ribonucleic acid with phloroglucinol[57] after treatment with hot ferric chloride–acetic acid; tryptophan by diazotized naphthylethylenediamine;[58] purine and pyrimidine by the copper-orcinol reagent.[59] Fluorimetry is also developed for the separate estimation of α-chlorophyll and β-chlorophyll as these two isomers fluoresce differently when excited by violet and by blue light; advantage is taken of this for their separate measurement.[60]

Cleanliness of foods

Mention was made in the Report for 1945 and for 1946[61] of the publications, mostly in America, of methods designed to measure and identify dirt in food. Attention has been particularly focussed on insect particles and on rodent hairs as the latter are associated usually with excretal matter from these animals. The subject can be overdone, and some references in the press have been rather unfortunate on this account. There is not the slightest ground for supposing that cereals or other basic foods produced in Britain are any worse in this respect than those produced in the U.S.A. or elsewhere, notwithstanding the high degree of extraction required from our millers. The methods used have been subjected to careful study by the American Association of Official Agricultural Chemists, and reports on the best microanalytical techniques for particular foods have been published.[62] These methods are of a high degree of precision, but we are still without adequate knowledge or guidance on the proper standards or limits which should be adopted. Moreover it might be stressed that the conclusions to be drawn from tests should be strictly limited. If as the result of a test on say 25g. of sample one mouse hair is found, it is doubtful whether the conclusion is justified that there are 4 per 100g., or that such finding indicates any particular degree of contamination. Those interested in the question of insects in cereal products will find a useful summary in a new publication by H. M. Stationery Office[63] which gives particulars not only of the life history and habits of such insects, but also of methods for their control and elimination. Control of insect pests being so very important a matter, much study continues to be given to fumigation and its attendant problems. The total of absorption of methyl bromide[64] by wheat is defined by the Freundlich equation, and rate of sorption by $R_t = R_o + kt$. R_o, the instantaneous physical absorption, is followed by a slow chemical reaction. The kinetics are of zero order, and sorption increases with temperature and, in the case of whole wheat but not of milled wheat, with moisture content. The removal of methyl bromide on subsequent aeration is not quite complete;[62] the residual amount is proportional to the protein content, which decomposes the methyl bromide by methylation of the carboxylic, phenol or sulphydryl groups in the protein.

Side by side with the study of fungicides and methods of control of infestation it is necessary to study methods for the culture identification and enumeration of moulds and bacteria, pathogenic or otherwise. Pathogenic fungi grow particularly well on potato-glucose-agar, which is a medium favouring abundant sporulation, and so is useful for identification purposes.[65] Christensen[66] advocates the use of a malt extract-salt-agar for the enumeration of mould colonies in flour; the salt concentration 7·5% and acidity p_H 5 restrict bacterial growth, and the use of a simple binocular microscope facilitates the counting and identification of colonies of moulds. The deterioration of some feeding stuffs by mould is a function of humidity as well as length of storage and nature of the material.[67] Some will grow with R.H. as low as 40%, but most of the common types, such as *Penicillium* and *Aspergillus* species, require 65, 70, or even 85% R.H. In canned fruits much can be done by effective washing, but, even so, mould growth may take place in the head space; this may be eliminated by replacement of air, including air trapped in berries, by an inert gas.[69]

Coffee

Some interesting work has been done recently on coffee and coffee essences. The flavour of coffee is believed to be due largely to 2-thiolfuran and its methyl and ethyl esters, together with some other sulphur compounds. This has suggested the use of some of these compounds for the artificial flavouring of coffee substitutes.[70] The nicotinic acid characteristic of coffee is derived from the decomposition of trigonelline;[71] it is found to the extent of 16 to 44 mg. per g. in raw coffee beans, and is increased by the roasting operation, which affects some decomposition of the trigonelline, so that there is much more nicotinic acid in a dark roast coffee than in a light roast coffee. Figures are from 95 to 263 mg. per g. The amount of nicotinic acid does not seem to be dependent on variety of the bean, but upon this decomposition. Dixson[72] describes a practical method of the separation by means of a Kestner climbing film evaporator and subsequent re-combining of the volatile aromatic substances in the preparation of coffee essences and coffee powder. A patent has also been issued for the addition of alkaline earth phosphate or tartrate, citrate or lactate to coffee and chicory blends, as this is said to improve the palatibility and flavour.[73] Another method of enhancing the flavour of coffee is by freezing the green beans and then exposing them to ultra-violet rays. This process is said to reduce the content of chlorogenic acid and so improve the flavour of beans which have not received sufficient sunlight during growth.[74] The roasting and cooling of coffee beans in an inert gas instead of air has also been patented.[75] The conversion of the green tea leaf into the black tea we are accustomed to see involves, amongst other things, the oxidation of leaf tannins. These are phenolic bodies, and the oxidation is brought about by oxidative enzymes liberated on crushing the leaf. This oxidase has been shown to be insoluble in water, and has been found to be located in the grana which is associated with the chloroplasts.[76] It does not appear to participate in the respiration of the plant, but is an oxidase having specificity like that of the known polyphenol oxidases, but it does seem that the respiration of the tea leaf involves other yet unrecognized oxidase systems.

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THE FERMENTATION INDUSTRIES

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As far as the fermentation industries are concerned, 1947 has been a year of steady progress rather than of any outstanding discoveries. In conformity with the change in policy which has been made in the presentation of this annual review, the number of individual contributions has been curtailed, and the papers chosen for discussion are described in greater detail.

Hops

A review of the 1946 crop has been made by J. Nott.[1] After the early stages of cultivation, during which weather conditions were considerably more favourable than in 1945, and consequently did not force precocious growth, conditions deteriorated right up to picking time, with the sole exception of a fortnight in July. The weather provided ideal conditions for the spread of downy mildew, and Goldings especially succumbed to this disease. The situation was complicated by the fact that routine spraying with copper fungicides was difficult owing to the wet state of the ground. Even Fuggles, which is relatively resistant to downy mildew, showed infection in many cases. Weather conditions also made it difficult to cope with aphis infection, and many tons of insecticide powder must have been wasted.

Mosaic disease, which is confined to Goldings and Golding varieties, appears to be advancing in the Midlands, while nettlehead seems to be on the increase in Fuggles. Apparently *Verticillium* wilt is not present in its progressive form in the West, but it is not generally realized that the fluctuating type of this disease is more widespread.

Apart from the difficulties caused by the weather of combating plant diseases and insect infestation, weather had a direct influence on the size and quality of the crop. The fall in average temperature led to the bine being short, and, although the burr was prolific, low temperatures may not have been suitable for complete fertilization, so that strigs and hollow ends of the cones were short. It is now estimated that the Hops Marketing Board had 155,355 pockets of hops, compared with the figure of 160,820 in 1945; a fall of 3·3%.

Two new hop varieties, "Pride of Kent" and "Sunshine Hop," have been described by E. S. Salmon.[2] "Pride of Kent" was obtained by a cross between Brewers' Gold and an unknown male parent, and "Sunshine Hop" was a cross between variety 0599 and an unknown male parent. Both these new varieties show features in common, such as habit of growth and shape of cone, which belong to the Golding class of hops. They are said to need only light "pulling," and in training require two bines to each string. They have the advantage that they can be picked as late mid-season or late crops. They proved to be better for machine picking than either Fuggles or Goldings, and apparently were immune from mosaic. " Pride of Kent " showed slight susceptibility to Downy Mildew, while both varieties proved to be satisfactory in brewing trials.

The long-term research scheme set up in the U.S.A. for the study of the genetics of hops is reviewed by R. E. Fore and J. D. Sather.[3] The discussion ranges over the production of improved varieties, such as earlies and lates and varieties resistant to various diseases such as Downy Mildew. Hybridization rather than simple selection is used.

E. S. Salmon and A. H. Burgess[4] point out that no really satisfactory comparative test of hop varieties can be made without adequate knowledge of the preservative value (P.V.) of the hops used, both as regards control and experimental varieties. There is a great body of evidence to show that the temperature at which hops are stored affects the rate of deterioration. Salmon and Burgess also point out that it appears to be a likely possibility that deterioration may also be a varietal characteristic.

Propagation trials with hops have been conducted.[5] The first successful experiments of propagating hops by means of soft-wood cuttings were made by Bailey in 1939. Attempts were made in this investigation to see if Bailey's original procedure could not be simplified. Fuggles and four wilt-resistant strains were tried, and both basal and lateral cuttings were used. It was found that the time of planting had no significant influence, but weather conditions were found to be important. The effect of phytohormones, such as β-indolylbutyric acid on basal cuttings, proved to be very harmful. All attempts to propagate Fuggles from lateral cuttings failed, and treatment with phytohormones merely hastened death. Experiments with lateral cuttings from wilt-resistant varieties proved to be more successful. Further tests are to be made on the effect of phytohormones on these cuttings, because of the conflict of evidence with the earlier work of Bailey.

According to F. H. Beard,[6] 1945 was the first year in which a serious outbreak of Downy Mildew occurred at East Malling. Dusting with flowers of sulphur failed to control the disease, and of 181 seedlings planted in short rows of approximately 15 hills, 13 were attacked in the burr stage and bore no crop, and 28 were very severely attacked in the cones. Of the remaining plants, 41 were severely attacked, 30 only slightly attacked, 22 showed trace of infection, and 44 were completely free. When the close proximity of the seedlings is considered, these 44 seedlings must be considered to be practically immune to *Sphaerotheca humuli.* Two forms of the wild hop, *H. americanus,* one from New Mexico and the other from Manitoba, showed high susceptibility to mildew attack. It was further found that of eight named new commercial varieties none was free from the disease, but the actual severity of the attack showed a good deal of variation. For instance, the variety " Quality Hop " (0063) was almost destroyed, whereas the varieties " Early Promise " (X 35) and " Malling Midseason " (BB 28) showed merely a trace of infection.

A general review of the *Verticillium* wilt problem in hops up to 1946 has been made by W. G. Keyworth.[7] An outline is given of the history of the disease, and a distinction is drawn between the fluctuating and progressive types of the disease. The general consensus of opinion now appears to be that these two types of the disease are due to two different strains of the fungus, *Verticillium albo-atrum*. Soil disinfection on a large commercial scale has proved to be impracticable, although it has its uses in keeping in check a new outbreak. Even the growing of other non-susceptible vegetable crops for as long a period as four years in infested soil has proved to be of little or no value, as the onset of the disease is only slightly reduced in intensity and the pathogen is not eradicated from the soil, and in two or three years' time the disease will be as severe as ever if hops are replanted. Investigations are now being made into the effect of the nature of the soil and of the nutrition of the hop plant on the incidence of the disease, but the practical value of such investigations appears to be very problematical.

The search for resistant varieties to this disease has shown that all the commercial varieties grown at the present time are highly susceptible to infection, whereas a number of hybrids that have been produced by E. S. Salmon, at Wye, show great powers of resistance, although complete immunity has not been obtained. Up to the present time approximately a dozen varieties have passed their initial resistance tests. Whether these new hybrids will prove to be suitable for grower and brewer has yet to be shown. Two new hybrids (OR 55 and OJ 47) have so far proved themselves to be the best varieties from the grower's point of view. The difficulty of rapid propagation of a new variety has been overcome, and it is now possible to produce sufficient stock within a few years for planting commercial plots of any selected variety. Another aspect of the wilt problem that is at present under investigation, is the evidence provided by the commercial variety " Tutshams " and possibly some Goldings, which, when mature, are less severely affected by wilt than mature plants of Fuggles. If this evidence be confirmed, it is always possible that such slightly resistant strains might remain reasonably free from infection if they were planted on clean soil.

Barley and malt

The season's barley has been reviewed by A. Cory-Wright.[8] In 1946 the harvesting weather was bad and most cereal crops were garnered in poor condition, in fact some fields were not harvested at all. In spite, however, of shocking weather conditions, barley, and for that matter all winter-sown cereals, survived remarkably well. A feature of the harvest was the enormous crop of weeds, especially fat hen, creeping thistle, and sow thistle. Combine harvesters are blamed for this state of affairs because they would allow weed seeds to go back on to the land, and thus the fields would not be properly fallowed. The Eastern Counties were troubled with a barley disease often known as " Gold Death "; a feature of this disease is that the ears, instead of bending over when ripe, continue to stand upright and a number of kernels are missing in each ear, with the result that the chaff is translucent, and seen against the sun gives this golden appearance. The disease is due to the stamens being unable to make viable pollen at the critical time, so that there is failure of pollination and, of course, fertilization. The reason for the failure of the stamens to produce pollen is not known. The fine, warm weather in August led to a great deal of the barley being cut too soon, with the result that it was unsuitable for malting. Comparison of the 1946 with the 1947 crop shows that the 1946 crop was potentially a bumper one, whereas the 1947 crop could not possibly have given a good yield. While, however, a large part of the 1946 crop was ruined by the appalling weather at harvesting time, the 1947 crop was harvested in good condition, and as long as brewers will accept barley with a high nitrogen content there should be no shortage.

L. R. Bishop[9] has discussed post-war malting problems. Low nitrogen content is an important factor for the production of malt of good quality. The reasons leading to this desirable state of affairs are now known, with the result that British barleys are amongst the lowest in nitrogen content in the world. Maturation of the grain is the process of recovery of the power of germination by the grain from the dormant state. This condition of dormancy of barley is apparently due to the presence of a membrane in the inner skin of the grain which is impermeable to oxygen, and the breaking of the dormant state and recovery of the power to germinate is associated with restricted fungal attack on this layer. When grain is stacked with a moderate moisture content it matures satisfactorily and is ready for malting towards the end of the year. When, however, a wet season is encountered and fungal activity in stack is excessive, a condition known as " secondary dormancy " may set in, when the embryo of the barley grain is progressively damaged from the radicle upwards, until eventually a stage is reached when the grain can no longer germinate, dies, and infects other grains.

Careful control of malting is required to prevent the defects of under or over-modified malt. J. de Clerck[10] claims that the chief external factors controlling the process of converting barley into malt are temperature, aeration, and humidity. The time factor is also of importance, *i.e.*, the duration of the process. De Clerck has employed the respiration rate of the germinating barley (expressed on a dry weight basis) as a test of conversion. The claim is made that to secure the best results in malting, respiration should be accelerated to the maximum point in the early stages of the process, so as to favour modification and obtain the rapid formation of enzymes. When respiration reaches a steady rate it should be checked to prevent heavy malting loss.

A so-called four-mash method for the evaluation of malt for brewing has been described by B. D. Hartong.[11] The method consists in obtaining extracts at 25°, 45°, 65°, and 85° C. (77°, 113°, 149°, and 185° F.), which are then calculated as percentages of the " fine grind " extract obtained by Congress Method to give four extract-indices, 58 is subtracted from the sum of the indices, and this is termed the " brewing value " (V.B.). Hartong claims that a sound barley properly malted will give a V.B. between 2·6 and 6·2. In general terms values of V.B. below 2·6 indicate a defective barley, while values above 6·2 indicate over-modification.

W. O. S. Meredith[12] has made a comparison of the malting quality of a new Canadian variety smooth-crowned barley, Montcalm, and variety OAC 21, over a period of seven years. The new variety was grown over a wide range of environment, and was found to compare favourably with OAC 21 in all its properties. The nitrogen content was lower and the saccharifying power higher, and it gave approximately 1% more extract when malted than OAC 21.

An examination of the data available over the 55 years 1880-1935 of the yields per hectare of barley in Sweden has been made by R. Prakken.[13] The main improvements that have been sought in recent years in Sweden have been in the direction of larger yields, stronger straw, increased resistance to disease, early and regular ripening, maturation, and general improvement in malting qualities. At first attempts were made to improve barley varieties by selection of suitable strains. Later on, however, hybridization was resorted to with the best strains obtained by selection.

Biochemistry and nutrition of yeast

R. S. W. Thorne[14] has given a review of the problem of hybridization in general in plants, followed by a detailed résumé of the Danish School of Winge and his co-workers on hybridization in yeast.

Detailed studies of yeast growth in bottom brewing fermentations have been made by E. Helm and B. Trolle.[15, 16, 17] Special care was taken to maintain the purity of the yeast in this investigation, and fresh cultures were introduced from time to time as required. The authors define a non-flocculating yeast as one which has not completely settled after the primary fermentation has been completed; whereas a flocculating yeast is defined as one which settles quickly to the bottom of the fermenting vessel. With a flocculating yeast attenuation may be poor and the beer biologically unstable. The yeast may change in character for no known reason from a flocculating to a non-flocculating variety. Particular attention was paid to any irregularities in the course of primary fermentation, and observations were also made on secondary fermentation and the properties of the finished beer. The following determinations were made for this investigation: alcohol, real extract, p_H, and total nitrogen content of wort. Suspended yeast was estimated by filtration and weighing the dried yeast. It is possible to calculate the dry weight of newly formed yeast from the total nitrogen content of the original wort, pitching yeast, and fermented wort. The weight of the settled yeast can then be determined by difference from the total yeast (pitching yeast and newly formed yeast) and suspended yeast. The curves drawn of the results indicated that the amount of suspended yeast shows a regular increase at first, rising to a maximum in approximately 75–100 hours, whereas on the whole there is a minimum of settled yeast during this period. Settled yeast now increases steeply, and at the close of fermentation approaches the figure for total yeast. The total nitrogen content of the wort decreases from the very commencement of fermentation and reaches a fairly constant level when settling begins, and the formation of new yeast is approximate to the fall in nitrogen content. The p_H curve is similar in shape to the nitrogen curve. The alcohol produced during the entire course of fermentation shows an inflexion at the point when suspended yeast is present in maximum amount.

It was also found that variations in the pitching rate had an influence upon the process. The higher the rate of pitching yeast added, the higher is the rate of fermentation. The maximum amount of yeast contained in suspension is reached at a time which roughly coincides with the inflexion found in the production time curve (see above).

The mechanism of selective fermentation by yeast has been fully investigated by A. Gottschalk,[18, 19] and the original papers should be consulted.

The investigations of M. T. G. Custers[20] on the genus *Brettanomyces* has been reviewed by J. L. Shimwell.[21] In 1904 Claussen gave a description of this genus, and claimed that it was responsible for secondary fermentation in beers and gave to them their pleasant vinous smell. Their importance to-day is not so great owing to the fall in the gravity of English beers. Custers has described some 17 different strains of *Brettanomyces* obtained from different sources, mainly British and Belgian top fermentation beers. These strains have certain features in common, *e.g.*, frequent occurrence of a particular shape of cell termed "ogivie" (*i.e.*, pointed at one end). All the strains were able to produce marked quantities of acid from glucose. Custers has recognized four species, *B. anomalus*, *B. claussenii*, *B. lambicus*, and *B. bruxellensis*. Under anaerobic conditions *B. claussenii* forms only carbon dioxide and ethyl alcohol from glucose, but under aerobic conditions considerable quantities of acetic acid are produced. The most remarkable observation, however, was that aerobic fermentation is greater than anaerobic, so that under experimental conditions *B. claussenii* shows a negative Pasteur effect. It should be noted, however, that this anomaly does not exist with old cultures, and the behaviour of any particular culture is much influenced by the previous conditions of growth.

Beer and the brewing process

J. de Clerck and C. Konovaloff[22] have studied the brewing of beer with low alcoholic content. Apparently the first requisite for such a fermentation is to use a wort containing the minimum amount of fermentable sugar. This condition is achieved by restricting β-amylase activity in the mash tun, so that the malt starch is only degraded to a small extent beyond the stage of dextrins. In actual practice it was found that the greatest restriction of β-amylase activity compatible with complete liquefication of the starch was most readily obtained by maintaining the temperature of the mash at 76°C. (169°F.). Beers made by this method were found to have an alcohol content of 1–1·5% by weight. They kept well, possessed a normal beer flavour, but lacked fullness. This lack of fullness may be connected with lack of colloidal nitrogenous matter in the wort.

R. Rayet[23] and J. de Clerck[24] have discussed the treatment of brewing waters from the point of view of its mineral salt composition and its effect on the flavour of beer. It is a well-established fact that the presence of bicarbonates in brewing liquor exerts an alkaline effect by reason of the fact of their conversion of primary into secondary phosphates in the mash tun with loss of carbon dioxide. Calcium ions, on the other hand, have an acid reaction by reason of their interaction with phosphate (mainly organic) and proteins. Magnesium ions have a similar effect, but their action is not so strong as calcium ions. The specific effects of individual ions is less widely understood. Sulphate ions are said to produce a beer with a dry flavour; chloride, on the other hand, is considered to produce a full flavour; while ferric ions cause colloidal haze and yeast degeneration, and nitrates and nitrites are toxic to yeast. Sodium ions give a poor-flavoured beer. The disadvantage in the use of cationic and anionic exchange resins are also discussed. The two main disadvantages are that water containing considerable amounts of bicarbonate is left with a high carbon dioxide content, and that the resins are slightly soluble in water. This solubility is sufficient to interfere, in the case of an anionic exchange resin, with saccharification in the mash tun by its toxic action on amylase.

J. de Clerck and C. Duganquier[25] have investigated the effect upon beer flavour of adding various mineral salts to brewing liquor. The ions used were Ca, Mg, Na, Cl, SO_4, and NO_3. The brews were all of the same strength, and after boiling and cooling sweet worts were all reduced to the same p_H by the addition of acids correspondings to the salts added. The worts were now hopped, cooled, and pitched with yeast from a pure culture. The effect of the various salts varied according to whether tap or distilled water was used. When tap water was used the flavours of the beers were placed in the following decreasing order of the salts added: $CaCl_2$, $MgCl_2$, Na_2SO_4, $MgSO_4$, tap water alone, NaCl. On the other hand, with distilled water the order was: $CaCl_2$, distilled water, NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$. The calcium ion was found to yield better flavours than the sodium ion with each of the anions used. Calcium chloride gave a beer with a sweeter and fuller flavour than calcium sulphate. Similarly, sodium chloride gave a better flavour than sodium sulphate. These results were found to be more marked with bottom fermentation yeasts than with top fermentation ones.

The problem of " stench " due to the liberation of hydrogen sulphide in the course of fermentation has been investigated by E. Urion and P. Chevalier.[26] They found that the liberation of hydrogen sulphide during fermentation is due to the reducing action of yeast or some infecting organisms on either sulphur-containing compounds, *e.g.*, cysteine, glutathione (arising from the autolysis of a weak yeast), or reduction of sulphates and sulphites (possibly arising from the presence of calcium sulphate in the brewing liquor or heavily sulphured hops). The hydrogen sulphide is considered to be completely swept out by the carbon dioxide evolved during fermentation, and thus has no effect upon the flavour of the finished beer.

Microbiology

A. Lund[27] has carried out experiments on the thermal death points of a variety of micro-organisms which are found in beer. It was found that most of the organisms used for this experimental work, e.g., *Torula, Acetobacter, Mycoderma, Saccharomyces, Pediococcus,* and *Lactobacillus pasteurianus,* were killed within 15 minutes when heated in bottom-fermented beer at 56°C. (132·8°F.). Some organisms were killed at an even lower temperature (50°C., 122°F.). The organism which proved to be most heat-resistant was *Lactobacillus lindneri* (the common rod form of lactic acid organism found in bottom-fermentation beer). Some strains of this organism survived a temperature of 58°C. (135·4°F.) for 20 minutes, but succumbed to a temperature of 60°C. (140°F.). The essential point established by the author is that pasteurization of beer at 60°C. (140°F.) for a period of 20 minutes ensures that the development of micro-organisms is prevented.

The sterilization of drinking vessels in licensed houses has been investigated by J. G. Davis and J. C. L. Resuggan.[28] Disinfectant detergent preparations were tested to see if the necessary requisites of adequate sanitation were given to the glasses, without at the same time imparting any undesirable flavour to the beer which subsequently filled them. Eventually it was found that a synthetic quaternary ammonium compound mixed with certain detergent salts had a high killing power against many common pathogenic organisms and coliforms, and no undesirable flavour was imparted to the beer.

T. K. Walker and J. Tošić[29] have continued their investigation on the characterization and identification of the acetic acid bacteria. They draw attention to the fact that until recently there was no standardized procedure available for the examination of members of this genus. They[30] have now given details of a systematic procedure for the characterization of a number of species of acetic acid bacteria.

The influence of *Acetobacter* infection on the condition and flavour of beer has been examined by S. Kulka and T. K. Walker.[31] The experiments were directed to see what resistance was shown by bottled beers stored at 53° F. to infection by acetic bacteria. Two series of trials were carried out and a comparison made with the same organisms in beer to which air had access. It was found that *A. gluconicum* and *A. xylinum* were innocuous in a brewery. *A. pasteurianum* was also found to be not dangerous to beer stability, although there is always the possibility that certain strains of this species may be more virulent than others. Similarly, *A. acetigenum, A. ascendens, A. kutzingianum, A. acetosum,* and *A. suboxydans* are unlikely to cause serious damage to beer in storage. Nevertheless, if conditions be favourable and sufficient time be allowed for these organisms to exert their action they can produce a certain degree of spoilage. The organisms *A. acidum-polymyxa, A. mobile, A. turbidans,* and *A. viscosum* were found to be the most virulent types of infection, while *A. aceti* and *A. capsulatum* were less virulent in their action. *A. capsulatum* is a strongly aerobic form, and therefore growth in bottled beer is weaker than when free access to air is allowed, whereas *A. viscosum* grows almost as strongly in bottle as in air.

In a general review on the biological stability of beer, B. M. Brown[32] emphasizes the fact that an organism must be considered in relation to its environment, and that the biological significance of a medium is subject to the organisms present in it. After a reference to the early work of Pasteur on the bacteria which are most dangerous to beer, the author pointed out that it was only within recent times that further investigations were made on this subject, when Shimwell showed that Gram-positive organisms are sensitive to the antiseptic action of hops, whereas Gram-negative are little, if at all, affected. The bacterial spoilage of beer is mainly due to two Gram-positive genera, *Lactobacillus* and *Streptococcus,* and the Gram-negative *Acetobacter.* A low p_{H}, acting in conjunction with alcohol and hop resin, tends to suppress the two former organisms, but their subsequent development depends upon the amount of sugar present. Beer offers little resistance to species of *Acetobacter,* but the exclusion of oxygen tends to inhibit their development and activity. At the present time the chief and most troublesome infection of beer is wild yeasts, and very little can be done to control their activity; the sole remedy is to prevent their access to beer.

J. L. Shimwell[33] considers that the generic name "*Sarcina*" is a misnomer when applied to the beer disease organism. Similarly, he objects to the name "*Pediococcus*." No true *Sarcina* or *Micrococcus* species are able to grow in beer. Shimwell places those organisms in the *Streptococcus* genus of the Lactobacteriaceae. Their cultural behaviour in the laboratory is very similar to other saprophytic *Streptococci*. "Sarcina-sick" beer has a characteristic honey-like odour due to the production of diacetyl by these organisms. The production of diacetyl is a secondary phenomenon to the formation of lactic acid, which is controlled by the p_{H}, carbohydrate content, alcohol content, and concentration of hop antiseptic in beer. One important feature of these organisms is their relatively low temperature optimum (21–25° C.; 70–75° F.) and their ability to develop even at the low temperatures of lager beer brewing.

A general discussion on brewing bacteriology has been given by Shimwell,[34] and in a further communication[35] he also discusses the question of air-borne infection in breweries. He is of the opinion that direct danger from air-borne bacteria has been greatly exaggerated, and from the practical standpoint is virtually insignificant.

An important communication on "ropy" beer has appeared by Shimwell.[36] The state of this subject has lain in a good deal of confusion in the past. A number of different organisms have been described as being responsible for this disease of beer, and although numerous organisms have been isolated from ropy beer and wines, when they have been reinoculated into beer they have failed to reproduce the disease. It is therefore unlikely that they are the casual organisms responsible. In 1912, however, Baker, Day and Hulton were able to isolate 11 strains of bacteria from different breweries which all produced ropiness in beer. These organisms apparently belonged to the acetic acid bacteria group. Baker *et al.* included these rope-producing organisms under the comprehensive title, *B. aceti-viscosum*. They were later renamed *Acetobacter viscosum* (Baker, Day and Hulton), Shimwell. In 1936 Shimwell was able to isolate from fresh stout another rope-producing organism, which was called *Acetobacter capsulatum*. It appeared to be closely related to *A. viscosum*, but differed in certain particulars, such as temperature relations, which warranted specific differentiation. The problems of ropiness in beer has now been completely reinvestigated by Shimwell in the hope of throwing new light on some earlier results which appear difficult to explain, and in some cases are definitely contradictory. The active mechanism of production of ropiness in beer is due to the production of gelatinous capsules by the organisms concerned. These capsules dissolve or disperse in the surrounding beer, and this produces the viscous condition so characteristic of this disease. For beer to become ropy three conditions must be satisfied: (1) the organism must gain access to beer either during or after fermentation, (2) the physical condition and nutrient composition of the beer must be satisfactory to allow of the growth of the particular spoilage organism concerned, and (3) when growth does take place something must be present in beer which not only allows growth to take place, but also enables the organism to manufacture material on which the production of ropiness depends. It was found that the slime which is so characteristic of ropy beer is formed by the organisms concerned from the residual non-fermentable carbohydrate or dextrin, and either stable dextrin or maltodextrin can function for this purpose.

Industrial fermentations

The increase in the amount of synthetic ethanol produced from ethylene and the development of production by the Fischer-Tropsch process has naturally led to the suggestion that synthetic methods may eventually replace fermentation as the source of industrial alcohol. In Britain and also in America, apart from the war years when grain was used, molasses is the raw material for alcohol production by yeast fermentation. In a recent discussion[37] it is argued that in the near future sufficient molasses will be available at a reasonable price to enable alcohol produced by fermentation to compete with the synthetic product. In an efficiently operated molasses distillery the yield of alcohol and carbon dioxide from the sugar in molasses is quite close to the theoretical value, so that substantial reductions in production costs by advances in the fermentation technique cannot be anticipated. As the cost of molasses forms a large proportion of the production cost it is evident that low cost molasses means reasonable production cost for fermentation alcohol.

Research on the production of industrial alcohol from domestic farm crops, particularly cereals, was one of the projects of the U.S. Department of Agriculture which received considerable attention during the years 1941-1945.[38] It has been suggested[39] that part of the cereals produced might be fermented in a small unit on the farm to yield alcohol for power and protein concentrates which would be fed to livestock. An interesting model continuous process alcohol unit has been described[40] which was devised to study the feasibility of such a process. The unit will produce about five gallons of alcohol from two bushels of grain in 24 hours. Every process is carried out continuously, even cooking and fermentation. Cooking of the slurry is achieved in six minutes by 1·25% H_2SO_4 at 340° F. After neutralization by chalk the cooled mash is fermented in a continuous process involving two fermenters. The capacity of the primary fermenter allows an eight-hour fermentation time, which, with a three-hour holding period in the secondary fermenter, is sufficient to ferment the mash completely, using a yeast concentration of about 100 million cells per ml. Wash containing about 5% by weight of alcohol is produced and distilled in a 3in.-D column, the lower section of which acts as a stripping section and the upper section as a rectifying column. The unit is fully instrumented and is automatic in operation. The yeast population is self-perpetuating, and inoculation is necessary only when the process is started.

During the processes of fermentation a " biological ennoblement " of the plant materials used frequently occurs.[41] This may take place during the preparation of the raw material, as in the synthesis of vitamins during the germination of cereals, or during the actual fermentation as when riboflavin is produced during the acetone-butanol fermentation of molasses. When a distilled product is the primary object of the fermentation the nutrients produced pass into the " spent wash " or " stillage," the soluble portion of which is often lost in the effluent. The disposal of this potentially valuable effluent has often presented a serious problem to the fermentation industry. An excellent presentation of the position in the U.S.A. was given in a Symposium on Industrial Waste at the 111th Meeting of the American Chemical Society. One of the papers presented[42] dealt with the recovery of materials to be used as fodder from fermentation residues at breweries, alcohol distilleries, and acetone-butanol plants. The brewers and grain distillers have developed equipment and an attractive market for their recovered grains. Before the war the average recovery of grains from distilleries was only about 20% of the potential 17lb. per 56lb. bushel of grain processed. During the war there was a large increase in the production of grain spirit for industrial purposes, and, because of the demand for protein and vitamin concentrates, the recovery of distillers' feed was increased to about 90% of the potential value. In addition to dried distillers' grains, dried distillers' solubles, *i.e.*, evaporated screened stillage, is produced in increasing amounts (100,000 tons in 1946). This material has a high soluble protein content and is also rich in water soluble vitamins, since it contains most of the vitamins from the grain and from the yeast developed during fermentation. The dried slop from the acetone-butanol fermentation finds a ready market as a feeding stuff because of its high content of riboflavin.

In view of the possibility that much of the simpler compounds, such as ethanol and acetone, may in the future be produced by synthesis rather than fermentation, it is interesting to note that in recent years the fermentation industry has expanded in other ways. Progress has been in the direction of producing more complex compounds secreted by living organisms during fermentation under carefully controlled conditions. Examples are the antibiotics such as penicillin and streptomycin, the vitamins such as riboflavin, and organic acids. The production of penicillin has now become an important commercial fermentation. Although the synthesis of this antibiotic has been reported, the yields from the complex processes involved are so low and, consequently, the costs so high that synthetic penicillin is unlikely to compete with that produced by the improved methods of fermentation now in operation. The earlier methods of production by surface culture[43] have, as anticipated, been largely replaced by the more economical fermentations employing submerged mycelium. The increased yields now obtained are due partly to the introduction of higher yielding strains of *Penicillium* and partly to improvements in the medium and in the technique of the deep fermentation process.[44] Strains developed by *X*-ray and ultra-violet treatment of spores have been reported to give yields in laboratory fermentations up to 1500 units per ml. of broth on the best medium and under optimum conditions of aeration and agitation.

Methods of penicillin production in submerged culture on a pilot plant scale have now been described.[45, 46] Descriptions[44, 47] of the processes employed by two of the largest producers in this country—the Distillers' Company, at Speke, and Glaxo Laboratories, at Barnard Castle—indicate that the magnitude of the volumes involved in the fermentation is not much smaller than that in the older ethanol or acetone-butanol fermentations. At Speke a battery of 14 x 10,000 gallon fermenters is employed, for which several hundreds of thousands of gallons of sterile broth consisting of corn steep liquor, lactose, and nutrient salts are needed each week. The fermentation is conducted for several days with aeration. Since many forms of bacterial infection rapidly destroy the penicillin produced, the sterilization of the large volumes of air employed and the maintenance of sterility in pipe lines and valves is a major problem to which very careful attention must be paid.

Details made public during the past year indicate the very large amount of research and developmental work which has been carried out to improve the fermentation process. The elucidation of the structure of penicillin and the demonstration that differences between the various known penicillins can be ascribed to differences in the side chain[44] led to attempts to induce the mould to utilize added " building stones " of known constitution so as to obtain an increase in the total penicillin production or the preferential formation of a desired penicillin. For example, the formation of penicillin 11, which is characterized by a benzyl side chain, is increased by the addition of phenylacetic acid.[48] This method of inducing the formation of a known penicillin by the addition of an appropriate compound has been extended to the formation of novel penicillins. One patent,[49] for example, lists several score monosubstituted acetic acids, each of which it is claimed may be metabolized by penicillin-producing moulds and incorporated in the molecule of a novel penicillin.

An interesting industrial fermentation, in which advantage is taken of the ability of living organisms to produce optically active compounds, is based on the so-called carboligatic reaction of Neuberg. When benzaldehyde is added to yeast fermenting sugar solution the benzaldehyde is condensed with acetaldehyde formed during fermentation, and L-phenylacetylcarbinol is formed. This optically active ketol is subjected to reductive methamination to yield L-ephedrine. A process based on this fermentation is in operation in Germany[50] and in the U.S.A.[51]

A review of recent advances in fermentation[52] outlines the technological developments in industries using yeasts, moulds, and bacteria. The emphasis is on the chemical engineering side, and special attention is paid to the development of continuous processes for the production of alcohol from grain and for the propagation of yeast. A more detailed review[53] deals with American industrial fermentations during the war period; alcohol production from grains and wood products, organic acids, and antibiotics are among the subjects reviewed.

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[48] Moyer, A. J. and Coghill, R. D., J. Bact. 1947, **53**, 329
[49] Lilly, Eli, B.P. Appl. 1130/47
[50] B.I.O.S. Final Rept. No. 1404, Item Nos. 22 and 24
[51] Neuberg, C., Ann. Rev. Biochem. 1946, **15**, 462
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MEDICINAL SUBSTANCES

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THE extent to which medical science is dependent upon the production of pure substances, either by synthesis or by extraction from natural sources, increases from year to year. This section is concerned chiefly with organic compounds of medical significance, and an attempt is made to indicate advances made during the year in certain classes of medicinals. It is quite impossible to cover the entire field, and subjects have been chosen with a view to presenting the more generally interesting material.

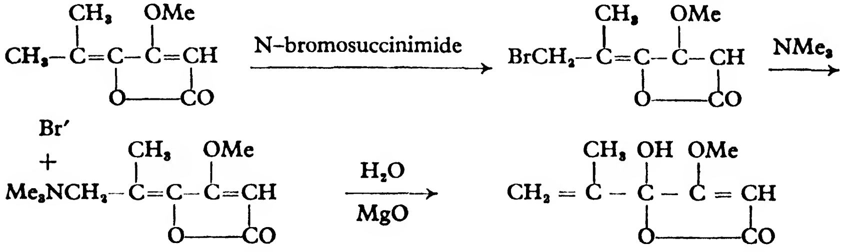
Antibiotics

General.—The general trend during 1947 has been for interest to shift from the well-established penicillin on to streptomycin, which has the most important property of activity against Gram-negative organisms. There is a further batch of new antibiotics on which further work will be necessary before their practical application can be assessed, and a warning note is sounded through the literature on the growing tendency to find organisms which have acquired immunity to penicillin and other antibiotics.

Penicillin.—The Editorial Board of the (American) Monograph on the Chemistry of Penicillin have given a brief history of the chemical study of penicillin,[1] with sixty-eight references to the American and British literature, and a brief summary[2] of the findings, up to the end of 1945, on the biosynthesis of penicillin, with an interesting list of precursors and their corresponding penicillins. W. A. Winsten and A. H. Spark[3] have reported on the penicillin types produced by *P. chrysogenum* Q-176. The principal types include benzyl, pent-2-enyl, *n*-amyl (?), *n*-heptyl, and *p*-hydroxybenzyl penicillins.

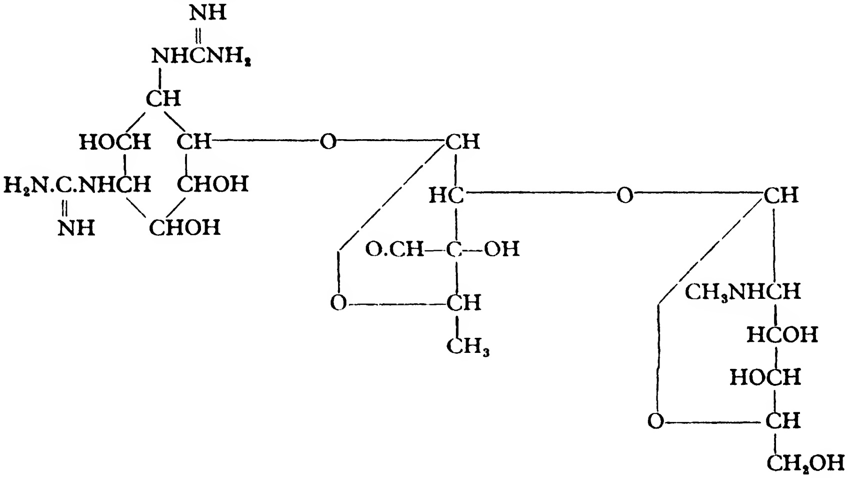
Counter-current distribution has been employed[4] by L. C. Craig, G. H. Hogeboom, F. H. Carpenter, and Vincent du Vigneaud for the separation and characterization of some penicillins.

R. A. Raphael has given a preliminary report on the synthesis of penicillic acid[5] from a lactone, the synthesis of which is not yet published.



Streptomycin.—The Merck & Co. research group[6] have proposed a full structure for streptomycin based on evidence supporting attachment of streptobiosamine to carbon 4 of streptidine, as shown opposite.

H. C. Carter, Y. H. Loo, and P. S. Skell[7] consider that evidence is more strongly in favour of attachment at C_5, though C_4 is not excluded. J. Fried and O. Wintersteiner, of the Squibb Institute for Medical Research,[8] have produced evidence for the aldehyde group in the above structure, and state that dihydrostreptomycin, in which the aldehyde group is reduced to an alcoholic group, has antibiotic activity of about 700 units/mg. against *K.pneumoniae*. The presence of an aldehyde group is also supported by evidence put forward by the Ohio State University Group.[9]



G. P. Mueller has recommended large-scale purification of crude streptomycin by partial adsorption on alumina,[10] and the method of counter-current distribution applied by E. Titus and J. Fried, has yielded streptomycin B, isolated as the reineckate.[11]

Citrinin.—This antibiotic, first isolated from *P.citrinum* Thom., has been isolated from five other *Penicillium* varieties, widely separated morphologically from *citrinum*.[12] These are *P.lividum* Westling, *P.phoeojanthinellum* Biourge, *P.implicatum* Biourge, *P.chrzaszczi* Zaleski, and *P.citreo-sulphuratum* Biourge. A report from Chinese sources on some independent investigations on the antibiotic activity of citrinin[13] indicates that, although adversely affected by citrinin, certain Gram-negative organisms are less susceptible to it than Gram-positives; clinical trials in local staphylococcal and streptococcal infections have given promising results.

Aerosporin.—G. C. Ainsworth, A. M. Brown, and G. Brownlee[14] have made a preliminary announcement of a new and interesting antibiotic produced by *Bacillus aerosporus,* to which they have attached the name aerosporin. This substance is active against several Gram-negative organisms, including the somewhat impervious *Haemophilus pertussis,* and has a high intrinsic potency, comparable with that of penicillin against Gram-positive organisms. Further important points include ready production by methods similar to those used for streptomycin, and relative stability. More information, particularly relative to toxicity, will be awaited with the greatest interest.

Other newly-described antibiotics include actidione from *Streptomyces griseus,*[15] lavendulin from *Actinomyces lavendulae,* and actinorubin from a not well-defined strain of *Actinomyces*,[16] and sulphactin from a soil *Actinomyces* (R-30).[17] Raphanin, an antibacterial substance isolated from aqueous extracts of radish seeds by G. Ivanovics and S. Horvath,[18] has been found to be active against a variety of bacteria, Gram-negative as well as Gram-positive, and also to prevent the germination of the seeds of certain plants; it is moderately toxic.

J. Ehrlich, Q. R. Bartz, R. M. Smith, D. W. Joslyn, and P. R. Burkholder have isolated chloromycetin from a *Streptomyces sp.* occurring in a Venezuelan soil sample.[19] This substance is claimed to be active against certain Gram-negative organisms (notably *Shigella paradysenteriae* Sonne) and to show activity against *Rickettsia prowazcki.* A further report from J. E. Smadel and E. B. Jackson confirms the activity against several *rickettsiae.*[20] J. G. Kidd[21] has examined the effects of an antibiotic from *Aspergillus fumigatus* Fresenius on tumour cells. This substance, which may be identical with gliotoxin, has been found to inhibit the growth of Gardner lymphosarcoma and Brown-Pearce carcinoma cells when tested *in vitro.*

Amino acids

Methionine.—A most useful paper on the semi-technical production of DL-methionine has come from the Ministry of Supply Research Establishment, Sutton Oak.[22] C. H. G. Hands, A. F. Millidge, and B. Y. Walker are responsible for this publication, which gives full details for semi-technical and pilot scale working together with a provisonal flow-sheet for a batch estimated to yield 100lb. methionine. Diagrams of plant are given, including one of a climbing film still used for the continuous distillation of diethylbromomalonate. The method employed involves the reaction together of ethyl phthalimidomalonate (prepared in stages from chloroacetic acid) with methyl β-chloroethyl sulphide (prepared in stages from ethylene oxide), in the presence of sodium ethoxide. The product is hydrolysed to the corresponding tricarboxylic acid, which, on hydrolysis by acid and removal of hydrogen chloride by pyridine, yields crude methionine in good yield. It is stated that by this method the cost of production has been very greatly reduced below the last quoted price.

J. R. Catch, A. H. Cook, A. R. Graham and I. M. Heilbron[23] have drawn attention to the great inconvenience experienced in the above and similar method attendent upon the use of a dangerous vesicant such as methyl β-chloroethyl sulphide. They also have pointed out that commencement from γ-butyrolactone involves a lengthy procedure, and offer a new method giving a 29% yield of methionine from acrolein by the following series of reactions:

$$CH_2{=}CH.CHO \xrightarrow{MeSH} CH_2(SMe).CH_2.CHO \xrightarrow{HCN}$$

$$CH_2(SMe).CH_2.CH(OH).CN \xrightarrow{NH_3/EtOH} CH_2(SMe).CH_2.CH(NH_2).CN$$

$$\xrightarrow[\text{at } 100^\circ]{\text{conc.HCl}} \text{DL-methionine.}$$

The configuration of methionine has been further studied by G. S. Fonken and R. Mozingo,[24] who have obtained *laevo*rotatory α-aminobutyric acid by treatment of *dextro*rotatory methionine with excess of Raney nickel. It is concluded that natural methionine, derived from proteins, is L(–)-methionine.

β-Alanine.—A new and convenient synthesis for β-alanine has been described by S. Chodroff, R. Kapp, and C. O. Beckmann,[25] who employ β : β′-iminodipropionic acid or its nitrile or diethyl ester as starting materials. Fusion with phthalic anhydride yields the appropriate acid phthalimide, which is then converted by heat to the β-phthalimidopropionic acid derivative. Hydrolysis of this produces β-alanine in good yield.

Following a study of the reaction of acrylonitrile with aqueous ammonia, J. H. Ford, S. R. Buc and J. W. Greiner[26] have found that 60–80% yields of β-aminopropionitrile are obtainable by rapid addition of acrylonitrile to aqueous ammonia preheated to 110°. This effects great improvement to the yields claimed by S. R. Buc, J. H. Ford and E. C. Wise (see Ann. Repts. 1945, 30, 517).

Lysine.—A. Galat[27] has improved the von Braun synthesis of DL-lysine;[28] he converts ε-caprolactam or ε-aminocaproic acid to ε-benzoylaminocaproic acid, chlorinates to the α-chloro acid with sulphuryl chloride in the presence of iodine, and converts to DL-lysine by ammonolysis and hydrolysis of the benzoyl derivative.

General methods.—A. Galat[29] has described the use of ethyl formylaminomalonate as an intermediate in the synthesis of amino acids. This ester is prepared in 55% yield from ethyl malonate by nitrosation with sodium nitrite and acetic acid, followed by reduction with zinc and formic acid; nitrosation with butyl nitrite gave a 63% yield. The ester has been used under the conditions employed generally for ethyl acetylaminomalonate, and thus have been obtained DL-phenylalanine (60%), DL-aspartic acid (55%), and DL-glutamic acid (57%).

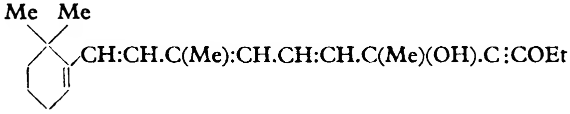
The esters of certain α-amino acids have been prepared directly, without isolation of the free acids, according to J. C. Shivers and C. R. Hauser,[30] who have used a method indicated by Fischer and Weigert.[31] An alkylated malonic ester is converted to an α-oximino acid ester by reaction with ethyl nitrite and sodium ethoxide, and the product reduced by hydrogenation over Raney nickel at high pressure. Prepared by this means, through ethyl α-oximinocaproate, norleucine ethyl ester has been hydrolysed to norleucine in good yield.

Aspartic acid.—H. J. Klosterman and E. P. Painter[32] have published a new synthesis of aspartic acid which they claim to be more convenient than methods employed previously. Over-all yields of aspartic acid amounting to approximately 40% have been obtained from γ-butyrolactone by treating the α-bromo derivative with aqueous ammonia, benzoylating the aminohydroxybutyric acid and oxidizing the product with alkaline potassium permanganate; the resulting DL-benzamido-aspartic acid was then hydrolysed to aspartic acid.

Vitamins and Growth Factors

Vitamin A Group.—R. A. Morton, M. K. Salah and A. L. Stubbs[33] have produced evidence to support the view that vitamin A_2 differs from vitamin *A* by an additional conjugated double bond in the ring. An aldehyde indistinguishable from retinene$_2$ has been obtained by Oppenauer oxidation of vitamin *A*, and, in better yield, from retinene; retinene$_2$ (prepared from vitamin *A*$_2$) has been found to yield the same crystalline 2:4-dinitrophenylhydrazone as that from the aldehyde from vitamin *A*.

A new synthesis of the "C18 ketone," an important intermediate in the synthesis of vitamin *A* and of "vitamin *A* acid," has been described by N. A. Milas and T. M. Harrington;[34] ethyl β-ionylidene acetate was reduced with lithium aluminium hydride to β-ionylidene-ethyl alcohol, and the product oxidized by Oppenauer's method to the desired ketone. This ketone has been used by D. A. van Dorp and J. F. Arens[35] as a starting material for a synthesis of "vitamin *A* aldehyde"; reaction with ethoxyethynyl magnesium bromide yielded the alcohol—

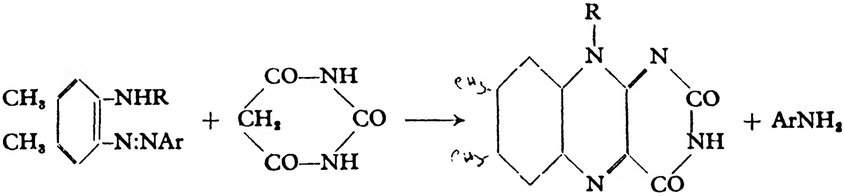


This alcohol was reduced by hydrogen over palladium on barium sulphate, and the product hydrolysed by aqueous hydrogen chloride to "vitamin *A* aldehyde."

C. D. Robeson and J. G. Baxter[36] have isolated a geometric isomer of vitamin *A* from shark liver oil. This substance, called by them *neo*-vitamin *A*, has also been found to occur in cod, dog-fish, halibut, and California jew-fish liver oils to the extent of 35% of the total vitamin *A*.

Folic acid (pteroylglutamic acid).—J. J. Pfiffner, S. B. Binkley, E. S. Bloom and B. L. O'Dell have published[37] an account of their researches into the isolation of pteroylglutamic acid from liver and from yeast, and have produced evidence suggesting that another anti-anæmic compound is also present in liver, differing from pteroylglutamic acid in being very acid labile. The same group (Parke, Davis, & Co., U.S.A.) have hydrogenated pteroylglutamic acid to a dihydro derivative which is readily re-oxidized back to the starting material,[38] and have also published an account of their work on oxidative degradation.[39]

Riboflavin.—A new synthesis of riboflavin has been announced by a group of workers in the research laboratories of Merck & Co., Inc.[40] Use is made of a reaction between 1-(D-ribitylamino)-2-arylazo-4:5-dimethyl benzene and barbituric acid.



(where R = D-ribityl)

This method is claimed to be simpler and more direct than the two methods previously published, which employ reaction of *o*-phenylenediamines with alloxan or with halogenated barbituric acids. A yield of 65·8% of the theoretical quantity of pure riboflavin has been obtained by this means from 1-(D-ribitylamino)-2-*p*-nitrophenylazo-4:5-dimethylbenzene.

δ-Tocopherol.—M. H. Stern, C. D. Robeson, L. Weisler and J. G. Baxter[41] have found that δ-tocopherol constitutes approximately 30% of the mixed tocopherol in soya bean oil. The mixture of tocopherols has been separated by them from the soil by molecular distillation and freed from glycerides by saponification. Selective adsorption on zinc carbonate removed *a*-tocopherol, and the resulting concentrate was separated by fractional crystallization of the palmitoyl derivatives. δ-Tocopherol was then isolated as the crystalline *p*-phenylazobenzoyl derivative.

The new tocopherol has been found the most active of the group as an antioxidant for vitamin *A* acetate and β-carotene, but has only one-hundredth of the activity of *a*-tocopherol in the Evans resorption sterility test for vitamin *E*. The structure is believed to be that of 8-methyl tocol.

Steroids

From the point of view of the "applied" or industrial chemist there can be no doubt that the publication of the details of sterol and steroid hormone production in Germany during the late war is of paramount importance. Methods have been acquired which give a sobering insight into the essential thoroughness of German production research and development, and which give instructions to production personnel in meticulous detail.

Sterols.—The production of cholesterol and of stigmasterol in satisfactory purity and at economic prices is fundamental to the production of the usual steroid hormones. The subject is dealt with in F.I.A.T. Final Report No. 902.

The method used by Boehringer and Soehne for extraction of cholesterol from wool-wax is based primarily on hot methanol extraction, which yields a crude cholesterol containing about 25% of pure sterol. From spinal cords the same firm obtain crude cholesterol by extraction with ethylene dichloride in a modified Soxhlet apparatus. The crude product from either source is purified by recrystallization from alcohol or from acetone.

Stigmasterol was produced by Hans Muehle (of Hamburg) from crude soya bean oil by preliminary extraction with alcohol in place of the more usual hydrolysis; the oil was thus eventually available for refining to edible oil. The alcohol extract was then hydrolysed and the unsaponifiable part purified by crystallization from alcohol.

The purification of crude soya phytosterols and details of the evaluation of the product in terms of stigmasterol content are given in B.I.O.S. Final Report No. 449.

Steroid hormones.—Two reports deal with this subject generally. The more useful one is F.I.A.T. Final Report No. 996, but some information is also given in B.I.O.S. Final Report No. 449.

*Dehydro*iso*androsterone.*—This is the principal intermediate in the synthesis of many hormones from cholesterol. The oxidation has been described by various competent authors, but little modern work has been published since the original papers of Ruzicka, Butenandt, and Wallis and Fernholtz. Such patents as have appeared may be regarded as interesting more for the information not given than that actually made available. We now have, in remarkably full detail, the method used by Schering A.-G. to obtain yields up to 8% of dehydro*iso*androsterone acetate semicarbazone from pure cholesterol. The most obvious deviation from previous published methods is in the use of a mixture of ethylene dichloride and acetic acid as a solvent for cholesteryl acetate dibromide during the chromic acid oxidation, but also noteworthy is the use of pyridine tetrabromide solution at low temperature for preparing the dibromide of cholesteryl acetate. This latter, presumably, is designed to reduce substitution to a minimum. Of interest also is the removal of chromium compounds from the oxidation mixture before working up, but the very obvious attention to the practical difficulties arising in development generally is perhaps the most important point of all.

It has been stated, and reported earlier, that the use of ethylene dichloride has resulted in the disappearance of pregnenolone from the oxidation products; it now appears that this does not necessarily apply, and may be based on the fact that this important by-product is not mentioned in the documents available.

Testosterone propionate.—Production details for this do not show any fundamental deviations from previously published methods; hydrogenation with Raney nickel is used for the reduction of dehydro*iso*androsterone acetate to androstenediol-3-acetate. No account is given in this report of the production of 17-methyl testosterone, which shares with testosterone propionate the distinction of wide clinical application.

Progesterone.—Two methods are given for the production of this "natural" progestational hormone. The first commences with dehydro*iso*androsterone acetate, which is converted to the cyanohydrin; this cyanohydrin has been found difficult to dehydrate economically in the past, and in this case the dehydrating agent employed is phosphoryl chloride in pyridine. It perhaps may be assumed that the reaction proceeds satisfactorily since a yield of 82·6% on the dehydro*iso*androsterone acetate is claimed. The dehydronitrile is brought into reaction with methyl magnesium bromide, and the resulting dehydropregnenolone (71%) hydrogenated over Raney nickel to pregnenolone (81 to 86%). Oxidation by Oppenauer's method (83%) gives progesterone. If these yields receive confirmation the method should become of considerable practical importance. The second method uses purified phytosterol as starting material, and proceeds along well-established lines via 3-hydroxybisnorcholenic acid (ozonization), which is converted to the methyl ester and acetylated. By a modified Curtius degradation 3-acetoxyternorcholenylamine is obtained; treatment with hypochlorous acid, followed by sodium ethoxide and hydrolysis, yields pregnenolone in approximately 2% over-all yield from phytosterol acetate (containing about 18% stigmasterol acetate).

Ethynyltestosterone.—This orally active substitute for progesterone is covered by manufacturing details; dehydro*iso*androsterone acetate is caused to react with potassium acetylide in anhydrous ammonia. The resulting 17-ethynylandrostenediol is oxidized by Oppenauer's method to ethynyltestosterone; the over-all yield for the two reactions is 67%.

Oestradiol.—Some information is given relating to the production of the ovarian hormone from dehydro*iso*androsterone by Inhoffen's method. Dehydro*iso*androsterone acetate is converted to androstenediol-17-benzoate as in the preparation of testosterone propionate, but the diol benzoate is then hydrogenated to androstandiol 17-hexahydrobenzoate and the product oxidized by chromic acid to the benzoate of androstan-17-ol-3-one. Bromination of the ketone yields the 2:2-dibromo derivative which rearranges in the presence of hydrogen bromide in acetic acid to the isomeric 2:4-dibromo ketone. Removal of hydrogen bromide with collidine and saponification of the product gives androsta-1:4-dien-17-ol-3-one. Aromatization is then carried out by heating with excess of tetralin in an atmosphere of nitrogen to 600°.

A secondary process for the production of oestradiol from 17-*cis, trans*-androstenediol 3-acetate is of interest. This substance is a by-product from the hydrogenation of dehydro*iso*androsterone acetate, which is the first step in the above process and in the production of testosterone propionate. By the same method as employed for the *trans* isomer the corresponding androstenediol-17-benzoate is prepared, but is then saponified and hydrogenated to the *cis, trans*-androstandiol. Oxidation with chromic acid to androstan-3:17-dione is followed by preparation of the 3-diethyl acetal, reduction and hydrolysis to androstan-17-ol-3-one. The acetate of the ketol is then subjected to the same series of reactions as the hexahydrobenzoate in the foregoing. The successful economic development of this process might enable oestradiol to become available for clinical use at a lower price, and so become less hampered in rivalry with the stilboestrol class of synthetic oestrogens. A. L. Wilds and C. Djerassi[42] have confirmed this partial synthesis (originally reported by Inhoffen and Zuhlsdorff[65]) in all essential detail; they have, moreover, improved the procedure given in the original report for preparing androsta-1:4-dien-17-ol-3-one, and as a result of further study of the aromatization stage have claimed yields of 10%, by employing dihydrophenanthrene at 390°.

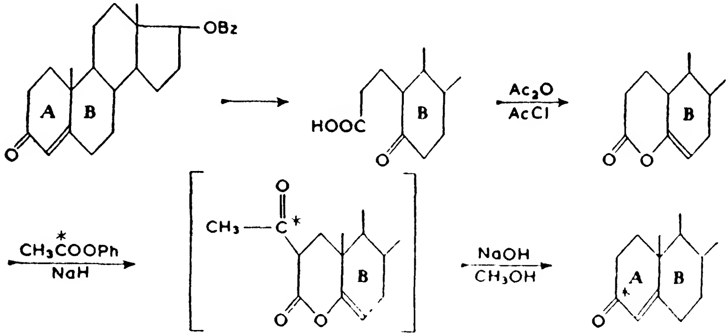
Oestriol.—This characteristic hormone of the placenta has been synthesized from oestrone methyl ether by reaction with *iso*amyl nitrite in *tert.*-butyl alcohol to give 16-*iso*nitroso-oestrone methyl ether; reduction with zinc and acetic acid gave 16-hydroxyoestrone methyl ether, which was then reduced and demethylated to oestriol. The name of Butenandt is associated with this synthesis, but essentially the same method has been published by M. N. Huffman,[43] who has claimed yields of 22 to 26% of oestriol from oestrone.

Deoxycorticosterone acetate (DOCA).—Two methods are given for the production of deoxycorticosterone acetate, one from the acid products of chromic acid oxidation of cholesteryl acetate dibromide and the other from phytosterol via pregnenolone (see above). The first is particularly interesting to manufacturers producing dehydro*iso*androsterone by cholesterol oxidation since the starting material 3-acetoxyaetiocholenic acid is a by-product from that reaction. 3-acetoxyaetiocholenyl chloride is brought into reaction with diazomethane, and the resulting diazopregnenolone converted to 21-acetoxypregnenolone by reaction with acetic acid. Final oxidation is by Oppenauer's method.

The second method follows the corresponding progesterone synthesis up to the production of pregnenolone, which is then condensed with ethyl oxalate and the product saponified. Reaction with iodine and potassium hydroxide yields an iodo ketone which on acetolysis gives 21-acetoxypregnenolone as in the first method. This second method does not appear to have been developed into a manufacturing process.

Radio-active testosterone.—R. B. Turner,[44] of Harvard University, has prepared testosterone having radio-active carbon in the 3 position.

Testosterone benzoate was treated with ozone, and the keto acid so produced lactonized and brought into reaction with phenyl acetate (containing radio carbon) in the presence of sodium hydride. Treatment of the product with methanolic sodium hydroxide yielded radio testosterone, which was purified by chromatography.



Alkaloids

Quinine.—W. E. Doering, G. Cortes and L. H. Knox have studied the partial racemization of quinine, the subject of earlier work by Rabe.[46] A new and possibly general method for racemization or epimerization of secondary alcohols has been developed; quinine has been partially racemized in toluene by treating with sodium *tert.*-butoxide and an oxidation-reduction system such as fluorenone-fluorenol.

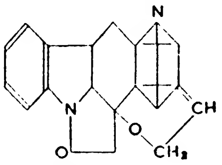
Curare alkaloids.—P. Karrer and H. Schmid[47] have published two further papers on the subject of the alkaloids of calabash curare. Nine alkaloids have so far been isolated, and empirical formulæ for eight of these have been suggested.

An important advance has been announced by F. B. Mallinson,[48] who finds that " Myanesin " [2 : β-dihydroxy-γ-(2-methylphenoxypropane)] has well-marked advantages clinically over curare. Twelve cases are quoted and the results analysed. Myanesin has been described by F. M. Beyer and W. Bradley[49] (British Drug Houses Ltd.); it has been found to be the most active of a series of glycerol ethers examined by them. In doses insufficient to cause paralysis myanesin has been found superior to hexobarbitone as an antagonist against strychnine convulsions, and it has been suggested that the pharmacological action may be due to a depressant action on the spinal cord.

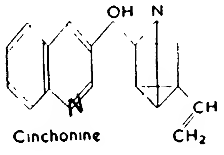
Febrifugine.—This is one of two new alkaloids isolated by J. B. Koepfli, J. F. Mead and J. A. Brockman[50] from the Chinese plant *Dichroa febrifuga* Lour. Febrifugine, isolated from both roots and leaves of the plant, is stated to be approximately one hundred times as active as quinine against *P.lophurae* in ducks. *iso*Febrifugine, isolated from the roots, has relatively slight activity.

Capauramine.—The structure of capauramine, isolated from *Corydalis pallida* Pers., has been given by R. H. F. Manske[51] as a dihydroxy trimethoxytetrahydroprotoberberine.

Strychnine.—The structure of strychnine continues to claim considerable attention. The relationship of *neo*strychnine to strychnine is now considered to be established, according to R. N. Chakravarty and R. Robinson,[52] and the structure suggested by R. Robinson, reported last year, has received support from R. B. Woodward, W. J. Brehm, and A. L. Nelson.[53] However, R. Robinson has now propounded a novel structure for strychnine which shows its relation to cinchonine closer than heretofore, and which he considers to be " the best working hypothesis at present available."



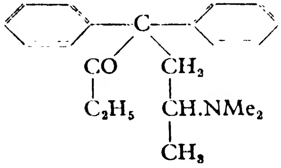
Strychnine



Cinchonine

Miscellaneous

Amidone.—This new analgesic, originally known as Hoechst 10820, was first announced in a B.I.O.S. report,[54] where it was described as the most active of a series of related compounds, and approximately ten times as active as Pethidine (Dolantin).



Amidone

During the year much interest has been shown in the substance; E. M. Schultz, C. M. Robb, and J. M. Sprague[55] have investigated the German process for its manufacture, and have discovered that the essential reaction between diphenylacetonitrile and 1-dimethylamino-2-chloropropane results in a mixture of two isomeric nitriles, the high melting one of which yields Amidone on reaction with ethyl magnesium bromide. This higher melting nitrile is not the one resulting from the reaction taking the normal course, and this disposes of some uncertainty which had existed of the structure of the German material.

N. R. Easton, J. G. Gardner, and J. R. Stevens[56] have completed the synthesis of *iso*amidone by reaction of the lower melting nitrile with ethyl magnesium bromide, and a note by W. R. Brode and M. W. Hill on the rearrangement of the isomeric 1:2-dimethylaminochloropropanes has confirmed the above.[57]

In this country Amidone has been taken up by the Wellcome laboratories, and the name Physeptone has been added by these workers to the steadily growing list of synonyms. They have published[58] an interesting account of the analgesic activity of compounds related to Amidone, and have compared them with morphine and pethidine. Amidone has been found approximately equal to morphine, but the *laevo* form is responsible for most of this effect, which itself is approximately twice as active as morphine or the DL mixture. Separation of the isomers was not found successful by these workers, but separation of the penultimate 1:1-diphenyl-3-dimethylaminovaleronitrile was readily effected by the use of D-tartaric acid.

British Anti-Lewisite.—Since 1940, when Stocken and Thompson[59] carried out an investigation into the nature of the reaction between arsenical compounds and proteins, interest has gradually grown in the uses of 2:3-dimercaptopropanol, known as British Anti-Lewisite (BAL). This substance, found effective as an antagonist to Lewisite used as a test substance, is the subject of a paper by L. A. Stocken,[60] who has compared the physical constants of various specimens. The method given for a standard preparation involves the reaction of 2:3-dibromhydrin with sodium hydrogen sulphide solution, yielding 64% of crude BAL. An account of the original work on Lewisite was published by R. A. Peters, L. A. Stocken, and R. H. S. Thompson[61] in 1945, and now a report on the use of BAL in arsenical intoxication, from the BAL conference, Medical Research Council, has been published.

During the year many papers have been published on the biological and clinical aspects of BAL; R. H. S. Thompson and V. P. Whittaker[63] have demonstrated the ability of the substance to detoxicate compounds of antimony, gold, and mercury, and L. A. Stocken[64] has shown it to be effective in acute mercury poisoning.

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characters $d_{15^\circ}^{15^\circ}$, 0·8938; n_D^{20}, 1·4588; α_D −32°50′; free menthol 44·7%. The lighter fraction (13·6% approx.), after treatment with boric acid and saponification of the borates, was found to contain methanol, ethanol, *n*-butanol, 1-pentanol, *iso*butylcarbinol, hexene-3-ol-1, methyl-3-pentanol-1, hexanol and ethyl-*n*-amyl carbinol. Some chemical aspects of the ageing of essential oils and perfume mixtures were discussed by Strausz,[6] who explained that the main factors in the deterioration of lemon oil are citral and D-limonene. Citral is a mixture of at least two isomerides, citral *a*, which amounts to about 90% of the total in lemongrass oil, and citral *b*. Citral from lemon oil, on the other hand, consists mainly of an isomeride γ-citral. In 1939 Schmidt prepared *iso*citral which possessed the fine lemon peel odour of lemon citral, in fact it is probable that the two substances are identical; γ- and *iso*citrals are more sensitive than the *a* and *b* isomers to cyclization, resinification and conversion into *p*-cymene. D-Limonene, which is present to the extent of about 90% in both lemon and orange oils, readily oxidizes to carvone and carveol. Bergamot oil, unlike lemon and orange, is subject to very little deterioration on storage, due to the fact that it contains no citral and the content of limonene is low, and it is evident that linalol, linalyl acetate, nerol, bisabolene and bergaptene, which constitute more than 50% of the oil have a stabilizing effect. The author recommends that citrus and peppermint oils be dried with anhydrous magnesium sulphate and then stored in glass containers at 5–10°, filled to the neck. It was pointed out that essential oils which improve on ageing, such as patchouli, vetivert and ylang-ylang, contain considerable amounts of sesquiterpenes and sesquiterpene alcohols. The storage of aldehydes in 10 to 50% alcoholic solutions has proved satisfactory. The formation of acetals and Schiff's bases in perfume mixtures on storage is discussed, as also are the effects of certain odorous resins and the large ring ketones and lactones of musk, civet, angelica oil and ambrette seed oil. A number of the published suggestions for shortening the time of maturing are considered, but the author doubts the efficacy of these methods when applied to perfumes, although some have proved useful when applied to the alcohol used as a solvent. The determination of carbonyl compounds by means of 2 : 4-dinitrophenylhydrazine was the subject of a paper by Scholtens,[7] who claimed that by his method it is possible to determine many ketones and aldehydes for which no accurate means was known previously. By a study of citronellal, citral, geraniol and linalol, Carroll[8] has endeavoured to determine whether acyclic isolates of essential oils are mixtures of the terpinene (I) or dipentene (II) forms, or whether certain of them consist only of one or other of these forms:

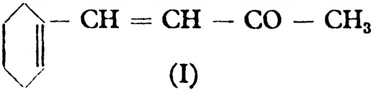
$$(CH_3)_2C = CHCH_2{\cdot}R$$

(I)

$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C}{\cdot}CH_2CH_2R$$

(II)

The conclusions arrived at are that most, if not all, of the acyclic terpene derivatives occurring in nature are of form (I), but it is difficult to prove that no isolates of form (II) exist, owing to technical problems involved in the separation of the two forms. In this paper are described methods for the preparation of semicarbazones and phenylurethanes, also for the estimation of carbonyl groups. Jones and Richardson[9] described two syntheses for a ketone (I) which is similar in constitution to β-ionone. The structure of this analogue was proved by degradative experiments



(I)

The controversial question of the genesis of essential oils in plants has been opened again by Naves[10] in an interesting article. The author shows that the formation of the oils in plants is not such a simple process as Charabot and his colleagues supposed, and that present knowledge no longer permits us to accept the hypotheses of these workers. The production of essential oils within the Empire continues to receive attention, the work being encouraged by advice and assistance from the Imperial Institute, from which department a number of reports have emanated during the year. Cosgrove and Islip[11] have attempted to prepare a fraction of Seychelles cinnamon leaf oil equal in quality to the Ceylon product, but although the lighter fractions were of better odour value than the entire oil, they were not sufficiently good to compete with Ceylon oil. A decrease in the citral content of Tanganyika lemongrass oil had been noted and with a view to ascertaining the causes of this, Coomber and Cosgrove[12] examined a number of samples distilled from grass cut at different times of the year and also after partial drying. The conclusions reached were that the grass should be fully mature before cutting, probably reducing the number of cuttings per year, and that cutting should be carried out during dry weather. Consideration should be given to frequent transplanting of the grass tufts into manured ground and also to distillation without partial drying. Trinidad lemongrass oil was found by Cosgrove and Islip[13] to compare favourably in odour, citral content and solubility with East Indian or Cochin oil. A sample of *Ocimum suave* oil from Kenya was examined by Coomber and Cosgrove[14] and found to differ from oils previously received from Tanganyika and the Belgian Congo, in that it contained much less eugenol but a high proportion of methyleugenol. The composition per cent was aldehydes and/or ketones 2·1; phenols, eugenol 8·3; phenol esters, methyleugenol 56·2; free alcohols, probably linalol 7·5; esters as linalyl acetate 0·8; acids as acetic 0·2; terpenes, etc., 24·9. Four samples of Palestinian orange oil were reported upon by Islip and Major;[15] three were found to differ only slightly in characters from normal sweet orange oil, while one sample had the rather high specific gravity of 0·8565 and an aldehyde content of only 0·94%. According to a local grower, N. C. Lanitis,[16] the potentialities of Cyprus as an essential oil producing island are great, owing to its favourable climate. Among the oils distilled from wild plants are bay laurel, juniper, pine needle, sage, origanum and thyme, and from cultivated plants, anise, bitter almond, cummin, lavender, lemon, neroli, orange, peppermint and rosemary.

Bennett,[17] commenting upon a paper on Seychelles cinnamon bark oil (*Bull. Imp. Inst.* 1946, 44, 188), points out that the B.P. does not require an oil of high eugenol content; on the contrary, oils from Ceylon have in recent years been of fine aroma and almost free from eugenol. Islip,[18] of the Imperial Institute, replied to the effect that three commercial samples of cinnamon oil B.P. examined recently contained 10·5, 8·5 and 8·5%

of eugenol. Each of these passed the B.P. ferric chloride test, as did the composite Seychelles oil upon which C. T. Bennett commented. According to d'Argila,[19] the cultivation of lavender should be developed in Spain, since present production yields an oil with 25 to 40% of linalol. With selected plants the linalol content in the second year was 58% plus 1·9% esters. Lemongrass should do well in the warm humid parts of the north-east of Buenos Aires province,[20] and it should be possible to take one to three cuttings per annum for three to six years. The yields of oil from two samples of grass were 0·391 and 0·416% v/w, with citral contents of 71·9 and 72·7%.

Dalmatov,[21] in a Russian patent, claims increased yields of oil from rose petals when they are covered with a salt solution, such as saturated sodium chloride, before steam distillation. By this method the loss of oil is reduced from 20 to 30% to from 5 to 8%.

Composition and characters

Angelica archangelica, [22] grown in Holland, yielded an essential oil containing D-α-phellandrene, α-pinene, hydroxypentadecanoic acid and α-methyl butyric acid. A secondary alcohol, probably borneol, was isolated.

Araucaria excelsa[23]—*iso*phyllocladene (m.p. 110–111°) was isolated from the final fraction of the oil.

Boronia megastigma.[24]—Naves and Parry have reviewed our knowledge to date of the odorous constituents, together with an account of some original work on the ketonic fraction of the extract of the flowering tops. The semicarbazones of the ketonic fraction were separated into the semicarbazone of β-ionone and a mixture of semicarbazones of racemic α-ionone and D-α-ionone.

Cinnamomum camphora var. *glaucescens*[25] leaves yielded an essential oil containing L-linalol 34%, cineol, DL-α-terpineol, geraniol, safrol, camphor and terpenes.

Cinnamomum kanahirai[26] oil was separated into an acidic portion containing palmitic, piperonylic, cumic and caprylic acids together with a new monobasic acid $C_{10}H_{18}O_2$ called "shogyu acid", and a neutral portion consisting of D-cadinene, bisabolene, α-and γ-campholene, and two new sesquiterpenes, α- and β-shogyuene.

Clausena anisata[27] leaves from trees cultivated in Java yielded an oil containing from 74·3 to 89·6% of anethol, together with a small amount of anisaldehyde. The author considers that the oil would find a ready market and would probably be cheaper than star anise oil.

Wild clove oil.[28]—The oil content of ten wild varieties of cloves of the Moluccas varied from 3 to 3·5%. Eugenol was absent but the presence of two crystalline compounds was determined—eugenin $C_{11}H_{10}O_4$ and eugenone $C_{10}H_{12}O_4$.

"Davana oil".[29]—*Artemisia pallens* Wall. yielded 0·13 to 0·3% of oil, having the characters $d_{15\cdot5^\circ}^{15\cdot5^\circ}$ 0·9605; $n_D^{20^\circ}$ 1·4880; α_D + 35°; acid value 2·4; ester value 52·9.

Eucalyptus cneorifolia.[30]—Berry has made field observations of seasonal variations in the essential oil from the growing tips of this Eucalypt, paying special attention to the occurrence of cymene. The yield of oil increased from September onwards, culminating with rapid growth of young tips in a " flush " period of 3 to 4 weeks, which varied from season to season according to the weather.

Eucalyptus globulus[31] oil from Nilgiris contained cineol 62·2%, pinenes 24%, sesquiterpene alcohols 5% and aromadendrene 1%. Phellandrene was absent.

Evodia elleryana[32] yielded to steam distillation of the leaves about 0·2% of oil, the chemical composition of which varied with the locality. Oil from Stradbroke Island contained evodione ($C_{16}H_{20}O_5$), elleryone ($C_{15}H_{22}O$) and an unidentified compound of formula $C_{16}H_{20}O_5$, a mixture of phenols and sesquiterpenes. Oil from the Mackay area contained elleryone and a compound $C_{16}H_{20}O_4$ of m.p. 107°.

The constituents of Lavandin oil[33] were identified by careful fractionation and analysis of the fractions.

Lavandula delphinensis.[34]—Oil from this plant grown at Moustiers-Ste.-Marie was examined and a large number of constituents determined.

Lavandula pedunculata[35] oil from Morocco was found to contain carvacrol, L-β-pinene, cineol 5·5%, L-borneol free and combined, L-camphor, acetic acid (combined) and L-cadinene.

Ledum palustre L.[36]—Leaves from Saghalien yielded 0·72% of essential oil, consisting of *p*-cymene, a terpene alcohol $C_{10}H_{15}OH$, geranyl acetate, geranyl formate, a bicyclic sesquiterpene $C_{15}H_{24}$ and ledol $C_{15}H_{26}O$.

Libanotis montana All.[37]—The oil from the fruits of this Umbellifer contained esters of geraniol and a bicylic sesquiterpene $C_{15}H_{24}$.

Lilium candidum L.[38]—Two samples of absolutes from these flowers yielded to distillation with ethylene glycol, under 3mm. pressure, colourless oils containing *p*-cresol, linalol, α-terpineol, phenylethyl acetate, cinnamate and palmitate. The author of this paper comments on the fact that perfumers have for some time succeeded in reproducing the odour of the flower by blends of linalyl and terpinyl cinnamates, which esters are undoubtedly present in the natural oil. Sweet orange oil from French Guinea was examined by Benezet and Igolen[39], who found that *n*-octanal constituted from 75 to 80% of the aldehydes present, together with nonyl- and decylaldehydes and citral. Nigam and Dutt[40], working on oil distilled in India from the peel of *Citrus nobilis*, found that the aroma was due to the presence of the caprylic esters of linalol and nonyl alcohol.

Phebalium beckleri[41] leaves and terminal branches yielded 0·15% of essential oil, containing about 60% of pinene, ocimene, sesquiterpenes and sesquiterpene alcohols.

Pinus caribaea, P. palustris and P. pinaster, according to Mirov,[42] produce most of the supply of commercial turpentine, this consisting of at least 90% of α- and β-pinene. The main constituents of the turpentines of a number of other species of Pinus are also given. Haagen-Smit, Redemann and Mirov[43] have determined the characters of Torrey Pine turpentine and have found it to contain L-limonene 75%, *n*-decylaldehyde 10%, *n*-undecane 5%, longifolene 4%, and lauryl aldehyde 0·2%.

Pistacia integerrima (Kakra-Sringi) oil was found by Shaukar[44] to contain α-pinene, camphene, DL-limonene, 1:8-cineol, α-terpineol, aromadendrene, stearoptene and free caprylic acid.

Ridolfia segetum (Moroccan "harvest fennel") yielded an essential oil which was reported by Gattefosse and Igolen[45] to consist of about 50% of D-α-phellandrene and 33% of myristicin.

Sphacele lindleyi leaves and stems were distilled by Oberhauser and Behn[46] and the oil gave a positive Zeisel test for phenolic ethers, cineol was also present. The oil was considered similar to that of *Salvia officinalis.*

Thymus serpyllum.—Voss[47] reports that the oils of wild thymes of this species collected in the hills of Silesia varied considerably, the odour of lemon or turpentine being observed most frequently; in a few cases the odour of rose and bergamot was detected, but the pure odour of thyme was scarcely ever present.

Valerian.—Wallis and Sanyal[48] found that the roots of both *Valeriana officinalis* and *V. wallichii* yielded a higher proportion of essential oil than either the rhizomes or stolons. This result indicates that some specimens of Indian valerian, which consist of rhizomes only, is of slightly inferior quality to those containing roots also.

Isolates and derivatives

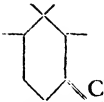
An investigation[49] of alliin extracted from garlic showed that this substance could be prepared in the form of colourless and odourless crystals which melted with decomposition between 163° and 165°. The empirical formula is $C_{12}H_{24}O_7N_2S_2$; it is non-bactericidal, but an enzyme present in garlic causes the formation of allicin, which is highly bactericidal. Further decomposition yields allyl sulphides.

Citral was isolated by Sabetay and Traband[50] from bergamot oil by the Guenther-Grimm method.

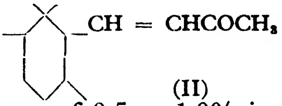
Vandoni and Govinelli[51] suggest that atlantone acetate prepared from the terpeneless oil of *Cedrus atlantica* might be substituted for vetiveryl acetate in perfumery.

Sixteen compounds have been studied[52] as possible cinnamaldehyde substitutes; of these only five were found to be sufficiently similar in odour to cinnamaldehyde to warrant further study. These were furanacrolein, cinnamaldehyde dimethyl acetal, α-methylcinnamaldehyde, α-methylfuranacrolein and *p*-methoxycinnamaldehyde. Correlation of structure with organoleptic properties suggested certain structural arrangements essential to cinnamon-like odour and flavour. The ring structure must not be modified too greatly by organoleptically active groups. Partial or total hydrogenation of the benzene ring in cinnamaldehyde destroys most of the cinnamon character. The presence of a methoxy group in the *p*-position tends to impart a floral note to cinnamaldehyde while in the *o*-position it increases the pungency. The introduction of two methoxy groups or a methylenedioxy group destroys most of the cinnamon character. The acrolein nucleus is necessary to impart cinnamon characteristics. The aldehyde group must be free or easily regenerated and long side chains must be absent.

The constitution of γ-irone, which is a tetramethyl*cyclo*hexanol derivative (I), has been worked out by Ruzicka[53] and his collaborators and α-irone (II), which exists in the concrete oil obtained by distillation in the presence of acid, has been synthesized. The latter substance has a similar odour to natural γ-irone.



(I)



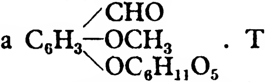
(II)

n-Hexanol has been discovered[54] to the extent of 0·5 to 1·0% in oil of "lavandin" and as esters (about 0·2%) in oil of lavender.

In a U.S.S.R. patent[55] methods are described for the production of menthol. The terpenes of the peppermint oil are polymerized by prolonged heating with concentrated alkali solution and the oil is removed by distillation. Trimenthyl borate is prepared, washed with butyl alcohol, and recrystallized. The purified borate is steam distilled to yield pure menthol. An alternative method is to convert the menthol into an alcoholate by heating purified peppermint oil with solid sodium hydroxide in the presence of low-boiling fractions of peppermint oil. The water produced by the reaction is removed and then the menthol is steam distilled.

The preparation of musk materials is the subject of a British Patent[56] in which the unsaponifiable matter of the fat from the musk glands of the musk rat is fractionated *in vacuo*; the fraction of b.p. 130–170°/1mm. being oxidized to musk ketones. An "animal alkaloid", $C_{16}H_{25}N$, has been isolated[57] from natural musk and named muscopyridine.

New sources of nerolidol and farnesol have been noted.[58] An essential oil from Brazil, oil of Cabreuva, obtained from *Myrocarpus fastigiatus* Allem. and *M. frondosus* Allem., contained about 80% D-nerolidol and about 2·5% farnesol. Oil of *Myrospermum erythroxylon* Allem. (Páo Vermelho, red wood) is also rich in nerolidol. The presence of both *α*- and *β*-nerolidols in Cabreuva oil has been established, and it is suggested that the presence of *α*-nerolidols may explain why the rotation of Cabreuva oil nerolidol is lower than that of preparations obtained from oils of petitgrain, neroli and balsam of peru.

A glycoside responsible for the odour has been isolated from rose petals by Langlais and Bollinger.[59] Goris[60] has prepared three glycosides from vanilla, the main glycoside, vanilloside had a rotation of -88°50′, mol. wt. 314 and formula  $C_6H_3\begin{cases}CHO\\OCH_3\\OC_6H_{11}O_5\end{cases}$. Two further glycosides existing in small quantities were isolated, one yielding on hydrolysis vanillic alcohol and the other an ester of fine odour, more penetrating than vanillin.

Analytical

The Essential Oil Association of America[61] has issued standard specifications for lemongrass oil, terpineol, terpinyl acetate and heliotropine, also a method for the determination of mineral oil in Ceylon citronella. This test is a modification of the standard Schimmel test using fuming sulphuric acid.

Sabetay[62] claims that steam distillation methods for the evaluation of essential oils in drugs and spices can be replaced with advantage by one using distillation under reduced pressure in presence of ethylene glycol. It is considered that this procedure is better suited for small samples, and that there is less risk of saponification.

The determination of essential oil in garlic is described.[63] The garlics are ground, macerated with water and then steam distilled with alcohol and oil, and the allyl sulphide determined in the distillate.

A number of microchemical tests to aid in distinguishing between cassia, cinnamon bark and cinnamon leaf oils are described.[64] The reagents used are: a saturated solution of sodium hydroxide in absolute alcohol, 30% aqueous sodium hydroxide, 20% sodium phenate, saturated solution of potassium hydroxide in absolute alcohol, phenylhydrazine and benzidine.

Discussing the " London Solubility Test " for citronella oil in the correspondence columns of a London journal, Salaman and Seaber[65] consider that the name of this test is unfortunate since the ten volume test adopted in London Market contracts has been known under the same name for some years. The writers advocate the adoption of the more stringent four volume test, but under a new name.

A colorimetric method for the determination of cinnamaldehyde in essential oils, tinctures, spirits or powdered bark is described.[66] The reagent used is a freshly-prepared solution of 5% *p*-phenylenediamine in alcohol with an equal volume of glacial acetic acid.

A sample of copaiba balsam was examined by Salaman and Seaber[67] and found to contain about 50% of a fatty oil with characters corresponding fairly closely with those of coconut oil.

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PHOTOGRAPHIC MATERIALS AND PROCESSES

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THE year 1947 is noteworthy in the annals of the photographic industry in this country. For nearly a decade there has been little or no opportunity of expanding or improving production facilities, indeed, it is difficult under present circumstances to maintain normal efficiency by repairing the effects of wear and tear. Nevertheless, on outdated and outworn plant, more material has been manufactured during the year than in any previous year. The use of photography in science, industry and commerce has advanced to such an extent as a result of the war, that in spite of this achievement market requirements are still unfulfilled, and the unfortunate amateur still has difficulty in obtaining his materials. Under these circumstances, it is not surprising that few new materials have appeared on the market—indeed " rationalization " has been responsible for the disappearance of many products which were in small demand.

The published literature has shown no diminution in volume, however, and we look to future years to see the commercial exploitation of much valuable research.

Latent image theory

During the last year or two, English speaking workers have learned of an interesting and important series of papers on latent image theory which were published in Belgium during the war. Some thirty of these have been admirably summarized by W. F. Berg.[1] The Belgian workers distinguish between three types of latent image, rather than the two originally postulated by Belliot,[2] the difference being merely that of position in the silver halide grain. The three types are surface latent image, sub-surface (or shallow internal) latent image, and deep internal latent image, and they may be separated and studied by a combination of treatments with " surface developers " containing no silver halide solvents, with " internal developers " containing solvents, and with bleaching solutions which may remove surface or surface and shallow internal latent image. The deep internal image has been studied in some detail, and has been found to require much heavier exposures ($\times 10^4$) than surface image. Moreover, it shows no solarization, whereas the surface image shows marked solarization but no second reversal. The second reversal often found on treatment of photographic materials in normal developers is shown to be due to the solvent (sulphite) in the latter, which gives a composite curve due to external and internal characteristics.[3] As might be expected from the large speed difference, the deep internal image shows low-intensity reciprocity-law failure at those intensities which show high-intensity failure of the surface image[4, 5], confirming the observed relative increase in ratio of internal to external latent image with increasing intensities.

One of the most interesting contributions is that of Falla[6] who studied the fogging effect of hydrogen peroxide and found that, although prolonged treatment gave a marked solarization, no internal latent image of any kind was formed—a surprising result which may necessitate revision of our present ideas of the mechanism of solarization.

The same authors carried out a very comprehensive investigation of the Herschel effect (*i.e.*, the reduction of density caused by exposing the latent image of a blue-sensitive emulsion to red or infra-red illumination). They showed that the red light post-exposure gives no reciprocity-law failure, though this observation was first made by Lescynski,[7] and that when the red light post-exposure is sufficient completely to destroy the potential density produced by a white light exposure, the sensitivity of a material is increased. Repeated cycles of white and red light exposures give progressively higher sensitivity. They showed also that the Herschel effect is largely confined to surface latent image, the internal latent image being generally enhanced by subsequent red light exposure. With normal development, both effects are shown, giving a decrease in density at low densities, and an increase at high densities. Debot[8] exposed an emulsion to blue light and bleached the surface latent image. On subsequent exposure to red light, the surface latent image was re-formed confirming that the Herschel effect is due to a redistribution rather than destruction of latent image.[9] This general conclusion explains the experimental results of investigations of the Herschel effect carried out by Belliot[10] (see also [11, 12, 13]). Meĭklyar[13] found a parallel shift of the characteristic curve along the log E axis, on illuminating a pre-exposed plate to red light > 650 mμ. He found that the extent of the Herschel effect increased with increasing intensity of the pre-exposure, and concluded that the latent images formed at different levels of intensity differ in quality, a fact which is well known and has been investigated by numerous workers. Burton,[14] for example, in a continuation of his studies of latent image by the valuable double-exposure technique has investigated the stability of the undevelopable sub-image caused by an exposure along with the normal latent image, and found rearrangement of the silver atoms during the interval between exposure and development. The larger sub-specks grow to developable size, while the smaller sub-image specks disappear.

A comprehensive investigation by Bernanose[15] of the sensitivity of colour sensitized products at various wavelengths has confirmed Webb's conclusion[16] that the shape of the reciprocity curve is independent of wavelength.

K. E. Zimens[17] has published experiments which are of importance in connexion with latent image problems. By radioactive tracers, he studied ionic exchange between solution and silver bromide grains in emulsions, for both silver and bromide ions, and found that whereas the former was rapid, with a half value time of 5 to 9 minutes, bromide ion exchange was unmeasurable even after 31 hours. The self-diffusion coefficient for silver ions calculated from his results was higher than that of silver ions in crystals found from silver halide melt, indicating an abnormally high interstitial silver ion concentration for photographic emulsions.

De Vaucouleurs and Viollet[18] have published a useful investigation of what they term the Cabannes-Hoffman effect. Cabannes[19] and Hoffman[20] independently noted that the rate of development was considerably influenced by the intensity of exposure, an observation which was described by Kron[21] in 1913, and which has been investigated by several workers subsequently.

Thus, if two areas of a sensitive material are exposed to low and high intensities for times which will give the same density on full development, the density of the low-intensity area is higher at short development times. The difference rises to a maximum at about 1 min. development, and decreases to zero as development proceeds. De Vaucouleurs and Viollet found that the maximum density difference increases, as would be expected, with increasing ratio of light intensities. They also determined that the low intensity exposure caused a higher proportion of larger grains to be developable than the high-intensity exposure, and found that treatment with a solvent—sodium sulphite—decreased the low-intensity density to a greater extent than the high-intensity density. These and other results are fully explained by consideration of the different types of latent image formed by light of different intensities. Probably the most authoritative discussion of the subject is that of Burton and Berg,[22] who conclude that both high and low intensity reciprocity failures conspire to cause a larger average surface silver speck when the same density is produced by lower intensity of exposure. The greater rate of development is due to this cause, no doubt aided, when normal developers are used, by a higher proportion of surface to internal specks.

Such experiments as these give valuable confirmation of the validity of the general picture of latent image formation which is emerging today. This is, of course, the Gurney-Mott mechanism, which has been reviewed by Mott[23] and to which has been added an explanation of optical sensitizing, and of development. From the fact that an unsensitized emulsion exhibits an absorption tail in the red and infra-red, Mott deduces the presence on the grain of specks at which electron transfer to the conductance levels can occur with less than the normal energy. The enhanced absorption in the sensitized region induced by the dye provides a source of energy which contributes to latent image formation. In support of this argument, Mott shows that the dye remains excited for about 10^{-8} seconds after quantum absorption, before reradiation occurs, and that during this period the energy is transferred from molecule to molecule many times, thus having a large probability of reaching the sensitive specks.

Two papers of great interest and importance have been published by West and Carroll, who have succeeded in measuring photoconductance in silver halide gelatin emulsions. In the first paper[24] they investigated dye sensitized emulsions and found the spectral range of photoconductance to follow the spectral sensitivity curve. An isomer of the sensitizing dye of comparable spectral absorption, which adsorbed satisfactorily to silver bromide, but which gave no induced sensitivity, did not extend photoconductance beyond the naturally sensitive region, and this was also true of a dye of intense green absorption which did not adsorb to the silver halide grain.

In the second paper[25] they investigated a supersensitizer which had little effect on the light absorption of sensitized emulsion, and found that the photoconductance was enhanced corresponding to the optical sensitivity. Desensitizers, on the other hand, while having a profound effect on the sensitivity of an emulsion, had practically no influence on photoconductance, proving that their effect was a secondary one, unconcerned with the primary photolytic action. The Becquerel effect, which is concerned with print-out red sensitivity induced by the presence of print-out silver was found to hold for photoconductance as well as for light action.

The light sensitivity of thallous bromide-gelatin emulsions has been investigated by Ritchie and Thom[26] who found many similarities with silver bromide emulsions. The authors conclude that the Gurney-Mott mechanism applies to thallium emulsions.

The nature of sensitivity nuclei of the silver halide grain has been studied by Chibisov, Titov, and Mikhailova[27]. They examined quantitatively the reactions between silver nitrate and gelatin, and between silver halides and gelatin and attempted to correlate these reactions with the increase in sensitivity of an emulsion during the ripening and digestion stages. The authors conclude that Ag_2S fulfils the subsidiary function of temporarily trapping electrons during photolysis so as to hinder recombination with bromine; the permanent electron traps which are converted after exposure into development centres are assumed to consist of specks of metallic silver.

New materials and techniques

During the war a method was devised for marking metal templates and jigs by sensitizing the surface of the metal and projecting thereon a photographic image of the required design. When the surface of the metal is flat, it can conveniently be sensitized by transferring thereon an emulsion layer from a temporary support such as paper. Several patents[28, 29, 30] cover the manufacture of such transfer sensitizing papers, which consist essentially of paper base coated with a layer of wax or resin, then with emulsion, and finally with an adhesive layer. It is stuck, emulsion downwards, on to the metal surface, and the paper base is then stripped off, leaving an even emulsion coat on the metal. Alternatively, adhesive may be coated on the back of ordinary photographic paper, which is attached to the metal, emulsion upwards.[31]

Photographic paper on waterproof base has definite advantages where rapidity of processing (especially the washing and drying operations) or lack of undue distortion is required, and a number of patents has appeared covering its manufacture.[32, 33, 34, 35, 36]

Two new supports have been developed, one consisting of a vinyl fluoride polymer,[37] the other of a fine wire mesh coated with soft gelatin which is used as a temporary support on carbon or carbrotype colour photographic processes,[38] and a number of references to new sub-layers occur including two for the normal cellulose base[39, 40] and one[41] for use with hydrophobic supports such as polystyrene.

Considerable interest has been aroused by the publication by E. H. Land, of the Polaroid Corporation, of a new one-step photographic process whereby a finished positive picture is produced in the camera about 1 minute after exposure.[42] The principle of the one-step method has been previously disclosed;[43] see also discussion by L. E. Varden.[44]

A specially constructed camera leads a strip of paper through pressure rollers in contact with the exposed negative. The paper carries periodically a "pod" containing a viscous developing and fixing solution, which is burst by the pressure rollers, so that the developer is spread uniformly between paper and negative. The silver halide solvent in the developer transfers undeveloped silver salts from the negative to the paper, where they are reduced to metallic silver to give a positive image.

Development in the positive layer is encouraged by the inclusion in the paper of finely dispersed metallic sulphides, which act as nuclei for physical development.

Finally, an interesting photosensitive compound has been prepared by Staehle[45] which reverses the usual action of dichromated colloids. A dichromated hydrophilic colloid, for example, gelatin, containing an aqueous dispersion of a soft synthetic resin and a pigment, for example, titanium dioxide is coated rather thickly and after exposure and washing, it is the *exposed* portions which are washed away. The mechanism of this process would seem to be that the resin is present in the form of globules separated by thin walls of the hydrophilic colloid. Before exposure, the colloid is sufficiently soluble to be extracted during water washing, allowing the resin globules to coalesce to a water insoluble layer, whereas in the exposed portions the colloid has been rendered sufficiently insoluble to prevent coalescence of the resin globules, though not sufficiently strong mechanically to prevent disruption of the whole layer and its removal, globule-wise, by the stream of water.

Emulsions

Of the large number of papers published on photographic emulsions, those by Knott and Stevens represent perhaps the most important advance of the year. They have been experimenting with emulsions which, under normal conditions of exposure, give a latent image only in the interior of the silver halide crystal, and hence give no developed image when processed in a normal " surface " developer. Development of the latent image may be achieved, however, by using an " internal " developer, *i.e.*, one containing a solvent for silver halide. They discovered that after normal exposure a reversed image is obtained upon development in a surface developer, if the material is given a uniform exposure to light during development.[46] The mechanism of this interesting observation seems to be that the surface treatment during second exposure allows surface latent image to be formed, unless internal latent image is already present, in which case the second latent image preferably builds up thereon. Other solutions which sensitize the emulsion so as to produce a surface latent image during second exposure include solutions of developing agents, the p_H of which is too low for them to function as developers, and in the case of certain dye sensitized emulsions, even soaking in water during second exposure will give a reversed image on subsequent development in a surface developer. Contrast is increased by treatment with a silver oxidant after first exposure, in order to remove any traces of surface latent image which may be formed.

Knott and Stevens[47] have applied their observation to colour photography by patenting a monopack containing such emulsions. They are processed to produce positive images in surface colour developers by simultaneously giving a uniform exposure to light complimentary to the colour produced by the developer. In B.P. 581,790,[48] these investigators have patented bipacks containing one emulsion of normal type sensitivity and another having no surface sensitivity. Such bipacks may be used for the preparation of improved colour-masking images, for producing differences in contrasts between image and sound track in motion pictures, and for correcting under- or over-exposure.

A number of papers indicate activity in the preparation of materials suitable for recording subatomic particles. The choice of screens, emulsions and developers for the photographic recording of cathode ray tube screen traces was the subject of a symposium,[49] and the relative properties of extremely fine grain emulsions to light and to direct electrons were determined by Kopp and Möllenstedt.[50]

The use of thickly coated emulsion of high silver : gel ratio is now standard practice for the recording of nuclear particles of large energy,[51, 52] though the rapid fading of latent nuclear track images is a general defect which will have to be cured.[53] One worker in the nuclear particle field, Pierre Demers,[54, 55] of the National Research Council, Montreal, Canada, successfully makes his own emulsions, and describes the preparation of a Lippman type emulsion particularly suitable for showing the tracks of ionizing particles.

There has been further activity in attempts to perfect a synthetic substitute for gelatin as an emulsion medium. Techniques for improving emulsions made from hydrolysed cellulose acetate, polyamide, and hydrolysed polyvinyl acetate have been patented.[56, 57, 58, 59, 60]

Steigmann[61] has continued his studies of photographic gelatins, and finds that the intrinsic restraining effect of gelatin on Ostwald ripening of silver bromide emulsions depends largely on its cystine content. If cystine-rich gelatins are heated 3–4 hr. at 80° at p_{H} 7·5, the fog tendency and speed are increased.[62]

The general principles of manufacture of high sensitivity photographic emulsions have been discussed by Charriou[63] and by de Langhe[64], the latter suggesting changes which are taking place in the grain structure during digestion. A new and interesting phenomenon has been described by A. Vassy, P. Schonne and E. Vassy;[65] Lippmann emulsions which have been stored for about three months develop a secondary maximum in spectral sensitivity at about 325mμ, this maximum becoming more marked, and shifting towards longer wavelengths with degree of ripening.

A few improvements in emulsions applicable under special conditions have been patented, *e.g.*, the inclusion of a higher fatty acid reduces the tendency of an emulsion to become scratched[66, 122] and fungus growth on photographic materials is prevented by supercoating and backing with gelatin containing a small quantity of colloidal silver.[67]

The Polaroid Corporation[68, 69, 70] continue to investigate methods of converting a photographic image into an iodine image which plane polarizes light, presumably for the Vectograph and similar processes.

Sensitizers and desensitizers

Research on optical sensitizers has continued, and numerous patents have appeared during the year, covering the use of new sensitizers, supersensitizers, desensitizers, and methods of preparation of dyes and intermediates. Of these, a patent by E. I. du Pont de Nemours & Co.[71] claims that the use of cyanine dyes as sulphamates imparts greater blue light speed than when used as iodides.

The publications on theoretical aspects of sensitizing again come from Russia. Natanson has published three papers which confirm the connexion between degree of sensitizing and molecular aggregation of sensitizing dye.[72, 73, 74] The first describes the potentiometric titration of some fifty cyanine dyes with silver ions, and although Natanson found no connexion between complex formation and sensitizing action, there was a definite relation with the fogging action of the dye, the fog increasing with increasing dissociation constant of the complex. Of the various nuclei investigated, quinoline, especially 4 : 4′ derivatives, showed the greatest tendency to complex formation and fog. The well-known increase in fogging action caused by lengthening the polymethine chain was shown to run parallel with increasing ability to form silver complexes.

A phenomenon of sensitization shown by some dyes is a sudden increase in intensity and range of sensitizing above the normal (first type) sensitizing, when the concentration of added dye reaches a critical higher value. The latter sensitization is known as " second type " sensitizing and is considered to be due to aggregation of the adsorbed dye, or change in molecular arrangement of the adsorbed layer. In his second paper, Natanson concludes that capacity for sensitizing of the second type is shown most strongly by thia- and selenacarbocyanine dyes, the latter being in general superior in this respect to thia dyes. From a study of over 500 dyes, he evaluates the effect of substituent groups in the molecule and places them in order of influence. In his third paper, Natanson finds a connexion between the peaks of the sensitizing band of a dye with several forms of molecular aggregation. Of the two bands usually given by thia- and selenacarbocyanines, that in the shorter wavelengths is considered to be due to dye in the same polymeric state as in aqueous solution, while the second peak is associated with dye in the molecular form, as in solution in solvents. Dyes capable of second type sensitizing show a third peak which is considered to be due to dye in a highly aggregated form, as in the presence of electrolytes. In this connexion, Solov'ev[75] claims to have demonstrated very different optical absorptions of different aggregations of dye molecules by a technique of diffusion of dyes into gelatin. Pinacyanol, for example, gave an upper layer of deep violet, a middle layer of raspberry red, and a light blue lower layer.

Three attempts have been made to explain the mechanism of dye sensitization. That of Mott[23] has already been mentioned in the section on latent image formation. Meiklyar and Stepanov[76] deduce that the extra energy in addition to that of the absorbed light quanta necessary to raise an electron to the conduction levels in the dye sensitized region is supplied by the thermal energy of the dye molecules. Simpson[77] explains optical sensitizing on the concept of a triplet state associated with unsaturation electrons in the dye, which couples with a hypothetical triplet state in the crystal.

A further paper[78] on hypersensitization by mercury vapour, while confirming the effect, does not throw light on the mechanism.

Sheppard, Lambert and Walker[79] have shown that under certain conditions of p_{H} and p_{Ag}, desensitizing dyes form reversible oxidation-reduction systems, whereas powerful optical sensitizers behave irreversibly.

Colour photography

The progress during the year is confined to improvements in detail on the well-established multilayer subtractive process, though there has been no diminution in research work. The majority of patents on colour photography have been concerned with couplers for colour development. The range has been enlarged,[80, 81] more stable couplers have been investigated,[82] and further efforts have been made to decrease diffusion of the coupler by increasing the size of the coupler molecule.[83, 84, 85, 86, 87]

A major advance has been made by Hanson and Vittum[88] who have patented couplers which are themselves coloured in such a way as to give automatic masking in a negative-positive process. The necessity of masking arises from the fact that the three subtractive dyes (cyan, magenta and yellow) each absorb more than one of the three primary regions, red, green and blue. The yellow dyes are nearest to the ideal, their absorptions in the red and green being negligible, but magentas invariably absorb in the blue as well as the green, while cyan dyes are the least satisfactory as they have a strong absorption in the blue and green, as well as in the red. This unwanted absorption in the blues and greens degrades these colours relative to reds in the final print. Hanson and Vittum describe couplers which are coloured by the presence in the molecule of a group which is expelled during the coupling reaction. The groups are chosen so that the unreactive couplers absorb those colours which the final dye absorbs *undesirably*. Thus a yellow coloured (blue absorbing) coupler is used for forming a magenta dye, and an orange coloured (blue and green absorbing) coupler for the cyan dye. The undesirable absorption in green and blue in the negative is thus no longer image wise, but is uniform over the whole negative, giving it an overall orange colour, which can be compensated in the final print by such means as alteration in colour of printing light, giving a correctly masked print of greatly improved colour rendering. Several other methods of automatic masking have been patented, but they represent variations of conventional methods.[89, 90, 91, 92]

Work on sensitizing dyes specifically for use in colour photography has been directed towards preventing their wandering to adjacent layers. Anish and Hensley[93] have patented cyanines with a methylenedioxy ring structure in the thiazole or selenazole nuclei. It is claimed that this component gives much stronger absorption to the silver halide grains. Knott[94] hinders the wandering of sensitizing dyes from one layer to an adjacent layer by including an extremely fine grain (Lippmann type) emulsion in the layer.

The new processes of colour photography call for little comment, as they represent further and often minor variants of the three colour subtractive process. A significant departure is made by Knott and Stevens,[95] however, who utilize their emulsion giving internal latent image only, in order to obtain differentiation between the components of a layered or mixed monopack.

Colour development has been investigated by Flannery and Collins,[96] who determined the silver to dye ratio under different development conditions. The dye yield was found to be greater than the 1 : 4 ratio given by the usually accepted equations, when sulphite was absent, but addition of sulphite to the developer increased the silver yield. Solov'ev[97] has studied the fastness of dyes to light, and finds that this property increases with increasing state of aggregation of the molecules.

Processing

Certain uses of photography demand very short processing times and a remarkable apparatus which projects a positive image some ten seconds after exposure is described by Brown, Blackmer and Kunz.[98] An electrically heated metal cylinder is dropped on to a frame of 16mm. film and a few c.c. of high energy developer is introduced. After 3 to 4 seconds, the developer is removed by vacuum line, and either a rapid fixing solution or a dichromate bleach is introduced to give a negative or positive image respectively. The film is rinsed in developer containing ethylene glycol to prevent crystallization and the near dry film passed to a projection system within ten seconds of exposure. Although the positive image given by the reversal process consists of unchanged silver halide, it gives a contrast which is adequate for most purposes. The rate of processing of non-gel emulsions has been investigated by Crabtree and Eaton[99, 100] and is found to be greatly increased by the presence of a thiocyanate, preferably inorganic, in the processing solutions. Henn and Crabtree have devised and published formulae for developer and fixing solutions suitable for use at low temperatures.[101]

The theory of development has been further advanced by James,[102] who has investigated the kinetics of reduction of silver ions in solution in the presence of metallic silver by hydroquinone and by catechol. He found that the rate of reduction was directly proportional to the concentration of the reducing agent, and deduced therefrom that adsorption of reducing agent to the silver catalyst is not an essential step in the reaction. On the other hand, the rate of reduction of silver bromide grains varies with the 0·6 power of the concentration of developing agent, indicating that adsorption to silver bromide or to the silver bromide-silver interface is necessary before development can take place.

He has further examined his charge theory of development, finding little variation of the charge effect with grain size or iodide content of the emulsion,[103] but the kinetics of development by catechol[104] were interesting. During the induction period of development, catechol functions as a univalent ion, but subsequent development is due largely to the bivalent ion, though the univalent ion is still active.

New constituents for developing solutions have been suggested,[105, 106, 107, 108, 109] including several suitable for single solution developer-fixing baths.[110, 111, 112]

Some work has been published on the analysis of developers containing Elon and hydroquinone, including an examination by Levenson[113] of Stott's method, which resulted in increased accuracy. Shaner and Sparks[114] recommend the use of methyl ethyl ketone for the extraction of Elon and hydroquinone and use the method of Baumbach[115] for estimating the compounds.

In a Dutch patent[116] Philips have claimed to be able to reduce the loss of precious metal in physical development from reduction occurring independently of the latent image. The quantity and metal content of the developer are strictly controlled by the amount of surface and the blackening desired.

Fierke and Staud[117] have described emulsions which can be dry developed. The silver gelatin emulsion contains the developing agent and a compound which generates ammonia or an amine on heating, decomposition, or reaction with other compounds. A number of such compounds is given.

An ingenious differential fixer has been devised by Hanson,[118] whereby layers of different silver halides may be differentially fixed by treating them with a fixer saturated with the less soluble of the two halides. The more soluble is then preferentially dissolved. The technique can be applied to the reversal process.

Intensification has been the subject of a few patents, among which is one claiming the intensification of the latent image by treatment with sulphur dioxide.[119, 120]

Processes designed to improve the physical characteristics of film are one by Russell and Houck,[121] in which the film is treated with a fatty derivative which reacts with the surface layer and offers protection against scratches (see also Dimsdale and Challis[122]), and one by Swan,[123] which reduces curl by immersing the film after processing in a dilute aqueous solution of an amide.

Muehler and Crabtree[124] have investigated the effect on stainless steel of rapid fixing baths containing ammonium chloride or ammonium sulphate, and find that the latter compound is not corrosive but is equally effective photographically.

Diazo processes

Several modifications of the diazo process have been patented during the year, two of which refer to the application of such sensitive layers to metal. Sease and Woodward[125] prepare a coating composition in water-insoluble polyvinylacetate which can be applied directly to ferrous metal without subsequent corrosion and decomposition, owing to the presence of a stabilizer which may be a metal or alkyl nitrite, or alkyl or aryl phosphate. Alink[126] cites the coating of aluminium with a diazonium compound in organic solution, with a water-insoluble binder. By separate coating of a slightly water-soluble diazo compound, and a coupler, Hall, Harding Ltd. and Leuch[127] obtain paper free from premature coupling, and having good keeping properties. A colour difference between halftones and full densities has been produced by the use of a coupler of slow coupling potential.[128]

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SANITATION AND WATER PURIFICATION

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IN 1947, a year in which many good papers on sanitation and water purification have appeared, the most impressive advances have been in the treatment of industrial waste liquors. This is a noteworthy trend, since for many years much less attention was given to the development of methods of treating these wastes than, for example, to the improvement of methods of treating domestic sewage. Previous reviewers have commented on the comparatively small volume of research in this country on the development of methods of treatment of water for domestic supply. The Institution of Water Engineers has now set up a Research Committee,[1] whose objects are to encourage research in this field and to ensure that the results of new work are brought to the notice of the industry.

The field covered by the term "sanitation and water purification"—a very wide one—includes the examination of liquids ranging from natural waters to a great variety of industrial liquids containing nearly all the substances used in manufacturing processes. The methods of analysis required are equally varied, and it is a major difficulty to keep pace with advances in analytical technique. In this review papers on analytical methods have not been referred to, but special mention may be made of an important American publication[2] which includes details of many methods of examination of natural waters, with particular reference to the effect of the waters on animals and plants. Accounts of recent advances in analytical methods have also been included in the 9th Edition of "Standard Methods for the Examination of Water and Sewage," published by the American Public Health Association.[3]

Water

Biology

One difficulty which confronts water undertakings in all parts of the world is the growth of microscopic green plants in storage reservoirs. Fundamental work on this subject is being undertaken by the Freshwater Biological Association, and a review of the progress so far made has been given by Pearsall and others.[4] Houghton and Rushton[5] have followed the growth of phytoplankton in a British reservoir for a period of five years, and have correlated the changes with changes in the dissolved constituents of the water. A detailed survey has been made of a lake system in Wisconsin.[6] It was found that the weight of nitrogenous material entering the lake in treated sewage effluent from a population of 750 persons was equivalent to that in the surface drainage from 1 sq. mile of agricultural land. Research so far has not led to any important advances in the management of reservoirs to reduce algal growths, and the most common method of reducing the trouble is by addition of algicidal substances to the water. In one American lake[7] addition of copper sulphate alone reduced the numbers of algae, but their decay led to unpleasant tastes in the water; satisfactory results are reported from addition of copper sulphate and activated carbon together. Some species are particularly resistant to copper sulphate; a case is reported where addition of nearly 5 ppm. of the crystalline salt failed to control growth of *Anabaena,* which subsequently gave rise to very bad taste and odour in the water.[8]

Pipe-packing

Experiments by the Metropolitan Water Board[9] during the war indicated that a paper packing material, treated with a water repellent, had possibilities as a substitute for yarn for the caulking of joints in water mains. Many investigators have found that yarn, unless specially sterilized, supports the growth of bacteria, including coliform bacteria, and may cause much difficulty in a distribution system. It is now reported that good results have been obtained in America with a chemically treated paper known as Fibrex,[10] and with jute sterilized by quaternary ammonium compounds.[11]

Corrosion

Joint research by a number of laboratories is in progress to determine the effect of chlorine on corrosion of metal fittings by water.[12] Rice[13] has published an account of experiments at Pittsburg in which addition of sodium hexametaphosphate to water partially inhibited tuberculation in iron mains. In California extensive corrosion of iron pipes exposed to treated water (p_H value 9·4 to 9·5) containing a profuse growth of the blue-green alga *Oscillatoria* was traced to the depolarizing effect of the oxygen given off during photosynthesis.[14] The corrosion stopped when the tank containing the water was covered, thus preventing the growth of the alga.

Softening

Some interesting experiments are being made with semi-scale plant on the softening of water by electro-osmosis.[15] The equipment consists of a tank divided longitudinally by a porous diaphragm into an anode compartment and a cathode compartment. When a direct current is applied, calcium ions pass into the cathode compartment, where they interact with calcium bicarbonate to give a precipitate of calcium carbonate. In one series of tests the total hardness of a water was reduced from 370 ppm. to about 125 p.p.m.

Plumbosolvency

There is a report[12] on some work carried out before the war by the Water Pollution Research Laboratory in an attempt to develop a method of treating a soft peaty moorland water to reduce its corrosive action on lead. The object was to devise equipment which could be used in a remote rural district without much supervision. The water was passed at different rates through tanks containing pieces of limestone, of which the smallest grade tried was $\frac{1}{8}$ to $\frac{1}{16}$in. This work was unsuccessful since the limestone rapidly became coated with a deposit of peaty material, and it is now clear that satisfactory results would only be obtained if the water were passed upwards through a bed of the particles of limestone at a rate high enough to expand the bed and to remove continuously the deposited organic matter.

Coagulation

Results of some work on treatment with coagulants of water containing humic material have been reported.[16] The optimum p_H value for different coagulants was determined, and the effect of addition of phosphate and other ions were investigated. Phosphate and, to a smaller extent, sulphate and chloride interfere with removal of organic matter, as a result, it is thought, of formation of basic compounds. Interest is being shown[17] in coagulation by compounds of aluminium formed by passing a direct or alternating current between aluminium electrodes immersed in the water to be treated. It is claimed that the floc formed is tougher than that formed by addition of aluminium sulphate to water; no new quantitative data, however, have been noticed. Bonilla,[18] after experiments with semi-scale plant, tentatively estimated that under American conditions the cost of the electrolytic treatment would be from 1·5 to 2·5 times the cost of treatment by addition of aluminium sulphate. " Activated " silicates as an aid to coagulation are in use at a number of water works in America, and it is understood that the method has been tried at one or two works in Great Britain. A review of the published literature has been given by Hay.[19]

Filtration

In an important paper[20] Boucher discusses the filtrability of liquids. He uses an apparatus based on one employed for many years in the laboratories of the Metropolitan Water Board. The liquid under examination is passed through a filter at a constant rate, and the loss of head after the passage of different volumes of the liquid is observed. It is shown that these quantities are related by the equation $H = me^{nV}$, where H is the hydraulic resistance, V is the volume of liquid filtered, n is a constant, and m is the value of H when V = O. F, the reciprocal of n, is called the filtrability of the water. The author gives a graph showing the filtrability of water from Lake Vyrnwy before and after passing through 14 miles of 42-in. trunk mains. At the outlet the filtrability was in general higher and much less subject to fluctuation than at the inlet, and it is suggested that this is due to the deposition of solid material in the main. Filtrability of a water was reduced as increasing concentrations of chlorine were added, but after the breakpoint had been passed the filtrability again increased.

The use of anthracite in filters treating water is increasing in Great Britain. It is reported[21] that at a mill at Bristol where very polluted water is treated with alum and is passed through rapid gravity filters after sedimentation, the average length of filter runs when sand was used was one hour, and that this was increased to five hours when anthracite was substituted. Filters containing diatomite were used by the U.S. Army during the war, since filtration through sand at the high rates employed did not remove cysts of *Endamoeba histolytica* nor the cercariae of *Schistosoma*.[22]

Chlorination

Many American water authorities report that they are adding increased amounts of chlorine to water to give breakpoint chlorination.[23, 24, 25, 26] By applying this treatment before addition of coagulants and filtration the amounts of coagulant necessary have been reduced, the period between backwashings of the filters has been increased (from 36 hours to 195 hours at one works[23]), and the total cost of treatment has been reduced. Tastes and odours in water have been eliminated by breakpoint chlorination, though it is generally agreed by the American workers that complaints are usually received when the treatment is first begun, as a result of dislodgment of organic matter from the mains. There have been complaints of chlorinous odours in the water drawn from taps, particularly in the early morning, but with some of the waters used in America this has apparently caused less complaint than the taste which would have been present if large amounts of chlorine had not been added. Treatment with chlorine dioxide is reported to have eliminated taste and odour from the very polluted water of the Ohio River.[27] Chlorine in large amounts has been applied to filters to kill nitrifying bacteria which were causing oxidation of ammonia during passage of the water through the filters; when nitrification was active the filtered water contained high concentrations of nitrite and had a high chlorine demand.[28]

Several papers have appeared on the effect of chlorination on viruses. Kempf[29] worked with the virus of eastern equine encephalomyelitis as being similar to the virus regarded as responsible for poliomyelitis. In the absence of suspended organic matter and with a period of contact of 10 minutes the virus was inactivated by chlorine added in a concentration of about 0·65 ppm., but not by a concentration of 0·35 ppm. The virus was always inactivated with breakpoint chlorination. Neefe[30] worked with the virus of infectious hepatitis, using distilled water to which had been added small quantities of fæces known to contain the virus. This water was then drunk by human volunteers; coagulation, sedimentation, and filtration did not remove the virus, but it was destroyed when the treated water was chlorinated to give, after 30 minutes, a concentration of total chlorine of 1·1 ppm., and of residual free chlorine 0·4 ppm. With a total residual concentration of 1 ppm., after a period of contact of 30 minutes, in water which had not been settled or filtered, the virus was not inactivated.

In an interesting paper, Milton and Hoskins[31] discuss the properties of hypochlorite formed by electrolysis of a dilute solution of brine. They found that, for a given concentration of available chlorine, hypochlorite produced electrolytically had a greater bactericidal effect than a solution of chlorine in water or a solution of hypochlorite as sold commercially. They conclude that the bactericidal action of electrolytic hypochlorite is due to the liberation of nascent oxygen in the reaction $HClO \longrightarrow HCl + O$. Commercial solutions of hypochlorite do not normally contain free HClO since, to avoid premature decomposition, alkali has been added to give a p_H value of at least 10, and at this p_H the free acid is not present. Another factor responsible for the rapid bactericidal effect of electrolytic hypochlorite is the presence of small quantities of metals, particularly iron and manganese, which catalyse the reaction $NaClO \longrightarrow NaCl + O$; it is stated that these metals are removed during the preparation of commercial solutions of hypochlorite which are intended to be kept for some time before being used. The bactericidal properties of chlorine dioxide are discussed by Ridenour and Ingols,[32] and a bibliography of papers on disinfection of water by iodine has been published.[33] No papers have been noticed during the year on the properties of ozone as a disinfecting agent, but Howlett[34] gives an account of the preparation and use of ozone in the treatment of water.

Fluorides

An interesting plant has been brought into operation in America for removing fluoride from the drinking water used by a mining company.[35] The concentration of fluoride varies seasonally from 2 to 14 ppm. F. The water, after softening and filtering, passes through four gravity filters containing a bed, 45in. deep, of calcium phosphate. In regenerating, the filters are backwashed until the water is clear, a 1% solution of NaOH is passed through to extract NaF, the filters are again washed, are then treated with water containing CO_2 in solution until the effluent has a p_H value of 7, and are finally again washed with water. Regeneration occupies about three hours for each filter, and one or two filters are treated daily. The concentration of fluoride in the treated water ranges from 0·5 to 0·7 ppm. The practice of adding small quantities of fluoride to domestic water supplies with the object of preventing dental caries is still growing in America.[36] Usually sodium fluoride is added, but one town is to use hydrofluoric acid. The total quantity of fluoride in the treated water is usually from 1·0 to 1·3 ppm. F. Addition of fluoride is regarded in America as in the nature of a large-scale experiment, and is by no means universally recommended. Detailed dental surveys are to be made during a long period—15 years is mentioned—to determine the effect of the treatment.

Boiler feed water

There are several patented processes in which water used as boiler feed is first passed through a device in which a very small potential difference is maintained between two electrodes; it is claimed that this treatment reduces the formation of hard adherent scale in the boiler. So far as the reviewer is aware no results of detailed quantitative tests of this method of treatment have yet been published. During 1947, however, two papers have appeared which bear on the subject. Evans[37] prevented deposition of hard scale in a laboratory still by passing the water over a glass plate which supported plates of zinc and copper which were not in contact. Willey[38] considered that the action of a very small electric current is to cause some change in colloidally dispersed matter in water, and that this, in turn, affects the form in which calcium carbonate is deposited when the water is subsequently heated. He states that the treatment has no effect on a water from which organic matter has been carefully removed.

Purification of mussels

Many of the areas around the British coast from which mussels are obtained are now heavily polluted by sewage. It has long been known that mussels and other shellfish from such areas may contain viable pathogenic bacteria, but that they can be "purified" comparatively easily. The method used in Great Britain was adopted after a long series of experiments by the Ministry of Agriculture and Fisheries,[39] and consists in exposing the mussels in specially constructed tanks to the action of sea water previously disinfected by addition of compounds of chlorine. One important factor is that the salinity of the purified water used in the cleansing tanks must not be less than about 22g. per 1,000g. In the cleansing stations now operated it is always possible to obtain water with a higher salinity than this, and the method adopted is to pump water to the station, disinfect it by addition of chlorine, use it in the cleansing tanks, and then discharge it to waste. Some mussels, however, are landed at ports on estuaries where the salinity of the water available is sufficiently high at high water of spring tides, but at other times is too low to give satisfactory cleansing. A method was therefore required by which water of the required salinity could be disinfected and used for cleansing, and could then be treated and used again, this process being repeated at least until water of the required salinity was again available from the estuary. Experiments on a large scale have now shown that this can be done; after use with one batch of mussels the sea water is chlorinated, and, after a period of contact, residual chlorine is removed by blowing air through the water; it can then be re-used for a further cycle of cleansing.[40] A special technique is required for determining the numbers of bacteria in shellfish; revised standard methods, generally similar to those used in Great Britain, have recently been published by the American Public Health Association.[41] Several papers have appeared on the cleansing of polluted shellfish in France·[42] where in some districts the industry is an important one.

Sewage

Work has been begun in America, and a first report has been published,[43] on the testing of various materials used for making joints in sewers. The tests included determination of resistance to penetration by the roots of plants under standard conditions. Incorporation of toxic materials in jointing compounds—for example, copper oleate in a concentration of 5% —had little effect on growth of roots. The most important properties were found to be adhesiveness, hardness, strength, and stability, and of the materials tried the best were certain preparations made from coal tar.

Rudolfs[44] has collected published data, and has himself carried out some work on the occurrence of phosphates in sewage, sewage effluents, and sludges; he shows[45] that addition of lime to sewage increases the amount of phosphate in the sludge deposited, and that very little of the lime added may be precipitated as $CaCO_3$. An account has been given of a plant[46] in which carbon dioxide, from the burning of sludge gas, is passed through diffusers into sewage before alum is added for flocculation; the cost of chemicals has thereby been greatly reduced. As a result of experiments on a small scale, Finch[47] has suggested a method of treating settled sewage in which a portion of the flow would receive complete treatment in an activated-sludge plant; the effluent, containing activated sludge, would then be mixed with the remainder of the settled sewage and the mixture would be given further treatment in a bio-flocculation plant.

Biological filtration

Further results of large-scale experiments by the Water Pollution Research Laboratory on the treatment of settled sewage by different methods of biological filtration have been published.[40] In one series of experiments the settled sewage was treated by alternating double filtration at a rate of 170 to 200 gallons per day per cubic yard in the two filters together, but not all the effluent from the primary filter was passed through the secondary filter; the rate in the primary filter was 330 to 400 gal./cu. yd./day, and in the secondary filter about 250 gal./cu. yd./day. The results were not always entirely satisfactory, and it is evident that the method has only limited application. In other experiments settled sewage was treated first by bio-flocculation and then by single filtration at a rate of 160 to 200 gal./cu. yd./day; the effluent usually had a biochemical oxygen demand of 20 to 30 ppm. Work generally similar to that carried out at Minworth has been begun at Coventry with filters 12ft. in diameter. Vosloo, working in South Africa, has reported that in large-scale experiments the performance of a percolating filter, 12ft. in depth, was not significantly improved when it was covered and operated with forced ventilation. Hitherto the detailed results of these experiments have not been available, but a brief summary has now been given at second-hand.[48] Some interesting experiments, of which much fuller details would have been welcome, have been described by Dreier.[49] In a small filter, with a rotary distributor, he inserted trays on different radii and at different depths. When the interval at which successive arms of the distributor passed over a given spot on the surface was 15 seconds or less there was a substantially constant rate of flow of liquid through trays placed below the surface at a depth equivalent to not less than twice the average diameter of the pieces of filtering medium. From this and similar experiments the author recommended that the interval of dosing at any point on the surface of a filter should not exceed 15 to 20 seconds. He had not found that continuous application had any beneficial effect.

In an American plant which included filters operated with recirculation of effluent severe ponding occurred; Shepherd[50] describes the very powerful remedies which were applied to remove it. Chlorine, bleaching powder, and sodium hydroxide were applied without success. The ponding was then found to be due to an excessive growth of *Beggiatoa alba,* the decay of which was producing so much hydrogen sulphide as to discolour paint on adjacent buildings. After further addition of chlorine the growth was finally removed by flooding the filters and allowing them to stand for a fortnight, when the organisms died and underwent anaerobic fermentation. They were then removed by alternate flooding and flushing.

It is clear from the work of Tomlinson and others[12, 40, 51] that emergence of flies from percolating filters can usually be controlled by the application of DDT or Gammexane without at the same time killing worms and springtails. Experiments to determine the optimum amounts of insecticide and the frequency of application are still in progress. The substances appear to have no effect on the quality of the filter effluent, or on the extent of nitrification, but under some conditions sufficient insecticide may be washed through the filter for the effluent to be toxic to fish. There have been many cases in America in which application of DDT to surface waters to kill insect larvæ has led to widespread fish mortality.[52] It appears, from the information available, that if the concentration of DDT in a sewage effluent is insufficient to harm fish it is unlikely to cause any damage to planktonic organisms or invertebrates.[53]

Activated-sludge process

The important work on purification of sewage begun over 10 years ago by the U.S. Public Health Service at Cincinnati has been continued by

Placak and Ruchhoft,[54] who studied the treatment of sewage by the activated-sludge process under controlled conditions in the laboratory. They used a buffered solution containing inorganic nutrient substances, including ammonia, to which known quantities of activated sludge were added. In each experiment a different organic substance was added to these mixtures, which were then aerated, the air being circulated in a closed system. There was usually rapid adsorption of the added organic material by the activated sludge, and this was followed by partial oxidation. The most extensive oxidation occurred with organic acids (other than certain toxic acids), and the least extensive with carbohydrates.

The inhibitory effect of chromate on nitrification during treatment of sewage by the activated-sludge process is confirmed by some observations at a works in America.[55] There was no evidence of reduction of chromate to chromic salts, and the chromate had no effect on the digestion of sludge at the works. It is reported[56] that nickel sulphate (1 to 3 ppm. Ni) inhibited nitrification and caused some deterioration in the quality of effluent from the treatment of sewage by the activated-sludge process in laboratory experiments. Concentrations of 6 ppm. Ni caused noticeable deterioration in quality and entirely stopped nitrification. On the other hand[57] nickel sulphate (up to 500 ppm. Ni) did not retard production of gas from digesting sewage sludge; there was a retardation with 1000 ppm. Ni, and much greater inhibition with 2000 ppm.

Garbage

Experience continues to accumulate in America on the discharge of ground garbage to sewers.[58] There seems to be a general opinion that the garbage does not interfere with digestion of sludge, and many consider that the most economical method of disposal is by collection in the dry state and addition to digestion tanks after grinding. The composition of the gas is not usually affected.[59]

Sand filtration

In the last few years there has been a revival of interest in the process of filtration of sewage effluents through beds of sand. Vosloo,[60] in South Africa, estimated that the cost of treatment in rapid gravity filters would be considerably less than in slow sand filters, and has begun experiments with a pressure filter; he gives curves showing the relation between rate of flow and hydraulic resistance after different volumes of effluent had been filtered.

Sludge disposal

Keefer,[61] in small-scale experiments, added ferric chloride and lime to mixtures of raw and digested sewage sludge and removed part of the liquid by filtration. He then incubated the treated sludges, containing different proportions of water, at 37°, but found that the amount of gas produced decreased as the moisture content decreased from 85% to 67·5%. If the method were satisfactory it would enable a reduction to be made in the size of digestion tanks. It has been reported[62] that digestibility of sludge is reduced by addition of phosphates, and it is suggested that digestion may be retarded if more than a quarter of the phosphate content of a sludge is derived from industrial wastes. Buswell[63] considers that control of digestion of sewage sludges should be based on determinations of total volatile acids (including their salts) rather than on determinations of p_H value; this method has proved very satisfactory in controlling digestion of industrial liquors. Several very good summaries of digestion practice in America have appeared; Gould[64] discusses utilization of gas, especially in gas engines, and Schroepfer[65] incineration of sludge, in a paper which includes useful figures for calorific value of sludges of different types. Miles[66] gives details of methods of heating sludge, and gives valuable information on the physical constants involved; both he and Gunson[67] consider that there are many advantages in heating sludge by direct injection of steam. It had been thought that this might cause partial sterilization, but in practice it does not do so.

Inkster[68] has studied the changes in viscosity of humus sludge after addition of ferric chloride. The filtrability increases with increasing viscosity. When ferric chloride is added in increasing amounts the viscosity rises to a maximum value and then decreases; the value is also dependent on the extent to which the sludge is stirred. Rudolfs and Falk[69] have found that the filtrability of sludge, after addition of conditioners, is dependent on the phosphate content. In general, when ferric chloride is used, the filtrability of the sludge decreases as the concentration of phosphate is increased, but the filtrability also depends on p_H value being greater at low values than at high. In some well designed experiments the authors greatly increased the filtrability of a sludge by removing phosphate by electro-osmosis. The careful and thorough experiments on a small scale by Wishart and others, reported previously, have been continued with semi-scale plant.[70] In the earlier experiments it had been found that of the chemicals reasonably available ferric chloride was the most efficient as a conditioner, and this was used in the semi-scale work; the treated sludges were then partially dewatered on a rotary vacuum filter. Aeration of sludge for about two hours before addition of ferric chloride reduced the amount of conditioner required; so also did elutriation with tap water, but not to so great an extent as aeration. The authors estimated that the cost of preparing a fertilizer containing 15% water at Manchester would be not less than £3. 10s. per ton. Instances are reported from America[71] in which lime slurry from the manufacture of acetylene from calcium carbide has been used as a conditioner for sludge before vacuum filtration; under favourable conditions the cost is less than that of lime. An account has been given[72] of the operation of the plant at Luton, where sludge is treated by the Porteous process, the filter cake after drying being used either as fuel or as fertilizer.

An outstanding event during the year was the publication of a paper by Hillier[73] giving a detailed account of the operation of the Esholt works of the Bradford Corporation and of the numerous products which are now manufactured from the crude grease separated from the sludge by filter pressing. These products, which are the result of many years of research and development at the Bradford works, are finding increasing use in industry as lubricants, rust preventives, constituents of paint, detergents, and polishes.

Chlorination

A very difficult problem of sewerage arises in Los Angeles, a district covering an area of 450 square miles and with 3000 miles of sewer; the longest flow before the sewage is discharged to the sea is 55 miles, occupying 18 hours. There has been much difficulty from the production of sulphides by anaerobic action in the sewers, and special methods of ventilation have been necessary. It is now reported[74] that the difficulty has been overcome by adding the proprietary substance Cloroben at a number of points in concentrations of 1 to 3·5 ppm. The risk inherent in chlorination of certain treated sewage effluents, however, has again been emphasized.[40] Addition of chlorine in amounts below the chlorine demand to effluents from a number of works caused them to become markedly toxic to fish. Where this occurred the treated sewage effluents always contained thiocyanate (from 2 to 8 ppm. NH_4CNS) derived from gas liquors in the sewage, and the toxicity was due to the formation of cyanogen chloride.

New works

A report has been published[40] of a brief examination of the waste waters from farm premises, a subject on which much more work is required. A preliminary account is also now available of the large sewage-disposal works under construction near Rickmansworth, Herts., for the Colne Valley Sewerage Board.[75] These works, in which the settled sewage is to be treated by the activated-sludge process, are to include grit channels, comminutors, rectangular primary sedimentation tanks with Mieder scrapers, aeration tanks for diffused air, and circular final settling tanks. Primary sludge is to be treated in three primary heated digestion tanks with stirrers and floating gas holders and in a single unheated secondary tank. The digested sludge will be elutriated with effluent in two stages, and will then be mixed with surplus activated sludge; the mixture will be treated with chlorinated copperas made on the works and will be filtered on rotary vacuum filters. The wet cake will be flash-dried and the granulated dried sludge may be burned in furnaces or sold as fertilizer.

Trade waste waters

Oils

Much pollution has been caused by the discharge from engineering factories of liquids containing neat oils and cutting oils. Measures taken at a large engineering works to remove both neat oil and emulsified cutting oils are described by Hogg, Pettet, and Collett.[76] The liquid containing emulsified oils was treated by adjusting the p_H value and adding aluminium sulphate. A somewhat similar method has been described[77] for treatment of washings from tanks at an oil refinery.

Metal pickling

A summary of the position reached in the important work which is being undertaken in America by the Mellon Institute on treatment of waste waters from the pickling of steel is given by Hoak.[78] At many mills ferrous sulphate is now removed from pickle liquor, which, after addition of acid, is re-used in the process. A major difficulty is to devise some economic way of disposing of the ferrous sulphate so recovered. It has now been shown on a small scale that ferrous sulphate can be substituted for gypsum in

Portland cement, and that the properties of the product are generally satisfactory; it seems to be expected, however, that there may be some difficulty in getting this process adopted on a large scale. Work is also in progress, as yet only on a small scale, on the manufacture of ammonium sulphate from ammonia and spent pickle liquor. Great improvements have been made in recent years in the neutralization of liquids containing ferrous sulphate and sulphuric acid by powdered limestone. Important factors in this process are the cost of the limestone and neutralizing plant and the volume and filtrability of the sludge produced. A survey of the properties of dolomitic limestone has been made by Hoak and others,[79] and an account of a large-scale plant in which diluted pickle liquor is neutralized by passage upwards through an expanded bed of powdered limestone is given by Reidel.[80]

Chemical industries

Publication of the reports of the Alkali Inspectors, interrupted by the war, was resumed during the year.[81] During the war it became necessary to control fires in spoil banks, to prevent their being used as reference points by enemy aircraft. This was done successfully either by spraying with water or by washing fine material to the base of the bank to prevent entry of air. The report contains accounts of many methods by which the emission of dust, smoke, and vapours has been reduced; an interesting example is the work which is being carried out by Messrs. Courtaulds Limited on the removal of hydrogen sulphide from air drawn off from spinning machines making viscose rayon yarn; the air is scrubbed by an alkaline liquid containing oxides of iron and manganese in suspension. The Liquor Effluents and Ammonia Committee of the Institution of Gas Engineers has published its Eighth Report.[82] This summarizes the work of the Institution, carried out over many years, on treatment and disposal of liquors from gas works. The main conclusions are that evaporation should be used only when no better method is available, and that the most convenient method of disposal is usually by discharge to municipal sewers. The most suitable spent liquor for disposal in this way is one containing the minimum concentration of higher tar acids and thiocyanates, since these are difficult to decompose by biological action. The Committee recommends early separation of tar from gas liquor and isolation of retort-house liquor from scrubber and condenser liquor; retort-house liquor can be used as fertilizer or can be evaporated for recovery of ammonium chloride. Methods are suggested whereby the concentration of thiocyanate in gas liquors can be reduced. An account has been given[12] of liquors from small gas producers, using coke as fuel, and installed as a standby at many factories during the war; the liquors represent a very small polluting load and disposal is not difficult.

Many difficulties have arisen recently in the treatment of liquors from the manufacture of artificial resins. Some of these liquors contain so high a concentration of soluble substances that the only practicable method of disposal at present appears to be concentration and incineration. It was shown in semi-scale experiments[12] that a waste water from the scrubbing of air containing vapours removed from asbestos after impregnation with resins of the phenol-formaldehyde type can be treated biologically in percolating filters. Effluents of good quality were obtained even when the liquid contained as much as 240 ppm. formaldehyde. A useful bibliography of papers published during the past 10 years on treatment of waste waters from the chemical industries is given by Hess.[83]

Cyanides.—Much work is in progress, both in Great Britain and abroad, on the treatment of waste waters containing simple and complex cyanides, particularly from the electro-plating industries. The two most promising methods of treatment so far worked out involve addition of ferrous sulphate to form insoluble complex cyanides, or addition of chlorine or compounds of chlorine to form cyanate, which under certain conditions undergoes decomposition to compounds of ammonia. By the first method it is possible to reduce the concentration of cyanide, but not usually to remove it entirely.[12] The p_H value of the liquid after treatment should be between 7·5 and 10·5 and an excess of ferrous sulphate is required, the amount being greater with complex cyanides than with simple cyanides. An excess of chlorine, in alkaline solution, will completely remove CN from a solution of a simple cyanide, though less is known of its action on complex metallo-cyanides.[40, 84] A complication in the use of this process is that if the treated liquid is to be discharged to a stream it is necessary to remove the excess of chlorine, which is itself toxic. An account has been given of a full-scale plant in which both these methods have been tried,[85] the process finally adopted being chlorination. When solutions containing cyanide are added to sewage and the mixture is treated in percolating filters the whole of the cyanide is usually not removed at first, though the proportion removed increases if the application is continued.[12, 40] Apart from its effect on the processes of sewage treatment, discharge of cyanide may be a danger to men working in sewers. Lockett and Griffiths[86] have developed equipment for determining the concentration of HCN in air drawn from sewers, and have concluded from laboratory experiments that cyanide in a concentration of 1 ppm. HCN or more would have a deleterious effect on treatment of sewage by the activated-sludge process.

Chromates.—The effects of chromate on sewage treatment are well known, and at many factories chromate is removed, by one of the several effective processes now available, before waste waters are discharged to a sewer. One major source of chromate, at least in America, is the waste liquor from air-conditioning plants. It is stated[87] that these waste waters may contain chromate in a concentration of the order of 250 ppm., and that very large volumes of liquid may be involved. The chromate is added to prevent corrosion of the plant in which the air is washed with water.

Explosives.—An account has now been given[88] of the measures taken in Great Britain during the war to dispose of waste waters containing TNT and other constituents of explosives from shell-filling factories. Precautions were taken to reduce the volume of these liquors as far as possible, and they were then treated in admixture with sewage from the factories. There were some difficulties, but on the whole the liquors were disposed of without causing undue pollution. A similar method was used for disposing of waste waters containing picric acid and dinitrophenol;[12] here elaborate precautions had to be taken to reduce the quantities of these toxic substances discharged, since only very small concentrations can be added to sewage without causing deterioration in the quality of the final effluent.

DDT.—A difficult problem of disposal of waste waters arises from the manufacture of DDT. There are usually two waste liquors, one being a strong solution of sulphuric acid containing chlorobenzenesulphonic acid and other substances and the other a much weaker washing water.[40] So far as is known, no satisfactory method of dealing with the strong acid has yet been developed, and where there are not good facilities for disposal it has been taken away in tank waggons and discharged into the sea. It has been shown that, provided certain precautions are taken at the factory, the weaker washings can be treated in admixture with domestic sewage.

Canneries

Experiments on treatment by sedimentation and biological filtration of waste waters from the canning of fruit and vegetables are described by Dickinson;[89] they confirm that these liquids can be treated satisfactorily by biological processes. In a full-scale plant in America[90] pre-treatment is given in a roughing filter, 3ft. deep, containing medium graded 3½ to 4in.; a very high load is applied—between 6 and 10lb. of biochemical oxygen demand per cubic yard of medium per day. There is always some difficulty in treating food wastes by sedimentation since anaerobic decomposition may occur if too long a period of retention is given. A Vacuator is in use at one American works; with this system the waste waters are aerated and are then passed into a vertical cylindrical vessel in which a partial vacuum is maintained above the liquid, the suspended solids which rise to the surface, buoyed up by bubbles of air, being skimmed off. In the plant described the average removal of suspended solids was 29%.[91]

Cellulose

Data are now accumulating on the production of alcohol and yeast from waste waters from the manufacture of cellulose from wood by the sulphite process. An account of the operation of one plant is given by Joseph,[92] who says that the waste waters resulting from the manufacture of alcohol have a biochemical oxygen demand of about 57% of that of the original sulphite liquor. This figure is in agreement with data given by Tyler.[93] Boruff,[94] in a review of American practice, states that most of the slop from the alcoholic fermentation of molasses, except in the area of New Orleans, is being concentrated in multiple-effect evaporators to contain 50 to 60% solids, and is being used as a constituent of cattle food. The amount which can be incorporated is limited by the high mineral content of the concentrate. Typical concentration plant is described by Spanyer.[95]

Penicillin, etc.

No detailed results of treatment of the very polluting waste liquors from the manufacture of penicillin have yet been noticed; these waste waters have caused much difficulty in Great Britain and are reported to have done so in America. It has been reported that waste waters from the manufacture of riboflavin from a mash containing protein, sugar, and mineral substances are being mixed with the separated mould and dried in a spray-drier.[96]

Meat industries

Useful data on the volume and composition of liquors from different sections of the meat industry are given by Mohlman.[97] One method of treating such liquors in America is by biological filtration in filters provided with facilities for back-washing with water and air. An interesting account of the operation of one of these plants has been published.[98] Effluent from the back-washed filters is treated in secondary filters of conventional design. The load on the primary back-washed filters is from 3 to 5lb. of biochemical oxygen demand per cubic yard of medium per day; the filters are back-washed about once in three weeks, and it is stated that they regain their activity immediately after washing.

Textiles

Accounts have now appeared of the aerobic process of retting flax developed by the Water Pollution Research Laboratory during the war.[99, 100] There are no waste waters from this process, the retting liquor being used with successive batches of flax. Some of the organic matter leached from the straw is decomposed by bacterial action during retting and some is removed on the wet flax after retting.

In Great Britain wool-scouring wastes are usually treated by addition of sulphuric acid in order that the greasy matter may be separated. Success is reported with another method, first described many years ago, in which the liquors are treated first with calcium hypochlorite and after sedimentation are again treated with sulphuric acid to give a p_H value between 4 and 5.[101] It is stated that up to 98% of the grease and 80 to 90% of the BOD have been removed by this process; the remaining oxidizable matter consists largely of soluble nitrogenous compounds. At Halifax the sewage, which contains large amounts of greasy textile wastes, is usually treated by addition of sulphuric acid. Lumb, Barnes, and Blackburn[102] have carried out experiments on the use of chlorinated copperas. They found that this would be more costly than sulphuric acid, though the cost could be reduced by adding the copperas in conjunction with sulphuric acid or lime.

Beet sugar

Results of an investigation, during several seasons, of waste water from the manufacture of beet sugar have been reported.[40, 103, 104, 105] In the early days of the industry these liquors caused much pollution; in Great Britain, at factories where there is particular difficulty in disposing of waste waters, they are now re-used in the process of manufacture. This has reduced by a very large amount the volume of waste liquor to be discharged, and the waste waters remaining can be purified in a plant of reasonable size. One difficulty which results from the re-use of process water is that corrosion in the diffusion batteries and auxiliary plant is increased. The effect of chlorination of the recirculated waste water is described; corrosion was reduced but by no means eliminated. It has often been objected that re-use of process water reduces the efficiency of extraction of sugar; in experiments with small-scale plant, however, this was found not to be so.[105]

Paper

No important papers have been noticed on treatment of the types of paper-mill effluent produced in large quantities in Great Britain, but a detailed investigation of methods of treatment of wastes from the de-inking of papers for re-use has been begun in America.[106] Addition of coagulants or of acidic gases removes a large proportion of the suspended solids, but this process would be costly to operate. Promising results have been obtained with treatment by bio-aeration. Some very interesting work has been done on the rate of oxidation of constituents of paper-mill wastes under different conditions; in the test for BOD, cellulose fibre prepared by different processes is oxidized at different rates,[107] and it has been shown that during a period of incubation of 10 days the uptake of oxygen by clarified paper-mill effluent is greater than for a similar liquid to which fibre has been added; with longer periods of incubation, however, the reverse is true.[108] In a discussion on this work experiments were quoted in which addition of activated carbon to sewage reduced the rate of oxidation during incubation.

A process somewhat similar to the manufacture of paper is that of pre-digestion of straw with caustic soda to increase its digestibility for farm animals. Many small plants were built on farms in Great Britain during the war. The waste waters from the process represent a rather high polluting load;[12] they cannot usually be treated in a specially built plant and most usually be disposed of by irrigation on farm land. Discharge without treatment to a small stream may cause noticeable pollution. There is still no very satisfactory method of treating waste waters from tanneries, though partial treatment by mixing the various types of liquor in constant proportions, adjusting the p_H value, and removing sludge are common in America. The practice of evaporating spent tan liquors for recovery of saleable by-products seems to be growing.[109]

General

Treatment of certain types of industrial waste waters by passage through beds of base-exchange or acid-absorbing materials is a process which has great potentialities. No large-scale use of this method has been noticed during the year, but work is proceeding actively in elucidating the factors which are of importance in determining the course of absorption of cations and anions from complex systems. A useful summary of the position reached and an account of some original work have been given by Melsted and Bray.[110]

It will have been noticed that success in the treatment of many types of industrial liquors depends on re-using them as far as possible in manufacturing processes. Instances where this method has been adopted have been discussed by several writers, who give as examples the treatment and re-use of water from the washing of sand,[111] of liquors from the manufacture of starch from corn, of synthetic rubber, of textiles,[112] and of liquors from the retting of flax and manufacture of beet sugar.[113]

Effects of pollution

Preliminary accounts have now been published of a bacteriological survey of the River Avon, in Warwickshire.[12, 40] Treated sewage effluents from Coventry are discharged into this river at points where very little water is available for dilution. These discharges greatly increased the numbers of bacteria in the river water, but the counts fell rapidly at increasing distances downstream. This work led to the development of a new method of checking the accuracy of counts of bacterial colonies.[114] Among the types of bacteria counted and examined were fæcal streptococci; the importance of this group as indicators of pollution by fæcal matter has been stressed by other workers.[115]

In assessing the effects of different types of polluting substances the determination of the toxicity to fish of constituents of industrial effluents is of importance. Satisfactory methods of determination have not yet come into use; they would require facilities for controlling the temperature, p_H value, degree of oxygenation, and other factors, in large volumes of water. Nevertheless, with existing methods approximate values for toxicity can be obtained; data on some constituents of industrial wastes commonly discharged to rivers have been given by Grindley,[116] and further information on the toxicity of acids and alkalis has been published.[117] Some very interesting observations on the consumption of oxygen and the rate of opercular movement of fish in solutions of different poisons are described by Jones.[118]

A matter of great importance from the point of view of public health is the efficient washing of utensils used in catering establishments. Much work is at present in progress in America on this subject. Methods of determining bacterial counts of washed utensils under standard conditions are being examined,[119] the efficiencies of different types of washing machine are being compared,[120] surveys of present practice in a large number of restaurants are being made,[121] and the bactericidal action of various detergents is being evaluated.[122, 123]

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