

and viscosity of solutions, light scattering and other techniques have contributed to the present conception of the structure of polythene, but even now it is not fully resolved. Each finite sample of polythene is made up of molecules having quite a wide spread of molecular weight. The physical properties of the polymer depend upon both the chemical features and also on the arrangement of the molecules in relation to one another in the solid state. Polythene is partly crystalline: in the commercial material, probably about 70 per cent of the molecules are in the ordered state. The authors of this paper correlated chemical and structural features with electrical conductivity, melt viscosity, melt elasticity, softening point and mechanical and physical properties in the solid state. A point of interest which the discussion evoked was that, under the action of gamma-rays, cross-linking is caused, resulting in the transformation of polythene to a glassy, brittle solid. This effect is similar to that produced by a very prolonged photo-oxidation; the mechanism of the change is a matter for speculation.

A second paper from Imperial Chemical Industries, Ltd., on butane dehydrogenation, by Mr. E. Beesley and Dr. B. Whipp, was equally creditable as a record of the rapid development, in collaboration with Universal Oil Products, Ltd., of a process under the stress of war-time conditions of emergency and improvisation. A mixture of *iso* and *normal* butanes (usually 70 per cent *iso*) was dehydrogenated over an alkali-promoted chromia-alumina catalyst to the corresponding butenes. This essential step in the production of *isooctane* for aviation gasoline was brought to successful operation; one major difficulty, namely, the random choking of the reaction tubes due to excessive and unpredictable coke formation, was cured by introducing 30-40 p.p.m. carbon disulphide in the charge. The carbon disulphide was thought to passivate the tube material against alternate oxidation and reduction, thus preventing the catalysis of carbon formation by finely divided metal. In the discussion, it was said that the process is now in operation for the production of *isobutene* from *isobutane* in an integrated plant, wherein this step fits in with other industrial processes.

The separation and utilization of  $C_4$  olefines, which are becoming increasingly available from the new oil refineries and petroleum chemicals cracking-plants, was reviewed by Dr. E. T. Borrows and Mr. W. L. Seddon (Petrochemicals, Ltd.). It is of particular interest that whereas the  $C_4$  stream from oil-refinery catalytic crackers contains virtually no butadiene, the plants installed by petroleum chemicals works for the cracking of naphtha, gas oil, etc., yield a  $C_4$  stream containing substantial amounts of butadiene. This constitutes both an opportunity and a problem. Considerable interest was shown in the authors' suggestion that, from a mixed  $C_4$  stream containing butadiene, the *isobutene* may first be removed by selective absorption in sulphuric acid without absorbing appreciable amounts of the butadiene present; in fact, more than 90 per cent of the butadiene may be afterwards recovered.

The series of specialist papers was concluded by the paper by Dr. D. P. Dodgson (Monsanto Chemicals, Ltd.) on the use of additives based on petroleum for improving the quality of various petroleum fractions. A wide range of products, including chlorinated waxes, sulphonation products, naphthenic acids, viscosity index improvers, pourpoint depressants,

etc., were dealt with. In the discussion, interest was shown in the use of additives to give oils of both high- and low-viscosity indices, and in the liability of viscosity index improvers to break down at high rates of shear. Dr. Dodgson gave the assurance that conventional lubricating oils containing additives from different manufacturers are, in general, mutually compatible.

Sir Robert Robinson, in the closing address, pointed out that the world chemical industry is highly competitive, and, if the British complement is to survive, it must keep in the race: any early financial losses in establishing the petroleum chemicals industry must be accepted; national and strategic interests make it imperative that the necessary capital to sustain development and growth of the industry must be found. The symposium, he said, rightly laid stress on an essential theme of this new industry: that is, its facility for developing alternative processes which do not require the use of substantial quantities of heavy inorganic chemicals, for example, in the production of acetone and phenol by the Distillers Co., Ltd., process, and of ethylene oxide by the catalytic oxidation of ethylene. This theme should be vigorously developed. Research over a broad front on catalysis should be conducted, and in this attack, continued Sir Robert, government departments such as the Chemical Research Laboratory and the Fuel Research Station of the Department of Scientific and Industrial Research should play an outstanding part. Recent research has demonstrated that there are many reactions and processes which hold high promise of industrial exploitation in Britain: the Fischer-Tropsch reaction and the Oxo syntheses are well-known examples. The recent work of Ziegler on the use of lithium and aluminium hydrides as catalysts in controlled polymerization processes may also lead to economic routes to both known and new products. These are only examples of the many opportunities, some known, some awaiting discovery, that lie before us, and only by our own energy and unsparing effort can they be won.

## CLAY - WATER RELATIONSHIPS

A MEETING of the Clay Minerals Group of the Mineralogical Society, held at the laboratories of the British Ceramic Research Association, Stoke-on-Trent, during November 7-8 last, was devoted to a discussion upon clay-water relationships. The meeting was preceded, on the morning of November 7, by a visit to the laboratories of the Association. At the scientific sessions the chair was taken on the afternoon of November 7 by Dr. G. W. Brindley (University of Leeds), and on the morning of the following day by Dr. G. Nagelschmidt (Safety in Mines Establishment, Sheffield).

The discussion was opened by a review of the significance of clay-water relationships in ceramics by D. A. Holdridge and F. Moore (British Ceramic Research Association). Plasticity and strength data as well as the Pfefferkorn and modified Pfefferkorn numbers for ball and china clays were related to dehydration data, and discussed in relation to the concept of 'planar' and 'broken-bond' water; the former is removed below 110° C., but removal of the latter is incomplete below about 250-275° C. In describing the rheological properties of importance

for clay slips and pastes, particular attention was paid to the methods for determination of viscosity and plasticity and their applicability. The rheology of thixotropic gels was also discussed. In the discussion, the different dehydration characteristics of china clay and ball clay were commented upon by R. Greene-Kelly (Rothamsted Experimental Station, Harpenden) and by Dr. Brindley, who also referred to recent dehydration data for nacrite<sup>1</sup>. G. K. Jones (Fuller's Earth Union, Redhill), Dr. N. O. Clark (English Clays, St. Austell) and Mr. Moore discussed the relationship of dilatancy, turbulence and shearing, and R. H. S. Robertson (Glasgow) inquired about the relationship of the modulus of rupture to the moisture content.

Soluble salts may have deleterious effects upon clay products—for example, efflorescence in bricks—and the determination of these in clayey raw materials was discussed by Prof. H. Lehmann (Bergakademie, Clausthal-Zellerfeld), who showed that extraction by a percolation method after firing gives the most useful information. Using this technique, it has been found that efflorescence is not related to the amount of soluble salts alone, but that it is also dependent upon pore space, pore characteristics, firing temperature and the density and chemical characteristics of the specimen. Correlation of efflorescence with firing temperature, the effect of various ions and the possibility of control of conditions leading to efflorescence were discussed. In reply to comments by B. Butterworth (Building Research Station, Watford), Prof. Lehmann stressed that he had considered only clays in which his laboratory is interested, and agreed that higher sulphate contents are not uncommon; he also mentioned that, in Germany, determination of soluble salts in the raw material is still used to assess a clay. Other speakers referred to the effect of association of bricks with cement products and the question of the total soluble salts. In reply to W. Noble (British Ceramic Research Association), Prof. Lehmann remarked that the effect of the pH of the extracting solution has not yet been considered.

The deflocculation of kaolinite suspensions and its relationship to chloride adsorption has been investigated by Dr. R. K. Schofield and H. R. Samson (Rothamsted Experimental Station), who found that a flocculated sodium-kaolinite suspension in contact with less than a critical amount of sodium hydroxide takes up chlorine ions from dilute sodium chloride solution; when deflocculation occurs, full negative adsorption is observed. These results are related to questions of cation-exchange by kaolinite, since, from the observations made, exposed hydroxyl groups at the surface would only be expected to give exchangeable hydrogen ions under alkaline conditions. In addition, montmorillonoids might, under certain conditions, be sorbed by kaolinite to neutralize positive charges. Mr. Greene-Kelly and Dr. Clark both commented upon the significance of the above results in work involving dispersion of mixtures of clay minerals, where one mineral may be preferentially deflocculated. Dr. D. M. C. MacEwan (Rothamsted Experimental Station) pointed out that the remarks upon dissociation of hydroxyl groups were in disagreement with the views of Edelman and Favejee<sup>2</sup>, and that the results might be significant in determining the true structure of montmorillonite<sup>3</sup>.

To investigate the relationship between viscosity and concentration for three clays of the kaolin group, T. E. Currie and Dr. R. W. Grimshaw (University of Leeds) employed electron-optically checked samples

of uniform particle-size. The viscosity/concentration curves were all similar in shape and could be derived from equations employing a series of constants dependent upon degree of dispersion, upon particle-size, and upon type of clay mineral present. In general, the viscosity was more dependent upon particle-size than upon type of mineral. Dr. Grimshaw, replying to Dr. Nagelschmidt, reported that constant shearing stress had been used, although the same general conclusions were applicable under different conditions. Dr. Clark questioned whether the relatively constant thickness-ratio for kaolinite grains in the various fractions could be taken as a universal rule, and in this connexion Mr. Robertson referred to some work upon the relationships of viscosity to rugosity<sup>4</sup> and to particle size for various kaolin clays<sup>5</sup>. The rigidity of the water envelope around clay particles and its effect upon results were also discussed by Dr. Clark and Dr. Grimshaw.

In a review of the subject of thixotropy and the internal swelling of crystals, Prof. U. Hofmann (Technische Hochschule, Darmstadt) described a very neat method, employing freeze-drying technique, of obtaining dry undisturbed clay-gel structures for examination under the electron microscope. These structures alter very little in volume during drying, and it is considered that the relative positions of particles are virtually unchanged; the framework is reasonably solid, very stable and even has a certain elasticity—properties which were demonstrated by a sample passed among members of the meeting. The effect of electrolytes upon the volume of coagulated clay gels, and the forces operative here and in maintaining the solidity of the framework were discussed. Prof. Hofmann also reported the results of an investigation upon thixotropy in non-aqueous liquids, for example, hexane and benzene. In the discussion, Dr. Nagelschmidt referred to the occurrence of thixotropy in systems with spherical particles, and Mr. Samson, Dr. Clark and Prof. Hofmann discussed general questions upon thixotropy and the arrangement of particles in flocculated systems. The formation of dipoles, and the dielectric constants of suspensions were referred to by Dr. Clark and Mr. Jones, and finally Prof. Hofmann, in addition to Dr. Clark and Dr. P. Howard (University of Leeds), suggested other methods whereby dry, undisturbed clay structures might be produced.

The conditions under which montmorillonoids lose their expanding properties on heating were described by R. Greene-Kelly, who related the changes occurring with crystal structure<sup>6</sup>. For example, if lithium-saturated montmorillonoids are heated to 200° C. and treated with glycerol, only dioctahedral components with the charge in the tetrahedral layer (that is, the beidellite type) will swell. Reference was made to the sorption of water by sodium-montmorillonoids, and some notes were given upon the information to be derived from such measurements. Mr. Greene-Kelly, in reply to Dr. R. C. Mackenzie (Macaulay Institute, Aberdeen), reported that he had not examined beryllium-montmorillonoids because of the hazards of the acidity of stable solutions of Be<sup>2+</sup> salts. Further discussion took place upon the effect of lithium ions upon the cation-exchange capacity of montmorillonoids and the possibility of such ions entering the lattice, these points being raised by Dr. Nagelschmidt and Dr. B. S. Neumann (Fuller's Earth Union).

Dr. G. W. Brindley and R. F. Youell (University of Leeds) showed that, during the oxidation of

ferrous to ferric chamosite, there occurs a partial dehydration which can be related to the lattice positions of the hydroxyl groups. The retention of water and structural order to high temperatures during the dehydration of nacrite<sup>1</sup> was also demonstrated. These results were considered in relation to oxidation-dehydration processes in other minerals, and, as an example, it was shown that chemical analyses for decomposition products of biotite<sup>2</sup> can only give reasonable structural formulæ using assumptions derived from the above experiments. The derivation of good structural formulæ was commented upon by Dr. MacEwan, Dr. Nagelschmidt and Dr. Mackenzie, while Dr. S. J. Gregg (University College, Exeter) compared the retention of water by silicates to a high temperature with the retention of water and carbon dioxide by other compounds. Dr. H. P. Rooksby (General Electric Co., Wembley) referred to the retention of water by  $\gamma$ - $\text{Al}_2\text{O}_3$ , and, in reply to his questions on the structural dehydration data, Dr. Brindley stressed the slowness of heating and the reproducibility of results even with broken crystals. The mechanism of the dehydration of kaolinite, with special reference to the work of White *et al.*<sup>3</sup>, was also discussed by Dr. Nagelschmidt, Dr. Grimshaw, Dr. Howard, Mr. Youell and Dr. Brindley.

The final paper was not upon the subject for discussion although it had an indirect connexion. In order to determine the effect of grinding on kaolinite, Dr. S. J. Gregg, T. W. Parker (English Clays, St. Austell) and Mrs. M. J. Stevens (University College, Exeter) ball-milled a sample for a thousand hours, withdrawing aliquots at intervals for various physical and chemical tests—for example, X-ray examination, air sedimentation, loss on ignition, etc. Up to six hundred hours, the primary particles were decomposed chemically as well as broken physically, and the products formed an amorphous layer on the somewhat disorganized, undecomposed particles. The resultant particles, which possess an internal area, resisted complete dispersion and, after six hundred hours, the proportion of stable aggregates increased. During discussion, questions were asked by Mr. Greene-Kelly, Mr. Henderson, Mr. Jones, Dr. Neumann, Dr. MacEwan, I. L. Freeman (London Brick Co., Stewartby) and Dr. Mackenzie upon the method of sampling, the wear on the ball-mill, the uniformity of particle size, density measurements and the stability of aggregates. The possibility of interference of electrostatic charges with air-sedimentation tests was suggested by Dr. P. L. Plesch (University College, Stoke-on-Trent), and, in reply to a question by Mr. R. Johnson (British Ceramic Research Association), Dr. Gregg pointed out the significance of the inter-relationship of measurements of bulk density, sedimentation and surface area. The X-ray results were discussed by Dr. Brindley and E. K. Cundy (English Clays) and the amorphous coating, or 'Beilby layer', by Mr. Robertson.

Before the end of the meeting, two brief reports—one on the conference on clays and clay technology, held at the University of California during July 21-52, 1952, and one on the meetings of the Comité International pour l'Étude des Argiles, held in conjunction with the Nineteenth International Geological Congress, Algiers, during September 8-15, 1952—were presented by Dr. MacEwan and Dr. Mackenzie, respectively.

This meeting, as a whole, proved most valuable, giving ample proof of the significance of clay-water

relationships in all aspects of clay studies, both pure and applied. Its value was enhanced by the concentration on problems which our present knowledge is insufficient to solve, but which might well form the subject of future research.

ROBERT C. MACKENZIE

<sup>1</sup> von Knorring, O., Brindley, G. W., and Hunter, K., *Min. Mag.*, **29**, 963 (1952).

<sup>2</sup> Edelman, C. H., and Favejee, J. Ch. L., *Z. Krist.*, **A**, **102**, 417 (1940); and Edelman, C. H., *Verres et Silicates Indust.*, **12** (Supp.), 3 (1947).

<sup>3</sup> For example, see *Nature*, **168**, 107 (1951).

<sup>4</sup> Robertson, R. H. S., and Emödi, B. S., *Nature*, **152**, 539 (1943).

<sup>5</sup> Meldau, R., and Robertson, R. H. S., *Ber. deut. keram. Ges.*, **29**, 27 (1952).

<sup>6</sup> For earlier work see Greene-Kelly, R., *Clay Min. Bull.*, **1**, 211 (1952).

<sup>7</sup> Walker, G. F., *Min. Mag.*, **28**, 693 (1949).

<sup>8</sup> For example, see Vassiliou, B., and White, J., *Clay Min. Bull.*, **1**, 80 (1949); and Murray, P., and White, J., *ibid.*, **1**, 84 (1949), and *Trans. Brit. Ceram. Soc.*, **48**, 187 (1949).

## RADIO RESEARCH IN THE BRITISH COMMONWEALTH

AT the meeting of the British Commonwealth Scientific Official Conference in 1946, a Specialist Conference on Radio Research was convened and was held in London during August 1948 under the chairmanship of Dr. R. L. Smith-Rose. The proceedings of this Conference, which were published (S.O. Code No. 47-148-1949; London: H.M.S.O.; 4d. net), included a number of recommendations designed to encourage the Commonwealth countries to participate more actively in a comprehensive programme of fundamental radio research. This programme included such items as proposals for the location of ionospheric recorder equipment for determining the characteristics of the ionosphere at vertical incidence, the study of the propagation of radio waves at oblique incidence and the comparison of radio transmission forecasts with the results of the practical operation of radio circuits. Other matters were concerned with radio noise of both terrestrial and extra-terrestrial origin, the investigation of meteors by radio methods, and with a study of the effect of meteorological conditions on the propagation of very short radio waves. Suggestions were also made for extending the limited services of standard frequency transmission, and for collecting information to increase our knowledge of the electrical constants of the ground in all parts of the Commonwealth.

The progress made towards the implementation of these recommendations has been reviewed on two occasions by correspondence through the British Commonwealth Scientific Liaison Offices in London; and last August in Sydney, Dr. Smith-Rose held another meeting of the Specialist Conference, taking advantage of the presence there of a number of radio scientists attending the General Assembly of the International Scientific Radio Union. It was noted that considerable progress has been made in extending the network of ionospheric recording stations throughout the Commonwealth. In addition to the stations in Great Britain at Slough and Inverness, the United Kingdom has maintained similar stations at Singapore and in the Falkland Islands; and more recently an experimental equipment has also been in operation at Port Lockroy in Antarctica. Furthermore, similar recorder equipment has been installed by the United Kingdom Department of Scientific and Industrial Research at Ibadan, Nigeria, and at Khartoum, where it is now being operated by the University