BRITISH CHEMICAL ABSTRACTS

B.—APPLIED CHEMISTRY

APRIL 22, 1927.

II.—FUEL; GAS; DESTRUCTIVE DISTILLATION; MINERAL OILS.

Hydrogenation of lignite in the presence of aqueous bicarbonate solution. F. Fischer and A. Jäger (Abh. Kenntn. Kohle, 1925, **7**, 141—143; Chem. Zentr., 1926, II, 1915).—Hydrogenation by the action of hydrogen under pressure in the presence of aqueous sodium bicarbonate solution is preferable to the use of sodium formate or mixtures of carbon monoxide and steam. L. A. Coles.

Colorimetric determination of humus substances. U. Springer (Brennstoff-Chem., 1927, **8**, 17—20).—The colour intensity of solutions of humic acids in aqueous alkalis (*e.g.*, sodium hydroxide and carbonate, ammonia, and, to a less degree, pyridine) decreases on keeping, rapidly at first and then more gradually. This decomposition effect increases with increasing concentration and degree of dissociation of the base.

W. T. K. Braunholtz.

Methane fermentation of peat. E. Melin, S. Norrbin, and S. Odén (Ingeniörs Vetenskapsakad. Handlingar, 1926, [53], 1—42).—Fermentation of unheated peat with inoculating sludge from sedimentation and decomposition chambers (Imhoff tanks) proceeded very slowly. The rate of fermentation was considerable only when the bacteria were vigorously stimulated at the start. The rate of fermentation was greatest at 25—30°, and at p_H 6·5—7. Addition of 0·05—1% of calcium acetate increased the rate of fermentation considerably. Analyses of the gases evolved during fermentation showed 62—78% CH_4 and 30—13% H. The constituents of the peat which seemed to be fermented were the hydrocelluloses and mucilage substances, hexoxanes in general, cellulose, and to some extent the pentosans. No indication of attack of the humic acids or lignins was found. Experiments on the removal of water from the fermented peat by pressure indicated that the water could not be squeezed out of fermented peat any more readily than from raw peat. Obviously, the colloids were not destroyed by the micro-organisms. W. Clark.

Recovery of carbon dioxide from waste flue gases. M. A. Rabinovitch (J. Russ. Phys. Chem. Soc., 1926, **58**, 518—526).—To ascertain the best conditions for the recovery of carbon dioxide from waste flue gases, the absorption and subsequent evolution of carbon dioxide by potassium hydroxide absorbers was investigated. The gas was passed at various pressures (1—8 atm.) and temperatures (19—80°) through potassium hydroxide solutions, and the rate of adsorption, and its relation to the concentrations of potassium carbonate and potassium hydrogen carbonate, as also the rate of their decomposition and recovery of the gas, were determined. Both rates increase with rise of temperature. Increase of potassium hydrogen carbonate lowers the rate of absorption. The dissociation pressure decreases with rise in potassium carbonate concentration. Experiments with mixtures of air and carbon dioxide were also carried out. The equation

$$[KHCO_3]^2\{[K_2CO_3]^2 \times P_{CO_2}\} = K$$

holds over a considerable range of concentrations. Addition of small quantities of potassium sulphate, which is formed in practice from the sulphur dioxide present in the flue gases, decreased the efficiency of the absorbers; potassium chloride had the same effect. Traces of soluble calcium or magnesium salts restored the efficiency almost to its original level. M. Zvegintzov.

Thermal relations in a Scottish oil-shale retort. L. C. Karrick (Chem. Met. Eng., 1926, **33**, 740—744).—In the average Scottish oil-shale retort, which is 26 in. in diam. in the distilling zone, the importance of steam and water-gas as internal heating media is indicated. It is shown that 55% of the heat necessary to distil the shale is transferred from the hot zone to the low-temperature distillation zone by these fluid heat-carriers, and that 86% of this heat is recovered from the spent shale. If the size of shale particles is reduced from 4 in. to 1 in. it is possible to increase the capacity of the retort by the use of larger quantities of steam which reduce the temperature in the hot zone to below that required for water-gas production. This conserves heat within the retort, but necessitates the provision of external means for generating fuel gas for heating the retort setting.

S. Pexton.

Petroleum oils of Grozny. A. Sachanen-Sachanov (Petroleum, 1926, **22**, 1240—1244).—Crude oil rich in wax is found in the deeper layers of the new oil-field. It has *d* 0·840, solidif. pt. 15°, greatly affected by hysteresis, contains 7% of wax (m.p. 53—54°), and 0·25% S. The yield of benzine is 23·31%, and of kerosene 13·31%. The residue after removal of lubricating oils contains 9% of wax (m.p. 75°). Oil poor in wax is found in the Solenaja Balka field; it has *d* 0·840, solidif. pt. —10°, and yields 27·79% of benzine and 12·54% of kerosene. Oil free from wax (containing 0·1—0·5% only) is found in almost all horizons of the old field and in the highest layer of the new field. It has *d* 0·850—0·860, but at the refineries 0·870 owing to weathering; solidif. pt. below —20°, and contains 0·2—0·3% S. The yield of benzine is 28·53% and of kerosene 12·55%. The residue contains 18·9% of asphaltenes. The natural gases of Grozny have a temperature of 80—90°, and are generally of *d* 1·30—1·40.

They yield 1 kg. of benzine per cub. m., consisting of 30—40% of condensable hydrocarbons and 60—70% of methane, ethane, and propane. H. Moore.

Valuation of commercial benzine by the "index number" of Ostwald. E. Kroch (Petroleum, 1926, **22**, 1245—1247).—The index number is not a new conception, being represented in American practice by the average b.p. It is misleading as an indication of the commercial value of spirits, as is shown by distillation graphs of various benzines. H. Moore.

Resinification value of transformer oils. F. Hoeg (Petroleum, 1927, **23**, 116—117).—The author confirms Typke's suggestion (cf. B., 1926, 523) that in examining transformer oils, the resin content should be determined both before and after heating; of two oils having the same resin content after heating, that which has the higher content before heating, and consequently shows the smaller increase, would probably prove the better in use. The acid value of the oils increases to about 2·5 times its original value during heating, and is approximately proportional to the resinification value. L. A. Coles.

Deleterious properties of lubricating oils. J. E. Hackford (Oil Eng. Tech., 1926, **7**, 325—327; Chem. Abstr., 1926, **20**, 3561).—Air is bubbled (1 per sec.) through the oil at 150° for 9 hrs.; the rate of acidity formation is the difference between the total acidity (c.c. of 0·1*N*-potassium hydroxide per 10 g. of oil) and the inherent acidity. To determine the acidity which will cause damage to bearings, 50 c.c. of oil are extracted with boiling distilled water for 1 hr., the solution is filtered, poured to a definite mark in a 50 c.c. U-tube, and the voltage obtained between zinc and copper electrodes is measured. A. A. Eldridge.

Determination of small quantities of water in mineral oils. W. Boller (Petroleum, 1927, **23**, 146—148).—The method serves for the determination of water in transformer and other oils containing up to about 0·01% of water. A current of a purified and dried non-reacting gas, preferably hydrogen, is passed successively through a vessel containing the oil at 130—140°, a tube packed with calcium carbide, and an absorption vessel containing an ammoniacal solution of copper sulphate and hydroxylamine hydrochloride, After the hydrogen has been passed through the apparatus for 1 hr., the carbide tube is heated at 180—200° for 1 hr., and the precipitated copper acetylide is washed, dissolved in dilute sulphuric acid, precipitated as sulphide, ignited, and weighed as cupric oxide, or is dissolved in excess of acidified ferric sulphate solution, and the reduced iron titrated with permanganate. L. A. Coles.

Determination of paraffin scale in crude paraffin wax. E. Belani (Petroleum, 1926, **22**, 1347—1348).—A small fireclay crucible, thoroughly porous, glazed on the sides but unglazed at the bottom, is inverted on a cork, through which a tube communicates with a vacuum flask. By the use of gelatin a space is moulded on the bottom of the crucible, and is filled with wax mass. The adherent oil is drawn into the flask through the porous base of the crucible, the oil removed, and the amount of scale determined by difference. H. Moore.

Dopes and detonation. H. L. Callendar (Engineering, 1927, **123**, 147—148, 182—184, 210—212; cf. B., 1926, 618).—It appears probable from the nuclear theory of detonation that the reactions occurring in the cylinder during compression, but before ignition, determine the "knocking" or "anti-knocking" character of a fuel. The temperatures of initial combustion (T.I.C.) of a number of organic liquids have been determined by passing a mixture of the vapour and air through a glass tube, the temperature of which could be gradually raised; the T.I.C. was shown by the appearance of water, carbon dioxide, aldehydes, or acids. The T.I.C. of the aromatic hydrocarbons were higher than those of the alcohols (benzene, 670°; ethyl alcohol, to aldehyde, 445°; to carbon dioxide, 520°), and the latter higher than those of the paraffins (about 300° for pentane and hexane). The mixture strength, if above 10%, had no effect on the T.I.C. of benzene or alcohol, but the values for pentane and hexane passed through minima. The T.I.C. of detonating fuels, such as the paraffins or ether, are much lower than the recorded values of their ignition temperatures. The temperatures reached in the cylinder during compression are sufficiently high to initiate oxidation of the detonating fuels, but not to produce any appreciable action with other fuels. Increasing the engine speed diminishes the time available for such chemical changes to occur, and a corresponding variation of the highest useful compression ratio (H.U.C.R.) with speed is observed. The addition of small quantities of anti-detonating substances to detonating fuels raises the T.I.C. (as determined in the heated tube) sufficiently to prevent initial oxidation in the cylinder during compression; thus 1% of iron carbonyl raised the T.I.C. of undecane by 150°. The products of the initial combustion of hexane are principally aldehydes, with smaller quantities of carbon dioxide, water, carbon monoxide, ethylene, and other unsaturated substances etc. Addition of lead tetraethyl, iron carbonyl, or nickel carbonyl reduces very considerably the amount of oxidation, and entirely inhibits the formation of unsaturated substances. Some metallic surfaces, *e.g.*, iron, copper, lead, and, in particular, platinum black, lower the T.I.C. and diminish aldehyde formation; others, *e.g.*, tin, nickel, zinc, produce little effect. Alcohols are much less readily oxidised than the paraffins, and addition of dopes increases the amount of oxidation. The aldehydes which appear as oxidation products of the paraffins are not therefore produced by the intermediate formation of alcohols. Moreover, the formation of aldehydes cannot be regarded as a primary cause of detonation, direct addition of aldehydes in fact making possible a small increase in the H.U.C.R. Examination of the products of initial oxidation of the paraffins does not support the theory of the intermediate formation of hydroxyl compounds, but indicates that the first products of oxidation are peroxides. Peroxide formation occurs in the oxidation of ethers and paraffins, but not with alcohols, benzene, or phenols. Addition of dope completely inhibits peroxide formation. Small additions

of organic peroxides to fuels have a marked effect in promoting detonation. It is concluded that detonation is due to the accumulation of peroxides in the nuclear drops during rapid compression. The amount of peroxide is not sufficient in itself to cause the detonation observed, but acts as a primer, causing simultaneous ignition of the drops. The metallic dopes act by reducing the peroxides as fast as they are formed, and thus delay the ignition of the drops. A. B. Manning.

Patents.

Manufacture of gas. H. Nielsen and B. Laing (E.P. 262,834, 20.6.25).—Semi-coke produced by the low-temperature distillation of coals in a hot, gaseous heating medium is very reactive towards carbon dioxide, and can be utilised in a pulverulent form to reduce the carbon dioxide of industrial heating gases to carbon monoxide, thereby producing higher-grade gas of lower sp. gr. A combined plant for the process is described. The gases containing carbon dioxide from the distillation retort are stripped of tar and oils and preheated at 750—800° in one of two chequered chambers, the other meanwhile being raised to the desired temperature by the combustion of solid or gaseous fuel. The hot gases from the preheater are brought into contact with the semi-coke, which may be heated externally as well as by the hot gases, the carbon dioxide being thereby reduced. The resulting hot gases may be utilised for the internal heating of the low-temperature distillation retort. If gas of still higher calorific value is required, part of the distillation products may be led direct from the retort to the preheating chequers prior to the reduction of its carbon dioxide content, and the tar oils contained therein cracked. S. Pexton.

Purifying [coal] gases. J. B. Garner, R. W. Miller, and G. A. Shaner, Assrs. to Standard Development Co. (U.S.P. 1,609,872, 7.12.26. Appl., 30.12.22).—Coal or like gas containing sulphur and cyanogen compounds, and other impurities, is washed with dilute (1—7%) sodium hydroxide solution, containing 0·5—4% of oleic acid, or a soluble soap, or other soluble substance, which increases the tendency to film formation, and hence the interaction of the gas and liquid. The liquid is revivified by treatment with ferric oxide, which is regenerated by exposure to air. Alternatively, ferric, copper, or nickel sulphate (1—10%), or one of the corresponding hydroxides, is added initially to the alkaline film-forming liquor, which is then regenerated, when necessary, by aeration. T. S. Wheeler.

Continuous operation of retorts for the production of gas and coke. Stettiner Chamotte-Fabr. A.-G. vorm. Didier (G.P. 434,086, 27.3.24).—A part of the coal is preheated to a temperature just above the softening point before being fed into the retort. "Hanging" of the charge in the retort is thereby avoided. A. B. Manning.

Cracking coal, oils, and other hydrocarbons. Internat. Bergin-Comp. voor Olie- en Kolen-Chemie, Assees. of A. Debo (Can. P. 258,201, 15.5.25).—The starting material is introduced, in the form of a paste, by means of a screw conveyor, into a high-pressure container, in which it is heated in the presence of hydrogen, the products of the reaction being withdrawn from the container in such a way as to maintain a constant level therein. A. B. Manning.

Cracking of [hydrocarbon] oils. F. E. Wellman, Assr. to Kansas City Gasoline Co. (U.S.P. 1,615,779, 25.1.27. Appl., 10.7.22).—The oil is contained in several small stills connected together; these are externally heated intermittently in periodic rotation, the resulting vapours being drawn off into a central vessel, while a common liquid level with a comparatively large surface is maintained in the small stills to prevent foaming. W. N. Hoyte.

Production of hydrocarbons resembling natural petroleum. L. Paris-Durcy (F.P. 607,688, 23.3.25).—Bituminous coal, lignite, tar, heavy oils, or vegetable or animal oils are hydrogenated by heating with hydrogen or other hydrogenating gas to pressures between 200 and 800 kg. A. B. Manning.

[Hydrocarbon] vapour recovery. C. L. Voress and N. C. Turner, Assrs. to Gasoline Recovery Corp. (U.S.P. 1,616,242, 1.2.27. Appl., 14.6.26).—The gaseous mixture of hydrocarbons is treated by contact with a solid adsorbent for an insufficient time to let the selective action of the adsorbent displace a large proportion of the more volatile vapours with less volatile vapours. A substantial part of the vapours is volatilised from this adsorbent, cooled, and passed through a second adsorbent in which the full selective action is permitted. A substantial part of the adsorbed vapours from this second adsorber is volatilised and condensed. W. N. Hoyte.

Refining of [hydrocarbon] oils. E. B. Cobb, Assr. to Standard Development Co. (U.S.P. 1,616,352—3, 1.2.27. Appl., [A] 8.4.22, [B] 24.2.26).—(A) Sulphocompounds, which induce emulsification and are present in oils treated with sulphuric acid, are destroyed by maintaining the oils at 180—260° until such compounds are decomposed. (B) Heavy distillates are treated with large amounts of fuming sulphuric acid, and the oil is neutralised and distilled by direct heat and by steam to a 5—10% residue. The distillate is re-treated with a less proportion of acid, and the resulting oil maintained at 180—260° while steam is passed through until it becomes neutral and will not tarnish copper. It is finally filtered. W. N. Hoyte.

Separation of [liquid] hydrocarbons from mineral matter. M. Mallet (F.P. 607,269, 12.3.25).—Mineral matter containing oil is ground under water and a part of the oil is separated. The material then undergoes further mechanical treatment, during which the oil collects in drops on the surface of the water while the mineral matter sinks to the bottom. A. B. Manning.

Continuous distillation of oil. F. A. Howard and N. E. Loomis, Assrs. to Standard Development Co. (U.S.P. 1,613,754, 11.1.27. Appl., 15.6.22).—The oil is passed through a battery of stills heated externally; the vapours evolved from each still are passed through heat exchangers immersed in the preceding still; the vapours from each still are mixed with those from the succeeding still entering the heat exchanger. W. N. Hoyte.

Distillation of oil. C. W. Stratford (U.S.P. 1,613,298, 4.1.27. Appl., 19.8.25).—The oil is contained in a still heated externally at the required temperature; a quantity is continuously drawn off at the bottom and returned to the still under pressure, being discharged through a large number of small nozzles so that the streams impinge on the heated sides of the still. W. N. Hoyte.

Distillation of oil. J. Primrose, Assr. to Power Specialty Co. (U.S.P. 1,614,689, 18.1.27. Appl., 7.4.21).—The vapours evolved from a conventional still are passed through a series of air-cooled condensers, the resulting condensates are separately collected, and the hot air from the condensers is passed to the still furnace. W. N. Hoyte.

Cracking of oils. H. H. Armstrong (U.S.P. 1,613,010, 4.1.27. Appl., 9.7.23).—The oil to be cracked is heated almost to cracking temperature and passed as a fine spray into the reaction chamber; a light hydrocarbon is also heated to cracking temperature, and is expanded into the atomised heavy oil so as to maintain the reaction chamber at the desired temperature. W. N. Hoyte.

Cracking of oils. C. Owens (U.S.P. 1,613,124, 4.1.27. Appl., 28.5.21. Renewed 1.4.26).—The cracking stock is vaporised by a current of steam drawn through the oil; the mixture of steam and oil vapours is passed through a heating zone, and the products are subsequently condensed, the whole process being operated at atmospheric pressure. W. N. Hoyte.

Cracking of hydrocarbon oils. C. L. Parmelee, Assr. to Sinclair Refining Co. (U.S.P. 1,613,718, 11.1.27. Appl., 8.10.24).—The oil is heated to cracking temperature in a tube still, thence it passes to a separating chamber in which carbon and tarry matter are drawn off; the clarified liquid passes to the supply chamber which acts as a heat exchanger with the separating chamber. Vapours from both the chambers pass up a dephlegmator, and thence to a condenser. The run-back from the dephlegmator together with fresh cracking stock is returned to the supply chamber, whence the oil is pumped to the cracking still. W. N. Hoyte.

Cracking [hydrocarbon] oils. O. P. Amend (U.S.P. 1,613,735, 11.1.27. Appl., 3.3.22).—The oil contained in a still is heated to cracking temperature by electric heating elements immersed in it. A minimum pressure of 75 lb. is maintained on the still. W. N. Hoyte.

Cracking of hydrocarbons. A. J. Paris, jun. (U.S.P. 1,614,930, 18.1.27. Appl., 14.5.24).—The oil is distilled and the distillate is heated to cracking temperature under pressure, the boiling range of the fraction so treated being limited to less than 50°. W. N. Hoyte.

Process of cracking or treating oils and other similar hydrocarbons. H. T. Darlington and R. M. Steffen, Assrs. to M. B. Schuster (U.S.P. 1,614,660, 18.1.27. Appl., 2.6.23).—Hydrocarbons under conditions of temperature and pressure conducive to cracking are treated with a gel composed of bentonite and water. M. E. Nottage.

Production of liquid resembling petroleum. P. J. H. Baurier (F.P. 606,900, 25.2.25).—Tar, oil, or gases obtained by the distillation of carbonaceous material are treated with steam at 300—450° in the presence of metals capable of decomposing the steam. L. A. Coles.

Producing natural gas gasoline. F. E. Hosmer (U.S.P. 1,613,108, 4.1.27. Appl., 16.7.26).—The natural gas is compressed and cooled by spraying with a cooling medium which is chilled by cold gas obtained on releasing the pressure on the gas at a later stage in the plant. W. N. Hoyte.

Motor fuel. C. F. Kettering and T. Midgley, jun., Assrs. to General Motors Corp. (U.S.P. 1,605,663—4, 2.11.26. Appl., [A], 15.4.22. Conv., 7.5.19. [B], 3.5.24).—The fuel comprises a low-compression motor fuel and a compound (A) in which at least one univalent hydrocarbon radical, or (B) having more than one aromatic closed chain and in which at least one aromatic hydrocarbon radical is substituted for a hydrogen atom of ammonia. H. Moore.

Flash-point tester for oils and fuels. H. Jentzsch (G.P. 433,432, 12.2.25).—An ignition block which can be heated in a furnace has a receptacle in which are a number of borings for holding the substance to be investigated, and is provided also with a multiple-flame burner for igniting the substance. The results, which are much more accurate than those obtained with the known open crucible type of apparatus, agree with those given by a closed apparatus. A. B. Manning.

Motor-fuel-testing composition. V. Serravaoll and E. Weis (U.S.P. 1,615,143, 18.1.27. Appl., 16.8.23. Conv., 21.12.22).—The testing fluid consists of a mixture of phenol and amyl acetate, containing two differently-coloured dyes, only one of which is soluble in petrol, tetralin, and benzine. The colours of the layers formed when the fuel under test is mixed with the liquid give an indication of the composition of the fuel, as regards alcohol and benzene on the one hand, and petrol, tetralin, and benzine on the other. T. S. Wheeler.

Hydrocarbon fuel. Combustible fuel [for internal-combustion engines]. L. Kirschbraun (U.S.P. 1,614,559—60, 18.1.27. Appl., [A] 1.4.20, [B] 16.8.20. Renewed [A] 8.6.25, [B] 9.7.26).—(A) Naphthenic acid or a naphthenesulphonic acid (1 pt.) is dissolved in petrol (100 pts.), the mixture is heated above 100° under pressure, dry steam (10 pts.) is passed into it, and the whole is homogenised and cooled. The product is a stable emulsion. (B) Petrol (50 pts.), the sulphonic acid from the acid sludge obtained in oil-refining (50 pts.), and water (20 pts.) are mixed with petrol to give a product containing 0·5% of sulphonic acid, 6% of water, and the remainder petroleum. Both products are non-carbonising. T. S. Wheeler.

Motor spirit. J. Luciani (F.P. 608,186, 28.8.25).—Various alcohols, nitroglycerin, tetranitrotoluene, or a mixture of these is added to benzene or its derivatives. A. B. Manning.

IV.—DYESTUFFS AND INTERMEDIATES.

Patents.

Vat dyes. I. G. Farbenind. A.-G., Assees. of G. Kränzlein, H. Greune, and R. Sedlmayr (G.P. 430,558, 21.8.24; Addn. to 412,053).—Benzanthrone or one of its

derivatives containing at least one free *peri*-position is condensed with aromatic *o*-dicarboxylic anhydrides in the presence of aluminium chloride or other condensing agent. The dye from benzanthrone and phthalic anhydride dyes cotton yellow from the hyposulphite vat; similar products are obtained from α-hydroxybenzanthrone with phthalic anhydride, and from β-methylbenzanthrone with 3 : 6-dichlorophthalic anhydride. C. Hollins.

Benzanthrone derivatives. I. G. Farbenind. A.-G., Assees. of H. Neresheimer (G.P. 431,744, 17.8.22).—Benzanthrones having a free 2-position are treated with acid oxidising agents. Benzanthrone is converted by chromic and sulphuric acids into a *sulphate*, which, by boiling with water, gives an oxidation *product*, convertible by sulphonation into a yellow wool *dye*. Chlorobenzanthronecarboxylic acid gives with sulphuric acid and manganese dioxide an oxidation *product*, which may be purified by treatment with sodium hypochlorite and precipitation with acids. C. Hollins.

***iso*Dibenzanthrone.** I. G. Farbenind. A.-G., Assees. of H. Neresheimer (G.P. 431,775, 26.10.24).—3-Chlorobenzanthrone, when treated with alkaline hydroxides and alkoxides in an indifferent diluent, *e.g.*, with potassium hydroxide, *iso*propyl alcohol, and benzene at 10—15°, yields pure *iso*dibenzanthrone. C. Hollins.

[*Bz*-2^1-]Hydroxybenzanthrones. K. Schirmacher, K. Zahn, K. Wilke, and P. Ochwat, Assrs. to Grasselli Dyestuff Corp. (U.S.P. 1,614,398, 11.1.27. Appl., 28.4.24. Conv., 25.6.23; cf. E.P. 218,255 and 224,522; B., 1925, 538,583).—*Bz*-1^1-Nitrobenzanthrone is reduced to the amino-compound, which is acetylated with acetyl chloride, and treated with concentrated nitric acid at 50°, when nitration occurs in the *Bz*-2^1-position. The nitroamino-compound, obtained by hydrolysis on treatment with nitrosylsulphuric acid gives a diazohydroxy-anhydride, the nitro-group being eliminated as nitrous acid, which, on treatment with stannous chloride in alkaline solution gives Bz-2^1-*hydroxybenzanthrone*, m.p. above 280°; Bz-2^1-*acetoxybenzanthrone* has m.p. 201°. Bz-2^1-*Methoxybenzanthrone*, m.p. 171—173°, on heating with alcoholic potassium hydroxide solution gives a *dye* which yields fast bluish-green shades on cotton in a hyposulphite vat. Bz-2^1-*Ethoxybenzanthrone* has m.p. 169—170°. These compounds can also be obtained by heating *o*-alkoxyphenyl α-naphthyl ketones with aluminium chloride. T. S. Wheeler.

Manufacture of polynitroamines. W. H. Bentley, and W. Blyth & Co., Ltd. (E.P. 263,552, 2.10.25).—Halogen atoms in aromatic polynitrohalogen compounds are replaced by amino-groups by heating the halogen compounds with carbamide (or with an organic substance which produces carbamide or is produced from it during the reaction, *e.g.*, biuret, cyanuric acid, or ammonium cyanate), in an open vessel, at 130—150°, preferably with agitation, if necessary in the presence of an inert solvent. Examples are given of the preparation, using carbamide, of 2 : 4-dinitroaniline from 1-chloro-2 : 4-dinitrobenzene; 4-chloro-2 : 6-dinitroaniline from 1 : 4-dichloro-2 : 6-dinitrobenzene; and 2 : 4 : 5 : 7-tetranitro-α-naphthylamine from 1-bromo-2 : 4 : 5 : 7-tetranitronaphthalene. B. Fullman.

Manufacture of water-insoluble azo dyes. Farbenfabr. vorm. F. Bayer & Co. (F.P. 604,443, 12.10.25).—The diazo compounds of dyes obtained by coupling diazotised unsulphonated amines with sulphamic acids of aromatic amines are coupled in substance or on the fibre with second components containing no sulpho- or carboxyl groups, such as β-naphthol, arylides of 2 : 3-hydroxynaphthoic acid, or acetoacetic acid, pyrazolones, etc. Thus, by coupling diazotised *o*-anisidine in alkaline solution with α-naphthylsulphamic acid, diazotising the product, and immersing in the clear diazo solution a fabric padded with 2 : 3-hydroxynaphthoic-β-naphthylamide, black shades are obtained. Using in place of the last-named substance 1-phenyl-3-methyl-5-pyrazolone scarlet shades are formed, and with α-naphthol-4-carboxylic acid black shades. A. Davidson.

Manufacture of azo dyes. Chem. Fabr. Griesheim-Elektron (F.P. 601,709, 6.8.25. Conv., 16.8.24).—Sulphonated or unsulphonated diazo, tetrazo, or diazoazo compounds are coupled with arylides of 2-naphthol-6-carboxylic acid. The dyes can be formed on the fibre, whilst those prepared in substance can be used as wool dyes or for the preparation of lakes etc. From diazotised 4-chloro-2-nitroaniline and the anilide of 2-naphthol-6-carboxylic acid a light-fast, orange-red lake is obtained. Cotton padded with bis-2 : 6-hydroxynaphthoic-1 : 6-naphthylenediamide and developed with diazotised 2 : 5-dichloroaniline yields fast brown shades. The azo dye from diazotised aniline-2 : 4-disulphonic acid and bis-2 : 6-hydroxynaphthoic dianisidide dyes wool fast orange shades. A. Davidson.

Preparation of halogenated naphthasultones. I. G. Farbenind. A.-G., Assees. of K. Schirmacher and W. Langbein (G.P. 433,527, 5.8.24).—α-Naphthol-4 : 8- or -6 : 8-disulphonic acid is heated in presence of water with halogens or halogenating agents. No naphthaquinones are formed, and the products, which are used as dyestuff intermediates, are converted by alkalis into halogenated naphtholsulphonic acids. *E.g.*, an aqueous solution of the sodium salt of α-naphthol-4 : 8-disulphonic acid is treated with hydrochloric acid and the mixture saturated with chlorine at about 30°; more chlorine is introduced, and the mixture heated at 80° for 30 min. On cooling, 4-*chloro*-1 : 8-*naphthasultone*, m.p. 176—178°, crystallises. 4-*Bromo*-1 : 8-*naphthasultone*, m.p. 196—198°, and *sodium* 4-*chloro*-1 : 8-*naphthasultone*-6-*sulphonic acid* are described. E. H. Sharples.

Azo dyes. I. G. Farbenind. A.-G., Assees. of L. Laska and A. Zitscher (G.P. 430,580, 4.10.24).—Azo dyes, suitable especially as ice-colours, are made by coupling amino-*N*-arylbenz- or-naphtha-triazoles with arylamides of 2 : 3-hydroxynaphthoic acid. 2-o-, 2-m-, and 2-p-*Aminophenyl*-1 : 2-*naphthatriazoles* melt at 120°, 160°, and 203—205°, respectively; 2-(3-*amino*-4-*methylphenyl*)-1 : 2-*naphthatriazole* at 172—173°; 2-(3-*amino*-4-*methoxyphenyl*)-1 : 2-*naphthatriazole* at 185°; 2-(2-*amino*-4-*methylphenyl*)-1 : 2-*naphthatriazole* at 137°; and 2-(4-*chloro*-2-*aminophenyl*)-1 : 2-*naphthatriazole* at 192°. The dyeings are fast to bowking. C. Hollins.

Preparation of mercaptans of the naphthalene series. I. G. Farbenind. A.-G., Assees. of J. Haller

(G.P. 433,103, 24.2.25).—Diazo compounds of naphthylaminesulphonic acids by treatment with alkali sulphides or xanthates are converted into dinaphthyldisulphidedisulphonic acids which are reduced to mercaptans, the sulpho-group being removed either during or before the reduction. E. H. Sharples.

Preparation of 6-chloro-2-nitrotoluene-4-sulphonic acid and 6-chloro-o-toluidine-4-sulphonic acid. I. G. Farbenind. A.-G., Assees. of F. Henle and B. Vossen (G.P. 434,402, 2.9.24).—(1) 6-Chloro-2-nitrotoluene is sulphonated with fuming sulphuric acid; the sulphonic acid is separated as the sodium salt by treatment with sodium chloride and reduced to 6-chloro-*o*-toluidine-4-sulphonic acid. (2) The technical mixture of 6-chloro-*o*-toluidine and 4-chloro-2-nitrotoluene is sulphonated. (3) The unchanged 4-chloro-2-nitrotoluene is separated by the addition of weak sodium chloride solution in which the 6-chloro-derivative is soluble, and then the latter is salted out as its sodium salt by the addition of more sodium chloride. The oxidation of 6-chloro-2-nitrotoluene-4-sulphonic acid to 6-chloro-2-nitro-4-sulphobenzene-1-carboxylic acid and the preparation from the latter of the amino-derivative are described. E. H. Sharples.

V.—FIBRES; TEXTILES; CELLULOSE; PAPER.

Determination of isoelectric points of wool and silk fibroïn. L. Meunier and G. Rey (Compt. rend., 1927, **184**, 285—287).—Curves relating the percentage swelling with the p_H value of the solution in which this occurs have been constructed for wool and silk fibroïn. The degree of swelling was found by deducting the weight of the dry threads from that of the centrifuged swollen threads. Minimum values of the swelling are found for p_H values of 3·6—3·8 and 4·2 in the case of wool and silk fibroïn, respectively, the former being the more pronounced. This indicates that wool is more amphoteric in nature than silk, since the swelling of proteins is due to the formation of ionisable salts with acids and bases. This is confirmed by determinations of the amino-nitrogen by Van Slyke's method, mean values of 0·2% and 0·07% being found in wool and silk, respectively. Shrinkage is a minimum in solutions, the p_H value of which corresponds to the isoelectric point of the protein.
J. Grant.

Methods of studying cord tyre fabric. F. W. Stavely and N. A. Shepard (Ind. Eng. Chem., 1927, **19**, 296—301).—Fatigue in tyre cords is measured by hysteresis loss and flexing life, the former showing that the properties of the original cord are not maintained, and the latter being of value in determining the desirability of changes in cord construction. When well impregnated with rubber cements containing vulcanisers etc. (the solvents of which should readily wet the fibre) each strand of a cord is completely covered with rubber, and the flexing life is improved. Increased flexing life usually corresponds with increased mileage. The effect of factors such as humidity, temperature, and wax content in the testing of raw cords is emphasised. The removal of the acetone- and benzene-soluble constituents of the cotton cord lowered the flexing life by about 30%.
C. O Harvey.

Testing sulphite liquor. E. Schmidt (Zellstoff u. Papier, 1927, **7**, 56—57).—The determination of free sulphurous acid in sulphite cooking liquor by the potassium iodate method is not more accurate than by titration with sodium hydroxide and phenolphthalein. The latter method breaks down owing to the sensitiveness of the indicator to carbon dioxide and organic acids, but the former also measures the total acidity (due to sulphurous acid, carbon dioxide, and organic acids). The effect of traces of either carbon dioxide or organic acid added to potassium iodate–iodide solution is to cause liberation of iodine. Excess of water partially reverses the above reaction, as shown by experiments in which various quantities of water free from carbon dioxide were added to solutions of potassium iodate and iodide acidified with equal volumes of standard acid, and the mixtures titrated with sodium thiosulphate solution, the required volume of the latter diminishing as the quantity of added water increased. B. P. Ridge.

Recovery of condensed water in cellulose factories. R. Escourrou (Chim. et Ind., 1927, **17**, 21—24).—By condensing the steam from the heating tubes at just below the b.p. and using this water for further steam raising, a great economy in fuel is effected, but it is essential to ensure that there is no contamination by acid leaking into the heating tubes. For this purpose two electrodes, immersed in the stream of condensing water, are connected through an electric lamp, relay, and bell to a source of electric supply. When the condensed water is pure no current flows through the circuit, but the presence of acid increases its conductivity and causes the lamp and bell to function
F. R. Ennos.

Chlorine gas process in the paper industry. G. Consiglio (Papier-Fabr., 1926, **24**, 785—789).—Particulars are given of a factory at Naples where cellulose is prepared from esparto, straw, and hemp by the chlorine gas process operated in conjunction with an electrolytic caustic soda plant. The grass is first softened by treatment in open boilers with a 1—2% solution of caustic soda at 70—80°. The alkali solution is used repeatedly, being made up in strength and volume by the addition of fresh liquor. Soda solution and wash waters are circulated by pumps, the steeped grass being washed in the boilers. After washing, the grass is transported to the chlorinating chambers of concrete. The chlorinated material is first washed with water and then extracted with cold caustic soda solution. The other processes are as usual. The consumption of chemicals per ton of bleached esparto cellulose is caustic soda 160—180 kg., chlorine gas 400 kg., chlorine in the form of bleach liquor 20 kg. The process suitably modified has also been applied experimentally to the manufacture of cellulose from bagasse and from pine wood. J. F. Briggs.

VI.—BLEACHING; DYEING; PRINTING; FINISHING.

Patents.

Ice-colour process. I. G. Farbenind. A.-G., Assees. of W. Christ (G.P. 433,149, 2.12.24).—Improved fastness to rubbing is obtained in ice-colours by treating the impregnated material, with or without previous centrifuging, pressing, or draining, with a weaker impregnating

solution to which sodium hydroxide and an electrolyte have been added, or with a solution of an electrolyte containing a little sodium hydroxide, or with dilute sodium hydroxide solution alone, in all cases with or without the addition of formaldehyde. The process is applicable to ice-colours made from 2 : 3-hydroxynaphthoyl- or acetoacetyl-derivatives of arylamines and arylenediamines. C. Hollins.

Preparation of colour reserves with vat dyes under vat dyes. A. Lauterbach, and Gebr. Enderlin Druckfabr. u. Mech. Weberei A.-G. (Austr. P. 103,911, 10.6.25).—To the previously prepared goods one or more vat dyes are applied with neutral metallic compounds as reserves, and dyed, it may be after steaming, in a dye bath of a vat dye, when simultaneously the reserving of the dye by the dye bath takes place. The dye to be reserved can also be applied by cover-printing or padding, and then after-treated with an alkaline solution containing, if necessary, a reducing agent. As reserves, there may be used substances of alkaline reaction or reducing agents or both. A fabric is printed with a colour reserve of lead acetate, potassium carbonate, gum senegal, kaolin, and Indanthrene Yellow G, dried, and then dyed, without steaming, by a hyposulphite vat of Indanthrene Blue RS. It is then washed, soured, washed, and soaped at the boil, a yellow under blue being obtained. A. Davidson.

Developing salts [in dyeing]. I. G. Farbenind. A.-G. Assees of H. Krzikalla (G.P. 433,150—1, [A] 12.4.25, [B] 29.4.25. Addns. to 421,837; B., 1926, 318).—In the preparation of anhydrous mixtures containing a nitrite and the mineral acid salts of aromatic amines capable of yielding a diazo solution when dissolved in water as claimed in the chief patent, the mineral acid salts are replaced by (A) *N*-sulphonic acid derivatives of diazotisable amines or (B) salts other than mineral acid salts of diazotisable amines; *e.g.*, a satisfactory developing mixture comprises (A) Glauber's salt, sodium bisulphate, sodium nitrite, and the sodium salt of a naphthalenesulphoamino-compound, or (B) acid aniline oxalate (or aniline salts of phthalic or aromatic sulphonic acids, *e.g.*, benzenesulphonic acid), Glauber's salts, oxalic acid, and sodium nitrite. A. J. Hall.

Dyeing and printing cellulose esters. I. G. Farbenind. A.-G., Assees. of R. Metzger and C. Schuster (G.P. 433,349, 11.10.24).—Cellulose acetate etc. is dyed with azo dyes derived from aminoaldehydes. *p*-Aminobenzaldehyde, diazotised and coupled with salicylic acid, gives a yellow; with 1 : 7-aminonaphthol, maroon; with β-naphthol, subsequently treated on the fibre with phenylhydrazine, brown. *m*-Aminobenzaldehyde, diazotised and coupled with dimethylaniline gives a golden-orange; with diphenylamine a golden-yellow. C. Hollins.

X.—METALS; METALLURGY, INCLUDING ELECTRO-METALLURGY.

Macroscopical determination of carbon in Martin steel test pieces. M. Hamasumi (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 819—828).—In the acid process the final decarburisation is so slow that samples may be withdrawn and analysed chemically, but in the basic process a quick macroscopic method is essential. Specimens of typical steels with carbon contents from 0·1 to 0·9% were quenched from 850° and 900° and the hardness was measured with a Rockwell testing machine and plotted graphically against the composition. The angles through which the specimens could be bent without fracture were also measured, and the etching effects with picric acid are illustrated, and also the different types of fracture. All the above properties are suited for the approximate determination of carbon, but the accuracy from 0—0·3% carbon is much greater than that above 0·3%. The macrostructures are also illustrated, and the effects discussed from the point of view of the equilibrium diagram. W. Hume-Rothery.

Hardness of different structures in steel. K. Tamaru (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 829—850).—The hardness of the different constituents has been measured for both plain carbon and manganese steels. A carbon steel containing 1·69% C was heat-treated and quenched so as to give structures containing varying amounts of austenite and martensite, the hardness of which was found to be 155 and 720 respectively (Brinell scale), assuming that the hardness varies linearly with the proportion of the constituents. The impact hardness of 0·6% and 0·8% carbon steels was measured between 0° and 900°; both show slight minima at 400—500°, and maxima at 600°, above which the hardness falls rapidly. The hardness of the austenite in manganese steels diminishes as the carbon content increases from 0·1—0·6%, and also diminishes with increasing manganese content, but from 0·6—0·9% C the hardness (182) is independent both of carbon and manganese contents. These steels contained 12—20% Mn, and a little martensite may have been present; they were also examined at high temperatures and showed complex results. In martensite produced by the ordinary quenching of carbon steels the hardness shows a maximum at about 0·8% C, but such specimens always contain some γ-iron. The hardness of a quenched 0·89% carbon steel is increased by tempering at 112°, but higher temperatures cause a decrease. The natural hardness of cementite is about 620, but in cast specimens it may be as high as 820 owing to strain. W. Hume-Rothery.

Change in hardness and density of iron and steel on cold-working. T. Ishigaki (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 777—794).—The hardness and density of Armco iron and of steels of varying carbon content have been measured after various kinds of deformation. In specimens broken under tension, the hardness at different points along the test piece increases as the fracture is approached. In hammered specimens, no further increase in hardness occurs after the thickness has been reduced by 50%. Hydrostatic pressure causes a comparatively slight but quite definite increase in hardness. On tempering deformed specimens of Armco iron, the hardness increases up to 250°, then decreases until 470°, when a second slight hardening occurs between 470° and 560°, above which the material rapidly softens. Steels show a similar increase in hardness up to 300—400°. The decrease in density of specimens after deformation

has been measured. The densities of specimens which had been compressed in steel moulds were slightly less than those of the originals, but the pressure-density curves were complex. The magnetic changes produced on heating deformed specimens were studied, and the results are discussed theoretically.

W. Hume-Rothery.

Solubility of carbon in pure iron. Y. Yamada (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 851—855).—The electrical conductivities of specimens of iron containing 0·010—0·089% C have been measured; the impurities present were 0·008% S, 0·002% Si, and a trace of manganese. The continuous nature of the composition-conductivity curves indicates that the solubility of carbon in pure α-iron is less than 0·01%, and this is confirmed by micro-examination.

W. Hume-Rothery.

Dilatometric and magnetic researches on pure iron and on iron-carbon alloys. H. Esser (Stahl u. Eisen, 1927, **47**, 337—344).—From a review of the work of previous investigators, and from the fact that only a very slight change of volume takes place at the A2 point of iron, the author concludes that the A2 change in iron is not a true allotropic modification, and that β-iron is really only a special condition of α-iron over a certain temperature range associated with a change in magnetic properties. The peculiar hook-shaped deviation obtained at the Ar1 point in the temperature–differential expansion curve of steels also occurs in that of pure electrolytic iron, and cannot, therefore, be caused by a retardation of the pearlite separation, but is probably due to temperature differences between the test and standard bars. Dilatometric analysis of pure iron that has been de-gassed by repeated heating at 700—800° *in vacuo* places the Ar3 point at 898° and the Ac3 at 904°; the Ac1 point is detectable only when at least 0·06% C is present in a steel, and the Ar1 when there is 0·20% C. With 0·86% C both the A1 and A3 points coincide, the Ar points at 708°, and the Ac points at 736°. The line joining the Ac1 points of iron-carbon alloys containing up to 0·86% C is horizontal at 736°, whereas that joining the Ar1 points rises in a smooth curve from 685° with 0·1% C to 708° with 0·86% C. The Ar3 and Ac3 lines fall steeply in smooth curves to join the A1 lines at the eutectoid point. Magnetic tests on a hypereutectoid steel (1·2% C) showed that the ratio, length/diameter, of the test piece had an appreciable effect on the cementite transformation at 180—200°.

A. R. Powell.

Rational use of case-hardening compounds. Systematic case-hardening tests. J. Hébert (Techn. moderne, 1926, **18**, 481—491, 525—532; Chem. Abstr., 1926, **20**, 3428).—The case-hardening effect of wood charcoal alone increases with the temperature; the rate of variation in the carbon content from the surface inwards decreases with increase of time, and increases with fall of case-hardening temperature. Penetration of 1·40 mm. is effected at 950° in 3 hrs. Addition of sodium chloride, sodium carbonate, ammonium chloride (10%), pulverised bone, or bone-black retards, and that of potassium ferrocyanide (10%), rosin, barium carbonate, carbonised leather, or sodium hydrogen carbonate accelerates the action, the character of the effects being described. With 20% instead of 10%, sodium chloride and potassium ferrocyanide increased the depth of penetration; carbonised leather, pulverised bone, and bone-black increased the outer eutectic or hypereutectic layer; rosin, barium carbonate, and ammonium chloride reduced both the total depth of penetration and the outer zone of maximum carburisation. The formation of an outer hypereutectic zone can be prevented by carrying out the treatment in two stages: (*a*) at 900—950° until the depth of penetration is 50—75% of that required, and (*b*) at 760—780°. It is important to obtain a sufficiently thick outer eutectic zone, and an inner, transition, hypoeutectic zone thick enough to reduce to a minimum the danger of fissuring on quenching.

A. A. Eldridge.

Cementation of iron, nickel, and cobalt by means of boron. Feszczenko-Czopowse (Trav. ac. mines Cracovie, 1925, [5]; Chem. Abstr., 1926, **20**, 3429).—Tests were carried out on "normal" mild steel (0·075% C), "abnormal" mild steel (0·115% C, 0·197% O), hypoeutectic steel (0·4% C), hypereutectic steel (0·95% C), nickel, cobalt, nickel steel (5 and 25% Ni), and nickel–chromium steels (0·5% Cr, 2·5% Ni; 1·12% Cr, 4·2% Ni). In gases containing carbon, cementation by carbon and by boron takes place simultaneously; boronisation is successful in hydrogen or *in vacuo*. The boronisation of iron and steel progresses very irregularly. At high temperatures the superficial layer cemented by boron is a solid solution of boron and carbon in γ-iron; on cooling, the alloy assumes a eutectoid structure. The rate of diffusion of boron in iron and steel rapidly increases with the temperature, but the layer so obtained is porous, and may be removed by slight mechanical effort. Iron is deoxidised by boron. The mechanism of the diffusion of boron in iron is considered. Boronisation of nickel takes place more readily than that of iron. Giebenhausen's diagram should include the solid solution of boron in α-nickel. Boron also gives a crystalline solid solution in α-cobalt. With greater boronisation of nickel a new, easily-fusible eutectic is formed. The rate of boronisation of cobalt is intermediate between those of iron and nickel. Nickel steels and nickel–chromium steels are more rapidly cemented with boron than mild steels, and the latter more rapidly than steels of higher carbon content.

A. A. Eldridge.

Reduction of iron ores by hydrogen. I. G. Gallo (Annali Chim. Appl., 1927, **17**, 27—38).—The action of hydrogen on magnetite of the percentage composition, Fe_3O_4, 86·53; SiO_2, 4·12; MgO, 7·20; MnO, 0·32; Al_2O_3, 0·71; S, 0·008; CoO, 0·10; CaO, 0·86; P, 0·002, and on the same ore after torrefaction and conglomeration, when it contained 86·85% Fe_2O_3, is described. The apparatus used was free from rubber and ebonite joints, as these are attacked by the hydrogen at a comparatively low temperature, with liberation of hydrogen sulphide. Reduction of the natural magnetite by pure hydrogen begins at 180°, and that of the torrefied product at 220°, but as the temperature rises (to 550°) the action becomes more rapid with the latter than with the former. After the first point of arrest in the manometer used to follow the change—this point being different for the two materials—a second is observed at

340—360°, which apparently marks the commencement of the reduction of the ferrous oxide. If water vapour as well as hydrogen is present, initiation of the reduction is retarded and, for the torrefied material, occurs at about 280—290°. The second stage, the reduction of the ferrous oxide, is also retarded and begins at 370° (375—380°) if the partial pressure of the water vapour is 20 (92) mm.; the velocity of the reduction also is lowered considerably by the presence of water vapour.

T. H. Pope.

Behaviour of iron pyrites with hydrogen. II. G. Gallo (Annali Chim. Appl., 1927, **17**, 39—44).—The desulphuration of pyrites by means of hydrogen takes place in three successive stages: (1) $2FeS_2 + H_2 = Fe_2S_3 + H_2S$; (2) $Fe_2S_3 + H_2 = 2FeS + H_2S$; and (3) $FeS + H_2 = Fe + H_2S$, the temperatures at which these commence being respectively 228—230°, 280—285°, and 370—375°. The reaction may be arrested at the completion of phase (1) if the temperature is maintained for some time at 450°. But, although this and phase (2) may be completed in a short time, phase (3) requires longer for its completion, as well as a temperature appreciably higher than that at which it begins. This indicates that the heat of formation of ferrous sulphide from iron and sulphur differs widely from that of pyrites from ferrous sulphide and sulphur. The reversible reaction (3) is intensely endothermic, but if the temperature is raised gradually, the desulphuration of ferrous sulphide may be carried to completion. No sulphur compound analogous to Fe_3O_4 appears to exist.

T. H. Pope.

Anomalous internal friction of reversible ferro-nickels. P. Chevenard (Compt. rend., 1927, **184**, 378—380).—A three-dimensional diagram has been constructed to show the variation of the decrease in reversible ferro-nickels in iron–nickel alloys as a function of the temperature and of the nickel content. The decrease corresponds to the internal friction of the ferro-nickels. A marked anomaly in the decrease is shown up to 300° for alloys containing 30—60% Ni, a maximum being obtained for 38% Ni. The internal friction is sensitive to secondary influences, such as the state of oxidation, and the thermal and mechanical histories of the sample. In terms of the author's theory (A., 1921, ii, 484) of a progressive and reversible transformation of an α form stable at absolute zero to an isomorphic β form stable to heat, the α form possesses a greater internal friction than the β form. The reaction $\alpha \rightarrow \beta$ occurs in the neighbourhood of the alloy Fe_2Ni, accompanied by condensation and by an increase in the modulus of elasticity.

J. Grant.

Magnetic analysis as a means of studying the structure of non-magnetic alloys. K. Honda and H. Endo (Inst. Metals, March, 1927, advance copy, 21 pp. Cf. B., 1918, 586 A).—Magnetic analysis can be applied to the study of the structure of paramagnetic and diamagnetic elements and alloys in both the solid and the liquid phases. A detailed description of the apparatus used for measuring magnetic susceptibility is given. In the case of the elements, the magnetic susceptibility–temperature curves are continuous except during melting or allotropic transformation. With binary alloys forming an eutectic, the susceptibility–concentration curve is linear in the range of the eutectic mixture and bends generally in the region of solid solution; the solution of a small quantity of a feebly diamagnetic or paramagnetic element in a strongly diamagnetic element in the solid phase decreases the diamagnetic susceptibility of the latter to a marked degree. Where no eutectic is formed, and the two components form a continuous series of solid solutions with one another, and also in the liquid phase, where the structure is a true solution, the susceptibility–concentration curve is linear, or nearly so. The magnetic susceptibility of an intermetallic compound has a special characteristic value quite different from the susceptibilities of the components. Magnetic susceptibility measurements show that intermetallic compounds existing in the solid state up to the liquidus may also persist in the liquid phase, although in some cases the compounds are more or less dissociated; the degree of dissociation can be roughly determined. Magnetic analysis also gives satisfactory results for the solidus and solubility line of cementite in the iron–carbon system, which is difficult to determine by thermal analysis. M. E. Nottage.

Examination of a fifteenth-century "brass." J. N. Friend and W. E. Thorneycroft (Inst. Metals, March, 1927, advance copy, 2 pp.).—Fragments from an English ecclesiastical brass which was cast in 1453 have been found to contain 84·1% Cu, 8·2% Zn, 3·6% Sn, 2·6%Fe, and 1·2% Pb. Microscopical examination in the unetched state clearly reveals the presence of lead particles, and the etched structure shows the typical cored configuration of cast bronze. M. Cook.

Penetration of brass by tin and solder. Copper–tin equilibrium diagram. H. J. Miller (Inst. Metals, March, 1927, advance copy, 11 pp.).—The results of experiments upon the straining of brass test-pieces when surrounded by molten tin, lead, and lead–tin solder, show that the stress necessary to cause cracking and penetration is much greater than that leading to penetration by mercury. Penetration usually takes place between grain boundaries, and the phenomenon is associated with season-cracking. The cracking of brass and subsequent penetration by the solder is due primarily to the presence of stress, and no cases of cracking are noted in the absence of stress. Liability of brass to crack during tinning or soldering is overcome by low-temperature annealing to remove residual injurious stresses. Evidence obtained from annealing experiments and microscopic examination indicate that the eutectic at the tin end of the copper–tin series of alloys contains between 0·6 and 0·7% Cu, which figure is lower than that obtained by previous investigators. M. Cook.

Attack of molten metals on non-ferrous metals and alloys. H. J. Hartley (Inst. Metals, March, 1927, advance copy, 22 pp.).—Clean polished surfaces of brasses and bronze were exposed to the action of molten tin at 300°. With bronze (91% Cu) and α or β brass, there is no sign of selective attack at the grain boundaries. With $\alpha\beta$ and $\beta\gamma$ brasses, the phase of higher zinc content is the more resistant, but the $\beta\gamma$ brasses show signs of fairly deep penetration along the grain boundaries. Prolonged attack upon $\alpha\beta$ and $\beta\gamma$ brasses results in the formation of a brittle constituent contain-

ing approximately 43% Cu, 45% Zn, and 12% Sn, which, on the grounds of *X*-ray crystal analysis, is regarded as a solid solution of the two intermetallic compounds Cu_5Zn_8 and Cu_4Sn. Tensile tests were carried out on brass and copper wires immersed in molten tin, or solders containing tin, at 240°, the times required for fracture under different stresses being measured. Solution and penetration, by tin and solders, with resulting weakening effect, occur at stresses insufficient to produce a large plastic deformation. In all cases tin has a greater effect than have the solders, and of two solders, that with the higher tin content has the greater effect. The fractures were accompanied by the formation of cracks which were usually intercrystalline. Possible explanations are discussed.

W. Hume-Rothery.

Recrystallisation of silver, copper, and aluminium. R. Glocker and H. Widmann (Z. Metallk., 1927, **19**, 41—43; cf. Glocker and Kaupp, B., 1924, 1016; 1926, 15; and Glocker, A., 1925, ii, 272).—On annealing severely cold-worked metals, recrystallisation usually takes place in two stages, in the first of which the new crystals are formed irregularly throughout the mass, and in the second they become regularly oriented according to the laws of crystallography. In certain cases, however, one or the other of these stages does not occur; *e.g.*, commercial aluminium (98% Al) recrystallises directly in the second stage at 275°, whereas cold-worked copper that has been previously hot-rolled never recrystallises with regular orientation of the crystals. Intermediate annealings during rolling also appreciably affect the course of recrystallisation of some metals by lowering the temperature at which this action begins, and by suppressing one of the stages of recrystallisation. Small quantities of impurites have a similar action; *e.g.*, the presence of 0·05% Fe in silver lowers the recrystallisation temperature to 20° or less, so that the severely cold-worked metal undergoes recrystallisation after storing for varying periods and intercrystalline fractures occur; this action may be suppressed by the addition of 0·1% Cu, which raises the temperature of recrystallisation to about 150°. Larger amounts of copper raise this temperature still further; with 0·3% Cu it is over 220°.

A. R. Powell.

Effects of impurities on copper. III. Effect of arsenic on copper. IV. Effect of arsenic plus oxygen on copper. D. Hanson and C. B. Marryat (Inst. Metals, March, 1927, advance copy, 43 pp.).—The effect on copper of up to 1% As is investigated in the absence of other impurities. Sound castings of these alloys are difficult to obtain. The alloys are remarkably malleable and ductile, and can be worked hot or cold to any desired extent. Within the range of composition investigated arsenic produces only a very slight increase in the hardness, tensile strength, and ductility of copper; the effect of cold-rolling increases slightly with the arsenic content. The fatigue range is relatively high; the ratio of fatigue range to ultimate stress is approximately 0·9, due, possibly, to the great ductility of the material and its capacity for undergoing cold-work. The electrical conductivity falls rapidly as the arsenic content increases. Arsenic reduces the crystal size in castings, but this effect is not appreciable in annealed and worked material. The solubility of arsenic in copper is about 7·25% at all temperatures. In the case of alloys containing up to 2% As and 0·1%O, no difficulty was experienced in obtaining sound castings. The addition of arsenic to copper containing oxygen counteracts the embrittling effect produced by the latter element, and makes cold-rolling possible. Ultimate stress measurements show that, if the ratio of arsenic to oxygen is less than 10 : 1, the process of cold-work cannot be carried very far without damaging the material; it becomes "over-rolled." This relation indicates quantitatively the beneficial effect of arsenic in correcting the loss of ductility of copper due to oxygen; it is suggested that an increase in the arsenic content in commercial arsenical copper might be permitted with advantage. Copper containing arsenic and oxygen can be rolled hot without difficulty. The addition of oxygen to copper containing arsenic makes little difference to the results of mechanical tests and electrical conductivity measurements. In alloys of low arsenic content the oxygen exists as cuprous oxide; as the arsenic content increases up to 1% the cuprous oxide becomes darker, and is gradually replaced by a slate-grey constituent, which is generally associated with cavities, and which is shown to be a reaction product between cuprous oxide and arsenic; when present in small quantities it is not harmful to copper. Arsenic raises the softening temperature of cold-rolled strip very considerably, irrespective of the oxygen content, a small amount having nearly as much effect as 1%. Annealing in hydrogen shows that copper containing more than a trace of oxygen becomes embrittled by reducing gases, irrespective of the arsenic content.

M. E. Nottage.

Effects of impurities on copper. V. Effect of bismuth on copper. D. Hanson and G. W. Ford (Inst. Metals, March, 1927, advance copy, 10 pp.).—Copper–bismuth alloys containing 0·001—0·1% Bi were examined in which the oxygen content is kept as low as possible. Sound castings of these alloys were not easy to obtain owing to excessive oxidation; a process of bottom-pouring was finally used. The solid solubility of bismuth in copper was found to be less than 0·002%, the bismuth, when present in sufficient quantity, being found in the crystal boundaries. Small quantities of bismuth adversely affect the rolling properties of copper, particularly during hot-rolling, the limiting amount is less than 0·01%, whilst for cold-rolling it is about 0·05%. Tests on rolled bar showed that bismuth has a harmful effect when present in still smaller quantities, particularly on the cold-working properties; in material which has to withstand severe cold-work, bismuth should be excluded, whilst for most other purposes the maximum should be 0·005%. Bismuth lowers the electrical conductivity of copper slightly, but its effect is negligible within the limits that permit successful working. The effect on the ultimate stress and the fatigue range is also small. In the notched bar (Izod) tests, the energy absorbed at fracture appeared to be less than that for bismuth-free copper of similar oxygen content.

M. E. Nottage.

Brittleness in arsenical copper. C. Blazey (Inst. Metals, March, 1927, advance copy, 15 pp.)—Examination of cases of failure which occurred spas-

modically in arsenical copper tubing showed that brittleness was only developed after heating below 600—650°. The tensile strength in the brittle condition is much below normal, the elongation relatively slight, and the fracture non-necked and intercrystalline; this latter observation suggests that the brittleness may be due to the temporary setting aside to the boundaries of a constituent which interferes with the rearrangement of the copper atoms at recrystallisation, but which can be redissolved after the rearrangement has taken place. The bend test readily disclosed the brittleness in thin strip and wires. In wire form, the metal behaved well under twist test. Brittle samples could be cold-rolled but not cold-drawn. Susceptibility to brittleness is inherent in the metal, and 500° appears to be the critical temperature for developing it; it disappears rapidly at 600°. In the tensile test the rates of elongation and hardening were practically identical for susceptible and non-susceptible metal, and for any one sample in the brittle and the ductile states, which suggests that the weakness resides in the grain boundaries, as, if the grains themselves were different, differences in the rates of extension or hardening would have been found. Continued cold-drawing when in the brittle condition brought about a progressive lowering of tensile strength and false increase in elongation, due to the opening up of numerous minute fissures. Rate of cooling from the annealing temperature, ageing at room temperature for 1 year, the influence of the furnace atmosphere (oxidising or reducing), chemical constitution, and microstructure had no apparent connexion with the susceptibility or non-susceptibility to brittleness. It appears probable that the susceptibility is connected in some way with the melting operations, because susceptible material can be converted into non-susceptible by re-melting and re-poling. M. E. Nottage.

Copper–beryllium alloys. M. G. Corson (Brass World, 1926, **22**, 314—320; Chem. Abstr., 1927, **21**, 47).—Beryllium may be used as a hardening agent for copper. The maximum solubility of beryllium is 1·7%. From 3·8 to 9·5% Be, the crystals first obtained belong to a new type of crystal lattice corresponding with the β-phase, having a body-centred cubic lattice. The β-phase is unstable in that the maximum copper content cannot be kept constant through all temperatures, and that beryllium shows extreme activity in the molten state. Ternary copper–nickel–bismuth alloys exhibit a smaller tendency for precipitation of a secondary constituent than do copper–nickel–silicon alloys, any such precipitation being sub-microscopical. The properties of a copper–nickel–beryllium alloy containing 0·3% Be in the wrought and heat-treated state are listed.
A. A. Eldridge.

Sodium cyanide copper solutions. W. D. Bonner and B. D. Kaura (Chem. Met. Eng., 1927, **34**, 84—85).—A cupric salt in a copper plating electrolyte is wasteful since cyanide is used up to reduce it to the cuprous form, whilst of the cuprous salts available, the cyanide, although more soluble than the chloride in sodium cyanide, is so susceptible to atmospheric oxidation that much free cyanide must be present. An electrolyte containing cuprous chloride is the best, being more stable and yielding higher current efficiencies. The molecular ratio of cyanide to copper must not exceed 5, for when the amount of copper is less than 1 mol. to each 5 mol. of cyanide, solution of copper in the cyanide solution takes place and not deposition. Agitation of the bath by bubbling hydrogen, nitrogen, or coal gas freed from carbon dioxide raises the current efficiency, whereas mechanical or air agitation causes oxidation.
W. G. Carey.

Etching reagent for copper. B. W. Holman (Inst. Metals, March, 1927, advance copy, 1 p.).—A small, dry crystal of silver nitrate is placed on the polished surface to be etched, and a drop of water allowed to fall on it. A light deposit of silver is formed and turns grey in about 3 sec., when both deposit and crystal are washed off with a jet of water. A clean, evenly-etched surface is obtained free from silver, which tends to adhere if silver nitrate solution is used. A very fine structure is shown under high magnification.
W. Hume-Rothery.

Crystallisation of the lead–tin eutectic. F. Hargreaves (Inst. Metals, March, 1927, advance copy, 2 pp.).—Straining and etching methods applied to sections cut from a 30 lb. ingot of lead–tin alloy of eutectic composition showed that the outside was composed of large chill crystals about 0·15 in. long, which showed a laminated structure and no tendency to "colony" formation. Crystals of similar size but with a coarser structure were found adjacent to the chill crystals, and the middle of the ingot was composed of small crystals up to 0·05 in. in diameter, in which the "colony" type of structure was well developed. The transition from large to small crystals was sudden, but the coarsening of the eutectic structure was gradual. Large nodules possessing a coarse radial structure comprised the upper layer. M. Cook.

Silver contents of Roman lead from Folkestone and Richboro Castle. J. N. Friend and W. E. Thorneycroft (Inst. Metals, March, 1927, advance copy, 2 pp.).—A specimen of Roman lead from Folkestone contained 0·0072% Ag, with traces of bismuth, and possibly also copper and antimony. A specimen from Richboro Castle contained 0·0078% Ag, with slightly more bismuth than in the Folkestone specimen, traces of copper, antimony, and tin being indicated.
W. Hume-Rothery.

Influence of calcium on aluminium containing silicon. J. D. Grogan (Inst. Metals, March, 1927, advance copy, 13 pp.).—Aluminium alloys were prepared containing calcium and silicon in the ratio 1 : 1·4 as demanded by the compound $CaSi_2$; a similar series was prepared containing silicon alone, also two alloys containing, respectively, 1 and 2% Ca without any added silicon. Calcium forms with aluminium the compound $CaAl_3$ as a network round the primary aluminium grains and containing 8·5% Ca. When silicon is added to calcium–aluminium alloys, a new constituent, thought to be $CaSi_2$, appears, possibly containing aluminium either in combination or in solid solution, and resembling $MgSi_2$ in colour. Its solubility in solid aluminium is extremely low, but unlike the latter compound, $CaSi_2$ does not impart the property of age-hardening to the alloy. It is formed in preference to $MgSi_2$ in alloys containing calcium, silicon, and magnesium; conse-

quently, calcium is able to suppress the age-hardening phenomena associated with $MgSi_2$ unless excess of silicon be present. Microscopical examination shows that in alloys containing calcium and silicon in the ratio required by the compound $CaSi_2$, this constituent appears; addition of calcium to such alloys causes the appearance of $CaAl_3$ in addition to $CaSi_2$; no additional constituents of the types CaSi and Ca_2Si appear. Electrical conductivity measurements show that the limit of solid solubility of silicon in aluminium at room temperature is about 0·6%, at which concentration the conductivity curve flattens out; the tensile strength of the annealed material also shows a similar change at this composition. The addition of calcium to aluminium containing silicon rapidly raises the electrical conductivity until calcium and silicon are in the proportions required by the compound $CaSi_2$; additional calcium causes the conductivity to fall slowly. The addition of silicon to aluminium containing calcium produces little change in the conductivity until sufficient has been added to unite with all the calcium to form $CaSi_2$; further calcium causes the conductivity to fall rapidly. M. E. Nottage.

Determination of calcium in aluminium alloys. P. G. Ward (Inst. Metals, March, 1927, advance copy, 1 p.).—The alloy (2 g.) is dissolved in caustic soda, the solution diluted, and the precipitate after settling is filtered off, dissolved in hydrochloric acid, neutralised with ammonium solution, and the iron and aluminium are precipitated with excess of 10% ammonium benzoate solution. The calcium in the filtrate is precipitated as oxalate and weighed as oxide. M. E. Nottage.

Solubility of silicon in aluminium. W. Köster and F. Müller (Z. Metallk., 1927, **19**, 52—57).—The ratio of graphitic to soluble silicon in silicon–aluminium alloys varies with the heat treatment to which the metal has been subjected, and this is taken to indicate differences in the solubility of silicon in aluminium with the temperature. From chemical analyses, conductivity tests, and micrographical examination it is concluded that the solubility of silicon in aluminium rises linearly with the temperature from less than 0·1% at 300° to a maximum of 1·7% at 570°. The dissolved silicon is converted to silica on treating the metal with acid, whereas that present as eutectic or as inclusions of graphitic silicon remains as a black or brown powder. The greater the proportion of dissolved silicon in commercial aluminium the greater is its resistance to corrosion. A. R. Powell.

Transformation of zinc–aluminium alloys in the solid state. W. Fraenkel and J. Spanner (Z. Metallk., 1927, **19**, 58—60).—Aluminium–zinc alloys of the composition Al_2Zn_3 were annealed for 8 days at 380° and quenched, the time taken for the maximum rise of temperature associated with the spontaneous decomposition of the compound being measured. Addition of 0·5% Bi, Pb, Sb, or Ag had no effect on the action, whereas small proportions of copper, tin, or cadmium retarded the rate of decomposition without appreciably affecting the maximum temperature reached. Lithium and magnesium rendered the action so slow that no rise in temperature took place. In every case the retardation was greater the greater the amount of impurity present, and this fact probably explains the conflicting results of other investigators of the α and γ ranges in the zinc–aluminium system. A. R. Powell.

Reports of investigations: ore dressing and metallurgical laboratory. C. S. Parsons, J. S. Godard, and R. K. Carnochan (Canad. Dept. Mines, 1925, [670], 11—71).—The article contains seventeen reports dealing with experimental work on the concentration by flotation, table treatment, etc. of a number of lead, copper, zinc, gold, and silver ores, and on a pyritic molybdenite ore from various Canadian mines, and includes data on selective flotation of zinc–lead–copper ores. Thiocarbanilide in a pulp made alkaline with sodium carbonate usually gave a good lead concentrate, and zinc could subsequently be floated by addition of copper sulphate and potassium xanthate; the presence of cyanide reduces the zinc content of the lead concentrate much more than does sodium sulphite or phosphate. A. R. Powell.

Reports of investigations: electrochemical and hydro-metallurgical laboratories. Hydro-metallurgical treatment of iron sulphide ores for the production of electrolytic iron and of pyrrhotite of low gold and copper content. Treatment of ilmenite for the recovery of electrolytic iron and titanium oxide. R. J. Traill and W. R. McClelland (Canad. Dept. Mines, 1925, [670], 72—88).—Further tests on the wet treatment of pyritic ores for the recovery of electrolytic iron and elemental sulphur are recorded (cf. B., 1926, 670). The ferrous chloride solution obtained after leaching with ferric chloride the product obtained by heating the ore at 750° in a neutral atmosphere may be purified from most heavy metals by heating with powdered ferrous sulphide, but zinc cannot be precipitated in this way, and is co-deposited with the iron in the subsequent electrolysis. For this operation the electrolyte should have an acidity of p_H 3·7—3·9 and a temperature of 80—90°; a carbon anode and a rotating steel cathode are used, separated by an asbestos cloth diaphragm. From electrolytes containing only traces of zinc a deposit containing 99·94% Fe has been obtained with an efficiency of 93%. The method has been applied to an ore containing 1·2% Cu together with pyrrhotite, pyrites, and gold; heating at 750° in a neutral atmosphere caused some alteration to the pyrrhotite which resulted in a poor extraction. Better results were obtained by leaching out the pyrrhotite directly and heating the residue at 750° preparatory to a second leaching. Nearly 90% of the copper and iron were recovered together with 60% of the sulphur; cyanidation of the residue gave a gold extraction of over 75%. The process has been adapted to the extraction of titanium dioxide and iron from ilmenite; the ore is heated with carbon at 950° to obtain a sponge of metallic iron containing the titania in mechanical admixture. The product is separated from gangue material by magnetic treatment, and the magnetic product is leached with ferric chloride solution to obtain ferrous chloride for electrolysis after a preliminary purification with calcium sulphide. The insoluble residue from leaching is utilised for the recovery of titania. A. R. Powell.

Combined pyro- and hydro-metallurgical process

for the treatment of nickeliferous pyrrhotite and other sulphide ores for the recovery of iron and sulphur in addition to the other contained metals. H. C. Mabee and A. E. Smaill (Canad. Dept. Mines, 1925, [670], 89—94).—The ore is smelted with an alkali flux under non-oxidising conditions to obtain a low-grade matte containing all the copper, nickel, and precious metals. This matte, on exposure to the air, disintegrates into a fine powder, which is roasted in a two-stage mechanically-rabbled furnace, in the first stage of which the temperature is maintained at 400° and in the second stage at 600°. The product is mixed with 10% of its weight of sodium chloride, damped with water, and again roasted at 400°, the issuing vapours being absorbed in water. This water is then used to leach the roasted product, and leaching is continued with 10% sulphuric acid. The residue contains practically all the iron and the greater part of the nickel, but only a small proportion of copper and sulphur; it is amenable to direct smelting for the production of nickel steel. The leach liquor is electrolysed for the recovery of copper, then treated for the removal of iron, and again electrolysed to recover the nickel. Over 90% of the copper and 40% of the nickel are obtained as pure metals. A. R. Powell.

XV.—LEATHER; GLUE.

Official methods for analysis of vegetable-tanned leather (J. Soc. Leather Trades' Chem., 1926, **10**, 411—418).—The number of individual pieces to be sampled shall be $n = 0{\cdot}7\sqrt{X}$ where X = total number of pieces, not be less than 3 (methods of taking the sample are given). *Moisture.*—Dry 2 g. of the well-mixed pieces to constant weight at 100—103°. Greasy leathers must be degreased before drying. *Total ash.*—Incinerate 5 g. of leather in a tared dish at a dull red heat in a muffle furnace until all carbon is consumed. *Ash of solubles.*—Ignite the residue from total soluble matter in water-soluble matters determination (*q.v.*). *Oils and fats.*—Extract 20—25 g. of leather in a Soxhlet apparatus with light petroleum (b.p. 40—65°) until free from grease, and dry fatty matter at 95—100° to constant weight. Leathers which contain oils insoluble in light petroleum must be extracted a second time with anhydrous ether. *Water-soluble matter.*—(*a*) After the fat extraction, the leather is completely freed from solvent by leaving it exposed to the air (not heated), transferred to a Procter extractor, covered with distilled water, left overnight, and extracted at 45° by continuous extraction until 1 litre of extract has been obtained in 3—3½ hrs. The total solubles and non-tans are determined in the extractive by the usual official method. (*b*) The fat-extracted leather, freed from solvent, is divided into two equal parts, each shaken for 5 hrs. with 500 c.c. of distilled water at 18°, and the liquid is filtered and analysed as before. *Nitrogen and hide substance.*—Heat 1·5 g. of the leather pieces with 15—25 c.c. of strong sulphuric acid for 5—15 min., add 10 g. of powdered potassium sulphate and 0·5 g. of anhydrous copper sulphate, boil for 1 hr. after the liquid has become clear and nearly colourless, dilute with about 200 c.c. of water, add 50 c.c. of 35% caustic soda solution, distil off the ammonia into standard acid, and titrate with standard alkali, using carminic acid, alizarin red S, or methyl red as indicator. *Glucose.*—Mix 200 c.c. of leather extract with 25 c.c. of a saturated solution of lead acetate, shake frequently during 5—10 min., filter, add excess of solid potassium oxalate to the filtrate, mix, and filter, returning filtrate until clear. To 150 c.c. of this filtrate add 5 c.c. of strong hydrochloric acid and boil under reflux for 2 hrs., cool, neutralise with anhydrous sodium carbonate, make up to 200 c.c., and filter through a double filter. Determine the dextrose immediately by adding 50 c.c. of the clear neutralised solution to 25 c.c. each of the ordinary Fehling's solutions. Heat to boiling in exactly 4 min., boil for 2 min., filter immediately through asbestos, wash thoroughly with hot water, then alcohol, finally ether, dry for ½ hr. in water oven, and weigh as cuprous oxide. *Epsom salts.*—Ash 5—10 g. of leather, moisten with water, add 15 c.c. of strong hydrochloric acid, wash and dilute to 50—75 c.c., add 2—3 drops of nitric acid, boil, nearly neutralise with 1 : 1 ammonia solution, then add slight excess of weak ammonia solution. Boil for a few minutes, filter, wash the precipitate with hot water. Add 10 c.c. of a saturated solution of ammonium oxalate to the boiling filtrate, cover, allow to settle for 2 hrs. in a warm place, allow to cool, and make up to 250 c.c. An aliquot portion (equivalent to 2 g. of original leather) is made up to 150 c.c., acidified with hydrochloric acid, a slight excess of clear saturated sodium ammonium hydrogen phosphate solution is added, and the mixture rendered faintly ammoniacal. After 15 min. add 5 c.c. of strong ammonia, and keep overnight. Determine magnesium gravimetrically as $Mg_2P_2O_7$. *Mineral acidity.*—Weigh 2 g. of the leather in a platinum or rhotanium dish, add 40 c.c. of 0·1*N*-sodium carbonate solution, mix thoroughly, evaporate to complete dryness on steam bath, ignite at dull red heat, moisten with 25 c.c. of hot water, break up the residue, filter, and wash 4—5 times with hot water. Dry, and ignite filter paper and residue at dull red heat, cool, and add to the residue 40 c.c. of 0·1*N*-sulphuric acid, cover the dish, place on steam bath for 30 min., filter, if necessary, into the first filtrate, washing the paper free from acid with hot water. Cool the solution and titrate with 0·1*N*-alkali and methyl orange.

D. Woodroffe.

Urunday and urunday [tannin] extract. W. Vogel (Collegium, 1926, 535—541).—Urunday or urunday pardo (*Astronium Balansæ*, Engl.), belonging to the *Anacardiacæ* family, is very similar to quebracho colorado chaqueno. Urunday tannin belongs to the pyrocatechol group, and gives the same qualitative reactions as quebracho. Commercial urunday extracts show a bluish-violet fluorescence compared with the yellowish-green of quebracho solutions. The natural products gave no difference either in acid or alkaline solution, and the above bluish-violet fluorescence is not considered a characteristic of urunday. The composition of the heartwood, sapwood, and bark are: tans, 14·4, 1·4, 12·4%; non-tans, 1·5, 1·2, 3·3%; water, 19·0, 42·5, 12·4%. Urunday extract is manufactured in the same way as quebracho extract; 100 lb. of urunday wood yield 20 lb. of solid extract containing tans 63—65%, non-tans 6·1—7·2%, insolubles 5—8%, and ash 1·6—1·9%. The tans/non-tans ratio is slightly lower than

that for quebracho, 100 : 10 against 100 : 7. A sulphited extract is prepared with composition :—tans 67·2%, non-tans 10·5%, insolubles 0·3%, and ash 7·5%. Sulphited urunday extract always contains some insoluble matter, thus distinguishing it from sulphited quebracho. There is very little difference between leathers tanned with urunday and quebracho, respectively, until they have been exposed to light, when the urunday-tanned leather becomes a pure brown. The colour of leather tanned with sulphited urunday extract does not differ from that of leather tanned with the natural extract, but it darkens more on exposure to light. Urunday excels quebracho in giving greater firmness and better weight. They are of equal penetrating power.

D. Woodroffe.

Biological hydrolytic units from protein complexes. E. Kann (Collegium, 1926, 541—545).—Bromopropionylalanine was treated in the cold with a dehydrating agent. A cyclic compound separated out, which lost its bromine, and, on treatment with dilute hydrochloric acid, gave up its nitrogen and yielded racemic acid. This is the product obtained by the action of enzymes on alanine. Bromopropionylaspartic acid behaves similarly, also the halogenoacyl derivatives of tyrosine, phenylalanine, and arginine.

D. Woodroffe.

Standardised bacterial preparations in the leather industry. E. Lenk (Collegium, 1926, 556—560).—Bating materials should be tested on three kinds of protein at least, viz., casein, collagen or gelatin, and elastin. Gelatin is a favourable substrate. Samples of "Cutrilin" (a bacterial bate) and pure pancreatic bates were kept at 35° for several days, and the content of trypsin was determined at intervals. The pancreatic bates lost 60% strength in 1 day, whereas the "Cutrilin" was 50% strong after 7 days. The action of the trypsin in "Cutrilin" was not diminished so much by change in p_H value as that in pancreatic bates. "Cutrilin" showed maximum effect from p_H 5—9, and decomposed gelatin substrate more quickly than pancreatic bates at p_H values less than 7·3. D. Woodroffe.

A tanning accelerator. R. E. Liesegang (Collegium, 1926, 571).—Alkaline pyrogallol or pyrocatechol solutions render insoluble those portions of the silver bromide–gelatin layer which have been exposed to light, and therefore can be reduced. Large amounts of sodium sulphite, which are usually present in developers, restrain this tannage. The author placed a granule of silver chloride (diam. 5 mm.) in a 10% gelatin solution, and covered the gelatin with a concentrated "metol–adurol" developer which was renewed every 4 days for 2 months. Then the gelatin was melted to remove the granule, but a layer of insoluble gelatin 3 mm. thick surrounded the latter. A portion of the molten jelly was mixed with some silver chloride paste, allowed to set, and in ½ hr. it was insoluble in water, whilst the untreated portion was soluble. The silver chloride catalysed the tanning effect in spite of the sulphite in the developer. D. Woodroffe.

Theory of oil tannage. B. N. Mathur (J. Amer. Leather Chem. Assoc., 1927, **22**, 2—44).—It has been shown that of two samples of seal oil, a pale coloured and a very dark brown, the latter possessed superior tanning properties and yielded much stronger leathers. Tanning tests with the fatty acids of seal oil showed that acrolein was not necessary in chamoising, but that the unsaturated fatty acids had tanning properties. Experiments on partially-tanned chamois leather showed that the presence of water is necessary to obtain the best leather. Hide substance, in order to be converted into a strong oil leather, requires a certain amount of moisture during the tanning process. Pieces of cotton cloth treated with the unsaturated fatty acids of seal oil and exposed to heat remained greasy unless they were kept moist. The carboxyl-groups of the unsaturated fatty acids do not undergo any chemical change during the process of tanning, and the hydroxyl-groups produced during the oxidation unite with the hydrogen of the hide substance to form water. The soaps of unsaturated oils do not change into lactones under the conditions of chamoising. Sodium salts of the unsaturated fatty acids of seal, cod-liver, and shark-liver oils, in the presence of air and moisture form compounds quite different from those formed in an atmosphere of dry air alone. The brownish compounds developed in air under the influence of moisture on the sodium salts of the above fatty acids are capable of tanning and essential to the chamoising process. Air is not absorbed during oil tanning. The hydroxy-compounds are formed when the seal oil contains about 30% of moisture, and they combine with the pelt without the evolution or absorption of gas and form chamois leather. Any unsaturated fatty acid will tan, provided it can combine with a hydroxy-group from the moisture. The sodium salt of dihydroxystearic acid has tanning properties; α- and β-hydroxystearic acids do not tan. The best tanning agents among the fatty acids of the oleic acid series are those in which the unsaturated linkage is in a reactive place, *e.g.*, positions 10 and upwards. These will combine with water even at ordinary temperatures. Hence the superiority of fish oils in tanning. The unsaturated oils capable of chamoising first hydrolyse on the hide fibre, and the rise in temperature facilitates the hydrolysis. The unsaturated acids thus set free, having at least one double linkage in a reactive position, combine chemically with the hydroxyl of the moisture. The saturated acids thus formed, chiefly monohydroxy-acids, combine at 50° with the hide substance with the elimination of water at a fairly rapid rate. The hydroxy-acids containing two or more hydroxyl-groups in the molecule combine with two or more mols. of hide substance and produce leather of inferior quality and feel. In oils used for tanning purposes, acids containing a single double-bond are those most essential in chamoising.

D. Woodroffe.

Nature of one-bath chrome tannage. K. H. Gustavson (Ind. Eng. Chem., 1927, **19**, 81—83).—Hide powder tanned with a basic chromium sulphate solution (66% acidity and 2·1 g. Cr_2O_3/litre) absorbed 3·82% of chromium trioxide, and when this tanned powder was treated with an oxalato-chromium compound it absorbed a further 4·66%; untreated hide powder absorbed 5·15% from the latter liquor. Hide powder, which absorbed 5·46% of chromium trioxide from an oxalato-chromium solution and 7·09% from a basic

chromium sulphate solution (5 g. Cr_2O_3/litre), was tanned with the latter, and then treated with the oxalato-chromium solution and a further lot of stronger basic chromium sulphate, respectively. It absorbed a total of 11·36% of chromium trioxide instead of 12·55% with the basic chromium sulphate followed by the oxalato-chromium compound. It absorbed a total of 10·25% of chromium trioxide instead of 17·47% when treated with a weak basic chromium sulphate followed by a stronger one. Hide powder tanned with a basic chromium sulphate (63% acidity and 11·8 g. Cr_2O_3/litre) absorbed 17·43% of chromium trioxide, and when afterwards treated with the oxalato-chromium solution, the absorbed chromium increased to 20·96% instead of 22·58% as calculated. The stronger solution contained some anodic chromium complexes. Hide powder pretanned with the oxalato-chromium and then with a basic chromium sulphate absorbed 10·37% Cr_2O_3 instead of 15·41% as calculated. Apparently tanning with cationic chromium compounds does not involve the same protein groups as anionic tannages. Anionic chrome-tanned powder has not the same affinity for cationic chromium compounds as untreated hide powder. Such reactions affecting the basic protein groups appear to inhibit the fixation of cationic chromium. The fixation of basic chromium sulphate by hide protein comprises two separate, but mutually influenced processes, the combination of cationic chromium by means of the acidic protein groups, and of the hydrolysed acid by the basic protein groups. Chemical inactivation of the latter reduces the acid-fixative capacity of the protein, consequently the chromium fixation is decreased. It is possible that the chemical interaction with the basic protein groups induces structural rearrangements and redistribution of the valency forces. The data given support the view of the dual nature of anionic and cationic chromium fixation. Cationic chromium combines with the acidic groups of the hide protein, forming a very stable salt. Anionic chromium forms molecular compounds with the basic protein groups.

D. Woodroffe.

Behaviour of formaldehyde-tanned hide powder toward chromium compounds. K. H. Gustavson (Ind. Eng. Chem., 1927, **19**, 243—248).—Portions of hide powder tanned in formaldehyde solutions of different concentrations respectively at p_H 8·0 and then treated with chromium sulphate solutions, absorbed less chromium as the concentration of the formaldehyde solution increased. The diminution in chromium fixation was more marked with a chrome liquor containing cathodic and anodic chromium than with cathodic chromium alone. Formaldehyde-tanned hide powder prepared at p_H 7·0—8·0 fixed less chromium than powders tanned at other p_H values. Formaldehyde-tanned hide powder tanned at $p_H = 7·0$ absorbed less alumina from a basic aluminium sulphate solution and less tannin from a solution of hemlock bark extract. The anionic-sulphito and oxalato-chromium compounds were less fixed by formaldehyde-treated hide powder at p_H 7 and 8 than by untreated hide powder. The fixation of these complexes is partly by the basic protein groups. The formaldehyde treatment reduces the number of basic groups. The tanning mechanism of basic chromium sulphates consists of two separate but mutually influenced reactions, the fixation of the complex cations by the acidic protein groups and the fixation of the hydrolysed acid by basic protein groups. The diminution of the number of basic protein groups by the formaldehyde treatment at $p_H = 7$—8 diminishes the fixation of hydrolysed acid and thus represses the hydrolysis of the chromium salt, hence less chromium is fixed. Increased chromium fixation was observed with hide powder tanned with formaldehyde at p_H 12·2. This is attributed to the formation of alkali collagenate which leads to an increased activity of the acidic groups in the hide protein. There is also a considerable deaggregation of the protein. Chromium sulphates of high acidity and low concentrations gave practically the same fixation by hide powder, untreated and treated with formaldehyde at p_H values 7·0 and 12·2. With decreased acidity the differences in the chromium fixation became more pronounced. The more basic chrome liquors contain large quantities of anionic complexes which probably react with the basic protein groups. Cationic chromium fixation is less influenced because the reduced basic protein groups affect it indirectly only. Pre-treatment of the hide powder with formaldehyde at low p_H values, *e.g.*, p_H 2·5, is chiefly a process of peptisation and activation of basic protein groups. Hence, the more acid chromium salts are not affected by such pre-treatment, but the colloidal liquors give increased chromium fixation. The acidity of the resulting chromium–formaldehyde–collagen compounds was lower in all cases than the corresponding chrome–collagen compound. The experiments show the importance of the previous treatment of the collagen on its subsequent behaviour with tanning agents.

D. Woodroffe.

Extraction of nitrogenous matter from calfskins by salt water. H. B. Merrill (Ind. Eng. Chem., 1927, **19**, 249—251).—Samples of freshly-flayed and fleshed calfskin and skin cured with 25% of its own weight of salt and dried, were soaked in water, 0·125*N*, 0·25*N*, 0·5*N*, and *N*-sodium chloride, respectively, for 24 hrs., and then with a fresh portion of the same solution respectively for a further 24 hrs. The used solutions were analysed for nitrogen, and it was found that fresh calfskin contains a small amount of nitrogenous matter insoluble in water, but soluble in dilute sodium chloride. The quantity of material dissolved either by water or salt approaches a limit with increasing time or increasing salt concentration, indicating that collagen is only slightly attacked. After curing with salt, the amount of water-soluble matter is doubled, whilst that of salt-soluble matter is diminished slightly. With cured skin, the addition of salt to the solution has almost no effect on the amount of nitrogenous matter extracted.

D. Woodroffe.

Influence of hydrogen-ion concentration and valency of added anion on plumping in tan liquors. R. O. Page and J. A. Gilman (Ind. Eng. Chem., 1927, **19**, 251—252).—Pieces of soaked, limed, fleshed, and unhaired cow-hide butt were shaken with distilled water for 1 hr., the thickness was measured with a sensitive gauge, the pieces were shaken with water to restore their normal shape, and then put into a 12·5% solution of wattle-bark extract, to which had been added different

quantities of sulphuric, hydrochloric, or lactic acid, respectively. The thickness was measured again after 24 hrs., and the p_H value of the liquor determined electrometrically. There was a slight increase in plumping from the isoelectric point up to p_H 3·5, then a rapid increase to a maximum at p_H 1·8 or less, followed by a steady decrease in swelling with further reduction in the p_H. The plumping and p_H values were plotted on a graph. Lactic and hydrochloric acids give approximately the same curves, but the sulphuric acid curve was only about half as high as that for the others, showing that the plumping for sulphuric acid, which gives a bivalent anion, was half that for acids with a univalent anion. D. Woodroffe.

XX.—ORGANIC PRODUCTS; MEDICINAL SUBSTANCES; ESSENTIAL OILS.

Patents.

Production of dicyclic bases. J. D. Riedel A.-G. (G.P. 433,098, 5.7.24. Addn. to 423,027; B., 1926, 513).—Secondary aliphatic bases containing the phenylethyl residue or derivatives of these compounds are condensed with α-halogeno-carboxylic acids or their esters, and the acids thus formed are converted into the acid halides, which, on treatment with condensing agents such as aluminium chloride, lose carbon monoxide and hydrochloric acid giving *N*-substituted tetrahydro*iso*quinolines. *E.g.*, from *N*-methylphenylethylamine and ethyl bromoacetate is obtained *ethyl* N-*methylphenylethylaminoacetate*, $CH_2Ph\cdot CH_2\cdot NMe\cdot CH_2\cdot CO_2Et$, b.p. 152—154°/12 mm., which, on hydrolysis with hydrochloric acid and treatment of the resulting hydrochloride with potassium hydroxide, gives N-*methylphenylethylglycine*, m.p. 163°. By the action of acetyl chloride and phosphorus pentachloride this is converted into the *glycyl chloride*, m.p. 98—100°, and the latter on treatment with aluminium chloride in the presence of benzene and warming for a short time at 100° gives the hydrochloride of N-*methyltetrahydro*isoquinoline, m.p. 161°. E. H. Sharples.

Separation of amine mixtures of partly hydrogenated aromatic compounds. I. G. Farbenind. A.-G., Assees. of F. Mayer and K. Schirmacher (G.P. 434,403, 6.3.25).—The mixtures are treated with formaldehyde in acid solution whereby the bases unsubstituted in the *p*-position are converted into diarylmethane derivatives. *E.g.*, the mixture of aminohydrindenes obtained by the nitration and reduction of hydrindene is heated in hydrochloric acid solution with 40% formaldehyde for about 3 hrs. at 70—90°. It is then made alkaline and distilled in steam; pure 5-aminohydrindene, m.p. 34—35°, distils, and the residue, a diaminodihydrindenylmethane, may be purified by crystallisation. Similarly, by the action of 40% formaldehyde on a mixture of 5- and 6-*ar*-tetrahydronaphthylamine, pure 6-*ar*-tetrahydronaphthylamine, m.p. 148°, and a diarylmethane derivative are obtained. E. H. Sharples.

Preparation from carboxylic acids of the pyridine and quinoline series of derivatives which are easily soluble in water. Chem. Fabr. auf Aktien (vorm. E. Schering), Assees. of T. Brugsch and H. Horsters (G.P. 433,646, 15.9.23).—The acids are treated with alkali cholates. *E.g.*, 2-phenylquinoline-4-carboxylic acid is added gradually with shaking to a 0·1*N*-solution of sodium cholate at 50°. Up to 3·5 pts. of the acid can be dissolved without separation on cooling. The substances are used as medicaments. E. H. Sharples.

Preparation of α-indanone. Comp. Nat. de Mat. Color. et Manuf. de Prod. Chim. du Nord Réunis Établ. Kuhlmann, C. Courtot, and J. Krolikovski (F.P. 608,101, 19.12.25).—Pure indene or the coal-tar fraction containing it is treated with hydrochloric acid, the impurities are removed by distillation *in vacuo*, and the residual α-chlorohydrindene is oxidised with sodium dichromate and dilute sulphuric acid to α-indanone, b.p. 125°/15 mm., m.p. 40—41°, in 70—85% yield. E. H. Sharples.

Production of derivatives of oxindole-3-acetic acid and its homologues containing halogens substituted in the aromatic nucleus. Chem. Fabr. auf Aktien (vorm. E. Schering), Assees. of W. Schoeller and K. Schmidt (G.P. 433,099, 11.3.25).—The acids are halogenated by the customary methods. *Monoiodo-oxindole-3-acetic acid*, m.p. 204°, *di-iodo-oxindole-3-acetic acid*, m.p., 214°, *dibromo-oxindole-3-acetic acid*, m.p. 275°, *dichloro-oxindole-3-acetic acid*, m.p. 256°, *oxindoleacrylic acid*, m.p. 212° (from oxindolealdehyde and malonic acid), *oxindole-3-propionic acid*, m.p. 208° (by reduction of the preceding), and *monoiodo-oxindole-3-propionic acid*, m.p. 224°, are described. E. H. Sharples.

Preparation of water-soluble derivatives by means of salt-forming groups of substituted arylarsinic and arylstibinic acids and their corresponding oxides. I. G. Farbenind. A.-G., Assees. of K. Streitwolf and A. Fehrle (G.P. 433,105, 24.6.24. Addn. to 413,147; B., 1925, 783).—Amino-, or aminohydroxyaryl-arsinic or -stibinic acids or their corresponding oxides are treated with aldoses or ketoses under conditions described in the main patent. Examples are, the condensation products of dextrose with 3-amino-4-hydroxyphenyl-1-arsinoxide and 3-amino-4-hydroxyphenyl-1-arsinic acid, galactose with *m*-aminophenylstibinic acid, lactose with *m*-aminophenylstibinoxide, and arabinose with *p*-aminophenylarsinic acid. Condensation may be suitably effected by heating the components in aqueous solution at 50—55° with the addition, if necessary, of a little sodium hydroxide. E. H. Sharples.

Preparation of cadmium salts of phenols and phenol derivatives. Chem. Fabr. von Heyden A.-G., Assees. of R. Gebauer (G.P. 433,102, 25.11.24).—Cadmium salts of phenols and phenol derivatives are prepared by the usual methods for the preparation of metal phenoxides. The products possess a similar physiological action to that of the analogous bismuth compounds and may be used as dusting powders, and also in the form of oil emulsions for injection purposes. *E.g.*, aqueous solutions of cadmium sulphate and sodium phenoxide are mixed and the precipitate is washed first with water, then with 96% alcohol and dried at 50°. The product is a white, odourless, talc-like powder having the composition, $PhO\cdot CdOH$, and is suitable for the preparation of antiseptic powders. Cadmium *salts* of tribromophenol, salicylic acid, sulphosalicylic acid, guaiacol, guaiacolcarboxylic acid, and resorcinol are described. E. H. Sharples.