THE OXIDATION OF CAOUTCHOUC.

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Note:- The numbers above names indicate references to the literature. A list of references with corresponding numbers is given at the end.

PART I. GENERAL SURVEY.

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Occurrence of Rubber.

At present rubber is almost entirely obtained from Hevea brasiliensis, a plant of the botanical order Euphorbiaceae, which is native to the valley of the river Amazon. Rubber is a constituent of the latex, a milky secretion of the plant, the rubber content varying from 20 to 40 per cent. and depending largely on the age of the tree. The latex is usually present in a specialised system of cells or tubes which extend to all parts of the plant, those situated in the stem or trunk providing the main source of supply. Incisions are made in the lower part of the stem, and the latex which exudes is collected. The rubber is present in the latex as a dispersion in an aqueous medium, and is coagulated by heat, or by the addition of a small quantity of coagulant such as acetic acid or formic acid. Crude Para rubber contains, besides caoutchouc, resin, nitrogenous substances (mainly gluco-proteins), inorganic matter in small amounts and carbohydrates. The nomenclature relating to rubber is somewhat confused, the fundamental hydrocarbon which gives the crude substance its characteristic properties being variously described as "rubber" and "caoutchouc." The latter term is used by the Chemical Society in connection with the purified hydrocarbon and will be used throughout in this sense, the term "rubber" being applied to the crude natural substance. Unlike many naturally occurring/

occurring organic substances caoutchouc is optically inactive, though the resins associated with it in the crude state may show activity.

Physical Properties.

The caoutchouc hydrocarbon is not dissolved by alcohol or acetone, but crude rubber dissolves in benzene, chloroform, carbon tetrachloride and carbon disulphide with preliminary swelling, the nitrogenous constituent remaining undissolved, and forming a network in the solution which can be detected by the use of a suitable staining medium. The preliminary swelling is eliminated by grinding or "masticating," the rubber being repeatedly passed between steel rollers revolving at different speeds. Solution then takes place much more readily.

Rubber is usually regarded as consisting of an emulsoid system, in which both disperse and continuous phases are modifications of the parent hydrocarbon in different states of molecular complexity. The fact that rubber at low temperatures "freezes," losing its transparency and becoming hard and stiff, is in agreement with this. On heating in air rubber becomes sticky or "tacky" at about 160° and melts at about 220°, the solubility in solvents remaining unchanged where the heating is carried out in air but being reduced when an inert gas is substituted for air. "Tackiness," on the other hand, does not appear on heating in an inert gas. "Tackiness" is regarded as being due to a decrease in the complexity of the rubber aggregate, and is not apparently caused by the action of atmospheric oxygen, the resinous air oxidation products of rubber being hard and brittle. The terms "Aggregation" and "Disaggregation"

"disaggregation" have been suggested by Whitby[1] and Harries[2] in place of the terms "polymerisation" and "depolymerisation" commonly used to express changes in the physical state of complex colloids, the changes produced in rubber by "mastication" or heating in air being due to disaggregation. Atmospheric oxygen may cause disaggregation as a preliminary to oxidation. From a study of the resin esters of shellac, which exist in two forms, one soluble in alcohol, the other insoluble and only saponifiable to give 3 per cent of aleuritic acid, Harries[2] showed that the insoluble form became alcohol soluble after peptization with acetic or formic acid, and was then saponifiable to give the normal yield of 30 per cent of aleuritic acid. He therefore concluded that the reactivity of complex aggregates is influenced by the state of aggregation, several disperse phases forming by mutual adsorption a complex in which they are so arranged as to offer no sufficient point of attack to external chemical forces. Crude rubber, which normally resists hydrogenation, was readily hydrogenated after thorough mastication, light petroleum being used as solvent and the reaction carried out at ordinary temperatures under a few atmospheres pressure. Mechanical plasticising would thus appear to break up the mutual adsorption of the various phases, giving an effect similar to that of peptization with an organic acid. The action of concentrated sulphuric acid on rubber is of interest in this connection. Heim and Marquis[3] showed that a chloroform solution of crude rubber on shaking for 3 to 5 minutes with concentrated sulphuric acid gave on pouring into alcohol a white flocculent precipitate which could easily be filtered. There was no apparent change in the chemical composition of the product

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unless the action of the sulphuric acid was allowed to continue for a considerably longer period. Here again the chemical action of the acid would appear to be preceded by disaggregation of the rubber complex. Duclaux (4) has recently proposed a theory which accounts in a satisfactory way for the phenomena associated with the solution of rubber. A reversible gel is usually assumed to consist of two phases only, solvent and solid gel, but this does not agree with the properties of rubber solutions. An irreversible gel, like silicic acid, leaves on drying a porous sponge-like mass which reacts neither physically nor chemically with solvents and absorbs only by capillarity. Reversibility in a gel must therefore be due to the presence of a third phase not inert in the presence of a solvent. The solid phase is such that the cells are filled, not with solvent, as in an irreversible gel, but with this third substance. The latter is soluble in the solvent, forming either a colloidal or a molecular solution within the cells, but because it is incapable of passing through the semi-permeable walls of the cell through which solvent enters, it exerts a considerable osmotic pressure. Rubber is assumed to have such a structure, the cell walls being composed of a substance insoluble in benzene and similar solvents, the cell contents or plasma being a viscous liquid soluble in the same solvents and of high molecular weight. The viscous liquid does not escape even when the rubber is in colloidal solution. Swelling is thus purely an osmotic process. The solvent penetrates the walls of the cells and swelling thereby occurs, the extent of the swelling depending on the solvent. The soluble portion of the cell forming the plasma is assumed/

assumed to consist of a mixture of unequally polymerised substances not equally soluble in different solvents. The power of adherence of fresh rubber surfaces is thus due to tearing of the cells with efflux of their vicous contents and extensibility is due to deformation of cells containing plasma. The semi-liquid structure of rubber postulated above is not incompatible with its known mechanical strength. The general view of the physical structure of rubber is therefore that it consists of an aggregate of caoutchouc molecules, the state of aggregation depending on external conditions and being influenced by chemical action, heat, mechanical treatment and also by light. The effect of the latter is to cause a marked reduction in the viscosity of rubber solutions and in the case of the solid to accelerate the disaggregating effect of atmospheric oxygen.

Purification and Molecular Complexity of Caoutchouc.

The purification of caoutchouc has been fairly well standardised by numerous workers. The crude rubber is shredded, washed with water to remove traces of carbohydrates, etc., the resin is removed by extraction with acetone, the deresinised product is dissolved in benzene, and the solution filtered to remove the insoluble constituent. Precipitation of the benzene solution with alcohol gives a product the analyses of which agree well, considering the difficulty of removing traces of accessory substances, with the empirical formula C_5H_8. The insoluble residue removed by filtration from the benzene solution contains oxygen, according to Weber,[23] the oxygen content varying inversely with the amount of residue. The correctness of the C_5H_8 empirical formula has been questioned by Kirchhof,[5] who considers the composition of caoutchouc to be represented by $C_{10}H_{17}$, the molecule consisting/

consisting of aggregates of $C_{20}H_{34}$ arranged in open chain spirals. The C_5H_8 formula, however, receives support from the work of Pummerer and Burkard [6] on the catalytic hydrogenation of caoutchouc, purified with special precautions, the proportion of hydrogen taken up corresponding very closely with that required to convert $(C_5H_8)_x$ to $(C_5H_{10})_x$. The progressive purification of caoutchouc by Pummerer and Koch [7] has given interesting results. These may be summarised as follows:

(a) Caoutchouc was fractionally precipitated from a benzene solution by addition of alcohol. The oxygenated impurities were first precipitated as a yellow oil. Further addition of alcohol gave practically pure caoutchouc. The residual solvent was removed by washing with acetone.

(b) The same procedure followed as in (a) followed by fractional precipitation from hexahydro-toluene with acetone.

(c) Solution of the product (b) in light petroleum, followed by shaking with alcoholic potash, the ethereal solution of the final product being clarified by shaking with animal charcoal.

The product from (a) gave a clear solution in benzene, but was turbid in ether, petroleum ether or hexahydro-toluene solution.

The product from (b) was clear in hexahydro-toluene while that from (c) was clear in all four solvents. On cooling the product from (a) after extraction with acetone, crystals formed in the rubber mass, crystallographic examination showing three types of crystals in six modifications. These are ascribed to the presence of several individual chemical substances in the purified product. The benzene-alcohol mother liquors deposited on standing further fractions of caoutchouc /

caoutchouc which gradually set to a mass of yellowish white spherical aggregates, non-crystalline material being removed by washing with ether. This solvent could also be used for recrystallisation.

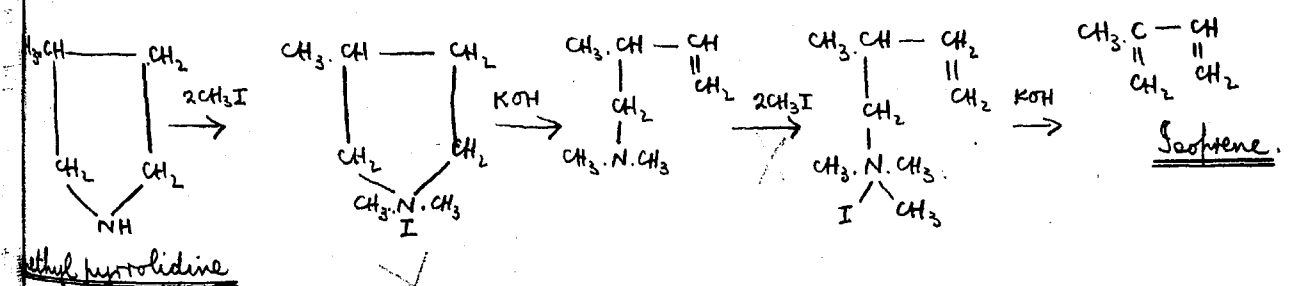
The crystals showed strong double refraction and became transparent and plastic at 60°, fusing completely at 92°. They were practically non-elastic. Molecular weight determinations gave negative results.

Owing to the colloidal nature of the hydrocarbon no satisfactory determinations of the molecular weight of caoutchouc have been made. The freezing point method has given results up to 8,000 but the depression observed in solutions of practicable strength is extremely small, and is more than covered by the experimental error. Hinrichsen and Kindscher (8) employed latex which was centrifuged with benzene to a clear solution, the depression of the freezing point was taken, the solvent evaporated and the residual caoutchouc and resin weighed. The latter was extracted with acetone and weighed, its molecular weight being then determined. The value for caoutchouc was found by difference to be 3137, giving an empirical formula of $(C_5H_8)_{47}$. From determinations of the combined sulphur in vulcanised rubber Bary (9) obtained the value 2720 corresponding to $(C_5H_8)_{40}$. Other values have been deduced from observations on the nitrosites, ozonides and halogen derivatives of caoutchouc, but no really satisfactory result has so far been obtained.

<u>The Constitution of Isoprene and Early Work on Rubber</u>.

The distillation products of rubber were investigated by Gregory, Dalton and Himly, the latter giving the name "Caoutchine" to the fraction boiling about 170°. A systematic examination of these/

these products was made in 1837 by Bouchardat[10] and in 1860 by Greville Williams[11], who gave the analysis and name for isoprene and commented on the coincidence between its composition and that of caoutchouc. He also obtained "caoutchine" and a hydrocarbon "Heveene" boiling above 300°, previously described and named by Bouchardat. Caoutchine was subsequently shown to be identical with dipentene. Gustave Bouchardat[12] isolated in addition butylene, ethylene and methane (probably decomposition products of the higher fractions) while Ipatiev and V.Wittorf[13] obtained trimethyl-ethylene along with the isoprene fraction. In 1882 Tilden[14] suggested that isoprene was β-methyl crotonylene (β-methyl butadiene) $CH_2{:}C(CH_3).CH{:}CH_2$. This was confirmed by the syntheses carried out by Kondakov, Ipatiev and V.Wittorf,[13] and Euler.[16] Ipatiev treated the isoprene-trimethylethylene mixture, obtained by the dry distillation of rubber, with hydrobromic acid in acetic acid solution, hydrolysed the products with potassium carbonate and obtained a mixture of β-dimethyl-trimethylene bromide and dimethyl-ethyl carbinol. The β-dimethyl-trimethylene bromide yielded isoprene on heating with alcoholic potash. Euler's synthesis, which is the most conclusive, consisted in converting β-methyl pyrrolidine into its methiodide, eliminating hydriodic acid to give a base, converting the latter into its methiodide and removing hydrogen iodide.



Addition Products of Caoutchouc.

(a) With Halogens.

Gladstone and Hibbert[17] in 1888 examined the behaviour of caoutchouc towards the halogens. In diffused light a chloroform solution of the hydrocarbon was found to yield addition products with chlorine, substitution taking place simultaneously with the addition. The final product was a white powder, corresponding to the formula $C_{10}H_{14}Cl_8$. With bromine under the same conditions the product, which was similar in appearance, had the approximate composition $C_{10}H_{16}Br_4$, excess of bromine giving as final product $C_{10}H_{15}Br_5$, in the formation of which substitution occurred as indicated by the free evolution of hydrobromic acid. The tetrabromide was prepared and described by Weber,[18] who attempted to form crystalline derivatives from it by heating with phenol, an amorphous compound corresponding to $C_{10}H_{16}(O.C_6H_5)_4$ being obtained. This split off phenol on boiling with caustic alkalies, polyhydroxy compounds being formed. The dihydrochloride $C_{10}H_{18}Cl_2$ was also prepared by the action of moist hydrochloric acid gas on a dilute solution of caoutchouc.[19] Hinrichsen, Quensell and Kindscher prepared and analysed both the dihydrochloride and dihydrobromide, the highest addition product obtained with hydriodic acid being $C_{10}H_{16}.HI$, a colourless sticky substance. These products were colloidal in nature, showing the Brownian movement in solution. The bromination of caoutchouc in ice-cold chloroform was found to be practically independent of the time or amount of bromine used, giving the tetrabromide as final product. It was further shown

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that caoutchouc absorbs iodine in sunlight, the reaction being photochemical and independent of temperature. The final product lost iodine on keeping, giving a final product $C_{20}H_{27}O_7I$. Oxidation would therefore appear to have occurred. Boswell, McLaughlin and Parker[20] have recently prepared a somewhat similar product $C_{25}H_{40}O_8I$ from the interaction of caoutchouc in carbon tetrachloride solution with iodine and hydrogen peroxide. Harries[21] prepared the hydrohalogen derivatives of natural and various synthetic caoutchoucs, the dihydroidide of natural caoutchouc being found to lose one molecule of hydriodic acid on treatment with solvents. Heating with pyridine or piperidine in sealed tubes to 125-145° was found to regenerate caoutchouc, the product, however, was not identical with the natural hydrocarbon. The "regenerated" caoutchouc gave hydrohalides on treatment with halogen acids, this property being retained after repeated addition and abstraction of the acid. Somewhat different results as regards the addition of bromine to caoutchouc have been obtained by Schmitz,[22] who used caoutchouc which had been "depolymerized" by heating for 10 hrs. with xylene at a pressure of 15 atmospheres. Bromination of this material in carbon tetrachloride solution gave as primary product $C_{20}H_{32}Br_{10}$ five atoms of bromine being taken up per $C_{10}H_{16}$ instead of the usual four. This product on standing lost hydrobromic acid to give $C_{20}H_{30}Br_8$ which was micro-crystalline. The first product is regarded as of open chain type, the second is possibly cyclic but with a smaller ring that the parent hydrocarbon. Of the above compounds the dihydrochloride of caoutchouc has been of considerable service

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in supplying material for Harries' work on "regenerated" rubber, thus giving a standard of comparison with the natural product, while the tetrabromide has been largely used for the technical estimation of the hydrocarbon.

(b) With Oxides of Nitrogen.

The action of nitrogen trioxide on caoutchouc was studied by Harries,[24] a product of variable composition being obtained, depending on whether moist or dry reagents were used. Moist nitrogen trioxide gave with a moist benzene solution of caoutchouc a yellow amorphous powder, soluble in alkalies and reducing Fehling's solution, corresponding to the composition $C_{20}H_{30}O_{14}N_6$. This substance, nitrosite "c" was regarded as a definite compound, its molecular weight in solution being 561, in agreement with the assigned formula.

Nitrogen peroxide was stated by Weber[25] to give a caoutchouc nitrosate $C_{10}H_{16}O_4N_2$, soluble in alkalies giving colloidal metallic derivatives. The composition of this product was verified by Alexander[26] but Harries[27] and Gottlöb[28] have contended that its composition varies with the period of exposure to the nitrogen peroxide and that it is more nearly described by the nitrosite formula. The action of nitrous fumes on caoutchouc does not consist of simple addition, oxidation taking place simultaneously as shown by the presence of small amounts of carbon dioxide in the issuing gases.

The nitrosite of caoutchouc has been of service in characterising the hydrocarbon, but has thrown no light on its structure.

Ditmar[29] in 1902 isolated, as a product of the action of concentrated nitric acid on caoutchouc, an acidic substance $C_{10}H_{12}N_2O_6$, having/

having the characteristics of a mono-basic acid, and melting at 142°- 143°. This was verified by Harries[24] and it was later shown by Ditmar[30] that the substance was probably 3:6 or 5:6 dinitro-dihydrocuminic acid $C_3H_7.C_6H_4(NO_2)_2.COOH$. It gave red, amorphous soluble alkali salts, and on reduction with tin and hydrochloric acid gave a dark brown powder corresponding to diamino-dihydro-paracuminic acid. The above substance would appear to be derived from a fairly complex degradation product of the caoutchouc hydrocarbon.

(c) With Chromyl Chloride.

Chromyl chloride, originally used by Etard[31] as a reagent for benzene hydrocarbons, has been employed to a considerable extent in connection with the terpenes. Addition products of the general formula $C_{10}H_{16}.2CrO_2Cl_2$ have been obtained, these yielding, on decomposition with water, aldehydes or ketones and, in some cases, acids or chlorinated products containing oxygen. The description of caoutchouc as a "polyterpene" and its intimate though obscure relationship with dipentene, together with the empirical resemblance in composition between its halogen derivatives and those of the terpenes, led Spence and Galletly[32] to investigate its behaviour towards chromyl chloride. An amorphous product, closely resembling those similarly obtained from the terpenes, and possessing an identical composition, viz. $C_{10}H_{16}2CrO_2Cl_2$ was isolated. This product, however, on decomposition with water gave entirely different results from those previously obtained with the terpenes. Two main products were separated as the result/

result of the reaction:

(a) A chloroform soluble resin of a dark brown colour. An alcoholic extract of this substance showed pronounced aldehydic properties, restoring the colour of Schiff's reagent, reducing Fehling's solution and giving a mirror with ammoniacal silver oxide. With phenylhydrazine a small quantity of a crystalline phenylhydrazone was obtained, melting about 92°.

(b) A brown powder insoluble in all organic solvents and in dilute mineral acids, but soluble in dilute alkalies. This substance contained both chromium and chlorine (Cr = 4.6%, Cl = 4.5%) and was obviously of very complex character.

The original addition product with chromyl chloride dissolved completely in water to give a perfectly clear greenish solution, from which a brown gummy mass, containing the constituents (a) and (b), separated only on standing for some time, or more rapidly on heating. This behaviour is very different from that of the terpene chromyl-chloride compounds, which are decomposed immediately by water with considerable evolution of heat, external cooling being necessary during the process. The addition of the chromyl chloride to caoutchouc, under the experimental conditions, was accompanied by very little rise in temperature, the reaction being much milder than with the terpenes, external cooling being necessary in this case also.

With the exception of this preliminary paper no further work on the action of chromyl chloride on caoutchouc has been published.

The Polymerisation of Isoprene and its Homologues.

Greville Williams[11] in his work on the dry distillation products of rubber observed that isoprene on standing in the air for some months became "ozonised," losing its fluidity and becoming viscous. On distillation unchanged isoprene passed over and the contents of the retort solidified to a pure white spongy elastic mass, only slightly sticky. This substance contained 10.6 per cent of oxygen (C = 78.8 per cent H = 10.7 per cent) and gave on burning the same odour as rubber. Bouchardat[12] in 1875 heated isoprene in sealed tubes at 280° for several hours, obtaining a viscous red fluid which he named "colophene," together with "terpilene" (dipentene). In 1879 he described the treatment of isoprene in the cold with concentrated aqueous hydrochloric acid, isoprene mono- and dihydrochlorides being formed, together with a non-volatile substance having the approximate composition of caoutchouc, resembling it in its behaviour towards organic solvents, and giving on dry distillation dipentene and isoprene.[33] Bouchardat therefore claimed to have prepared an impure synthetic caoutchouc by the polymerisation of isoprene. Tilden[34] in 1882 and 1884 described the preparation of isoprene (in small yield) by the pyrogenetic decomposition of turpentine, and stated that isoprene on treatment with nitrosyl chloride gave rise to caoutchouc. A similar product was claimed as a result of the action of concentrated hydrochloric acid on "colophene" (the heat polymerisation product of isoprene). No analyses or detailed descriptions of these supposed caoutchoucs were given. The formation of colophene by heating isoprene under pressure was confirmed by Wallach[35] who noted later that isoprene

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on long exposure to light was converted into a tough mass resembling rubber. This product was not further investigated. The formation of caoutchouc by the direct heating of isoprene was not observed by Bouchardat, Tilden or Wallach.

The spontaneous polymerisation of isoprene to a caoutchouc-like substance was first noted by Tilden (36) in 1892. Isoprene, prepared by the pyrogenetic decomposition of several terpenes, was found, on standing for several years, to have become partly converted into a yellow solid possessing the characteristic swelling properties of caoutchouc in presence of solvents, and capable of vulcanisation to an elastic solid. This synthesis was confirmed by Weber, (37) who put forward the suggestion that caoutchouc, in view of its relationships with isoprene and dipentene, might be regarded as a polyterpene, the term "polyprene" being preferable on account of its unknown molecular complexity. No analyses or specific tests of Weber's caoutchouc were given. Further confirmation was afforded by Pickles (38) in 1910, isoprene which had been allowed to stand for $3\frac{1}{2}$ years out of contact with air being found to give, on precipitation with alcohol, a white substance resembling immature rubber from young trees, and forming a tetrabromide and nitrosite exactly resembling those of natural caoutchouc.

The technical synthesis of caoutchouc from isoprene was first accomplished by the Bayer Company (39) in 1909, the method employed being the heating of synthetic isoprene, with or without the addition of acid, neutral, or alkaline catalysts, at temperatures under 250°. The polymerising action of sodium on isoprene was almost simultaneously discovered/

discovered by Matthews[40] and Harries[41] in 1910, the latter having succeeded in effecting the same result, by heating isoprene with acetic acid at about 100°, a little previously. An examination of the decomposition products of the ozonides, obtained from heat polymerised and sodium polymerised isoprene caoutchoucs, led Harries[42] to the conclusion that the former was identical with natural caoutchouc, the sodium polymerised product being different in structure. The two caoutchoucs were distinguished by the terms "normal" and "abnormal," the abnormal caoutchouc ozonide giving on decomposition acetonyl acetone and succinic acid in addition to laevulinic aldehyde and acid, the sole decomposition products from the normal substance. This difference is readily understood, since the position of the methyl group in isoprene is unsymmetrical with regard to the double linkages, and may thus give rise to a number of isomers during polymerisation.

Caoutchouc-like polymers have been prepared from the homologues of isoprene, notably from piperylene (α-methyl butadiene), from butadiene itself, from Ostromisslenski's so-called caouprene bromide (polymerised vinyl bromide) and from dimethyl-erythrene ($\beta\gamma$-dimethyl butadiene). The polymerisation of the latter was discovered by Kondakow,[43] who heated it with alcoholic potash for several hours, obtaining a leather-like elastic mass, nearly white in colour, non-volatile in steam, soluble in hydrocarbon solvents but insoluble in ether, alcohol and water. A later product obtained by the action of light on the hydrocarbon over a period of a year was amorphous and insoluble in all solvents, swelling in benzene. In 1909 this substance/

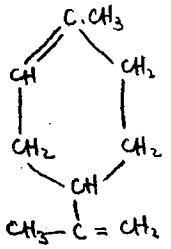
substance was stated to be converted into a technically valuable caoutchouc by heating under pressure at 150°-200°. Kondakow did not claim that his original product was a true caoutchouc and it has been shown by Harries that it is not identical with caoutchouc obtained by the heat polymerisation of dimethyl-butadiene, the ozonides of the two substances giving quite different decomposition products. In the technical preparation of dimethyl-erythrene caoutchouc it was found necessary to control the polymerisation of the hydrocarbon so as to give a product insoluble in alcohol but soluble in benzene, being thus intermediate in complexity to Kondakow's first and second polymers.

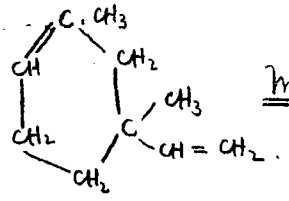
Bouchardat's[33] work on the polymerisation of isoprene has been repeated by Pond,[44] following exactly the details given by the earlier worker, but without any trace of a caoutchouc-like substance being obtained. The spontaneous polymerisation products of isoprene, as described by Tilden,[36] Weber,[37] Wallach[35] and Pickles[38] have also been examined by Harries,[45] who regarded them as being analogous to Kondakow's first dimethyl-erythrene polymer and not true caoutchoucs. Kondakow has expressed the opinion that the isoprene used by Bouchardat and Tilden, and which on treatment with aqueous hydrochloric acid gave caoutchouc, had already undergone spontaneous polymerisation on standing and thus contained caoutchouc, the chemical operations employed being without effect on the final result. Pond and Harries used freshly distilled isoprene which could thus contain no polymerisation products.

During the polymerisation of isoprene a variable proportion of dimeric /

dimeric hydrocarbons, dipentene and myrcene, is obtained together with caoutchouc. The relationship of myrcene to dipentene is probably

Dipentene





Myrcene

Butadiene and dimethyl-butadiene (dimethyl erythrene), being symmetrical in structure, yield only one dimeride, the latter also gives a trimeride. The dimerides are cyclic in structure.

In 1915 Ostromisslenski (46) showed that cautious heating of isoprene at 80°-90° gave a myrcene-like hydrocarbon with three double linkages, two of which were conjugated. This substance was termed β-myrcene and given the structure CH_2:CH.C(Me):CH.CH_2.CH_2. C(Me):CH_2. Heating of this substance with barium peroxide at 60°-70° converted it quantitatively into normal isoprene caoutchouc, isoprene itself under similar treatment giving an abnormal caoutchouc. It was also shown (47) that vinyl bromide gave on polymerisation a six-membered cyclic derivative, 1:3:5 tribromo-cyclohexane, in addition to the 32 membered erythrene caoutchouc bromide, this being regarded as analogous to the formation of dipentene and myrcene, both six-membered, in the polymerisation of isoprene, together with the supposedly 32 membered ring of caoutchouc.

The process of polymerisation was explained by assuming the dissociation of the parent hydrocarbon into a hydrogen atom and a free radicle, these immediately combined at the ethylene linking of a molecule of undissociated hydrocarbon to give the dimeride, in the case of/

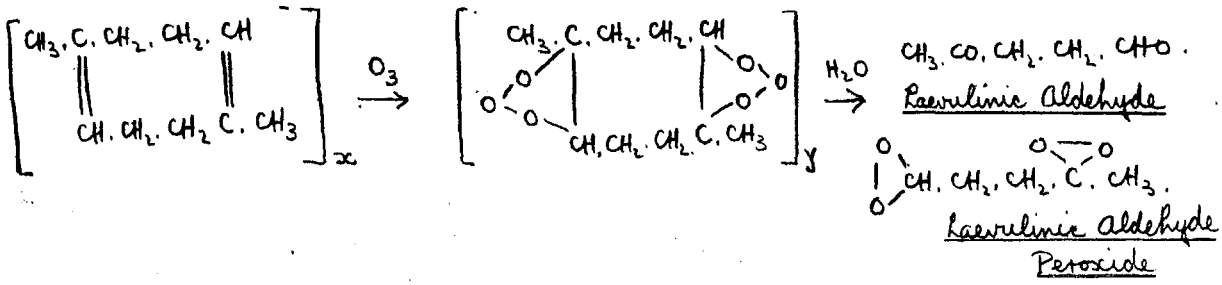
of isoprene β-myrcene. The latter similarly combined with another molecule of hydrocarbon to give the trimeride, the process being repeated to give the octameride, which underwent cyclisation to caoutchouc. With unsymmetrical hydrocarbons, such as isoprene, dissociation into a hydrogen atom and a free radicle could theoretically occur in different ways, this would account for the presence of normal and abnormal caoutchoucs in the products of polymerisation. With symmetrical hydrocarbons, such as erythrene and dimethyl-erythrene, no such isomerism could occur, in fact, as Ostromisslenski[48] has shown, only one form of caoutchouc derived from each of these is known.

The rate of polymerisation of hydrocarbons containing conjugated double linkages is affected in a marked degree by catalysts, especially those containing oxygen. Barium peroxide and other peroxides have been used in the technical synthesis of caoutchouc, and the action of atmospheric oxygen in accelerating the rate of polymerisation of conjugated dienes has been noted by Engler.[49] Sodium has also been employed as a catalyst in the preparation of synthetic caoutchouc but has not given satisfactory results technically; the only workable process has proved to be that of Kondakow, dimethyl-erythrene, prepared by dehydration of pinacone, being polymerised in sealed metal containers at about 60° over a period of several months.

So far no satisfactory theory of the mechanism of polymerisation has been given, the results given by various agents and methods being entirely empirical in basis.

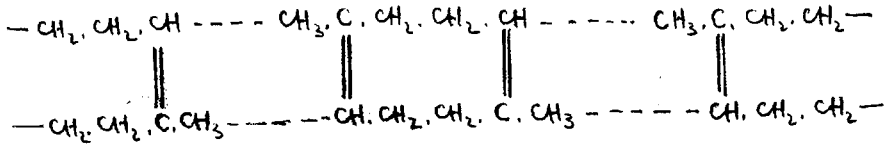
The Constitution of Caoutchouc and its Homologues.

Although the structure of isoprene had been established and its polymerisation to caoutchouc verified, the chemical nature of the polymerised product remained obscure, and its relation with the naturally occurring product was uncertain. The introduction of ozone as a reagent for caoutchouc in 1904 cleared up many of the difficulties. By passing ozone through a chloroform solution of caoutchouc kept at 0°, Harries[50] obtained on evaporation of the solvent a vitreous mass of caoutchouc ozonide. Purification by solution in ethyl acetate and precipitation with petroleum ether gave a product of the composition $(C_{10}H_{16}O_6)_x$ containing two ozone residues for each $C_{10}H_{16}$ and confirming the presence of one double bond for each isoprene nucleus. On heating with water the ozonide was found to give as products of hydrolysis, hydrogen peroxide and a substance with the reactions of a keto-aldehyde or di-aldehyde. Prolonged boiling gave laevulinic acid and an acid M.P.195°, apparently a succinic acid. When impure ozone was used a di-oxonozide $(C_{10}H_{16}O_8)_x$ was formed, which on hydrolysis gave the same products as the ozonide but in different proportions. In 1905 Harries[51] described the ozonisation by improved methods and stated that the only volatile products of the ozonide hydrolysis were laevulinic aldehyde and laevulinic aldehyde peroxide. On this evidence he formulated caoutchouc as a polymer of 1,5, dimethylcyclo-octadiene, the formation and hydrolysis of the ozonide being represented as follows:



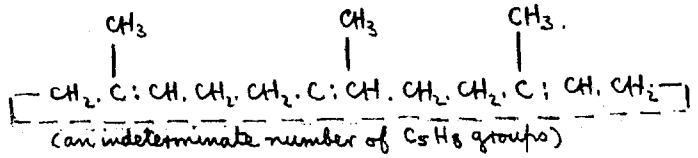
The presence of laevulinic acid was regarded as being due to a secondary reaction, probably oxidation of the aldehyde by the hydrogen peroxide set free during the hydrolysis of the aldehyde peroxide.

The polymerisation of 1,5 dimethylcyclo-octadiene to caoutchouc was assumed by Harries to occur through the saturation of partial valences according to Thiele's theory, the complex formed being easily depolymerised to give the parent hydrocarbon and thus retaining its unsaturated character. The complex would be represented thus, the dotted lines denoting partial valences:

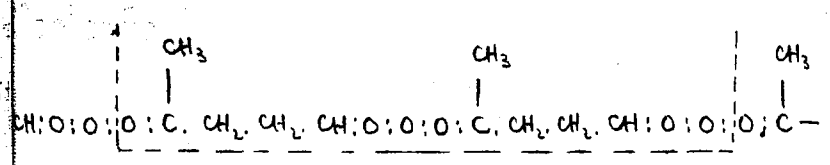


This structure was criticised by Pickles (38) on several grounds.
(a) If ozone is able to effect depolymerisation of the caoutchouc complex to dimethylcyclo-octadiene molecules, other reagents such as bromine should give similar results forming a relatively simple tetrabromide. The tetrabromide of caoutchouc is a complex substance of much the same order as the hydrocarbon itself. This makes the existence of a loose combination of dimethylcyclo-octadiene molecules improbable. If, on the other hand, the polymerisation is chemical it/

it must result in the elimination of double bonds and a reduction in unsaturation. The empirical formula of the tetrabromide $C_{10}H_{16}Br_4$ shows that the relative unsaturation of the complex is the same as that of two combined molecules of isoprene. Pickles formulated a mono-cyclic structure, the molecules of isoprene being chemically combined,



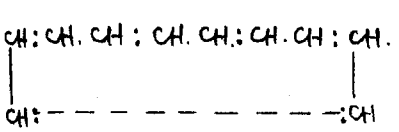
the union being accompanied by a re-arrangement of the double bonds. This allows two double bonds per $C_{10}H_{16}$ and accounts satisfactorily for the known unsaturation. The formation of the ozonide would be represented thus, the carbon atoms separating at the double bonds, and fission taking place as indicated to give



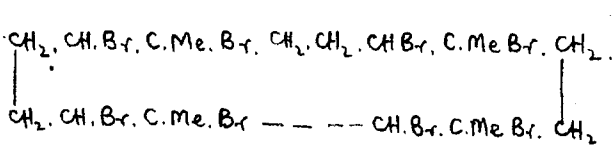
$C_{10}H_{16}O_6$ units which in turn break down to laevulinic aldehyde and its peroxide.

In 1912 Ostromisslenski (52) showed that vinyl bromide polymerises readily in sunlight to give what he called α-caouprene bromide. This was shown to exist in three different forms, styled α-, β-, and γ caouprene bromides, mutually convertible. The change α→β→γ form was brought about by exposure to ultra-violet light or by boiling with glacial acetic acid. Caouprene bromide is a simpler homologue (demethylated) of caoutchouc bromide. The latter was also stated to exist in three forms, differing only in their physical state of aggregation. A formula agreeing with that of Pickles was suggested. Dehydrocaouprene, obtained by removal of hydrobromic acid from caouprene bromide/

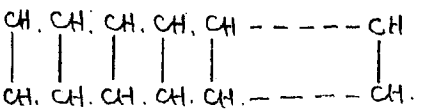
bromide, was given the formula



Dehydrocaoutrene

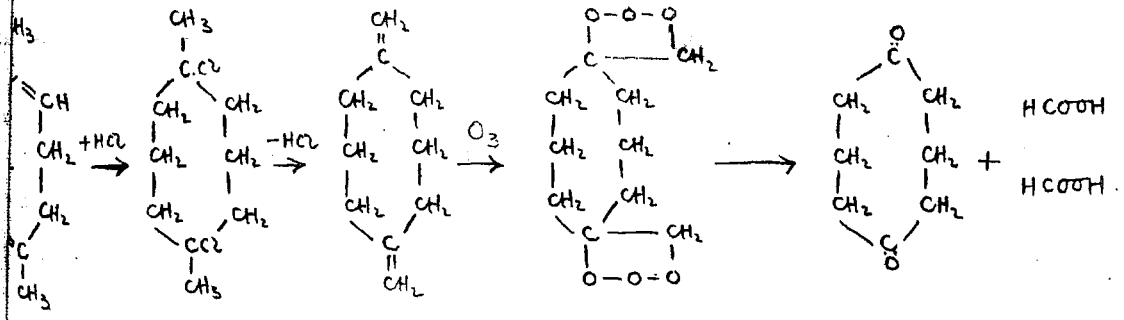


Caoutchouc Tetrabromide

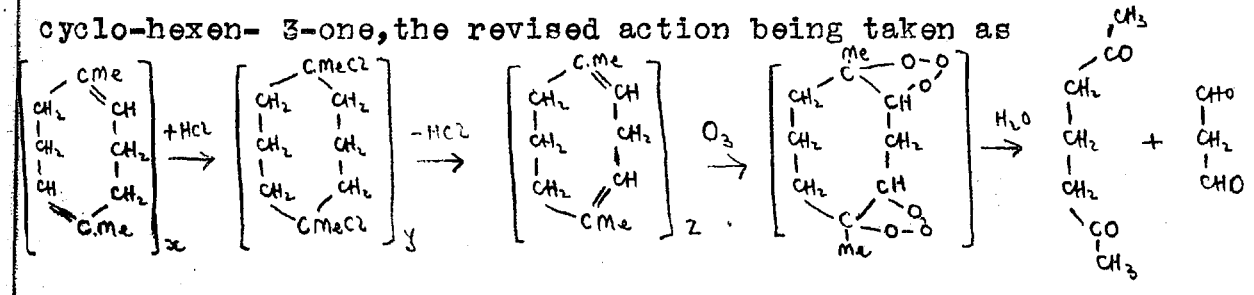
Dehydrocaouprene was regarded as a higher homologue of benzene, but Willstätter and Waser's (53) work on cyclo-octatetrene shows that dehydrocaouprene is not a higher homologue of benzene, but must be regarded as  bridging taking place with formation of tetramethylene rings.

Further evidence of the presence of an eight membered nucleus in caoutchouc was given by Harries (54) as a result of the study of the ozonisation products of regenerated caoutchouc. Crude Para rubber was treated with hydrochloric acid gas, the dihydrochloride was separated and purified, and the halogen acid removed by heating with pyridine in an autoclave at 125°-145°. The regenerated caoutchouc was ozonised, the ozonide isolated and hydrolysed, and the products of decomposition were examined. These were identified as laevulinic aldehyde and acid, 1,5 cyclo-octadione, formic acid and a keto-acid $C_7H_{13}O\cdot COOH$. This would appear to show that regenerated caoutchouc is a mixture of at least three different substances, the above products being irreconcilable with a single symmetrical formula. The addition and removal of the halogen acid may take place in several ways, thus affecting the distribution of the double bonds in the hydrocarbon. The formation of 1,5, cyclo/

cyclo-octadione may be represented thus:



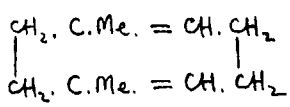
It was shown a little later by Harries (55) that the supposed 1,5, cyclo-octadione was really heptane$\beta\zeta$-dione ($CH_3 \cdot CO \cdot CH_2 \cdot CH_2 CH_2 \cdot CO \cdot CH_3$). This substance loses the elements of water very readily in presence of alkalies or acids to give 1-methyl cyclo-hexen- 3-one, the revised action being taken as

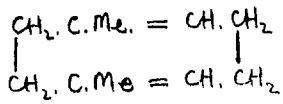


The latter should be identified as the mono-or dialdehyde of malonic acid, but was not detected. Under the conditions of decomposition of the ozonide the aldehyde acid would be broken up to give acetaldehyde and carbon dioxide, the presence of these was actually observed.

In an investigation of the decomposition products of the ozonides of synthetic caoutchoucs, prepared by the polymerisation of isoprene in the presence of ozonides or peroxides, or of sodium, Steimmig (56) identified, besides laevulinic aldehyde and acid, succinic acid and acetonyl acetone. To account for the presence of the two latter, synthetic caoutchoucs derived from isoprene were assumed to contain

1:6/

1:6 dimethyl, 1:5 cyclo-octadiene. 

as well as 1:5 dimethyl 1:5 cyclo-octadiene 

The two substances may be regarded as formed by the symmetrical and the unsymmetrical condensation of two molecules of isoprene. Caoutchouc obtained from the auto-polymerisation of isoprene gave approximately the same amounts of acetonyl-acetone and succinic acid. Natural caoutchouc gave neither of these substances and must therefore be of different constitution from the artificial products. This work was repeated by Harries (57) using carefully purified isoprene and polymerising by heating in a sealed tube for 6 weeks at 70°. No trace of acetonyl-acetone could be detected in the decomposition products of the ozonide. Steimmig's conclusions were therefore incorrect, Harries maintaining that the products of polymerisation even of pure isoprene vary greatly with treatment, and can therefore not be said to be isomeric. In addition the isoprene used by Steimmig was stated to be impure.

The dimethyl-cyclo-octadiene formula for caoutchouc was abandoned by Harries (58) in 1914 as the result of close examination of the decomposition products of a large quantity of ozonide prepared from regenerated caoutchouc. The latter was prepared as already described, by heating caoutchouc hydrochloride with pyridine in an autoclave. Distillation of the decomposition products gave the following fractions:

I. Up to 120° ($\frac{1}{2}$ mm.press). This contained laevulinic aldehyde, traces of methyl-cyclohexenone, diacetylpropane and laevulinic acid.

II. 100°-130°. This was mainly laevulinic acid.

III/

III. 130°-150°. This was mainly undecatrione $C_{11}H_{18}O_3$: leaflets M.P. 93°-94° Trioxime M.P. 123°-124°.

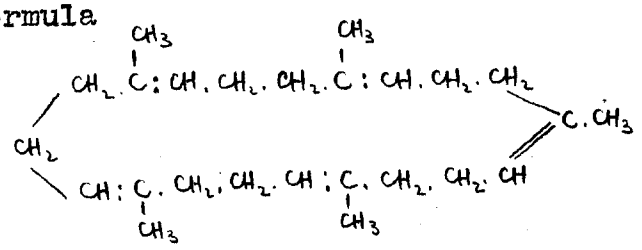
IV. 150°-250° This was mainly pentadecatetrone $C_{15}H_{24}O_4$: leaflets M.P 123° Oxime M.P. 112°-113°, together with an undefined residue of resin, etc.

The acids formed were separated by conversion into their calcium salts, acidification of the latter with dilute sulphuric acid giving the free acids. The mixture contained formic acid, acetic acid, oxalic acid, laevulinic acid, succinic acid, hydrochelidonic acid (laevulinic acetic acid) and methyl cyclohexenone carboxylic acid, together with 20 per cent of undefined residue.

The results showed that the decomposition products could not be harmonized with any possible rupture of a cyclo-octadiene ring. The molecular weight of the caoutchouc ozonide in acetic acid solution, which appears to indicate the formula $(C_{10}H_{16}O_6)$, is therefore unreliable, the molecule being of much larger dimensions. Harries assumed the probable existence of a ring system in which the group $CH_3\overset{\|}{C}\cdot CH_2\cdot CH_2\cdot CH =$ is regularly repeated, the degree of polymerisation being unknown. The presence of the tetraketone would indicate at least a ring of 20 carbon atoms. In the same paper Harries stated that the triketone and tetra-ketone already identified occur in a definite ratio to one another in the ozonide decomposition products, and would thus appear to be generated by rupture of the same cyclic structure. The molecular weight of caoutchouc ozonide in benzene solution was found to be 535 ($C_{25}H_{40}O_{15}$ requires 580). Taking this as basis, a ring of 20 carbon atoms would give the

required/

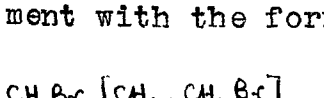
required formula



or $C_{25}H_{40}$

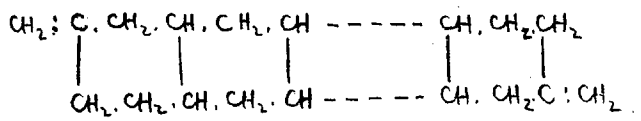
A ring of isoprene nuclei would only give laevulinic acid and aldehyde on decomposition of the ozonide, but the removal of hydrochloric acid from the hydrochloride would possibly give a rearrangement of double bonds, allowing of the formation of higher ketones. Regenerated rubber obtained by consecutive addition and abstraction of halogen acid from caoutchouc shows an increasing proportion of high boiling constituents in the decomposition products of the ozonide. This would point to a progressive shifting of the double bonds.

In continuation of his earlier work on caouprene bromide (polymerised vinyl bromide) it was shown by Ostromisslenski[59] that the molecular weight of the soluble modification of this substance, as determined by the cryoscopic method, was 1809. This is in agreement with the formula $C_{32}H_{48}Br_{16}$ or expressed structurally

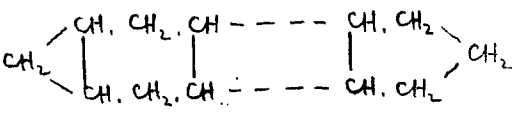


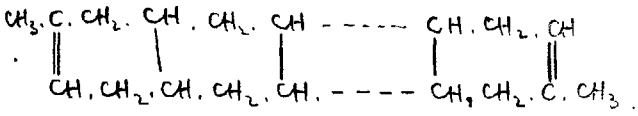
Removal of hydrobromic acid from this substance gave dehydrocaouprene: $C_{32}H_{48}Br_{16} - 16HBr = C_{32}H_{32}$ and a homologous substance $C_{32}H_{24}(CH_3)_8$ was obtained from the bromide of Para-caoutchouc $C_{32}H_{40}(CH_3)_8Br_{16}$. Reduction of caouprene bromide with zinc dust gave erythrene (butadiene) caoutchouc and isomeric caouprene/

caouprene in varying amounts. Caouprene was found to give no definite decomposition products with ozone. Formulae differing from that previously given were proposed:



or





Caouprene $C_{32}H_{32}$.

The bromide of natural caoutchouc, being homologous with caouprene bromide, must therefore possess a mono-cyclic structure, (-CH2.CH2.C(Me).Br.CHBR-)x and since by the action of zinc dust in alcohol it was converted readily and quantitatively into free caoutchouc, the latter must also have a mono-cyclic structure $(-CH_2.CH_2.C(Me):CH-)_x$, the positions of the CH_3 groups and double bonds being fixed by the decomposition products of the ozonide. Further reasons were advanced by Ostromisslenski for the abandonment of Harries dimethyl-cyclo-octadiene formula for caoutchouc. Willstätter's work on dimethyl-cyclo-octadiene having shown that the latter gives a crystalline tetrabromide with sharp melting point, not comparable with caoutchouc tetrabromide, and that it polymerises with almost explosive violence, yielding crystalline and horny compounds of varying complexity, but quite unlike caoutchouc. By analogy with caouprene bromide and caouprene itself, caoutchouc /

caoutchouc would therefore have the formula:

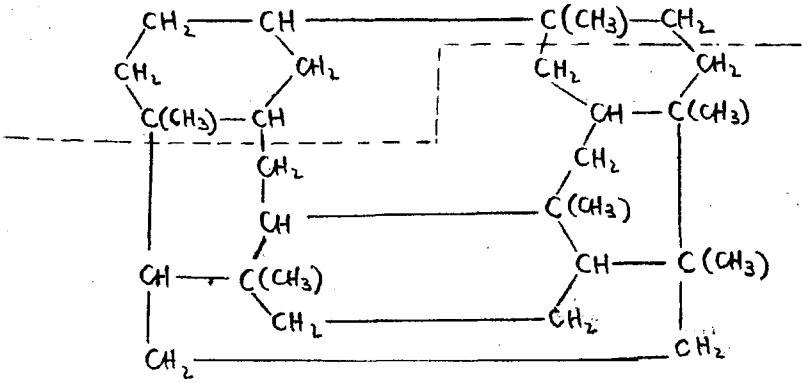
$$CH_2 . CH_2 . [C.Me:CH.CH_2.CH_2]_4 . C.Me:CH.$$

or $C_{40}H_{64}$.

This is identical with the formula proposed by Pickles,[38] who himself suggested the presence of at least eight isoprene nuclei in a closed chain. This formula is in agreement with the bromine saturation capacity of caoutchouc, as shown by the formation of the tetrabromide, with the known complexity of the molecule, and with the decomposition products of the ozonide prepared from the natural hydrocarbon.

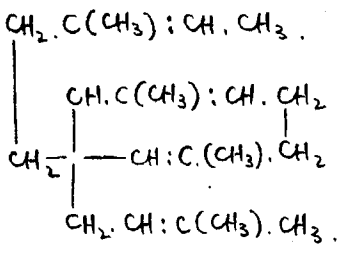
Olivier[60] has recently repeated Harries' work on the ozonides of caoutchouc, varying results being obtained in some cases. He holds the assumption of the homogeneity of the ozonide to be invalid, and that the molecular weight of the latter cannot serve as a basis for estimating that of caoutchouc, the available evidence being insufficient to allow of accurate conclusions as to the complexity of the caoutchouc molecule being drawn.

Alternative formulae have been advanced by Boswell[61] and by Kirchhof.[5] The former regards caoutchouc as represented by $C_{30}H_{48}$, the structural formula being given as



or $C_{30}H_{48}$

This corresponds to a combination of five isoprene molecules and such a compound could undoubtedly give rise on destructive distillation to dipentene and isoprene, in accordance with known results, the formation of dipentene being indicated by the dotted line. One residue is present which could react as dimethyl cyclo-octadiene, giving rise on ozonisation to laevulinic aldehyde and acid. The maximum yield would correspond to one-third of the caoutchouc taken, accounting for the discrepancy between the theoretical and actual yields of ozonide obtainable. The production of other hydrocarbons, such as dimethyl-butadiene, by destructive distillation should also be possible. The formula represents the caoutchouc molecule as saturated, oxidation being supposed to occur through the fission of a molecule of isoprene and subsequent addition of oxygen. The unsaturated nature of caoutchouc, as exemplified by its addition products with bromine and the halogen hydrides, is thus ignored. Kirchhof (loc.cit.) assumes an open chain spiral structure for caoutchouc, the fundamental unit being $C_{10}H_{17}$. This conclusion is based on the discrepancy between the theoretical composition of caoutchouc and that found by analytical methods, a discrepancy which can be attributed to the difficulty of preparing a pure specimen for analysis. The formula is as follows:



or $C_{20}H_{34}$.

Such a substance would give rise on destructive distillation to isoprene, along with other low-boiling hydrocarbons, the production of dipentene, by rearrangement, being also possible. The ozonide should yield decomposition products different from those known to be obtained. The most satisfactory test of the formula would be the establishment of a chemical difference between natural caoutchouc and synthetic caoutchouc prepared from isoprene, the decomposition products of the respective ozonides being compared. If the formula given above is correct there should be a marked divergence in the results. The chemical identity of natural caoutchouc with synthetic caoutchouc prepared from pure isoprene has been maintained by Harries,[57] this however has been denied by Steimmig[56] and doubts have been cast by Olivier[60] and Boswell[61] on the quantitative formation of the ozonide of natural caoutchouc.

The presence of methane, ethylene, butylene and trimethyl ethylene, in addition to isoprene, dipentene and higher boiling hydrocarbons, in the pyrogenetic decomposition products of caoutchouc, has been established by earlier workers.[62] Staudinger and Fritschi have recently shown that when caoutchouc is distilled in vacuo (0.3 mm.) at 275°-320° the products of decomposition include, besides isoprene and dipentene, a hydrocarbon $C_{15}H_{24}$ and small amounts of $C_{20}H_{32}$ and $C_{25}H_{40}$. $C_{15}H_{24}$ has two double linkages and is probably a hydro-naphthalene derivative, while $C_{20}H_{32}$ has three double linkages and has probably a long aliphatic side-chain. These results are interpreted on the basis of a chain formula, the chain being assumed to break up and union taking place in groups

of/

of 1, 2, 4, etc. carbon atoms.

The usually accepted view that caoutchouc is directly derived from a chemical union of isoprene nuclei, a monocyclic structure being assumed, has received support from the work of Pummerer and Burkard (6) on the hydrogenation of very pure caoutchouc by the method of Paal and Skita. One molecular proportion of hydrogen was found to be absorbed for every isoprene residue, i.e. $(C_5H_8)_x + x\ H_2 = (C_5H_{10})_x$. If the caoutchouc molecule consisted of a long open chain of isoprene residues a greater absorption of hydrogen would be expected. The accuracy attained in the experimental work enables the authors to conclude definitely that caoutchouc consists either of a ring system or of an unusually long open chain of isoprene nuclei $(C_5H_8)_x$. $x > 20$. The hydro-caoutchouc obtained resembled caoutchouc closely in physical properties, evidently retaining its very high molecular weight. In addition caoutchouc was found to react normally with per-benzoic acid, giving a viscous oxide $(C_5H_8O)_x$, evidence of the presence of two double linkages for each pair of isoprene residues.

The Hydrogenation of Caoutchouc.

In 1869 Berthelot (63) found that by heating caoutchouc with concentrated hydriodic acid solution to 280° under pressure a number of hydrocarbons boiling above 350° were obtained. These belonged evidently to the paraffin series, being very stable towards bromine, fuming nitric acid and fuming sulphuric acid, and did not solidify even on long standing.

Attempts at the hydrogenation of caoutchouc in the presence of catalysts have, until recently, given negative results. By

using/

using spongy platinum as catalyst, and hydrogenating at 270° under 100 atmospheres pressure, Staudinger (62) and Fritschi have succeeded in preparing a hydro-caoutchouc $(C_5H_{10})_x$, retaining the colloidal character of caoutchouc and proving stable towards bromine. On standing in sunlight absorption of bromine slowly took place, a caoutchouc-like product being obtained. Decomposition of hydro-caoutchouc at 350°-390° in vacuo gave a series of products of the type $(C_5H_{10})_x$, each possessing only one double bond. The lowest boiling product was a pentene, giving methyl-ethyl ketone on oxidation, being thus probably unsymm, methyl-ethyl ethylene. From the higher fractions were obtained, among others, a hydrocarbon $C_{15}H_{30}$ and, as highest boiling constituent, $C_{50}H_{100}$. The presence of this substance shows that hydro-caoutchouc must have a very high molecular weight. Objections were raised by Harries to this conclusion on the ground that at the high temperature employed the caoutchouc must be largely decomposed, the hydrogenation products obtained being not necessarily directly related to the original hydrocarbon. The later work of Pummerer and Burkard (63) has shown this objection to be invalid, a colloidal reduction product being obtained in the cold. From a study of the thermal decomposition products of the hydro-caoutchouc previously obtained Staudinger (64) has concluded that it is formed from the hydrocarbon $C_{50}H_{100}$ in the same way as caoutchouc is formed from isoprene, the relation between $C_{50}H_{100}$, the highest thermal decomposition product of hydro-caoutchouc, and methyl ethyl-ethylene, the lowest, being of the same type. From its stability towards bromine and oxidising agents Hydro/

hydro-caoutchouc is assumed to be a paraffin hydrocarbon, caoutchouc itself being regarded as an ethylene derivative of very high molecular weight, containing perhaps 100 or more molecules of isoprene, the ultimate molecule being of about the same order of magnitude as a colloid particle. Similar properties were ascribed to hydro-caoutchouc by Pummerer and Koch,(7) who prepared it by hydrogenation of dilute solutions (0.2 to 0.6 per cent) of very pure caoutchouc in presence of spongy platinum at half an atmosphere excess pressure. The hydro-caoutchouc was obtained as an opaque, viscous, non-elastic partly crystalline mass $(C_5H_{10})_x$ giving no depression of the melting point of camphor. Heating for three hours at 200°, then for twenty minutes at 300° in an atmosphere of carbon dioxide at 12 mm. pressure, caused no visible change in the product, but a molecular weight determination in camphor gave a value of 1700, this result being possibly due to disaggregation of the hydro-caoutchouc.

Crude hydro-caoutchouc on distillation in hydrogen at 350° gave a yield of saturated hydrocarbon $C_{45}H_{92}$. The residue, which was colourless and completely saturated, had the composition $(C_5H_{10})_x$, molecular weight in camphor 1500. Distillation at 1.5 mm. gave a colourless viscous mass $C_{50}H_{102}$, boiling at 354°. The hydro-caoutchouc itself was completely stable to air, bromine, or potassium permanganate at ordinary temperatures, agreeing in this respect with Staudinger's product. By reduction of caoutchouc under the same experimental conditions as before, but at atmospheric pressure a compound $C_{50}H_{86}$, stable to bromine, was obtained.

By/

By the reduction of caoutchouc dihydrochloride in dichloroethylene solution in presence of zinc dust Harries[65] obtained a large yield of α-hydro-caoutchouc. This substance was light yellow in colour, somewhat elastic and melted at 120°-130°, giving a molecular weight in bromoform solution agreeing with the formulae $(C_{35}H_{62})_x$ or $(C_{40}H_{70})_x$. It readily formed an ozonide and gave a hydrochloride and a bromide. The empirical formula led Harries to conclude that the caoutchouc molecule contains 35 or 40 carbon atoms, most probably the latter, thus bringing his views into agreement with those expressed by Pickles[38] and Ostromisslenski[52] years before.

The complex nature of the products resulting from the pyrogenetic decomposition of hydro-caoutchouc would seem to indicate that caoutchouc itself has a much larger molecule than that usually ascribed to it, the $C_{40}H_{64}$ formula being inadequate to explain the formation of hydrocarbons such as Staudinger's $C_{50}H_{100}$ and Pummerer's $C_{50}H_{102}$. These products can scarcely be formed by secondary condensation during distillation, since hydro-caoutchouc contains no double bonds and, according to Staudinger, leaves practically no residue after decomposition is complete. With such a large molecule no decision between a chain and a ring formula can be made.

The Oxidation of Caoutchouc.

In 1865 Spiller[66] examined a piece of fabric coated with unvulcanised rubber, the latter having become brittle or "perished," through long exposure to the air. A benzene extract of the rubber coating gave, on evaporation, a substance quite different from rubber, soluble/

soluble in alcohol, insoluble in carbon disulphide, and freely soluble in aqueous alkalies and alkali carbonates. Analysis of this substance showed it to contain oxygen, the approximate composition being $C_{30}H_{48}O_{10}$. It was hard and resinous in character and has been named "Spiller's resin." The action of gaseous oxygen on caoutchouc was subsequently investigated by Herbst,(67) who passed the gas through a boiling 1 per cent solution of the hydrocarbon in benzene for 140 hours. Two main products were isolated, a transparent reddish brown syrup of the composition $C_{10}H_{16}O$ and an amorphous friable yellow solid corresponding to $C_{10}H_{16}O_3$, the first being soluble and the second insoluble in petroleum ether. A very small amount of a hard brittle resin, similar in composition and properties to the second substance, was also obtained. The air oxidation of rubber was attributed by Kirchhof(68) to autoxidation, a study of the oxidation of raw and vulcanised rubber at ordinary temperatures and at 100° leading him to postulate the formation of an unstable peroxide $C_{10}H_{16}O_2$. The reaction was then supposed to proceed thus $C_{10}H_{16} + C_{10}H_{16}O_2 = 2C_{10}H_{16}O$ (Herbst's first product): $C_{10}H_{16}O + O_2 = C_{10}H_{16}O_3$ (Herbst's second product). The action of oxygen was more fully examined by Peachey,(69) who deposited thin films of purified caoutchouc (deresinised and filtered) on the walls of a flask electrically heated to 85°. The material was exposed to the action of moist oxygen, the action being sufficiently rapid to allow of the volume of gas absorbed being noted. It was observed

that/

that the presence of the normal amount of resin (about 3%) appreciably retarded the action, further, that the amount of oxygen taken up corresponded closely to two molecules per $C_{10}H_{16}$ of hydrocarbon. A later investigation by Peachey (70) and Leon confirmed this result, in addition the presence of variable amounts of carbon dioxide was detected (about one molecule of carbon dioxide per $C_{10}H_{16}$). This showed that the amount of oxygen reacting was rather greater than that found by the earlier volumetric method, a portion being used up in the formation of carbon dioxide. Moisture was found to exert no appreciable influence on the course of the reaction, while the natural resin only retarded the oxidation, having no effect on the final result. Fifty grams of purified caoutchouc were used in the later work, the material being exposed to the action of oxygen at 85° over a period of six months, extraction with alcohol every second day being employed to remove oxidised material and expose a fresh reacting surface. The reaction product was almost completely soluble in alcohol with formation of a yellowish red viscous gum. After fractional precipitation from various solvents this material was finally separated into four portions, distinguished as A, B, C and D.

A was a clear yellow resin, neutral in character, insoluble in water but soluble in all the usual organic solvents. Its composition corresponded to $C_{16}H_{26}O_3$. No derivatives were prepared.

B was a fawn-coloured amorphous powder, feebly acidic in character/

character. It had no definite melting point, swelling up at 130°, and not charring below 250°. It was insoluble in water, carbon disulphide or petroleum ether, soluble in alcohol and acetone. Oxidation with permanganate gave mainly oxalic acid. Attempts at molecular weight determination were a failure and no salts could be obtained, a neutral solution giving precipitates with metallic salts consisting of the original substance in colloidal form. The approximate composition was given by the formula $C_6H_9O_2$.

C was not closely examined. It was a brown amorphous substance insoluble in organic solvents but soluble in alkalies, having the composition $C_{11}H_{16}O_4$.

D was a reddish brown amorphous solid insoluble in all solvents, attacked by concentrated nitric acid to give a product $C_{11}H_{13}NO_6$. It had the composition represented by $C_6H_9O_2$ but did not resemble B. None of these products could be said to be a definite compound and their relationship to the original caoutchouc remains obscure.

A small quantity of hydrogen peroxide appeared to be formed during the oxidation, the presence of a peroxide, as shown by the liberation of iodine from potassium iodide and the development of a yellow colour with titanium sulphate, being observed in the aqueous extract of the oxidation product. A trace of laevulinic acid and also of laevulinic aldehyde or its peroxide also appeared to be present.

It was pointed out by Ostwald[71] in a note on Peachey's first paper that the rate of absorption of oxygen in these experiments was typical of an autocatalytic reaction, the formation of an unstable intermediate product which functioned as a catalyst, possibly a caoutchouc peroxide, being suggested. A similar view was held by Kirchhof,[68] as quoted above. Ostromisslenski[72] further showed that caoutchouc activates oxygen in a similar manner to the terpenes.

The action of oxygen on thin films of rubber at 75°-80° was also studied by Kirchhof,[73] who could not, however, obtain definite results. Great variations in the rate of oxidation were shown by different samples.

Resin free rubber, on exposure to the action of atmospheric oxygen in full sunlight for three months, was found by Boswell, McLoughlin and Parker[20] to have resinified to the extent of about 30 per cent. The resin formed was soluble in acetone and was separated into two fractions, one soluble in carbon disulphide, possessing properties similar to rubber and corresponding to $C_{10}H_{16}O$, the other insoluble in carbon disulphide, hard and brittle and corresponding to $C_{25}H_{40}O_9$.

The presence of laevulinic aldehyde in "tacky" rubber might be inferred from the occurrence of this aldehyde in the decomposition products of caoutchouc ozonide. The presence of an aldehydic substance in "tacky" rubber giving the pyrrole reaction, and therefore presumably laevulinic aldehyde, has been detected by Gorter,[74] whose observations have been confirmed by Bruni/

Bruni and Pelizzola[75] and by Whitby,[76] the latter preparing and characterising the well-known phenyl methyl dihydro-pyridazine derivative.

The disaggregating effect of concentrated sulphuric acid on chloroform solutions of caoutchouc, as noted by Heim and Marquis,[3] and already referred to, has been further studied by Kirchhof,[77] who treated carbon tetrachloride solutions of raw rubber with concentrated sulphuric acid in the cold. The rubber was found to give over ninety per cent yield of a brittle powder which was separated by extraction with acetone into two fractions, a reddish brown oxidation product and a hydrocarbon of the empirical formula $C_{10}H_{15}$. The latter gave with bromine and sulphur addition products corresponding to $C_{20}H_{30}Br_2$ and $C_{20}H_{30}S$, the disappearance of three double linkages being ascribed to the formation of tetramethylene rings in the rubber hydrocarbon under the influence of the concentrated acid. These observations were explained by reference to the supposed $C_{20}H_{34}$ empirical formula for caoutchouc, an open chain spiral structure being suggested. Prolonged treatment of the rubber solution with concentrated acid gave as final product $C_{10}H_{14}O$, assumed to be identical with the main product of the spontaneous oxidation of the caoutchouc hydrocarbon. Prolonged treatment of a benzene solution of rubber with concentrated sulphuric acid gave an acetone soluble reddish brown substance $C_{20}H_{30}O_3$, having the properties of an aldehyde acid. Precipitation of this substance from alcoholic potash solution with dilute sulphuric acid gave a product of the same empirical formula,

melting/

melting at 95°-96° after recrystallisation from acetone, reducing Fehling's solution and yielding a phenyl-hydrazone which sintered at 90° and melted at 120°-124°.

Oxidation of caoutchouc in glacial acetic acid - carbon tetrachloride solution with hydrogen peroxide was found by Boswell, McLoughlin and Parker (78) to yield as primary product a substance having the empirical formula $C_{30}H_{48}O$ which, on standing in air, absorbed oxygen to give a product $C_{25}H_{40}O_2$. This was explained by assuming the presence of a $C_{30}H_{48}$ nucleus in the caoutchouc molecule, the loss of a molecule of isoprene, followed by the addition of oxygen, giving rise to the more highly oxygenated product. A formula for caoutchouc was proposed on this basis and has already been referred to. The evolution of carbon dioxide during the oxidation was noted.

The action of potassium permanganate, which has proved of great value as an oxidising agent in the terpene branch of organic chemistry, has been investigated by Harries (50) and by Van Rossem (79). No oxidation products directly related to caoutchouc were isolated, the hydrocarbon itself being transformed into an oily modification, probably as a result of preliminary disaggregation. From the aqueous liquors after completion of the reaction Harries separated a small amount of fatty acids. Boswell and Hambleton, (80) by agitating a carbon tetrachloride solution of caoutchouc with aqueous potassium permanganate for several days, succeeded in effecting oxidation, a pasty mass having the composition $C_{25}H_{40}O$ being obtained. This product resembled caoutchouc in properties, being/

being insoluble in alcohol or acetone, but soluble in ether, carbon tetrachloride and petroleum ether. On standing in air it combined with oxygen, giving a substance of the composition $C_{25}H_{40}O_2$. Water soluble products were stated to be formed in addition to the above but no attempt appears to have been made to isolate or characterise them.

The action of perbenzoic acid on caoutchouc, with formation of a viscous oxide $(C_5H_8O)_x$ has already been referred to, and the same workers, Pummerer and Burkard,(6) found in addition that the final result of oxygen absorption by very dilute caoutchouc solutions was the same as with the peracid. Concentrated solutions of caoutchouc were found to absorb gaseous oxygen with extreme slowness. This can be readily understood on the basis of Harries' theory that the chemical reactivity of complex colloids varies inversely with their degree of aggregation. This may also help to explain some of the contradictory results quoted above.

PART II.

THE OXIDATION OF CAOUTCHOUC WITH POTASSIUM PERMANGANATE.

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The action of dilute aqueous permanganate has been studied by Harries,[50] Van Rossem[79] and Boswell,[80] only the latter being able to obtain a product definitely connected with caoutchouc. The work described beneath was undertaken in order to investigate the products obtained with increasing proportions of permanganate, the products at each stage being isolated and examined. The oxidation has been carried out both in aqueous and in alkaline solution, the neutral and acidic products being collected and, as far as possible, characterised.

The material used was plantation crêpe rubber, freed from resin by extraction for ten hours with acetone in a Soxhlet apparatus. The deresinised rubber was dissolved in carbon tetrachloride, in the case of the material for the neutral oxidations, and in benzene for the oxidations in alkaline solution, the solution being filtered through glass-wool to remove the insoluble matter. Sufficient solvent was distilled off to give an approximately 2 per cent solution of caoutchouc, quantities of the solution containing as nearly as possible 5 grams of hydrocarbon being used for each oxidation. The potassium permanganate solution used throughout was of 1 per cent strength, an equi-molecular proportion of caustic potash being added in the case of the oxidations in alkaline solution. The proportion of permanganate used was calculated on the basis of

one/

one atom of available oxygen for each $C_{10}H_{16}$ of caoutchouc, the proportion being 3.88 grams $KMnO_4$ to each 5 grams of hydrocarbon. Amounts of permanganate solution equivalent to 1, 2, 3, 4, &c. atoms of available oxygen were successively used, the weight of caoutchouc present being reduced in the higher stages of the oxidation so as to keep the volume of the reaction mixture at about two litres. The caoutchouc and permanganate solutions were mixed in stoppered bottles of two to three litres capacity, and the whole was mechanically shaken at room temperature until oxidation was complete, as shown by the disappearance of the purple permanganate colour in the aqueous layer. This operation required three or four days with the smallest proportion of permanganate, the time gradually increasing with the proportion of permanganate used, two to three weeks being necessary in the highest oxidations carried out.

The general procedure employed in the isolation of the oxidation products was the same throughout, the reaction mixture being allowed to stand after completion of the oxidation until separation into two layers was complete, the manganese dioxide remaining in every case in the layer consisting of the organic solvent and the dissolved oxidation product. The aqueous layer was removed as completely as possible by means of a siphon, and the manganese dioxide was separated from the benzene or carbon tetrachloride solution by filtration, a process which proved very tedious in the earlier stages of the oxidation, owing to the viscosity of the solution. This was especially the case with the benzene solutions of the alkaline oxidation products. The residue of manganese dioxide

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was washed with the solvent used during the corresponding oxidation and was then dried in air and powdered, a further digestion with solvent being resorted to in order to remove any adsorbed oxidation product. It was then repeatedly extracted with hot water to separate traces of soluble acid salts and was finally rejected.

The filtrate containing the oxidation product was dried over anhydrous sodium sulphate, the extract from the manganese dioxide being added. The solvent was then partly removed by distillation under reduced pressure and the oxidation product was precipitated by the addition of alcohol, being obtained as a white pasty mass. With increasing oxygen content this precipitation became less complete, the highest oxidation products only settling out after standing for a considerable time. With these it was found necessary to remove practically the whole of the solvent before adding alcohol. In all cases it was found advisable to remove the original solvent at the lowest possible temperature, resinification, as indicated by the development of a yellow colouration, taking place on heating to above 50°.

The precipitated oxidation product was thoroughly washed by decantation with alcohol and then with acetone, the last traces of solvent being removed by evaporation in vacuo. The final product was a clear syrup, slightly yellow in the lower oxidations, colourless in the higher, and of varying stickiness. It was finally dissolved in light petroleum, a clear solution in each case being obtained.

It was found that little change occurred in the oxidation products, even on long standing, in this solvent. This was not the case when carbon tetrachloride was used, as was discovered early in/

in the investigation. On standing for some time in this solvent, the flasks used being filled with carbon dioxide, two of the first neutral oxidation products were found, on analysis, to give higher values for oxygen than others which had been dissolved in petroleum ether. On examination chlorine was found to be present in both substances to the extent of over 16 per cent. The general appearance of these chlorinated products was similar to that of caoutchouc dihydrochloride.

The oxidation products were prepared for analysis by prolonged desiccation in vacuo over sulphuric acid, exposure to light being avoided and atmospheric oxygen being excluded.

It was found in every case that partial precipitation of the oxidation products took place on standing in petroleum ether solution, precipitation being very incomplete in the case of the substances containing small proportions of oxygen, and only occurring on standing for some time. The higher oxidation products, however, settled out after a few hours, the removal of the solvent being greatly facilitated by their assumption of a coherent form.

The aqueous layers from the original oxidation processes, together with the corresponding washings from the manganese dioxide residues, were saturated with carbon dioxide to neutralise free alkali and evaporated nearly to dryness on the water-bath. The solution of carbon dioxide during the oxidation of caoutchouc has been observed by Boswell (78) but, so far as could be ascertained, the aqueous extracts from the neutral oxidations were only faintly alkaline, so that no definite conclusion as to the production of carbonic /

carbonic acid could be drawn. The concentrated solution of potassium salts obtained by evaporation was acidified with dilute hydrochloric acid, saturated with salt, and thoroughly extracted with ether. The ethereal extracts were dried over anhydrous sodium sulphate, the bulk of the solvent was distilled off, and the remainder was evaporated in vacuo. The acid extracts from each oxidation were separately collected and set aside to allow of crystallisation taking place.

General Properties of the Oxidation Products.

The oxidation products obtained resembled one another in general appearance, varying from pale yellow, only slightly elastic, solids in the lower stages of oxidation, to colourless, non-elastic brittle resins in the higher. The lower members were completely insoluble in alcohol, even refluxing with alcohol failed to dissolve any appreciable amount. The higher members, particularly the three highest, were softened by alcohol, becoming semi-liquid and dissolving completely in presence of a little carbon tetrachloride. They were readily soluble in ether, benzene, chloroform, carbon tetrachloride, and petroleum ether; from the last solvent, however, more or less complete precipitation took place on standing, as has already been referred to. They showed no definite melting point, decomposition occurring to a greater or less extent in almost every case on heating. The property of swelling in solvents, so characteristic of rubber, was shown by all, the tendency becoming less with increasing oxygen content. This would indicate a decrease in molecular complexity with increasing oxidation and this is borne out/

ut by the very marked reduction in viscosity which takes place uring the addition of oxygen. The carbon tetrachloride and enzene solutions obtained after completion of the permanganate xodations were very much more mobile and less viscous than the riginal solution of caoutchouc.

Analyses of the various products, together with some special letails, are given below.

xidation in Neutral Solution.

I. One Atom of Oxygen per $C_{10}H_{16}$.

This was a pale yellow solid, slightly elastic, melting at 140°-145° with slight decomposition.

nalysis:

0.1787 gram substance gave 0.5098 gram CO_2 : 0.1669 gram H_2O.

his corresponds to a composition C = 77.81 per cent: H = 10.38 per ent : O = 11.81 per cent.

he empirical formula would be $C_{35}H_{56}O_4$. The composition on this asis should be

C = 77.78 per cent : H = 10.37 per cent : O = 11.85 per cent.

II. Two Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow solid, slightly elastic, melting at 130°-135° with slight decomposition.

nalysis:

0.1799 gram substance gave 0.5108 gram CO_2 : 0.1651 gram H_2O.

his corresponds to the composition

C = 77.45 per cent : H = 10.20 per cent : O = 12.37 per cent.

The empirical formula would be $C_{25}H_{40}O_3$. The composition on this basis should be

C = 77.32 per cent : H = 10.31 per cent : O = 12.37 per cent.

III. Three Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow brittle solid, melting at 150°-155° with slight decomposition.

Analysis:

0.1694 gram substance gave 0.4741 gram CO_2 : 0.1553 gram H_2O.

This corresponds to the composition

C = 76.32 per cent : H = 10.20 per cent : O = 13.60 per cent.

The empirical formula would be $C_{30}H_{48}O_4$. The composition on this basis should be

C = 76.27 per cent : H = 10.02 per cent O = 13.71 per cent.

IV. Four Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow brittle solid, melting at 115°-120° with very slight decomposition.

Analysis:

0.2007 gram substance gave 0.5534 gram CO_2 : 0.1792 gram H_2O.

This corresponds to the composition

C = 75.22 per cent : H = 9.92 per cent : O = 14.86 per cent.

The empirical formula would be $C_{20}H_{32}O_3$. The composition on this basis should be

C = 75.00 per cent : H = 10.00 per cent : O = 15.00 per cent.

V. Five Atoms of Oxygen per $C_{10}H_{16}$.

This was similar in appearance to IV, melting at 115°-120° with slight decomposition.

Analysis:

0.2008 gram substance gave 0.5440 gram CO_2 : 0.1628 gram H_2O.

This corresponds to the composition

C = 73.39 per cent : H = 10.11 per cent : O = 16.50 per cent.

The empirical formula would be $C_{30}H_{50}O_5$. The composition on this basis should be

C = 73.47 per cent : H = 10.20 per cent : O = 16.33 per cent.

VIII. Eight Atoms of Oxygen per $C_{10}H_{16}$.

This was a white brittle solid, melting at 110° - 115° with very slight decomposition.

Analysis:

0.1354 gram substance gave 0.3449 gram CO_2 : 0.1132 gram H_2O.

This corresponds to the composition

C = 69.47 per cent : H = 9.92 per cent : O = 21.24 per cent.

The empirical formula would be $C_{35}H_{56}O_8$. The composition on this basis should be

C = 69.53 per cent : H = 9.27 per cent : O = 21.20 per cent.

Oxidation in Alkaline Solution.

IA. One Atom of Oxygen per $C_{10}H_{16}$.

This was a pale yellow brittle solid, melting at about 90° with no decomposition.

Analysis:

0.1488 gram substance gave 0.3730 gram CO_2 : 0.1201 gram H_2O.

This corresponds to the composition

C = 68.37 per cent : H = 8.97 per cent : O = 22.66 per cent.

The/

The empirical formula would be $C_{24}H_{38}O_6$. The composition on this should be

C = 68.25 per cent : H = 9.00 per cent : O = 22.75 per cent.

IIA. Two Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow slightly elastic solid, melting at 105°-110° with very slight decomposition.

Analysis:

0.2014 gram gave 0.5665 gram CO_2 : 0.1860 gram H_2O. This corresponds to the composition

C = 76.71 per cent : H = 10.26 per cent : O = 13.03 per cent.

The empirical formula would be $C_{31}H_{50}O_4$. The composition on this basis should be

C = 76.54 per cent : H = 10.29 per cent : O = 13.17 per cent.

IIIA. Three Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow slightly elastic solid, melting at 115°-120° with slight decomposition.

Analysis:

0.2033 gram substance gave 0.5650 gram CO_2 : 0.1870 gram H_2O. This corresponds to the composition

C = 75.90 per cent : H = 10.22 per cent : O = 13.88 per cent.

The empirical formula would be $C_{29}H_{46}O_4$. The composition on this basis would be

C = 75.98 per cent : H = 10.05 per cent : O = 13.97 per cent.

IVA. Four Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow brittle solid, melting at 115°-120° with slight/

light decomposition.

Analysis:

0.1511 gram substance gave 0.4146 gram CO_2 : 0.1367 gram H_2O.

This corresponds to the composition

C = 74.83 per cent : H = 10.06 per cent : O = 15.11 per cent.

The empirical formula would be $C_{20}H_{32}O_3$. The composition on this basis would be

C = 75.00 per cent : H = 10.00 per cent : O = 15.00 per cent.

VA. Five Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow elastic solid, melting at above 190° with considerable decomposition.

Analysis:

0.1401 gram substance gave 0.4287 gram CO_2 : 0.1399 gram H_2O.

This corresponds to the composition

C = 83.45 per cent : H = 11.09 per cent : O = 5.44 per cent.

The empirical formula would be $C_{20}H_{32}O$. The composition on this basis would be

C = 83.33 per cent : H = 11.11 per cent : O = 5.56 per cent.

VIIIA. Eight Atoms of Oxygen per $C_{10}H_{16}$.

This was a pale yellow brittle solid, melting at 125°-130° with slight decomposition.

Analysis:

0.1825 gram substance gave 0.5082 gram CO_2 : 0.1640 gram H_2O.

This corresponds to the composition

C = 75.94 per cent : H = 9.98 per cent : O = 14.08 per cent.

The/

The empirical formula would be $C_{36}H_{56}O_5$. The composition on this basis would be

C = 76.06 per cent : H = 9.86 per cent : O = 14.08 per cent.

XA. Ten Atoms of Oxygen per $C_{10}H_{16}$.

This was a white brittle solid, melting at 100°-102° with slight decomposition.

Analysis:

0.1129 gram substance gave 0.2630 gram CO_2 : 0.0877 gram H_2O.

This corresponds to the composition

C = 63.53 per cent : H = 8.63 per cent : O = 27.84 per cent.

The empirical formula would be $C_{30}H_{48}O_{10}$. The composition on this basis should be

C = 63.38 per cent : H = 8.43 per cent : O = 28.19 per cent.

The preceding results show that with the neutral oxidation series the oxygen content increased steadily from member to member, the products obtained being generally very similar. In the alkaline series there were considerable irregularities, IIA showing a lower oxygen content that IA or IIIA, and VA having the lowest proportion of oxygen of any member of the series. These irregularities were not accidental, analyses of duplicate preparations, and also of samples of caoutchouc submitted to a continuous stage by stage oxidation, showing results in good agreement. The apparent discrepancy can be explained by assuming the fission of a more highly oxygenated portion from the caoutchouc molecule under the influence of the alkaline permanganate, leaving a more unsaturated residue. This is borne out by the nature of the acidic products from the alkaline/

alkaline oxidation, an appreciable amount of laevulinic acid being isolated from them. The ratio of carbon to hydrogen in caoutchouc is maintained throughout the series, the lowest carbon-hydrogen ratio being 7.26 in the case of V, the highest 7.62 in the case of IA, most of the others being within 0.1 of the calculated value 7.5. This would indicate that the oxidation products are intimately related to the parent hydrocarbon.

Chemical Properties of the Oxidation Products:

The oxidation products were, without exception, neutral, being unacted on by dilute alkali. They were unsaturated to bromine and were all acted on by aqueous alkaline permanganate, the higher members, however, were acted on only slowly by this reagent. The presence of aldehydic or ketonic groupings was tested for by refluxing portions of the oxidation products with alcohol, the alcoholic extracts gave no reactions for aldehydes with Schiff's reagent, Fehling's solution, or ammoniacal silver oxide, and did not form semicarbazones when treated with semicarbazide hydrochloride. It was therefore concluded that the oxygen was present either in the form of hydroxyl groups or in the anhydride form, the oxidation products being either alcohols of very high molecular weight, or inner oxides. To test for the presence of hydroxyl groups the oxidation products were heated with metallic sodium in dry benzene solution. No evolution of hydrogen could be detected but resinification slowly took place. As this usually happens when unsaturated substances are similarly treated, no conclusion could be drawn, regard being had to the work of Harries,(2) previously referred/

sferred to, on the chemical inertness of complex colloidal aggregates, pre especially in presence of a polymerising agent such as sodium. he action of gaseous hydrochloric acid on a glacial acetic acid-ther solution of the oxidation products was then investigated. onsiderable decomposition took place as indicated by the darkening f the reaction mixture, even when cooled in ice, this being most oticeable in the case of the higher oxidation products. After emoval of the solvents in vacuo and purification of the residue y solution in boiling ethyl acetate, a white powdery solid was btained, closely resembling the dihydrochloride of caoutchouc and elting about the same temperature, 115°-120°. This would indicate hat the oxidation products are still closely related to the original aoutchouc, though in what way is not clear so far as this method of ttack is concerned. Attempts to form p-nitrobenzoates, by heating the oxidation products with p-nitrobenzoyl chloride in pyridine solution, gave only sticky resins, which clung tenaciously to the p-nitrobenzoic acid formed after the removal of pyridine with dilute sulphuric acid. Similar attempts to form phenylurethanes by heating with phenyl isocyanate in benzene solution were also unsuccessful. Determinations of the bromine unsaturation capacity, however, gave some indication of the nature of the oxidation products.

Bromination of the Oxidation Products.

The proportion of bromine taken up in chloroform solution cannot be accurately determined by observations of colour changes, the addition of a few drops of the reagent to solutions of the higher oxidation products almost immediately producing a brownish colouration.

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The use of an external indicator, such as starch-potassium iodide, is unsatisfactory since substitution occurs if the titration be prolonged. The method employed by Gladstone and Hibbert (17) in their determinations of the bromine addition capacity of caoutchouc was used, a dilute solution of the oxidation product in chloroform being treated with a measured volume of a one per cent solution of bromine in chloroform, the addition of excess of bromine being ensured by the use of starch-potassium iodide paper as external indicator. The reactions were carried out at 0°, the mixture being well shaken after the addition of the bromine and allowed to stand for five minutes. Excess of a strong aqueous solution of potassium iodide was then added, the mixture was shaken so as to ensure complete absorption of residual bromine, and the liberated iodine was immediately titrated with standard sodium thiosulphate, using starch solution as indicator. Carbon tetrachloride was tried as solvent but was found to be useless, the brominated products being practically insoluble in it, forming a flocculent precipitate which rendered titration extremely difficult. It has been shown by various workers that iodine is only very slowly absorbed, even by caoutchouc itself, in dilute solution, and could not thus introduce any appreciable error into the determinations. The disaggregating effect of the bromine on the chloroform solutions of the oxidation products was very marked, the viscosity of the original solutions disappearing immediately on its addition. The chloroform solutions of the brominated products were perfectly fluid. No appreciable amount of hydrobromic acid was formed, as was verified by titration of

the/

he final reaction mixture with quarter-normal caustic sod. On standing, however, in almost every case, decomposition took place n the titrated solutions, iodine being liberated and the solutions becoming acid. Only the two first oxidation products in each series gave stable addition products. After separating and drying the chloroform solutions of the latter, the brominated products were obtained as white sandy powders by precipitation with alcohol. They have not been further examined. Several series of brominations were carried out, the results being in fair agreement. The solvent would appear to have some influence on the course of the reaction, the brominations carried out in carbon tetrachloride solution giving uniformly low results.

Results of the Bromination of the Oxidation Products.

Product.	Empirical Formula.	Gms. Bromine absorbed per gram of Product.	Gms. Br. per Gram. Mol. Product.
I.	$C_{35}H_{56}O_4$	1.79	967
II.	$C_{25}H_{40}O_3$	1.66	647
III.	$C_{30}H_{48}O_4$	1.65	779
IV.	$C_{20}H_{32}O_3$	1.45	464
V.	$C_{30}H_{50}O_5$	1.42	696
VIII.	$C_{35}H_{56}O_8$	1.42	858
IA.	$C_{24}H_{38}O_6$	1.88	793
IIA.	$C_{31}H_{50}O_4$	1.65	802
IIIA.	$C_{29}H_{46}O_4$	1.40	641
IVA.	$C_{20}H_{32}O_3$	1.46	467.

Results of the Bromination of the Oxidation Products (Contd.)

Product.	Empirical Formula.	Gms. Bromine absorbed per gram of Product.	Gms. Br. per Gram Mol. Product.
VA.	$C_{20}H_{32}O$	1.97	567
VIIIA.	$C_{36}H_{56}O_5$	1.54	875
XA.	$C_{30}H_{48}O_{10}$	1.58	897.

The approximate empirical formulae of these products would be, assuming the general structure to be mono-cyclic and of the type C_nH_{2n}.

I. $C_{35}H_{56}O_4Br_{12}$ or $C_{35}H_{53}(OH)_3Br_{12}O$:

IA. $C_{24}H_{38}O_6Br_{10}$ or $C_{24}H_{32}(OH)_6Br_{10}$.

II. $C_{25}H_{40}O_3Br_8$ or $C_{25}H_{38}(OH)_2Br_8O$:

IIA. $C_{31}H_{50}O_4Br_{10}$ or $C_{31}H_{47}(OH)_3Br_{10}O$:

III. $C_{30}H_{48}O_4Br_{10}$ or $C_{30}H_{45}(OH)_3Br_{10}O$:

IIIA. $C_{29}H_{46}O_4Br_8$ or $C_{29}H_{44}(OH)_2Br_8O_2$

IV. $C_{20}H_{32}O_3Br_6$ or $C_{20}H_{30}(OH)_2Br_6O$:

IVA. $C_{20}H_{32}O_3Br_6$ or $C_{20}H_{30}(OH)_2Br_6O$

V. $C_{30}H_{50}O_5Br_9$ or $C_{30}H_{45}(OH)_5Br_9$:

VA. $C_{20}H_{32}O\ Br_7$ or $C_{20}H_{31}(OH)\ Br_7$

VIII. $C_{35}H_{56}O_8Br_{11}$ or $C_{35}H_{49}(OH)_7Br_{11}O$:

VIIIA. $C_{36}H_{56}O_5Br_{11}$ or $C_{36}H_{53}(OH)_3Br_{11}O_2$

XA. $C_{30}H_{48}O_{10}Br_{11}$ or $C_{30}H_{38}(OH)_{10}Br_{11}$.

From these results it would appear that the oxidation products may be regarded as hydroxy compounds, at least after bromination, and therefore probably possess an initial hydroxy structure. The oxygen cannot be present in ketonic or aldehydic form, since such products would only require half as much bromine for saturation as that actually absorbed. This also applies to an inner oxide structure, unless rupture of the oxygen linkages by the bromine be assumed, which is not so probable. In any case the brominated oxidation products would have the general structure of highly complex cyclic bromo-hydrins. These substances would probably be very unstable, and this is borne out by the rapid decomposition of most of the brominated products, bromine being split off and the reaction mixtures becoming acid. It is interesting to note that while IV and IVA are almost identical in melting point, composition and bromine saturation capacity, V and VA are quite different in these respects, the latter being apparently more nearly related to the parent caoutchouc. On the other hand III and IIIA are of nearly the same empirical composition, but differ in melting point and in bromine saturation capacity. These facts seem to point to the conclusion that caoutchouc is much more complex than is expressed by the $C_{40}H_{64}$ formula, this is in agreement with the formation of a saturated hydrocarbon $C_{50}H_{102}$ in the pyrolysis of hydro-caoutchouc, as noted by Staudinger,(64) and Pummerer(7) and Koch. Staudinger (loc. cit.) has expressed the opinion that the caoutchouc molecule is very/

very large, containing possibly 100 or more isoprene nuclei, a hydrocarbon capable of giving rise to the product $C_{50}H_{102}$ by simple fission being necessarily of a high order of complexity. If the oxidation products described above be expressed as of the type $(C_5H_8)_xO_y$ which is approximately correct as regards carbon and hydrogen, the lowest common multiple of the values of $\frac{y}{x}$ is found to be 420. This would give a total of 420 isoprene nuclei in a caoutchouc complex, capable of giving rise to any one of the various oxidation products by simple addition of oxygen. This, however, is purely conjecture, the nature of the oxidation products being such as to render inapplicable all ordinary criteria of purity or chemical individuality.

Isolation of the Acid Products of Oxidation:

As already stated the acidic products of each separate oxidation were collected and set aside. On completing the series it was found that the quantity from each stage was not sufficient to allow of each being worked up separately, the products of the neutral oxidation were therefore combined, as were also those of the alkaline oxidation. The two series were then separately investigated.

Acid Products of the Neutral Oxidations.

All of these on standing deposited crystals in varying amounts, these were removed from the mother liquor by filtration, washed with ether, and separately examined. As the residual product, which was dark red in colour, viscous and somewhat sticky, obviously contained a considerable proportion of resin acids, which/

which would decompose on distillation, it was decided to esterify it. This was done by neutralising as exactly as possible with aqueous sodium carbonate, the resulting solution being evaporated to dryness and the mixed sodium salts dried in vacuo. Esterification was then carried out by refluxing the sodium salts with ethyl iodide in dry benzene solution for two days. The mixture was filtered to remove sodium iodide, and was then distilled under atmospheric pressure, two fractions being collected, one boiling below 60°, the other between 60° and 100°. Fractionation of the first gave a distillate boiling at 54°-56°, a pleasant smelling liquid which gave formic acid on hydrolysis with alcoholic potash and acidification of the potassium salt. The fraction boiling between 60° and 100° was further separated by fractionation into unchanged ethyl iodide and a liquid boiling at 75°-80°, smelling of ethyl acetate and giving acetic acid on hydrolysis, the latter being definitely identified by its conversion into acetanilide.

Distillation was then continued at 14 mm. pressure, a fraction boiling between 100° and 130° being obtained. Above this temperature practically nothing came over, decomposition of the residue of resin esters being indicated by darkening in colour and the appearance of traces of moisture in the distilling flask. This residue could not be distilled even in a high vacuum, being evidently complex in character. To separate the resin acid or acids the residue was hydrolysed with alcoholic potash, the excess of alkali was then removed by saturating with carbon dioxide. After distilling off most of the methyl alcohol the mixture was diluted with/

with water, acidified with dilute hydrochloric acid, and filtered. The precipitated resin acid was washed with water, redissolved in dilute aqueous sodium carbonate, and reprecipitated by the addition of dilute hydrochloric acid. After filtration and thorough washing with hot water it was dried in vacuo, the final product being a dark brown brittle resin, practically insoluble in water, readily soluble in alcohol, ether, and acetone, and in dilute aqueous sodium carbonate and bicarbonate.

Analysis of the Resin Acid.

0.1547 gram substance gave 0.3760 gram CO_2 : 0.0982 gram H_2O.

This corresponds to the composition

C = 66.32 per cent : H = 7.06 per cent : O = 26.62 per cent.

The empirical formula on this basis would be $C_{46}H_{58}O_{14}$, giving a composition corresponding to

C = 66.18 per cent : H = 6.96 per cent : 9 = 26.86 per cent.

In order to determine, if possible, the approximate molecular weight of this product, metallic salts were prepared with a view to analysis. It was found that the silver, calcium and barium salts were unsuitable, the first giving an unstable product which quickly decomposed on exposure to light, the second and third gave flocculent precipitates which would not settle out and filtered with extreme slowness. The lead salt, prepared by adding lead acetate solution to a neutral solution of the ammonium salt of the resin acid, settled out well and could be thoroughly washed by decantation before filtering. It was washed on the filter till free from lead salts and was then dried in vacuo and analysed, the lead being determined as sulphate by evaporation with concentrated sulphuric acid. The result of the analysis/

analysis was as follows:

0.3629 gram lead salt gave 0.1043 gram $PbSO_4$. Percentage of lead = 19.63. Assuming the acid to be dibasic, this would give a molecular weight of 1055-205 = 850. The molecular weight of the acid, assuming the formula $C_{46}H_{58}O_{14}$ would be 834, in fair agreement. The acid was colloidal in character, undergoing marked shrinkage on drying, in accordance with the usual behaviour of gels on removal of solvent.

The fraction described above, boiling at 100°-150° at 14 mm. pressure, was fractionated under ordinary pressure, being finally separated into two portions boiling at 185°-188° and 198°-205° respectively. The first fraction, on hydrolysis and extraction of the acid with ether, was found to consist of ethyl oxalate, the acid being identified by its melting point (189° for the anhydrous acid), by analysis of its calcium salt and by the preparation of oxanilide, M.P.255° by heating with aniline. The crystalline product separated, as already mentioned, from the original mixture of acids, was also found to be oxalic acid, a further small quantity of the acid being separated from the filtrate after final removal of the resin acid described above.

The fraction of ester boiling at 198°-205° gave on hydrolysis, acidification of the reaction mixture and subsequent extraction with ether, a thick yellow syrup which deposited crystals after removal of solvent and cooling in ice. These crystals melted at 25°-30° and were extremely soluble in water. The silver salt, prepared/

prepared from the neutral ammonium salt of the acid, was a white solid, crystallising in leaflets from hot water. A specimen gave on analysis the following results 0.2550 gram salt gave 0.1243 gram Ag. : 0.2501 gram CO_2 : 0.0689 gram H_2O. This corresponds to the composition Ag = 48.74 per cent : C = 26.75 per cent : H = 3.02 per cent : O = 21.49 per cent. This would give an empirical formula $C_5H_7O_3Ag$. This would require the composition Ag = 48.41 per cent : C = 26.91 per cent : H = 3.14 per cent : O = 21.54 per cent. The acid was therefore probably laevulinic acid $C_5H_8O_3$, a product which might reasonably be expected to occur in the oxidation products of caoutchouc.

The remainder of the acid was purified by conversion into the silver salt; the latter, after being purified by recrystallisation from hot water, was suspended in water and decomposed by passing in hydrogen sulphide. After removal of silver sulphide by filtration, the aqueous solution of the acid was concentrated by evaporation, the residue being dried in vacuo. No satisfactory melting point could be obtained, but the acid was positively identified by converting it into its semicarbazone. This was prepared by warming an aqueous solution of the sodium salt of the acid with semicarbazide hydrochloride. The semicarbazone was almost immediately precipitated, and after standing for some time was filtered off and recrystallised several times from hot water. After drying on porous plate the crystals were found to melt at 183°-184°, and showed no depression of melting point when mixed with a little laevulinic acid semi-carbazone similarly prepared. In addition the acid was found to give/

give iodoform immediately, on dissolving in cold sodium hydroxide containing iodine, a reaction characteristic of laevulinic acid.

The yield of laevulinic acid was very small, amounting to about one per cent of the caoutchouc oxidised.

Acid Products of the Alkaline Oxidations.

These were worked up in precisely the same way as those from the neutral oxidations, the products obtained being identical, with the exception of the resin acid. The latter was present in smaller amount and was apparently of more complex composition, though similar in solubility and in general appearance to the resin acid already described. Analysis gave the following results:

Analysis of Lead Salt of Resin Acid.

0.2204 gram substance gave 0.0511 gram $PbSO_4$. Percentage of lead = 15.84. Assuming the acid to be dibasic this would give a molecular weight of 1307-205 = 1102.

Analysis of the Resin Acid.

0.1728 gram acid gave 0.4109 gram CO_2 : 0.1019 gram H_2O. This corresponds to the composition

C = 64.85 per cent : H = 6.55 per cent : O = 28.60 per cent.

The empirical formula would be $C_{15}H_{18}O_5$, the composition on this basis being

C = 64.75 per cent : H = 6.47 per cent : O = 28.78 per cent.

The molecular weight of this product would be 278, which is much too low. $C_{80}H_{72}O_{20}$ gives a molecular weight of 4 × 278 = 1112, in fair agreement with that obtained from the salt of the acid.

The /

The proportion of laevulinic acid formed in the alkaline oxidations was considerably higher than that observed in the neutral series, amounting to three or four per cent of the caoutchouc used. Much less oxalic acid was formed, only one acid extract depositing crystals on standing. Both resin acids were unsaturated to dilute alkaline permanganate.

It was thought that a trace of higher fatty acid, possibly valeric acid, was present in the original acid extracts, as indicated by their odour, but none was actually isolated during the working up.

Owing to the small amount of the oxalic and laevulinic acid esters obtained during the final fractionation, it was found necessary to combine the highest boiling volatile products from both series of oxidations, the relative proportions of oxalic and laevulinic acids present being inferred from the amounts of ester obtained from the two series.

Conclusions.

The preceding work may be summarised as follows:

I. Caoutchouc on oxidation with dilute aqueous potassium permanganate in neutral and in alkaline solution gives a series of oxygenated products, regular in the case of the neutral oxidations, irregular in the case of the alkaline oxidations. These products are of the same general character as those obtained by other workers, differing however from the air oxidation products in being insoluble in alcohol or acetone. As has been pointed out, this is mainly a difference in degree, the insolubility in alcohol decreasing/

decreasing with increasing oxygen content. The complex structure of caoutchouc has been shown to persist throughout the series.

II. The chemical character of these oxidation products appears from the experimental evidence to be that of hydroxy-compounds, their inertness towards the usual reagents for the hydroxyl group being ascribed either to the complex nature of the aggregate, in accordance with the views of Harries,(2) or to the arrangement of the hydroxyl groups themselves. On the basis of the accepted structure of the caoutchouc molecule, these would be present as adjacent secondary and tertiary groupings, the latter in particular being easily dehydrated to give a non-reactive inner oxide structure. The presence of hydroxyl groups is further confirmed by the proportion of oxygen present in the lowest members of the oxidation series, the amount being greater in the case of I and IA than that available in the permanganate used. Having regard to the simultaneous formation of acidic products, though in small quantity, containing a much higher proportion of oxygen than the caoutchouc oxidation products, it must be concluded that the permanganate oxidation of caoutchouc in dilute solutions gives, as final product, a poly-hydroxy compound. Nothing definite can be said, owing to the impossibility of ensuring chemical purity, as to the chemical individuality of the oxidation products, but the characteristics of the products as a whole are those of a definite oxidation series, rather than those of a complex mixture of oxygenated substances.

III/

III. The suggestion has been made that the complex nature of the products is due to the presence in the caoutchouc molecule of a much larger aggregate of isoprene residues than is expressed in the usual formula.

IV. The acidic products of the oxidation have been shown to consist of the two lowest members of the fatty acid series, formic acid and acetic acid, together with oxalic acid and laevulinic acid. In addition complex resin acids, colloidal in character and of high molecular weight, have been isolated from both series of oxidations.

PART III.

The Oxidation of Caoutchouc with Chromyl Chloride.

The preliminary work of Spence (32) and Galletly on this reaction has already been mentioned. In view of the results obtained it seemed desirable to investigate more closely the nature of the products formed, both with regard to their bearing on the constitution of caoutchouc, and on the mechanism of the Etard reaction. The general procedure was that employed by Spence and Galletly, carbon tetrachloride, however, being used throughout as solvent in place of carbon disulphide. Preliminary trials showed this change of solvents to be desirable, the stability of carbon tetrachloride towards chromyl chloride in the absence of moisture being at least equal to that of carbon disulphide. The inflammability of the latter, in view of the very dilute solutions used and the large bulk of the reaction mixtures, made the use of another solvent almost necessary.

The caoutchouc used throughout was pale plantation crêpe, deresinised by extraction for 10 hours with acetone. The material was dissolved in carefully dried carbon tetrachloride and filtered through glass wool to remove insoluble matter, the resulting solution being concentrated to give as nearly as possible a caoutchouc content of 2 per cent. Freshly distilled chromyl chloride, in the proportion of 2.28 grams for each gram of caoutchouc to be treated, was similarly dissolved in dry carbon/

carbon tetrachloride to give a 5 per cent. solution. The weight of caoutchouc used in carrying out an oxidation was usually 25 grams, this being as much as could conveniently be dealt with in the later stages of extraction. The chromyl chloride solution was carefully added in successive small amounts to the caoutchouc solution, the mixture being well shaken after each addition to ensure complete reaction. The caoutchouc chromyl chloride compound separated immediately as a dark brown amorphous powder, the viscosity of the solution steadily diminishing with each addition of chromyl chloride, the final mixture being as fluid as the solvent used. As noted by Spence and Galletly, very little heat was evolved during the reaction, external cooling being unnecessary. The quantity of chromyl chloride required to complete the reaction was found to be as nearly as possible that corresponding to the formation of an addition product of the type $C_{10}H_{16}.2CrO_2Cl_2$, the reaction with caoutchouc being thus normal, no secondary reactions taking place. To ensure complete formation of the chromyl chloride compound, a few drops in excess of the theoretical amount of chromyl chloride were added and the reaction mixture was allowed to settle, the reaction was taken to be complete when the supernatant liquid remained slightly red in colour.

After completion of the reaction the insoluble chromyl chloride-caoutchouc compound was separated from the solvent by filtering/

filtering as rapidly as possible, the dark brown amorphous residue being washed on the filter with dry carbon tetrachloride till free from traces of chromyl chloride, and finally drained. Analysis of samples carefully dried in vacuo and ignited showed the composition to agree satisfactorily with that indicated above, further verifying the results of Spence and Galletley. When free from solvent the caoutchouc chromyl chloride compound is a light brown amorphous solid, insoluble in organic solvents not containing hydroxyl groups, slowly decomposed by atmospheric moisture and immediately decomposed by water.

The chromyl chloride compound was decomposed by adding it in small quantities to a large volume of ice-cold water, the mixture being vigorously shaken after each addition. Very little rise in temperature took place, the compound rapidly dissolving to give a pale green opalescent solution. When the whole of the chromyl chloride compound had been added the mixture was allowed to stand for some hours, the green colour becoming steadily darker, while a flocculent greenish white solid separated. To prevent oxidation of the decomposition products by liberated chromic acid a small quantity of sodium sulphite was added, this apparently had some effect in hastening the decomposition. When the latter appeared to be complete the mixture was thoroughly extracted with chloroform. Ether and carbon tetrachloride were tried as extraction media but were found to be unsatisfactory, the flocculent solid floating in

the/

the former and rendering separation almost impossible, while the decomposition products proved to be very much less soluble in the latter than in chloroform. The process of extraction proved to be very tedious, the chloroform being absorbed by the colloidal decomposition products and requiring several hours to settle in spite of its density. The soluble portion of the decomposition products was finally obtained as a dark brown brittle resin by distillation of the dried chloroform extracts and evaporation of the residue. As also found by Spence and Galletly, steam distillation of the decomposition mixture gave no volatile products.

To ensure complete decomposition of the chromyl chloride compound, the reaction mixture was refluxed on the water bath for several hours after completion of the preliminary extraction. Further extraction with chloroform gave a further small yield of the dark brown resin mentioned above. When extraction was complete the aqueous liquor, containing a considerable proportion of chloroform insoluble matter, was heated to expel the solvent and was then filtered while hot. The residue, which was pale greenish brown in colour, was washed free from chromium salts with hot water, and was then dried. After boiling with alcohol to remove traces of resin it was finally obtained as a light greenish brown, very finely divided powder, insoluble in water and in all neutral organic solvents.

Resin from the Decomposition of the Chromyl Chloride Compound.

This was obtained in a convenient form by evaporating a chloroform solution in vacuo and powdering the residue, the final product being a dark brown resin with a crystalline fracture, insoluble in water and in dilute alkalies, readily soluble in alcohol and acetone, somewhat less so in ether, leaving practically no residue. It has already been described by Spence and Galletly, who found it to be aldehydic in properties, and this has been verified. An alcoholic extract of the resin was found to decolourise dilute acid permanganate solution, restore the colour to Schiff's reagent, reduce Fehling's solution and ammoniacal silver oxide solution, and was also found to develop an intense yellow colour when heated with dilute caustic soda. From the alcoholic extract Spence and Galletly obtained a small quantity of a crystalline phenylhydrazone, melting at about 92°. Attempts to repeat this, by treatment of an alcoholic extract of the resin with phenylhydrazine acetate in acetic acid solution, have not been successful, this, however, will be referred to later.

Attempts to prepare a semicarbazone of the resin aldehyde were more successful. These were carried out by adding to an alcoholic solution of the resin a concentrated aqueous solution of semicarbazide hydrochloride and sodium acetate, turbidity being cleared by the addition of a little alcohol. The mixture was allowed to stand for a fortnight and was then fractionally/

fractionally precipitated with water. The precipitated semicarbazone was filtered off and dried, and was then purified by making a saturated solution in hot alcohol, cooling, and filtering off the precipitate. This was repeated until no change in the colour of the precipitate could be observed. The final product was a pale yellow very finely divided amorphous powder, readily soluble in alcohol, acetone, or ethyl acetate, insoluble in chloroform or carbon disulphide. It was obviously resinous in character, giving dark red solutions in alcohol and acetone and had no definite melting point, darkening in colour when heated and decomposing completely above 300° to give a black liquid.

Analysis of Semicarbazone of Resin Aldehyde.

0.1545 gram substance gave 11.4 ccs. moist N_2 at 16°C and 750 mm. pressure.

This gives a nitrogen percentage of 8.5

The usual method of separation of aldehydes by means of sodium bisulphite proved to be of little use in purifying the resin aldehyde. An alcohol-ether solution of the resin was treated with a saturated aqueous solution of freshly prepared sodium bisulphite, the mixture being shaken at intervals and allowed to remain for several weeks. The crystalline precipitate was removed by filtration, washed with alcohol and ether, and decomposed with dilute sodium carbonate. The mixture was thoroughly extracted with ether, a small quantity of a sticky yellow/

yellow syrup being obtained on evaporation of the solvent. A fresh quantity of bisulphite solution was added to the original solution of the aldehyde, and the precipitated crystals were separated, washed and decomposed as before. Several repetitions of this process gave as final product a small quantity of a white flocculent solid, possessing the characteristics of an aldehyde, but insufficient in amount to allow of characterisation. On prolonged standing in contact with the bisulphite the colour of the solution deepened to a dark red, and on evaporation of the mixture a very deep red solution was obtained, which on acidification with dilute hydrochloric acid gave a yellowish brown flocculent precipitate of a resin acid. This would indicate that the resin aldehyde had undergone oxidation, probably through absorption of atmospheric oxygen.

In order to characterise more completely the resin aldehyde, oxidation with dilute nitric acid was resorted to. The aldehyde was heated on the water bath with five per cent nitric acid, the operation being continued until a product completely soluble in dilute sodium carbonate was obtained. During the heating the colour of the solid slowly changed from dark brown to a much lighter colour, a small quantity of chromium salts passing into solution. The reaction would appear to give an almost quantitative yield of acid; with the exception of the chromium salt, which coloured the aqueous liquor dark red, and was only very slowly precipitated by sodium hydroxide or ammonia, no appreciable amount of soluble product was obtained. On

completion/

completion of the reaction the resin acid was filtered off, washed with hot water, and dried. It was purified by dissolving it in dilute aqueous sodium carbonate, filtering to remove traces of insoluble matter, and reprecipitating by the addition of dilute hydrochloric acid. It was filtered off, redissolved in sodium carbonate, reprecipitated by the addition of acid, and was finally filtered and washed on the filter with hot water till free from sodium salts. When moist it was a light brown gelatinous solid, obviously colloidal in character, shrinking on drying in vacuo to a dark brown brittle resin. This resin was insoluble in water, soluble in alcohol and acetone, and dissolved immediately in sodium carbonate and bicarbonate solutions and in ammonium hydrate, the solutions being dark red in colour.

With a view to obtaining some idea of the molecular complexity of this acid, one of its metallic salts was prepared. For the reasons given in connection with the preceding work on the resin acids from the permanganate oxidations, the lead salt was selected. This was prepared by adding lead acetate solution to a neutral solution of the ammonium salt of the acid, the precipitated lead salt being washed by decantation, and finally on the filter, till free from soluble lead salts. After drying in vacuo it was obtained as a dark brown resin, practically insoluble in the usual organic solvents. Owing to the presence of traces of chromium in the resin acid, which would have vitiated the usual method of estimating lead by evaporation with sulphuric acid, the organic matter in the samples analysed was destroyed by heating/

heating with nitric acid. After evaporation of excess of nitric acid the residue was dissolved in water, mixed with an equal volume of alcohol, and the lead was precipitated with sulphuric acid, being finally weighed as sulphate.

Analysis of Lead Salt of Resin Acid.

0.2810 gram substance gave 0.0855 gram $PbSO_4$ Lead = 20.79 per cent.

Assuming, as in previous cases, the acid to be dibasic, this would give a minimum molecular weight of 996 - 205 = 791 for a dibasic acid.

Analysis of Resin Acid.

0.1720 gram substance gave 0.3848 gram CO_2: 0.1167 gram H_2O: 0:0018 gram Cr_2O_3 (residue).

This would give Carbon = 61.1 per cent: Hydrogen = 7.5 per cent: Oxygen 30.3 per cent: Residue 1.1 per cent.

The chromium percentage is too low to allow of chromium being a possible constituent of the acid, and it may therefore be regarded as an adsorption. The results calculated on this basis would give

Carbon = 61.72 per cent: Hydrogen = 7.67 per cent.

Oxygen = 30.61 per cent. This would correspond to an empirical formula $C_8 H_{12} O_3$. The composition of this would be

Carbon = 61.55 per cent: Hydrogen = 7.69 per cent:

Oxygen = 30.76 per cent.

The molecular weight would be 156, a value much too low in view of the properties of the acid. The formula $C_{40} H_{60} O_{15}$ would give

a/

a molecular weight of 156 x 5 = 780, in fair agreement with the value 791 for the lead salt, or, allowing for the chromium residue, 778.

The acid $C_{40}H_{60}O_{15}$ should in turn be derived from a di-aldehyde of the composition represented by $C_{40}H_{60}O_{13}$. The di-semicarbazone of this aldehyde should have a nitrogen content of 8.6 per cent. That actually found by experiment, as previously stated, was 8.5 per cent.

The resin acid was unsaturated to dilute aqueous alkaline permanganate, in addition the deep red colour of its sodium and ammonium salts in solution might possibly indicate the presence of hydroxyl groups. It had no definite melting point, blackening when heated above 200° and remaining solid at 240°. It was thought that esterification of the acid might yield methyl esters which could be distilled under reduced pressure, thus affording a means of purification. The sodium salt of the resin acid was therefore prepared by adding a slight excess of the acid to a solution of sodium carbonate, filtering, and evaporating to dryness, the residue of sodium salt being dried in vacuo. Esterification apparently took place readily, the benzene solution soon becoming coloured. When the reaction was considered to be complete, the benzene was distilled off, the last traces being removed in vacuo. The residue was then extracted with hot alcohol, until practically colourless. Evaporation of the alcohol left a dark red brittle resin, evidently of complex nature, much more easily soluble in alcohol and/

[Esterification was then carried out by refluxing the sodium salt with the requisite amount of dimethyl sulphate, calculated on the basis of the formula given above, benzene being used as solvent]

and ethyl acetate than the original acid. It decomposed on heating and could not be distilled without breaking down. A very similar product was obtained by the Fischer Speier esterification method, a suspension of the sodium salt of the acid in absolute methyl alcohol being refluxed on the water bath while a slow stream of hydrochloric acid gas was passed through the reaction mixture.

Insoluble Residue from the Chromyl Chloride Compound.

This was finally obtained, as already described, as a light greenish brown powder, insoluble in all neutral organic solvents. On prolonged heating in glacial acetic acid or anhydrous formic acid, it passed completely into solution. It dissolved fairly readily in dilute sodium hydrate on heating, giving a very deep red solution, the same result being obtained, but much more slowly, with sodium carbonate solution.

The insoluble residue, on analysis, was found to contain both chromium and chlorine in approximately the same proportions, the values being about 1½ per cent; higher than those found by Spence and Galletly.

Analysis of Insoluble Residue.

Chlorine: 0.5280 gram substance gave 0.1276 gram.AgCl.
Chlorine = 5.98 per ct.

Chromium: 0.5360 gram " " 0.0504 gram.Cr_2O_3
Chromium = 6.46 " "

0.1658 gram substance gave 0.3065 gram CO_2: 0.1073 gram H_2O:
0.0174 gram residue (Cr_2O_3).

This corresponds to Carbon = 50.42 per cent: Hydrogen = 7.19 per cent
Residue = 10.49 per cent.

The complete composition is C = 50.42%: H = 7.19%: O = 29.95%: Cr = 6.46%: Cl = 5.98%.

No empirical formula of reasonable size can be calculated on this basis, it is therefore advisable to regard this substance as a colloidal adsorption product, the constancy of the chlorine and chromium content, as noted by Spence and Galletly, being due to the constancy of the conditions under which the whole reaction was carried out with different samples of caoutchouc. As will be shown later, it is not a necessary product of the decomposition of the caoutchouc chromyl chloride compound; it is perhaps best considered as representing an intermediate stage in the action.

As stated above, the insoluble residue was found to dissolve completely in glacial acetic acid on heating, a pale green opalescent solution, reminiscent of the original aqueous solution of the chromyl chloride compound, being obtained. Heating was continued until a small quantity of the reaction mixture, on dilution with water, gave no trace of green residue. The mixture was then cooled and largely diluted with water, a brown resinous solid being precipitated, and the chromium remaining in the aqueous liquor. The resin was filtered off, washed with hot water, and dried. It was finally obtained as a dark brown powder, almost completely soluble in chloroform, largely so in alcohol. The alcoholic extract gave similar aldehyde reactions to the chloroform soluble resin obtained in/

in the first part of the oxidation, and already described. A semicarbazone was therefore prepared exactly as in the first case. This was separated by fractional precipitation with water, and was purified as far as possible by repeated precipitation from a hot concentrated alcoholic solution.

Analysis of Semicarbazone of Intermediate Aldehyde.

0.1664 gram substance gave 10.4 ccs. moist N_2 at 16°c and 751 mm.press. Nitrogen = 7.2 per cent. The aldehyde semicarbazone was a pale yellow finely divided powder, very readily soluble in alcohol and acetone, insoluble in chloroform or carbon disulphide. It showed no definite melting point, darkening in colour when heated, and decomposing to a black liquid above 300°. It was evidently resinous in character.

The corresponding acid was prepared from the aldehyde resin as already described, by heating with five per cent. nitric acid, the final product being purified by precipitation of the sodium salt with dilute hydrochloric acid. It was finally isolated as a dark brown resin, soluble in alcohol and acetone, and dissolving readily in dilute aqueous sodium carbonate and bicarbonate, and in ammonium hydrate, to give deep-red solutions. From these the acid was precipitated by the addition of dilute mineral acid as a light brown flocculent solid, shrinking considerably on drying and evidently colloidal in character. It had no definite melting point, decomposing at about 210° to a black liquid.

Analysis/

Analysis of Intermediate Acid from Insoluble Residue:

0.1774 gram substance gave 0.4012 gram CO_2: 0.1143 gram H_2O: 0.0029 gram residue (Cr_2O_3). The chromium in this case also is too small in amount to be regarded as a constituent of the acid. Treating it as an adsorption, these figures would give the composition

Carbon = 62.67 per cent: Hydrogen = 7.27 per cent:

Oxygen = 30.06 per cent.

The empirical formula corresponding to this would be $C_{28}H_{38}O_{10}$.

On this basis the composition should be

Carbon = 62.92 per cent: Hydrogen = 7.12 per cent: Oxygen = 29.96%.

The lead salt of the acid was prepared and purified as far as possible by the method already given. It was very similar in general appearance to the lead salt of the aldehyde resin acid.

Analysis of Lead Salt of Acid from Intermediate Aldehyde.

0.2849 gram substance gave 0.0673 gram $PbSO_4$.

Lead = 16.13 per cent.

Assuming the acid to be dibasic this would give a molecular weight of 1284-205 = 1079, or if the chromium residue in the acid be allowed for, 1058.

The composition $C_{28}H_{38}O_{10}$ would give an empirical formula weight of 534. Doubling this formula would give $C_{56}H_{76}O_{20}$ corresponding to a molecular weight of 1068, in fair agreement with the value obtained from the lead salt and with the general properties of the acid.

The/

The acid should be derived from a di-aldehyde, $C_{56}H_{76}O_{18}$, the di-semicarbazone of which would have a nitrogen content of 7.3 per cent. That found experimentally, as stated above was 7.2 per cent.

This acid, like the acid from the original resin aldehyde, was unsaturated towards dilute alkaline pernanganate.

Acid from the Insoluble Residue.

The pale green insoluble residue from the decomposition of the chromyl chloride compound was found, as previously mentioned, to dissolve fairly readily in hot dilute sodium hydrate, the same action taking place, but more slowly, with sodium carbonate solution. The latter was used in preference to the former as being less likely to cause any drastic chemical change. After prolonged heating on the water bath, the sodium carbonate solution being periodically changed, practically the whole of the organic matter passed into solution, leaving a residue of chromium hydroxide. The alkaline extracts, which were deep red in colour, were acidified with dilute hydrochloric acid. A light brown flocculent precipitate separated, which was removed by filtration and purified by successive solution in sodium carbonate and reprecipitation with dilute hydrochloric acid. After washing with hot water till free from sodium salts the acid was dried in vacuo, undergoing shrinkage to a dark brown brittle resin, very similar in appearance and solubilities to the two resin acids previously described. Like them it was unsaturated to dilute aqueous alkaline permanganate.

Analysis/

Analysis of Acid from Insoluble Residue.

0.1771 gram substance gave 0.3977 gram CO_2: 0.1320 gram H_2O: 0.0035 gram residue (Cr_2O_3). Treating the residue of chromium oxide as an adsorption, as in the previous cases, this would give the composition Carbon = 62.48 per cent: Hydrogen = 8.45 per cent: Oxygen = 29.07 per cent. The empirical formula corresponding to this would be $C_{44}H_{70}O_{15}$, the composition on this basis should be Carbon = 63.01 per cent: Hydrogen = 8.35 per cent: Oxygen = 28.64 per cent. The lead salt of the acid was prepared and purified as already described, it was very similar in appearance to the corresponding salts of the two preceding acids.

Analysis of Lead Salt.

0.2912 gram substance gave 0.0838 gram $PbSO_4$. Lead = 19.65% Assuming the acid to be dibasic, this would give a molecular weight of 1054-205 = 849, or if the chromium residue in the acid be allowed for, 828. The formula given above, $C_{44}H_{70}O_{15}$, would give a molecular weight of 838, in good agreement.

This acid was of the same complex character as those already described, melting with decomposition above 240°C. Attempts were made to effect purification through its methyl ester, alternative methods of preparation being tried for this. The sodium salt of the acid when heated with dimethyl sulphate in dry benzene gave as final product a dark-red resin, very soluble in alcohol, acetone and acetic ester. This resin decomposed on heating/

heating and was as intractable as the original acid. Esterification of the acid itself by the Fischer Speier method gave a very similar product.

The relationships existing between the three acids described are completely obscure. In the absence of any satisfactory means of determining the actual molecular weights of these products, no indication of the degree of molecular complexity can be obtained. If the formulae be written so as to give the same number of oxygen atoms in each, they become, in the order in which the acids are described, $C_{40}H_{60}O_{15}$, $C_{42}H_{58}O_{15}$, $C_{44}H_{70}O_{15}$. The acid obtained by treatment of the insoluble residue with sodium carbonate thus contains the highest proportion of hydrogen, the lower hydrogen content of the other two being possibly due to the oxidising effect of the dilute nitric acid used in their preparation. The first two are of nearly the same empirical composition, but differ considerably in the proportion of lead present in their lead salts. If the first acid is regarded as dibasic, the second may be regarded as tribasic, the acids otherwise being very similar.

It is possible that the insoluble residue from the decomposition of the caoutchouc chromyl chloride compound represents an intermediate stage in the decomposition, but its complexity, as shown by the fact that the smallest empirical formula representing its composition is $C_{101}H_{171}O_{45}Cr_3Cl_4$, would indicate that it is merely an adsorption product of the aldehyde resin itself. Its solubility in acetic and formic acids/

acids, with formation of an aldehyde resin, may simply be due to disaggregation, these acids having been shown by Harries to effect "peptization" of complex organic colloids. The solution of the insoluble residue in sodium carbonate may similarly be due to slow oxidation of the resin aldehyde by absorption of atmosphere oxygen, the acid so formed passing into its sodium salt in presence of the alkali. In any case the results of the chromyl chloride oxidation of caoutchouc indicate that the hydrocarbon is of very complex structure and high molecular weight, the aldehyde resin and insoluble residue constituting practically the entire yield of decomposition product, and occurring in approximately equal quantities when the reaction is carried out in the usual manner.

Water Soluble Products of the Oxidation.

The occurrence of laevulinic acid as a normal product of the permanganate oxidation of caoutchouc made it very probable that it would be present among the decomposition products of the chromyl chloride oxidation. This idea was supported by the fact that Spence and Galletly isolated from the chloroform extracts of the oxidation products a substance, giving a phenylhydrazone which melted about 92° and was crystalline. Laevulinic aldehyde phenylhydrazone is an oil, and cannot be induced directly to crystallise, but the phenylhydrazone of laevulinic acid is crystalline and melts at 108°.

After complete extraction of the resin aldehyde and removal of/

of the insoluble residue by filtration, the aqueous liquor from the decomposition of the chromyl chloride compound was saturated with salt and extracted with ether. A small amount of a sticky yellow syrup was obtained on removal of the solvent, a drop of this substance gave a very distinct pyrrole reaction after heating with alcoholic ammonium acetate. This would point to the presence of laevulinic aldehyde in the aqueous residue, extraction being rendered difficult by the large bulk of the latter and the solubility of the aldehyde in water. In order to remove any laevulinic aldehyde or acid extracted by the chloroform along with the aldehyde resin, the latter was washed with a little ether, the washings being added to the ether extract from the aqueous residue.

The yellow syrup obtained by evaporation of the ether extracts was dissolved in alcohol, a strong aqueous solution of semicarbazide hydrochloride and sodium acetate was added, and the mixture was allowed to stand for a fortnight. The mixture was then evaporated to dryness in vacuo and washed with small portions of absolute alcohol. These extracts on evaporation gave a sticky residue from which nothing crystalline could be separated, the presence of the very soluble resin semicarbazone making purification almost impossible.

In order to protect the laevulinic aldehyde, if formed, from oxidation by traces of chromic acid set free during the decomposition of the caoutchouc chromyl chloride compound, the/

the latter operation was carried out in one case using water saturated with sulphur dioxide. Decomposition of the chromyl chloride compound took place very rapidly and completely, the sole product being the aldehyde resin, no trace of insoluble residue being formed. This would definitely point to the latter as being actually an intermediate product of decomposition, possibly formed by union of two or more molecules of partly decomposed chromyl chloride compound. The final result would be a product of more complex character than the aldehyde resin, but capable of decomposition to a similar substance. This is borne out by its behaviour towards sodium carbonate and glacial acetic acid, as already described. The insoluble residue, once formed, is perfectly stable towards sulphurous acid, it is thus probable that the action of the latter is to prevent intramolecular polymerisation during the decomposition. This method of decomposition was not generally used, extraction of the resinous products being rendered extremely difficult by the absence of the insoluble residue, which served to distribute them more completely through the aqueous liquor, and thus reduced their extreme stickiness in presence of the solvent used for extraction.

After complete removal of the resins by extraction with chloroform, the aqueous residue was heated to expel the remainder of the solvent. It was then cooled, saturated with salt, and extracted with ether. The ethereal extracts on evaporation yielded a small amount of a yellow syrup, a drop of which gave a very definite pyrrole reaction after heating with alcoholic ammonium acetate. This syrup was/

was dissolved in 50 per cent acetic acid and treated with an aqueous solution of phenylhydrazine acetate, the mixture being warmed and allowed to stand. No crystals separated and, even after evaporation to dryness in vacuo and extraction of the residue with alcohol, no crystalline product could be isolated. The alcoholic extracts, however, after evaporation to dryness and treatment with dilute hydrochloric acid, gave a small quantity of a product which crystallised from alcohol in pale yellow leaflets and melted at 195°-196°. It would thus appear to be 1-phenyl-3-methyl-dihydro-pyridazine, the most characteristic derivative of laevulinic aldehyde. The chromyl chloride oxidation of caoutchouc would therefore appear to give rise to a small amount of laevulinic aldehyde, this being oxidised to laevulinic acid under the ordinary conditions of the reaction.

Conclusions.

I. The oxidation of caoutchouc with chromyl chloride gives rise to two main products, a resin with aldehydic properties, oxidisable to a corresponding acid, and a complex insoluble product containing both chromium and chlorine.

II. The insoluble product undergoes decomposition on heating with glacial acetic acid, chromium and chlorine being eliminated and a resin of aldehyde properties being formed. This resin aldehyde is also oxidisable to a closely related resin acid.

III. The insoluble product is also decomposed on prolonged heating with aqueous sodium carbonate, a resin acid being formed with the elimination of chromium and chlorine.

IV. The insoluble residue does not appear when the caoutchouc chromyl chloride/

chloride compound is decomposed by sulphurous acid. This has been explained by assuming that the insoluble product arises through polymerisation of the chromyl chloride compound during decomposition. V. The probable presence of laevulinic aldehyde as a decomposition product has been shown. The relationships between the various products and the caoutchouc hydrocarbon are so far completely obscure, the impossibility of ascertaining the purity or otherwise of the oxidation products making conjecture useless.

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