CONSTITUTION
OF CAOUTCHOUC

OBSERVATIONS RELATIVE TO THE CONSTITUTION OF CAOUTCHOUC

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OBSERVATIONS RELATIVE TO THE CONSTITUTION OF CAOUTCHOUC.

Part I - Historical Review.

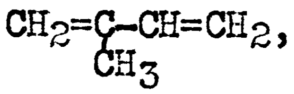
The constitution of caoutchouc is a problem which has interested and baffled organic chemists ever since the work of Williams (1) in 1860. This investigator discovered that the pyrogenic decomposition of caoutchouc yielded as one of the chief products, isoprene. Later in the same year he noticed that the isoprene fraction obtained from rubber, on standing for a period of months, was transformed into a viscous fluid. On attempting to distill this product a small quantity of isoprene passed over first, then the contents of the flask were suddenly transformed into a spongy, elastic mass, which, on burning, gave off the characteristic smell of burning rubber. The analysis of the elastic product agreed with the composition $C_{10}H_{16}O$.

In 1879 Bouchardat (2) obtained an elastic product by treating isoprene with aqueous HCl. Analysis of the product showed a small amount of Cl, which Bouchardat assumed could be regarded as an impurity. The carbon-hydrogen ratio agreed very closely with that required by $C_{10}H_{16}$.

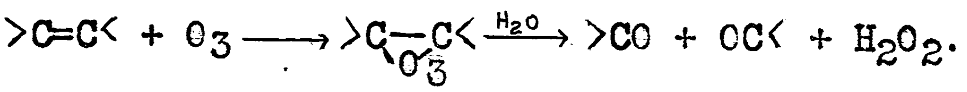
Later Tilden (3), Pickles (4), Wallach (5), Harries (6) and others observed that isoprene, treated under various conditions, polymerised to a product which appeared to be identical with the rubber hydrocarbon.

In 1888 Gladstone and Hibbert (7) published a paper dealing chiefly with the optical properties of caoutchouc. The samples they employed yielded, on analysis, values for carbon which were considerably lower than the theoretical. One sample only was obtained which gave a value for carbon within 1% of that required by $C_{10}H_{16}$. This difficulty persists to the present and it cannot be said that any investigator has ever obtained pure caoutchouc from crude rubber.

From the values found for the molecular refractive power and the molecular dispersive power of caoutchouc solutions these investigators concluded that caoutchouc must have three double bonds.per $C_{10}H_{16}$. This is the first recorded attempt to throw light on the structure of caoutchouc.

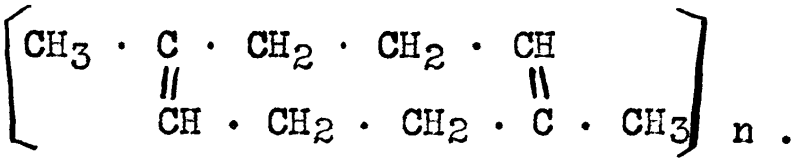
In 1884 Tilden (8) proposed the formula  $CH_2=\underset{CH_3}{C}-CH=CH_2$, for isoprene which was subsequently verified by Ipatiew and Wittorf (9). The way in which isoprene united to form caoutchouc, however, was a problem left untouched until Harries began his work on the action of ozone on the hydrocarbon.

Ozone has been shown by Harries (10) to act on ethylenic linkages in the following manner

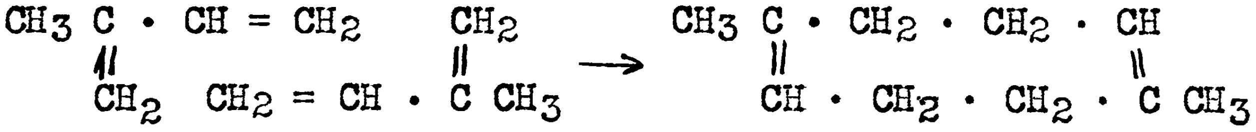


$$>C=C< + O_3 \longrightarrow >\underset{O_3}{C-C}< \xrightarrow{H_2O} >CO + OC< + H_2O_2.$$

By treating caoutchouc solutions with a stream of ozonised oxygen Harries obtained a product which he assumed was an ozonide with the above type of structure. As this product was explosive on standing it was treated directly with water and yielded as the only recognizable products laevulinic aldehyde, laevulinic aldehyde diperoxide and laevulinic acid. Hence, he assumed that caoutchouc contained the grouping, $CH_3.\underset{\parallel}{C}.CH_2.CH_2.\underset{\parallel}{CH}$, the double bonds being in the 1:4 positions. Molecular weight determinations in acetic acid solution gave a value of 233 for the ozonide, which approximated closely that required for a molecule with ten carbon atoms. From these facts Harries concluded that caoutchouc possessed the structure

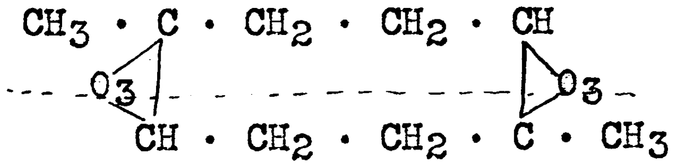


As the molecular weight of the hydrocarbon is known to be very much higher than that corresponding to the ozonide, it was assumed that the 8-membered rings were in turn polymerised to a complex of very high molecular weight, by means of partial valences (Kolloid Nebenvalenzen). The polymerisation of isoprene to the ring structure is represented by Harries as taking place according to Thiele's theory, the double bonds reacting in the 1, 4 positions.



The cyclo-octadiene rings were then assumed to polymerise to the higher complex.

The ozonide of caoutchouc was assigned the structure



By scission along the dotted line this ozonide would give laevulinic aldehyde, laevulinic aldehyde deperoxide, or, as a secondary product, laevulinic acid, presumably formed by the action of H_2O_2 which would be liberated on treatment of the ozonide with water.

By treating with ozone which had not been thoroughly washed with H_2SO_4 and NaOH, a product containing considerably more oxygen was obtained. This product was called an oxozonide and its formation was attributed to the action of a hypothetical allotropic form of oxygen, O_4, for the existence of which there has been no evidence advanced. It is far more probable that the washing with NaOH and H_2SO_4 merely reduced the strength of the ozone, instead of removing the O_4.

Later, Harries was forced to abandon the 8-membered ring structure, partly on account of the discovery of more complex scission products of the ozonide than could be accounted for by a ring of that size, and partly on account of the behaviour of the hydrochloride $(C_{10}H_{16} \cdot 2HCl)_n$ on heating in vacuo at 100°C. Under this treatment the hydrochloride gradually gave off HCl, and on analysis at the end of 5, 7, 14, and 20 days respectively, values were obtained which corresponded roughly with the compositions

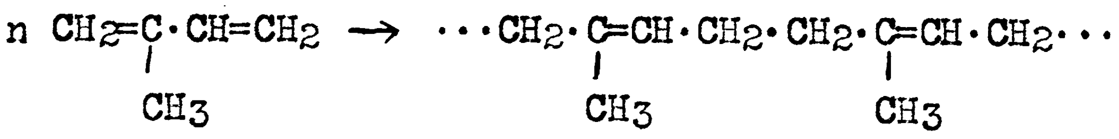
$$C_{25}H_{40}\cdot 5HCl \rightarrow C_{25}H_{40}\cdot 4HCl \rightarrow C_{25}H_{40}\cdot 3HCl$$

$$\rightarrow C_{25}H_{40}\cdot 2HCl \rightarrow C_{25}H_{40}\cdot HCl \ .$$

Further heating caused no further loss of HCl from the monohydrochloride.

These facts, then, led Harries to the belief that, instead of the 8-membered ring, caoutchouc possessed a 20-membered ring with the formula $(C_{25}H_{40})_x$. This ring would be built up from isoprene in a manner similar to that given for the 8-membered ring, but would contain 5 isoprene units. Molecular weight determinations on the ozonide, using benzene as a solvent, gave a value of 535, while $C_{25}H_{40}O_{15}$ requires 580. The molecular weight of 233, obtained in acetic acid solution was discarded on the assumption that acetic acid dissociated the ozonide.

In 1910 Pickles (11) advanced a formula for caoutchouc, which, to use his words, avoids "the vague and unnecessary conceptions of polymerisation" of ring systems. His formula represents caoutchouc as being built up of isoprene in the following manner



$$n\ CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\cdot CH{=}CH_2 \rightarrow \cdots CH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH\cdot CH_2\cdot CH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH\cdot CH_2\cdots$$

The oxidation results and the addition of halogens require that the two ends of the long chain thus formed be linked together. Pickles suggests that in each molecule there is only one such ring. This avoids the necessity of assuming two steps in the polymerization of isoprene to caoutchouc. The scission products of the ozonide are also accounted for quite as satisfactorily as by Harries formula.

The main objections offered by Pickles to the formula of Harries, although directed at the 8-membered ring structure, apply as well to the larger ring. They are as follows: The polymerization of the rings must be purely physical, or else the connection must be so loose, that the ozone first depolymerizes the caoutchouc aggregates and then acts on the double bonds. If the polymerization were chemical, some of the double bonds would be saturated, which is not borne out by the action of halogens and halogens acids, as they show the existence of two double bonds and still have very complex molecules. If ozone depolymerizes caoutchouc there is no reason why halogens and halogen acids should not do the same, producing products with as low molecular weight as the ozonide. In brief, according to whether or notthe polymerization were chemical or physical, we should expect to get,

1. Addition of not more than 4 molecules of Br_2 with the caoutchouc remaining in the polymerized state, or
2. Addition of 5 molecules of Br_2 with the production of simple molecules.

As neither of these results is obtained it is a case of reductio ad absurdum.

Olivier (12), in 1921, repeated some of Harries' work on the preparation of the ozonide of caoutchouc. In his experiments extreme precautions were taken to exclude all traces of moisture, the ozone being dried carefully and the solvent and caoutchouc freed from all traces of water. The passage of ozone was stopped as soon as a drop of the solution failed to decolorise immediately a few drops of a dilute solution of Br_2 in chloroform. The product was precipitated six times and dried in vacuo over $CaCl_2$ and KOH. Under these conditions constant weight could not be obtained, owing to persistent losses of volatile matter. The molecular weights obtained after 2 and 49 days respectively were 558 and 703.

Kept over H_2SO_4, after 2 and 13 days respectivbly, values of 869 and 636 were obtained.

A similar preparation, excessively ozonized, gave values of 325 and 487 after 1 and 19 days respectively.

From these facts Olivier argues that there is no reason for believing Harries' ozonide to be a homogeneous body, therefore the molecular weight cannot be used as an argument in favour of his formula. Again, as the normal ozonide is decomposed by ozone, it is probable that the same is true of caoutchouc itself.

Olivier also repeated Harries' work on the thermal dissociation of the hydrochloride, but states that the values obtained were by no means as significant as those of Harries. The latter, it may be pointed out, has offered no experimental evidence whatever in confirmation of his assumption that the various hydrochlorides were homogeneous, and as the periods of time between analyses were altogether arbitrary, there is no reason for assuming such to be the case.

The view that the polymerization of isoprene to caoutchouc proceeds in two stages has another protagonist in Aschan,[13] who studied the condensation of isoprene with unsaturated hydrocarbons such as amylene, pinene, and camphene, under the influence of $AlCl_3$. In all cases two classes of products were obtained, one insoluble in all organic solvents and one soluble in most organic solvents with the exception of alcohol. The two classes of products had the same percentage composition and almost identical additive capacity. From this evidence Aschan argues that the soluble compound is the simple polymer, and the insoluble, the complex aggregate. However, the crucial point in the establishment of this view was not even investigated, no evidence being offered in support of the view that the soluble product would polymerize to the insoluble. The possibility that the two are of altogether different structural types was not excluded.

Further evidence submitted as being in favour of the polymerized ring structure is that of W. C. Schmitz (14) on the bromination of what he calls depolymerized caoutchouc. By heating a xylene solution of acetone-extracted rubber at 285°C and 13 - 15 atmospheres pressure, a limpid solution was obtained, which, on centrifuging, was readily freed from all impurities. On distilling off the solvent an oily mass was obtained which gave a carbon-hydrogen ratio of exactly 10 to 16. Treatment with Br_2 in CCl_4 solution indicated a bromine absorption of 5 Br_2 per $C_{20}H_{32}$. On standing, the solution slowly evolves HBr until exactly two molecules have been given off. The author interprets the experimental evidence as follows : On depolymerization the rings are probably opened, yielding a product with 5 double bonds per $C_{20}H_{32}$. Bromine then adds on at these double bonds with the formation of $C_{20}H_{32}Br_{10}$. Then when 2 HBr has been split off there are probably smaller rings formed. Schmitz attributes all the inconsistencies in the previous work on the halogenation of caoutchouc to the interference of "colloidal phenomena" with the strictly stoichiometrical reaction. Finally, these results are said to be in accord with the more recent ideas of Harries.

Schmitz' process of reasoning, then, is this :

Three assumptions are made at the outset,

1. Caoutchouc possesses a polymerized ring structure.
2. Heat depolymerizes the complex and opens the rings, with

the production of more unsaturated chains.

3. Bromine adds on at the double bonds and then HBr splits off, with the production of rings smaller than the original.

Then without offering the slightest vestige of proof for any one of these assumptions, he submits the conclusion that caoutchouc must have a polymerized ring structure, that is, that assumption number one is correct. The fallacy is obvious.

The experimental method of Schmitz is open to even more severe criticism than is his reasoning. Caoutchouc starts to decompose in a high vacuum at 220°C. Heated in benzene solution in a sealed tube at 140° for 4 - 5 hours, the present author has shown it to undergo a change, and the original elastic material cannot be recovered. If ''depolymerization" in this case means decomposition, it is futile to mask the facts with a meaningless word. Even accepting Schmitz' own contention, that the rings are opened on heating, the process is still decomposition. It would be unprofitable to speculate further on the results of the work, as there is no reason to suppose that they have any bearing on the bromination of caoutchouc.

In 1921, Harries and Evers (15) submitted further evidence in support of the former's theory of the structure of caoutchouc, in a paper on the reduction of caoutchouc ~~hydrochloride~~ by means of the action of zinc on the hydrochloride. The product obtained was free from chlorine and was still partially unsaturated. The analytical results are not particularly conclusive as to the composition.

$C_{30}H_{50}$	requires	C 87.80	H 12.20
$C_{30}H_{52}$	''	C 87.29	H 12.71
$C_{40}H_{70}$	''	C 87.19	H 12.81
$C_{35}H_{62}$	''	C 87.05	H 12.95
	Found	C 87.80	H 12.99
	''	C 87.81	H 12.91

As the product was freed from zinc salts with water it would be natural to attribute the high hydrogen values to traces of moisture and to place more faith in the values for carbon, which correspond to $C_{30}H_{50}$. However, Harries decides the composition to be either $C_{40}H_{70}$or $C_{35}H_{62}$. On attempting to distill the product at 0.1 to 0.5 m.m., vigorous decomposition (starke Zersetzung) set in at a temperature of 120 - 130°C, continuing until a temperature of 240°C was reached. From 240 - 300°C about half the residue was distilled over, accompanied still by some decomposition. In spite of the fact that decomposition started 120° below the temperature at which distillation began, Harries assumed the distillate to be identical with the original hydrocarbon. Analyses of the product do not agree with those of the original substance.

Found	C 86.86	H 12.70
	C 86.61	H 13.52

Hydrochlorides of the original hydrocarbon and of the distillate were prepared, the analyses being as follows.

	I	II	III	IV	V	VI
C	79.47	78.64	78.63	77.39	79.74	79.87
H	12.07	11.21	11.18	10.58	10.80	10.63
Cl	8.80	8.64	9.18	9.08	7.70	7.88

V and VI were the figures obtained for the hydrochlorides of the distillate. The author's own analytical results disprove his contention that the two substances are identical.

The molecular weight found for the original substance in $CHBr_3$ solution was 6067, a value which Harries assumed to be abnormal as the solution was colloidal. No molecular weight determination on the distillate was published. Ozonization in chloroform solution gave, from the original hydrocarbon and the distillate, products which agreed fairly well in composition and which approximated $C_{40}H_{70}O_{15}$. In ether-ethyl acetate solution the ozonide obtained did not agree with any of the above optional formulae, so ozonization was continued for another 5 hours. The final product approximated in composition $C_{35}H_{58}O_{18}$, containing considerably more oxygen than the product mentioned above, and Harries concluded that there must have been a mixture of two isomers present in the hydrocaoutchouc, and hence in caoutchouc itself. As a matter of fact these results are only additional proof for Olivier's contention that the ozonides are not homogeneous. The two isomers supposed to exist in caoutchouc are both given ring structures; one a 28-membered ring, $(C_{35}H_{56})_n$, and the other a 32-membered ring, $(C_{40}H_{64})_n$. From the boiling point of the distillate above, the hydro-caoutchouc is concluded to consist of simple ring compounds, $C_{35}H_{62}$ and $C_{40}H_{70}$.

The idea of the existence of isomers is expressed in Harries book when he mentions the existence of three varieties of caoutchouc, the ordinary, insoluble, and oily. The latter was obtained from caoutchouc solutions which had stood for a long time at slightly elevated temperatures. It is stated that, on evaporation of the solvent and long standing, this is converted into the ordinary variety. This product has been obtained by the present author and will be dealt with later. It is probable that this has undergone chemical change and is no longer caoutchouc. The insoluble form is noticed in precipitated rubber which has been heated, or has stood for some time. Reasons will be given later for the belief that this is not different shemically from the ordinary variety.

A year later the hydrogenation of caoutchouc was studied by Staudinger and Fritschi (16), who employed a catalytic method. Extracted rubber was impregnated with finely divided platinum and heated in an autoclave, with 100 atmospheres pressure of H_2, at 270°C. Below 250° the reaction did not take place, at 260° only slowly, and at 270° fairly rapidly. The product obtained was a completely saturated, colorless, amorphous mass, which did not possess the physical properties of caoutchouc. It formed colloidal solutions in benzene, ether and CCl_4, hence must have a molecular weight comparable to caoutchouc. Dry distillation of the product at a maximum temperature of 390° in a high vacuum yielded a series of hydrocarbons ranging from C_5H_{10} to $C_{50}H_{100}$, each having one double bond. The results of this investigation are believed by Standinger to settle definitely the question of open chain versus polymerized ring structure. According to Pickles' argument, outlined above, we should expect from a substance possessing Harries' structure, simple ring compounds, which should not show colloidal properties. If, on the other hand, caoutchouc possesses a long open chain we should expect a hydrogenation product of comparable molecular complexity. As the latter was obtained by Standinger, there is only one possible conclusion.

In passing, one objection must be offered to Standinger's experimental method. On the dry distillation of caoutchouc itself in a high vacuum, he found that decomposition set in at about 220°. In spite of this fact he employed a temperature 50° higher, without showing first that caoutchouc did not decompose under these conditions. If there were bridge bonds in the original substance, they might conceivably be ruptured under such drastic treatment, and the hydrogen absorption would be greater than that required by the bridged structure.

However justifiable the above objection to Standinger's method may be, his main contention seems to be proved beyond doubt by the work of Pummerer and Burkard (17). These investigators hydrogenated caoutchouc in solutions in saturated solvents, using finely divided platinum black as a catalyst. The temperature employed was 70 - 80°, which is low enough to exclude any possibility of decomposition. In contrast, however, to the product obtained by Standinger, the hydrocaoutchouc obtained was a tough, elastic substance, similar to caoutchouc in physical properties. This fact offers further justification for the objection advanced against the employment of such a high temperature as 270°. The compositions of the two products, however, were identical, and they both indicate a very high molecular weight.

The hydrocaoutchouc of Pummerer and Burkard was readily autoxi~~d~~ized in the presence of platinum black, with the production of a substance which yielded analytical figures approximating those usually obtained for caoutchouc itself, and which was assumed to be isomeric with the latter. It is inconceivable, though, that a saturated hydrocarbon could be autoxized to an unsaturated one, and it is extremely probable that the oxidation product contained oxygen. As the hydrocaoutchouc gave analytical figures corresponding to a pure saturated hydrocarbon, there is no reason why the oxidation product should not be obtained in a corresponding state of purity. To compare the analysis of a pure compound with those usually obtained for impure caoutchouc is unjustifiable, and does not indicate identity of composition with pure caoutchouc.

A study of the action of perbenzoic acid on caoutchouc solutions by the same investigators revealed the fact that by excluding all traces of moisture and working at 0°C, a substance of the composition $(C_5H_8O)_x$ could be obtained. If moisture were allowed access, the product could not be obtained. The substance was a white, tough solid, insoluble in all organic solvents. Reference to this substance will be made later.

Recently, Kirchhof (18), in a sereis of three papers, has developed an altogether new conception of the structure of caoutchouc. By the action of H_2SO_4 on solutions of plantation crepe, two main products were formed, A and B.

A was insoluble in all organic solvents, but swelled in solvents used for caoutchouc. Its composition was calculated by the author, on the basis of a sulphur and ash-free substance, to be $C_{20}H_{30}$.

B was soluble in alcoholic KOH and in acetone, and had a composition of $C_{20}H_{30}O_3$.

Bromination of A was carried out by swelling the substance in CCl_4 and adding a solution of Br_2 in CCl_4. The mixture was shaken for 2 hours. Three products were obtained.

A_1, corresponded in composition with $C_{20}H_{30}Br_2$ (36.6% Br), and was insoluble in all organic solvents.

A_2 also corresponded farily well with $C_{20}H_{30}Br_2$ (37% Br), and was soluble in CCl_4, but precipitated by acetone.

A_3 contained a higher percentage of Br and was not investigated further.

From the Br-content of A_1 and A_2, Kirchhof argued that three double bonds had disappeared from each 20-carbon molecule, leaving only one. On purely experimental grounds this conclusion is open to very serious criticism. In the first place the original substance was not in solution when treated with Br_2. It is at least customary, if not necessary, to have reacting substances such as these in solution, if the reaction is desired to go to completion. If a substance is insoluble it is very difficult to determine from a single procedure whether or not the reaction is complete. Secondly, as the product of the action of Br on A consisted of at least three substances, there is no reason for assuming A to be homogeneous, ~~N~~nor for assuming that the normal course of the reaction with bromine leads to a compound $C_{20}H_{30}Br_2$.

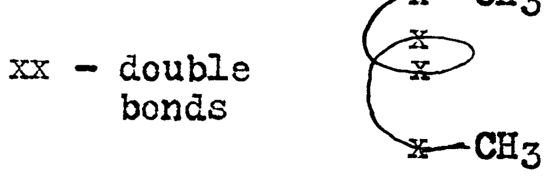
On heating A_1 at 100° to constant weight, a product D, corresponding in Br-content with $C_{20}H_{29}Br$ was obtained, showing that one molecule of HBr had been lost. On brominating this substance, which was also only swollen in CCl_4, a product containing 38.7% Br was obtained. This was not identical with A_1 or A_2. If a double bond resulted from the removal of HBr, substance D, on bromination, ought to give a product with three atoms of Br, which requires 47.15% Br. The result of this bromination is unexplainable on the basis of the 20-carbon molecule. As substance D was not in solution the bromination was possibly incomplete.

Heated with sulphur, A yielded a product, which, after extraction with acetone, showed a sulphur content of 24.75%. This was too high to correspond with the bromine compound, so the substance was extracted 4 hours with CS_2, when the sulphur values had fallen to 9.6%. The nature of the CS_2 extract was not described, namely, whether it was simply excess sulphur or organic sulphur compounds. For $C_{20}H_{30}S$ would be required 10.6% sulphur and Kirchhof assumes his substance to have that composition.

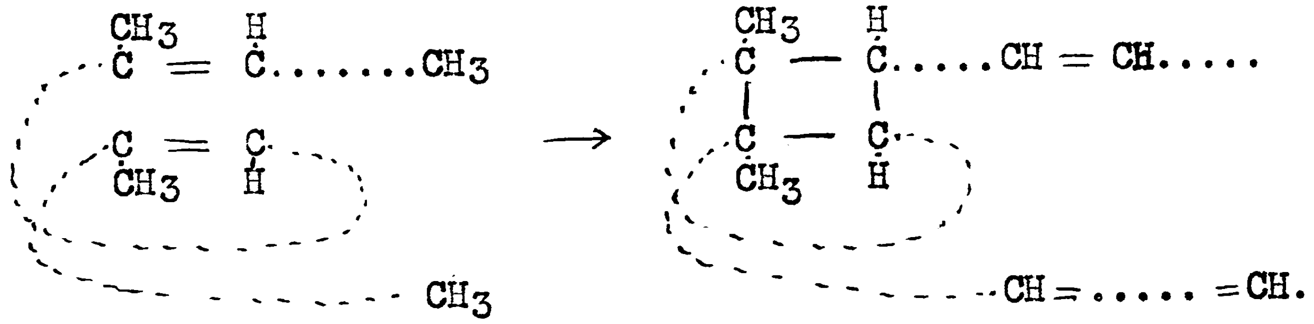
The acetone-soluble product B, from the action of H_2SO_4 on the caoutchouc solution, gave values corresponding to $C_{20}H_{30}O_3$. The substance reduced Fehling's solution, indicating an aldehyde group, and the saponification number indicated one carboxyl group per C_{20}. The molecular weight corresponded very well with $C_{20}H_{30}O_3$. On treatment with phenyl hydrazine there was obtained a product which is said to separate out from dilute HCl solution in spherical crystals, ("Sie [subst. B] liefert in schwach salzsaurer Losung ein rotbraunes Phenyl-hydrazon, das in Ausserst feinen anscheinend sphärischen Kristallen von ca. 2 µ Durchmesser, die sich sehr langsam absetzen, kristallisiert."). How the substance B was dissolved in an acid solution when it is precipitated from alkaline solutions by acids is a mystery left to the readers' imagination. It is claimed for this substance that it is the first really crystalline substance ever obtained from caoutchouc which has not been broken down to any extent. We will consider evidence later which will show whether or not the caoutchouc has been broken down a great deal.

The running fire of criticism directed at the experimental work of Kirchhof has been for the sole purpose of pointing out the insecure footing of the theory which will be developed now. Repeated disappointments in the endeavour to establish more or less simple stoichiometrical relationships in the oxidation products of caoutchouc, have made the present author rather sceptical of any results which would indicate such simple relationships as those of Kirchhof.

In interpreting the results just outlined, Kirchhof advances a formula for caoutchouc which is a spiral chain with the double bonds arranged spatially over one amother. The empirical formula, instead of being $(C_{10}H_{16})_n$ or $(C_{20}H_{32})_n$, is $C_{20}H_{34}$. A general scheme for the formula would be



In ordinary caoutchouc the molecular weight indicates a much more complex molecule than this, so Kirchhof assumes, with Harries, that the simple molecules are united by molecular forces, or " Kolloid-nebenvalenzen "[4], to form much higher aggregates. The action of H_2SO_4 is represented as a removal of 2 H atoms from each of the end methyl groups, thus forming the hydrocarbon $C_{20}H_{30}$. In addition, the double bonds are supposed to be destroyed by the formation of tetramethylene rings.



The unsaturated residues formed by the removal of 2 H atoms from each methyl group are supposed to polymerize indefinitely to $(C_{20}H_{30})_n$. This accounts for the insolubility and obviously high molecular weight of substance A. The aldehyde-acid B is supposed to result from the oxidation of one $-CH_3$ group to $-CHO$ and the other to $-COOH$. It will be noticed that the product of the reaction with H_2SO_4 has only one double bond per $C_{20}H_{30}$, this being based on the rather unconvincing evidence intended to show that three double bonds had disappeared during the reaction.

The empirical formula $C_{10}H_{17}$, as opposed to $C_{10}H_{16}$, must be admitted to have extensive justification in the analytical results found in the literature, but it must be remembered that the results in the literature are from analyses of impure caoutchouc. If, by coincidence, the analys~~i~~es of impure caoutchouc fit in with $C_{10}H_{17}$, it is no proof that pure caoutchouc will also give these results. The carbon-hydrogen ratio in caoutchouc will be discussed fully later.

In reference to the spiral chain it is difficult to see any essential difference between it and the ordinary straight chain. No organic chemist would entertain the idea that molecules which have their structure represented by straight chains actually have their carbon atoms stretched out in perfectly straight lines. If spatial arrangement, then, is admitted, the spiral chain is not different from the straight chain. In straight chains there is nothing known of any tendency to such a behaviour as is represented in the above formation of tetra-methylene rings, so the whole theory of Kirchhof is based on speculation, supported by fragmentary bits of doubtful evidence. What organic chemistry needs to-day is not new and useless theories, but correlation and explanation of some of the theories we have.

Still another new conception of the structure of caoutchouc has been advanced by Boswell (19) who proposed a fully saturated complex bridged structure, $C_{30}H_{48}$. In brief, the main experimental facts consist in the preparation of the following oxidation products:

1. Oxidation of caoutchouc in CCl_4 solution by shaking with aqueous $KMnO_4$ gave a product whose analysis gave the figures

Found	C 83.9 %	H 11.4 %
$C_{25}H_{40}O$ requires	84.3	11.2

2. On standing some time in the air substance 1 became oxidised and analyses of two different preparations gave figures approximating $C_{25}H_{40}O_2$.

3. Hydrogen peroxide acting on a CCl_4 solution of caoutchouc gave two products, a water soluble, sticky substance, and a substance insoluble in water. The former was not investigated. By evaporating the CCl_4, the latter substance was obtained. After precipitating twice from ether with methyl alcohol the analysis gave values the average of which was

	Found	C 85.54%	H 10.96%
$C_{30}H_{48}O$	requires	84.90	11.32.

This substance, on heating, became partially insoluble in ether.

4. A sample of 3 which had stood in the air was treated with ether. The soluble part was precipitated, dried and analysed.

	Found	C 80.33%	H 10.40%
$C_{25}H_{40}O_2$	requires	80.64	10.75 .

This substance was assumed to be identical with 2.

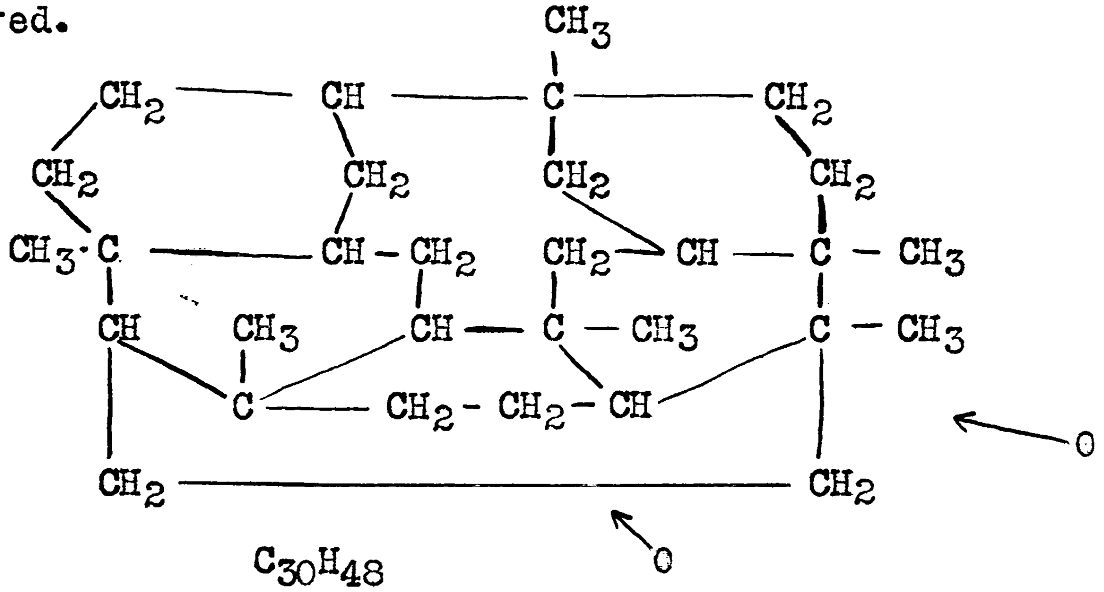
5. The ether insoluble part of the above sample of 3 was precipitated from CCl_4 with methyl alcohol, dried, and analysed.

	Found	C 81.39%	H 10.50%
$C_{15}H_{24}O$	requires	81.81	10.90.

6. By the action of air on thin sheets of extracted rubber two products were obtained, the first being soluble in CS_2. This substance corresponded closely in composition to $C_{20}H_{30}O_2$.

7. The part insoluble in CS_2 corresponded closely to $C_{25}H_{40}O_9$.

In interpreting the experimental results obtained, Boswell supported the formula below as representing best the facts observed.



$C_{30}H_{48}$

In all cases oxidation was represented by oxygen entering the ring between two carbon atoms, as indicated by the arrows above.

This interpretation of the results is open to several criticisms, the main ones being as follows :

1. In all cases the oxidation products were precipitated one or more times, washed, dried, and analysed. This procedure merely shows the composition of the precipitate and does not offer any indication of homogeneity. As we shall see later, there is no reason for assuming any of them to be homogeneous.

2. No molecular weight determinations were carried out and it is pure speculation to assume that the substances obtained corresponded to the formulae assigned to them.

3. The mechanism of the oxidation as represented by Boswell is without analogy. None of the oxidizing agents used are known to act in the manner indicated.

4. The structure assigned to caoutchouc is altogether contrary to present conceptions of ring stability. Incorporated in the complex structure is a 10-carbon ring, which does not exist.

In summing up the work that has been done on the constitution of caoutchouc, it must be pointed out first that the greater part of it is without value on account of very serious experimental defects. Of all the recent constructive work reviewed above, there are probably only two researches which are not open to criticism. Harries' study of the products of the action of ozone on caoutchouc is the first of these, and the second is the hydrogenation of caoutchouc carried out by Pummerer and Burkard.

One of the chief faults in most of the work is that there is apparently a tendency to look for evidence in favour of a certain structural formula rather than to obtain evidence which will eventually lead to a correct interpretation of all the facts. What is needed in the chemistry of caoutchouc is not formulae but evidence; not evidence which can be twisted into conformity with some particular structural formula, but plain experimental facts, sought out by an unbiased mind. In the study of a complicated substance such as caoutchouc, which yields derivitives with ill-defined physical properties, there is offered a great deal of latitude in interpreting evidence and this makes it all the more essential for the investigator to be unprejudiced.

THE OXIDATION OF CAOUTCHOUC

As oxidation has been one of the most fruitful methods in the determination of the structures of the terpenes, it is natural that this method should be extensively employed in the study of the structure of caoutchouc. The ozone method of Harries, which has already been dealt with, has probably been the most productive of significant results, the double bonds being shown to be chiefly in the 1, 4 positions. The use of $KMnO_4$ and H_2O_2 by Boswell has not contributed any definite information, as there is nothing known of the structure of the products or of their molecular weights. Neither has he shown any of the products to be homogeneous.

Atmospheric oxygen is the oldest and most widely studied oxidising agent but the results have been far from satisfactory, no two investigators obtaining comparable results. In most cases the rubber has merely been exposed in sheets or films and the degradation products studied. The incompatible results obtained by different investigators show that the mixture of end products must be very complicated. No attempt has ever been made to follow the course of the reaction from the initial stages to the end.

The earliest recorded examination of the products of the autoxidation of rubber was made by Hofmann (20) in 1860. He obtained samples of resinified rubber which had been used for insulating purposes in India. The substance had lost all the characteristic physical properties of rubber and was a brown, brittle mass. By the use of various solvents the substance was divided into three parts, none of which showed any simple ratio of C, H, and O. In 1865, Spiller (21) examined the oxidation products of some rubber which had been exposed to the air for several years, but the brittle resin obtained by him, although very similar in physical properties to one of the products of Hofmann, showed a very appreciable difference in composition.

Since these two investigations there have been many attempts to resolve the resinous oxidation products into constituents of simple composition, and, although some of the products approximate roughly the compositions $C_{10}H_{16}O$, $C_{10}H_{16}O_2$, and $C_{10}H_{16}O_3$, there has been no agreement between the results of different investigators. Probably the most careful study of the products of the oxidation of caoutchouc by oxygen was made by Peachey and Lean (22). Samples of acetone extracted rubber were oxidised in an electric ~~furnace~~ oven at 85°C in an atmosphere of oxygen over a period of 6 months. The samples were extracted with alcohol every 48 hours to remove the resinous products and expose fresh surfaces of caoutchouc to the action of the oxygen. When the oxidation was complete an examination of the products was made and four main products were obtained.

Substance A was soluble in all ordinary organic solvents, and was a brownish, neutral resin.

Found	% C	72.07	% H	10.01
		72.11		10.03
$C_{16}H_{26}O_3$ requires		72.18		9.81

Substance B was insoluble in petrolic ether, ether, CS_2, and water, but soluble in most organic solvents. This substance was a fawn-colored resin which appeared to be feebly acidic. Molecular weight determination by the ebullioscopic method in $CHCl_3$ and C_6H_6 showed no elevation of the boiling point. Analysis gave the following values.

Found	% C	63.41	% H	7.91
		63.69		7.82
$C_6H_9O_2$ requires		63.71		7.97

Substance C was insoluble in all ordinary organic solvents but soluble in alkalis, including NH_4OH. The substance was not studied chemically.

Found	% C	62.71	% H	7.62
		62.83		7.43
$C_{11}H_{16}O_4$ requires		62.46		7.55

Substance D was insoluble in all organic solvents and in alkalis. Analysis showed it to have the same composition as substance B. Prolonged boiling with formic acid gave a product closely resembling B in all its properties.

It will be seen from the above figures that there is no simple relationship between the oxidation products and the original hydrocarbon, $(C_{10}H_{16})_n$. In B, C, and D the H values are too low to correspond with a carbon-hydrogen ratio of 10 to 16, although in A this ratio is maintained.

The only recorded attempt to oxidise caoutchouc in solution by means of oxygen was made by Herbst (23). A 1% solution of rubber in benzene was heated to boiling under a reflux condenser and air was bubbled through for 140 hours. Three products were obtained.

I, a brown syrup which was the main product. Analysis corresponded well with $C_{10}H_{16}O$.

II, an amorphous, brittle solid, insoluble in petrolic ether, given the formula $C_{10}H_{16}O_3$.

Found	C	65.54	H	7.90
$C_{10}H_{16}O_3$ requires		65.22		8.69

It will be noted that the value for H is too low for a carbon-hydrogen ratio of 10 to 16.

III, a brittle solid, different in physical properties from II, but given the same formula by Herbst.

Found	C	67.33	H	8.51
$C_{10}H_{16}O_3$ requires		65.22		8.69

Here there is very poor agreement with the calculated values, and also low H values for a carbon-hydrogen ratio of 10 to 16.

Part II - Experimental

In beginning a study of the oxidation of caoutchouc the present author decided that the only way to control the action of atmospheric oxygen so as to ensure uniform reaction was to oxidise in solution. Several solvents were tried and finally xylene was selected as the most satisfactory for the main research. Its solvent action was good and the moderately high boiling point reduced loss by evaporation to a negligible quantity.

In all cases the concentration employed was 12 grams of extracted rubber in 100 c.c. of solvent, and the temperature used was 97 - 101°C. A wide-necked flask containing the solution was placed in an oil bath heated by means of a hot plate, and a very tall reflux condenser was used to prevent loss of solvent. Before passing air through, the contents of the flask were heated for 2 days to thin out the solution, then a gentle stream of dry air was bubbled through for varying lengths of time. A careful study was made of the products at the end of 24, 48, 72, 96, 120, and 144 hours respectively, and also of the products at the end of 18 and 22 days respectively.

The first treatment of the reaction mixtures was to distill the solution on the water bath to about 1/3 of its volume under reduced pressure, add the precipitant with vigorous stirring, wash the precipitate with the precipitant, then partially dry at 100° in an atmosphere of CO_2 for 1 to 2 hours. Heating in this manner coagulates the protein, and, by redissolving the product in benzene, the former may be completely removed by the suction filter. The process of filtration is usually slow, as the protein clogs the pores of the paper, and sometimes it is necessary to precipitate and heat a second time to coagulate the last traces of suspended protein. By this method it is always possible, though, to obtain a perfectly clear, transparent solution. The samples of protein thus obtained were given to Mr. Dolid, in this laboratory. This is the first time the protein has been obtained in reasonably large quantity from crude rubber.

The first precipitation of an oxidation product from such a reaction mixture will, if the precipitate is allowed to settle thoroughly, carry down all the protein and it is not necessary to filter solutions of products which may remain in the main solution. All precipitations were carried out by adding the precipitant to the solution with vigourous stirring, thus ensuring gradual separation and the greatest possible homogeneity of the precipitate. In the ensuing description of the experimental work, directions are given, except where otherwise stated, based on a volume of 350 c.c. of solution.

In carrying out analyses after each of several solutions and precipitations there was, in all cases, an insufficient amount of precipitant added to cause complete precipitation. In this way, relatively more soluble substances would be gradually eliminated, if such were present.

Investigation of the Products at the End of 24 Hours

After distilling the solution to 1/3 of its volume and adding about three times its volume of acetone, the protein was removed from the precipitate in the manner described above. Together with the protein there remained on the filter a small amount of an insoluble tough substance which appeared to be unchanged rubber. It could not be freed from protein for analysis. On treatment of the clear benzene solution with an excess of acetone a pale yellow oil was obtained, which was precipitated from its benzene solution once more, washed with acetone, and dried in vacuo at 100°. The substance, when completely freed from solvent, is a pale yellow, soft gum, which, on standing a few hours after removal from the oven, becomes tough and elastic. If a comparatively small amount of solvent be retained, this tendency to become elastic is greatly diminished. When freshly removed from the oven after removal of the solvent, the substance is miscible in all proportions with aromatic hydrocarbons, halogenated hydrocarbons, petrolic ether and ether. It is insoluble in, and precipitated by, ethyl acetate, acetone, alcohol, etc. On standing a few hours it becomes partially insoluble in ether, and on standing in vacuo for a few days, swells in rubber solvents in much the same way as rubber itself, finally forming a thin solution which shows no Tyndall effect. Solutions of the freshly prepared material, even when concentrated, are quite limpid and non-colloidal.

A sample was taken for analysis and was precipitated several times with analyses following successive precipitations.

Analysis -

1. Dissolved in ether, precipitated with ethyl acetate, dried. 0.1525 gm gave 0.4806 gm CO_2 and 0.1566 gm H_2O.
2. Dissolved in ether, precipitated with ethyl acetate, dried. 0.1726 gm gave 0.5440 gm CO_2 and 0.1751 gm H_2O.
3. Dissolved in ether, filtered to remove insoluble part, precipitated with ethyl acetate, dried. 0.1443 gm gave 0.4516 gm CO_2 and 0.1467 gm H_2O.
4. Dissolved in C_6H_6, filtered, precipitated with acetone, dried. 0.1449 gm gave 0.4489 gm CO_2 and 0.1449 gm H_2O.
5. Dissolved in petrolic ether, evaporated in vacuo at 100°. 0.1358 gm gave 0.4291 gm CO_2 and 0.1388 gm H_2O.

	1	2	3	4	5	Average.
% C	85.95	85.96	85.35	85.61	86.17	85.81
% H	11.41	11.27	11.29	11.26	11.35	11.32

The carbon-hydrogen ratio is 10 to 15.83.

The above substance will be designated as substance A.

The solution remaining after the first precipitation with acetone was distilled to about 50 c.c., and a large excess of acetone added. The very small amount of pale yellow oil which was precipitated showed exactly the same physical properties and solubilities as A. Only a trace was soluble in ethyl acetate. In the residues of the main solution there was detected an extremely small amount of petrolic ether-insoluble material.

Substance A, then, appears to be almost the sole product of this action. The substance reduces Fehling's solution on boiling for about 1 minute.

Molecular weights in benzene, by the cryoscopic method (24):

Weight of benzene	9.520 gms.	'K' = 5020	(25)
Weights of substance	0.2439 gm	.2401 gm	.2691 gm
Δ	.026°	.051°	.076°
M	4822	4761	4844

Average molecular weight 4809.

This value is probably low, as it is almost impossible to get substance A free from solvent without causing some of it to become insoluble. The substance becomes quite stiff as removal of solvent nears completion and this makes it more difficult to remove the last traces of solvent than in the case of A_1, below.

Examination of the Products at the End of 48 Hours.

Following the method above, a substance insoluble in acetone was precipitated, freed from protein, and the benzene solution treated with a large volume of acetone. The precipitated oil was washed thoroughly with ethyl acetate, and the washings added to the main solution. The part insoluble in ethyl acetate was then dried in vacuo at 100°: It was a pale yellow gum, identical in properties with A.

Analysis -

0.1474 gm gave 0.4627 gm CO_2 and 0.1562 gm H_2O.

% C 85.54 % H 11.77.

This substance is evidently identical with A.

The main solution, after the precipitation of A, was distilled to a volume of about 75 c.c. and 5 times its volume of acetone added, when a pale yellow oil was precipitated. After drying in vacuo at 100°, this substance was almost identical in color with A, but was much more fluid. It showed much less tendency to become tough and elastic, and, with a small amount of solvent present, this tendency was altogether inhibited. Solutions of this oil showed no colloidal particles. In addition to being soluble in all the solvents for A, this oil was soluble in all proportions in ethyl acetate and methyl ethyl ketone, which are precipitants for A.

Analyses - after the successive operations indicated -

1. 0.1526 gm gave 0.4778 gm CO_2 and 0.1582 gm H_2O.
2. Dissolved in ethyl acetate, precipitated with acetone, dried. 0.1500 gm gave 0.4688 gm CO_2 and 0.1545 gm H_2O.
3. Dissolved in ethyl acetate, precipitated with alcohol. 0.1580 gm gave 0.4952 gm CO_2 and 0.1578 gm H_2O.

4. Dissolved in ethyl acatate, precipitated with acetone, 0.1506 gm gave 0.4797 gm CO_2 and 0.1530 gm H_2O.

5. Dissolved in methyl ethyl ketone, precipitated with acetone. 0.1497 gm gave 0.4713 gm CO_2 and 0.1525 gr H_2O.

	1	2	3	4	5	Average..
% C	85.39	85.24	85.48	86.14	85.87	85.64
% H	11.52	11.44	11.10	11.25	11.32	11.30

The carbon-hydrogen tatio is 10 to 15.83.

It is evident, then, that analysis will not distinguish between this substance, which will be called A_1, and A. Only the sharp distinction in solubilities and physical properties will differentiate between the two. The aldehydic nature of the substance is shown by its reducing action on Fehling's solution on boiling.

Molecular weight of A_1, in benzene, as above :

Weight of benzene	10.023 gm		
Weights of substance	0.23~~1~~27 gm	.1373 gm	.1551 gm
Δ	.021°	.032°	.047°
M	5423	5588	5316

Average molecular weight 5442.

In the main solution there was contained a very small amount of alcohol insoluble material and a trace of petrolic ether insoluble. These were discarded.

Investigation of the Products at the End of 72 Hours.

After treating the solution in the manner described above, precipitating with acetone and removing the protein from the precipitate, the latter was washed thoroughly with ethyl acetate and the washings collected. The portion insoluble in ethyl acetate was dissolved in ether and precipitated with ethyl acetate. It represented roughly 1/4 of the total product and was identical in properties with A. Analysis confirmed this identity.

Analysis -

0.1355 gm gave 0.4227 gm CO_2 and 0.1409 gm H_2O.

% C 86.08 % H 11.55.

The main solution was distilled to a volume of about 75 c.c., and 4 or 5 times its volume of acetone added. The precipitated oil consisted exclusively of A_1, which was the main product at the end of 72 hours.

Analysis -

0.1362 gm gave 0.4288 gm CO_2 and 0.1389 gm H_2O.

% C 85.86 % H 11.33.

The ethyl acetate washings of A, above, gave a precipitate with acetone, the analysis of which corresponded with A_1.

0.1473 gm gave 0.4632 gm CO_2 and 0.1482 gm H_2O.

% C 85.76 % H 11.18.

The main solution was distilled to about 30 or 40 c,c. and a large excess of acetone added. By dissolving the precipitate in C_6H_6 and throwing out with acetone twice, and drying, a bright red, viscid oil was obtained, which became tough and elastic on standing. The oil, when freshly prepared, was miscible in all proportions with all the solvents for A_1, but after becoming tough and elastic, was partially insoluble in all orgnaic solvents, swelling like insoluble precipitated rubber. Although no solvent could be found to differentiate sharply between it and A_1, the relatively smaller amount of this substance, and the slight difference in solubility in the xylene-acetone mixture apparently gave a very clear-cut separation. This substance will be referred to as B.

Analysis - after successive operations -

1. Dissolved in ethyl acetate, precipitated with acetone, dried. 0.1371 gm gave 0.4236 gm CO_2 and 0.1387 gm H_2O.
2. Dissolved in ether, precipitated with alcohol, dried. 0.1392 gm gave 0.4323 gm CO_2 and 0.1428 gm H_2O.
3. Dissolved in ethyl acetate, precipitated with methyl alcohol, dried. 0.1455 gm gave 0.4503 gm CO_2 and 0.1467 gm H_2O.
4. Dissolved in C_6H_6, precipitated with ethyl alcohol, dried. 0.1366 gm gave 0.4248 gm CO_2 and 0.1375 gm H_2O.

	1	2	3	4	Average.
% C	84.26	84.69	84.40	84.81	84.54
% H	11.24	11.40	11.20	11.18	11.25

The carbon-hydrogen ratio is 10 to 15.99.

The aldehydic nature of this substance is shown by its reducing action on Fehling's solution on boiling.

Molecular weight of B, in benzene, as above :

Weight of benzene	9.813 gm		
Weights of substances	0.2462 gm	.2271 gm	.2244 gm
Δ	.025°	.049°	.072°
M	4916	4714	4628

Average molecular weight 4753.

A small amount of acetone soluble material and also of petrolic ether insoluble resin was obtained in the resudies of the main solution.

Investigation of the Products at the End of 96 Hours.

On treating the solution as above, adding a large excess of acetone, removing the protein by filtration of the benzene solution of the precipitate, and drying, a bright reddish oil, identical in properties with B, was obtained. This identity was confirmed by analysis.

Analysis -

1. Dissolved in C_6H_6, precipitated with acetone, dried.

0.1057 gm gave 0.3273 gm CO_2 and 0.1061 gm H_2O.

2. Repeated above.

0.1044 gm gave 0.3248 gm CO_2 and 0.1047 gm H_2O.

	1	2	Average.
% C	84.45	84.84	84.64
% H	11.15	11.14	11.14

The carbon-hydrogen ratio is 10 to 15.8.

Substance B is the chief product at the end of 96 hours. A_1 was not detected.

The main solution was distilled to about 75 c.c., and excess of alcohol added, when a yellowish oil was precipitated. After washing with alcohol and adding the washings to the main solution, acetone was added and part of the oil went into solution. The insoluble portion was washed several times with acetone and the washings added to the acetone solution. After dissolving in a very small amount of benzene, precipitating with acetone and drying, a reddish-yellow, viscid oil was obtained which was very similar in properties to B. It is soluble in all the solvents for A_1 and B, but is not easily precipitated from the main xylene solution by acetone. When re-dissolved in benzene, it is readily precipitated by acetone. It is insoluble in acetone, alcohol, amyl alcohol ~~alcohol~~, and methyl alcohol. After complete removal of solvent it becomes insoluble, only swelling in solvents. This insoluble modification is tough and elastic.

Analysis - after successive operations -

1. 0.1168 gm gave 0.3574 gm CO_2 and 0.1175 gm H_2O.
2. Dissolved in ether, precipitated with alcohol, dried. 0.1174 gm gave 0.3573 gm CO_2 and 0.1183 gm H_2O.
3. Dissolved in benzene, precipitated with acetone, dried. 0.1119 gm gave 0.3429 gm CO_2 and 0.1124 gm H_2O.
4. Dissolved in ethyl acetate, precipitated with methyl alcohol, dried. 0.1046 gm gave .3190 gm CO_2 and .1053 gm H_2O.

	1	2	3	4	Average
% C	83.45	83.00	83.57	83.37	$83.3\overset{5}{6}$
% H	11.18	11.19	11.16	11.18	11.18

The carbon-hydrogen ratio is 10 to 16.09.

Analysis shows this substance to be different from B, there being somewhat over 1% difference in the value for carbon. Relative ease of precipitation from the main xylene solution also differentiates it from B. This substance will be dssignated as substance C.

Molecular weight of C, in benzene, as above :

Weight of solvent	9.924 gms		
Weights of substance	0.2545 gm	0.2246 gm	0.2181 gm
Δ	.033°	.054°	.089°
M	3805	4380	3702

Average of the first and last concentrations, M = 3752.

Reduction of Fehling's solution on boiling shows this substance to be aldehydic.

The acetone solution of the part of the original precipitate which dissolved in that solvent, was treated with 95% alcohol, which precipitated the dissolved oil. After precipitating once more from C_6H_6 with alcohol, and drying, a red oil was obtained. This is much more fluid than B or C and does not show any noticeable tendency to become tough and elastic on standing. This substance was found in larger quantity at the end of 120 hours, and a further description of it will be found later.

Analysis -

0.1161 gm gave 0.3557 gm CO_2 and 0.1168 gm H_2O.

% C 83.55 % H 11.17.

Analysis will not distinguish between this substance and C. It will be called substance C_1.

The residue of the main solution was distilled in vacuo to a volume of about 25 c.c., and methyl alcohol added. A yellow oil precipitated, which was dissolved in acetone, precipitated with methyl alcohol and dried. This substance, when dry, was similar in appearance to C_1, but was very soluble in acetone, while C_1, when completely freed from solvent, was insoluble in acetone. Although not precipitated from the xylene solution by alcohol, when dry, it was insoluble in the latter solvent.

Analysis -

1. 0.1186 gm gave 0.3464 gm CO_2 and 0.1125 gm H_2O.
2. Dissolved in acetone, precipitated with methyl alcohol, dried. 0.1004 gm gave 0.2943 gm CO_2 and 0.0951 gm H_2O.

	1	2
% C	79.65	79.94
% H	10.54	10.52

Further analyses of this substance will be given later, as it is found in larger amount at the end of 120 hours. It will be referred to as substance D.

On evaporation of the residues of the main solution, dissolving the residue in acetone, and precipitating with petrolic ether, a dark brown, brittle resin was obtained. This substance was extremely soluble in acetone, alcohol, methyl alcohol, and less soluble in ether, aromatic hydrocarbons, etc. This is the first stage at which a sufficient quantity of material, insoluble in petrolic ether, could be obtained for analysis.

Analysis -

0.1486 gm gave 0.3872 gm CO_2 and 0.1234 gm H_2O.

% C 71.06 % H 9.23.

The carbon-hydrogen ratio is 10 to 15.59.

The substance has a strong reducing action on Fehling's solution on boiling.

A separate section is devoted to the solid resinous oxidation products, and those occurring in the products at the end of 120 and 144 hours will not be dealt with under those sections.

Investigation of the Products at the End of 120 Hours.

After treating the solution as above, with acetone, removing the protein from the precipitate, and treating the benzene solution with acetone, a pale yellow oil was obtained. This was very much similar to A_1, which was obtained at the end of 48 and 72 hours respectively. This substance showed very little tendency to become tough and elastic on standing, and resembled A_1 in consistency and color. In contrast to A_1 though, it was insoluble in ethyl acetate, although soluble in all the others solvents for A_1.

Analysis -

1. Dissolved in ether, precipitated with acetone, dried.
0.1120 gm gave 0.3462 gm CO_2 and 0.1141 gm H_2O.
2. Dissolved in benzene, precipitated with acetone, dried.
0. 1036 gm gave 0.3218 gm CO_2 and 0.1069 gm H_2O.
3. Dissolved in ether, precipitated with alcohol, dried.
0.1103 gm gave 0.3417 gm CO_2 and 0.1132 gm H_2O.
4. Dissolved in ether, precipitated with acetone, dried.
0.1211 gm gave 0.3576 gm CO_2 and 0. 1227 gm H_2O.

	1	2	3	4	Average
% C	84.30	84.71	84.49	84.57	84.52
% H	11.32	11.47	11.41	11.26	11.36

The carbon-hydrogen ratio is 10 to 16.14.

It is evident from these figures that this substance cannot be distinguished from B by analysis. Its color and other properties offer a marked contrast, though, as B is red, and tends to become elastic and insoluble on standing. This substance will be designated Substance B_1.

Molecular weight of B_1, in benzene, as above :

(see over)

Weight of solvent	9.872 gms		
Weights of substance	0.1950 gm	.2423 gm	.2264 gm
Dep Δ	.021	.048	.073
M	4628	4437	4328

Average molecular weight 4464.

From the molecular weight and the analysis it is evident that this substance is very closely related to B, with a molecular weight of 4753.

The solution was distilled to about 75 c.c., and excess of alcohol added. On digesting the precipitate with acetone, part went into solution. The acetone washings of the precipitate were added to this solution. The insoluble portion was dissolved in benzene, precipitated with acetone, and dried. The product was identical in properties with C.

Analysis -

0.1162 gm gave 0.3455 gm CO_2 and 0.1172 gm H_2O.

% C 83.42 % H 11.21.

Analysis confirms the fact that this is substance C.

The acetone solution was treated with 95% alcohol, the precipitated oil dissolved in benzene and again precipitated with alcohol. When dried, the substance was insoluble in acetone, although extremely soluble if a small amount of xylene ~~is~~ was present. It is also miscible in all proportions with amyl alcohol, a property which distinguishes it sharply from C. From this solvent, and from ether, it is precipitated by acetone. The substance does not show much tendency to become elastic on standing and is identical with substance C_1, which occurred in the product at the end of 96 hours. It is the chief product at the end of 120 hours.

Analysis -

1. Dissolved in amyl alcohol, precipitated with acetone.
0.1253 gm gave 0.3840 gm CO_2 and 0.1270 gm H_2O.
2. Dissolved in ether, precipitated with acetone, dried.
0.1229 gm gave 0.3760 gm CO_2 and 0.1233 gm H_2O.
3. Digested with acetone, dried.
0.1218 gm gave 0.3723 gm CO_2 and 0.1221 gm H_2O.
4. Dissolved in ether, precipitated with alcohol.
0.1156 gm gave 0.3542 gm CO_2 and 0.1147 gm H_2O.

	1	2	3	4	Average
% C	83.58	83.44	83.36	83.56	83.48
% H	11.26	11.14	11.13	11.02	11.14

The carbon-hydrogen ratio is 10 to 16.

The aldehydic nature of the substance is shown by its reducing action on Fehling's solution on boiling.

Molecular weight determination in benzene, as above ;

Weight of solvent 11.851 gms

Weights of substance	0.2790 gm	.1160 gm	.1330 gm
Δ	.040°	.057°	.078°
M	2887	2841	2751

Average molecular weight 2826.

On distilling the residue of the main solution to about 30 - 40 c.c., adding methyl alcohol in excess, and precipitating the oil obtained, from acetone by means of methyl alcohol, a red oil, identical in properties with D, was obtained. This substance was soluble in all ordinary organic solvents except ethyl and methyl alcohols. It could not be precipitated from the xylene solution with ethyl alcohol. It showed no tnedency to become elastic on standing for a long time in vacuo.

Analysis -

3. 0.1063 gm gave 0.3115 gm CO_2 and 0.1019 gm H_2O.

4. Dissolved in acetone, precipitated with alcohol.

0.0987 gr gave 0.2895 gm CO_2 and 0.0935 gm H_2O.

Taking analyses 1 and 2 from those of the corresponding products at the end of 96 hours, we get the following results.

	1	2	3	4	Average
% C	79.65	79.94	79.73	79.99	79.83
% H	10.54	10.52	10.65	10.53	10.56

The carbon-hydrogen ratio is 10 to 15.9.

The aldehydic nature of this substance was shown by its reducing action on Fehling's solution on boiling.

Molecular weight of substance D, in benzene, as above :

Weight of benzene	9.451 gm		
Weights of substance	0.2201 gm	.2098 gm	.1571 gm
Dep. Δ by	.061°	.124°	.175°
M	1874	1683	1677

Average molecular weight 1745.

The solid resins insoluble in petrolic ether were not investigated at this point.

Investigation of the Products at the End of 140 Hours.

The procedure was exactly the same as that adopted in the study of the products at the end of 120 hours, and the products obtained were the same, although occurring in different proportions. B_1, which was one of the chief products at the end of 120 hours, occurred only in very small amounts. C occurred in a smaller amount than in the previous investigation, and C_1 was still the chief product. D occurred in somewhat larger amount, but was evidently contaminated with a substance containing a larger proportion of oxygen, as indicated by the rising values of C and H after successive precipitations.

Analysis of B_1 -

0.1526 gm gave 0.4736 gm CO_2 and 0.1558 gm H_2O.

0.1389 gm gave 0.4308 gm CO_2 and 0.1429 gm H_2O.

	1	2	Previous Average
% C	84.64	84.44	84.52
% H	11.34	11.43	11.36

Analysis of C -

0.1127 gm gave 0.3432 gm CO_2 and 0.1137 gm H_2O.

0.1118 gm gave 0.3410 gm CO_2 and 0.1129 gm H_2O.

	1	2	Previous Average
% C	83.05	83.18	83.35
% H	11.21	11.22	11.18

Analysis of C_1 -

0.1161 gm gave 0.3557 gm CO_2 and 0.1168 gm H_2O.

% C 83.55 % H 11.17.

Previous average % C 83.48 % H 11.14

Analysis of D -

1. 0.1176 gm gave 0.3376 gm CO_2 and 0.1121 gm H_2O.
2. Dissolved in acetone, precipitated with methyl alcohol, dried. 0.1077 gm gave 0.3081 gm CO_2 and 0.1033 gm H_2O.
3. Dissolved in ether, precipitated with ethyl alcohol, dried. 0.1212 gm gave 0.3512 gm CO_2 and 0.1163 gm H_2O.
4. Dissolved in acetone, precipitated with ethyl alcohol, dried. 0.1159 gm gave 0.3355 gm CO_2 and 0.1095 gm H_2O.
5. Dissolved in ether, precipitated with methyl alcohol, dried. 0.1000 gm gave 0.2935 gm CO_2 and 0.0954 gm H_2O.

	1	2	3	4	5
% C	78.29	78.02	79.02	78.95	80.04
% H	10.59	10.65	10.66	10.50	10.60

The last figures correspond well with the previous figures for D (C 79.83% H 10.56%). The substance contaminating D is probably substance F, found at the end of 18 and 22 days, respectively.

Investigation of the Products at the End of 18 Days.

The volume of the solution in this case was 4 litres. At the end of the above period a large amount of resin had separated from the solution. The clear reddish solution was decanted off from this insoluble matter and filtered by suction. The resin had evidently carried down with it all the protein. The solid resins in the solution were precipitated by petrolic ether (B.P. 35 - 60°), after the solution had beendistilled to a volume of about 1 litre, These resins, including the insoluble material mentioned above, will be dealt with in the special section devoted to them.

After freeing from the resins, the solution was distilled to about 300 - 400 c.c. in vacuo, and an excess of alcohol added. The precipitated oil was dissolved in acetone, a very small amount of acetone-insoluble material allowed to settle out, the solution treated with alcohol, and the precipitate dried. When dry the substance was a light red, soft gum, insoluble in acetone, alcohol and methyl alcohol, but soluble in most of the other ordinary organic solvents. It shows no tendency to become elastic on standing. This substance will be called substance E.

Analysis of E -

1. 0.1403 gm gave 0.4276 gm CO_2 and 0.1388 gm H_2O.

2. Dissolved in benzene, precipitated with alcohol, dried. 0.1332 gm gave 0.4012 gm CO_2 and 0.1319 gm H_2O.

3. Dissolved in ethyl acetate, precipitated with alcohol, dried. 0.1295 gm gave 0.3880 gm CO_2 and 0.1273 gm H_2O.

4. Dissolved in ether, precipitated with alcohol, dried. 0.1362 gm gave 0.4065 gm CO_2 and 0.1343 gm H_2O.

5. Digested with acetone, dried.

0.1142 gm gave 0.3422 gm CO_2 and 0.1155 gm H_2O.

	1	2	3	4	5	Average
% C	81.17	82.15	81.70	81.40	81.72	81.63
% H	10.99	11.00	10.92	10.95	11.04	10.98

The carbon-hydrogen ratio is 10 to 16.14.

This substance readily reduces Fehling's solution on boiling.

Molecular weight in benzene, as above :

Weight of solvent	9.556 gms		
Weights of substance	0.2440 gm	.1991 gm	.2361 gm
Den Δ by	.061°	.118°	.182°
M	2049	1885	1831

Average molecular weight 1922.

The main solution was distilled to 150 - 200 c.c., and a large excess of methyl alcohol added. The precipitated oil was dissolved in acetone and ~~the~~ methyl alcohol added again. On drying, a dark red, semi-fluid was obtained, much similar in appearance to D. It was soluble in most organic solvents with the exception of alcohol and methyl alcohol, and showed no tendency to become elastic on standing. The substance will be referred to as substance F.

Analysis of F -

1. Dissolved in ether, precipitated with methyl alcohol, dried. 0.1467 gm gave 0.4225 gm CO_2 and 0.1372 gm H_2O.

2. Dissolved in acetone, precipitated with methyl alcohol, dried. 0.1401 gm gave 0.4044 gm CO_2 and 0.1305 gm H_2O.

3. Dissolved in ether, precipitated with ethyl alcohol, dried. 9.1425 gm gave 0.4069 gm CO_2 and 0.1319 gm H_2O.

4. Dissolved in benzene, precipitated with methyl alcohol, dried. 0.1294 gm gave 0.3734 gm CO_2 and 0.1219 gm H_2O.

	1	2	3	4	Average
% C	78.55	78.77	78.26	78.69	78.57
% H	10.42	10.35	10.28	10.46	10.38

The carbon-hydrogen ratio is 10 to 15.85.

This substance reduces Fehling's solution readily on boiling.

Molecular weight in benzene, as above :

Weight of solvent	11.862 gms	
Weights of substance	0.2147 gm	0.0852 gm
Δ	.060°	.086°
M	1486	1435

Average molecular weight 1460.

The main solution was distilled at 10 m.m. pressure on the water bath till no further xylene came off. The oily residue was then distilled with steam in order to determine whether laevulinic aldehyde had been formed. No trace of this substance was detected but about 20 c.c. of a liquid insoluble in water was obtained. This was carefully fractionated under reduced pressure, and found to consist of a mixture of toluic aldehydes. Only the meta compound was actually identified chemically, but the para aldehyde was recognised in the higher fraction by its pepper-like odor. The meta aldehyde was identified by means of its phenylhydrazone, which, when re-crystallized three times from 60% alcohol, melted at 87 - 88°C. It exhibited the characteristic change of color to a dull red after one day's exposure. The oxidation of a methyl group by means of gaseous oxygen is a type of reaction which has not hitherto been observed.

The heavy oil which remained after the steam distillation was treated with methyl alcohol, in which it was practically all soluble. On treatment with water a red oil was obtained, which, when dry, was a fairly stiff, dark reddish-brown gum, soluble in all ordinary organic solvents. If he~~ta~~ated at 100° for some time a small part becomes insoluble, and if heated much above 100° the whole will become a brittle, insoluble mass.

This substance will be called Substance G.

Analysis -

0.1313 gm gave 0.3515 gm CO_2 and 0.1185 gm H_2O.

0.0975 gm gave 0.2626 gm CO_2 and 0.0831 gm H_2O.

	1	2	Average
% C	73.01	73.45	73.23
% H	10.03	9.47	9.75

The carbon-hydrogen ratio is 10 to 15.98.

The values for carbon are slightly higher than those given by Peachey and Leon for their substance A, which had the composition C 72.09% - H 10.02%, but their substance was also soluble in all organic solvents.

Molecular weight in benzene, as above ;

Weight of solvent	9.891 gms	
Weights of substance	0.3155 gm	0.3102 gm
△	.148°	.289°
M	1048	1033

Average molecular weight 1040

This substance reduces Fehling's solution readily on boiling.

The products at the end of 22 days were exactly the same as those at the end of 18 days, and the proportions not noticeably different.

On reducing the volumes of the original solutions by distillation, water, formic acid, and an unsaturated acid were detected. The latter was not identified as a very small amount was available. Probably it was acrylic acid.

In order to show that the temperature of 97° - 101° did not change the normal course of the reaction at room temperature, an oxidation was carried out at 60°. After passing air through the solution for 8 days, the latter was treated as in the case of the solution at the end of 24 hours, and, in addition to a considerable amount of insoluble material which was probably unchanged caoutchouc, there was obtained a quantity of substance A.

Analysis -

0.1500 gm gave 0.4688 gm CO_2 and 0.1532 gm H_2O.

% C 85.23 % H 11.35.

Dissolved in ether, precipitated with ethyl acetate, dried.

0.1489 gm gave 0.4681 gm CO_2 and 0.1517 gm H_2O.

% C 85.74 % H 11.33.

It is not unreasonable, then, to extrapolate to room temperature and suppose that the elevated temperature merely increases the velocity of the reaction.

General Remark on the Precipitation of Oils from the Main Solutions in Xylene.

In order to conserve space and avoid tedious repitition, the above directions indicate a single addition of a given precipitant for the removal of each oil from the solution. In practice it is necessary to carry out a second precipitation in order to ensure complete removal of the substance in question. As a rule the solution should be distilled to the same, or slightly smaller,volume and a larger excess of precipitant added.

Although substance A was the first oxidation product of caoutchouc that could be isolated, there is no reason to assume that it is the first. If there are others, though, their properties are so similar to those of caoutchouc itself that they could not be separated from protein by the manner indicated above.

The Resinous Oxidation Products of Caoutchouc.

In a series of earlier investigations of the oxidation products of caoutchouc, a large variety of samples of solid resins were obtained. These were very soluble in acetone, alcohol, and methyl alcohol, less soluble in aromatic hydrocarbons, and insoluble in petrolic ether and CS_2. The samples described below either separated out from the solution undergoing oxidation or were precipitated by the addition of petrolic ether. These varied in color from a dark brown to a bright, lustrous yellow, and were all soluble in caustic alkalis with varying degrees of ease. In all cases, though, heating for a considerable length of time was required to effect solution. The substances were not soluble in NH_4OH. Attempts to obtain salts were a failure as the addition of an electrolyte merely precipitated the original substance. This confirms a similar observation of Peachey and Leon (26).

[illegible]

Solutions of these resins, even in the case of those of light color, were a ~~deep~~ reddish-brown, and showed some fluorescence. Solutions in aqueous alkalis were dark brown and opaque. The solubilities of the various samples obtained were so similar that no separation could be effected. On mixing two resins of altogether different appearance it was impossible to separate them again by the selective action of solvents.

No specimen was obtained which showed convincing evidence of homogeneity. A light yellow substance which separated from a cymene solution undergoing oxidation was at first thought to be homogeneous, but was later shown to consist of at least two individuals, one soluble and the other insoluble in ether. The earliest stage of oxidation at which the petrolic ether insoluble resins were noticed in appreciable quantity was at the end of 96 hours.

4 r These resins vary in composition from C 71.06% - H 9.23% to C 63.31% - H 7.24%. Thus the carbon-hydrogen ratio s vary from 10/15.59 to 10/13.72. By oxidizing for a suitable length of time almost any values intermediate between these may be obtained. It must follow, then, that there is a very large number of these resins, all possessing similar properties, and extremely difficult, if not impossible, to separate. This accounts for the incompatible results obtained by the various investigators who have investigated the resinous oxidation products of caoutchouc.

Peachey and Leon state that attempts to obtain a molecular weight of their substance B in benzene and in chloroform by the ebullioscopic method resulted in failure, no elevation in the boiling point being observed. The present author determined the molecular weight,in acetophenone, of a brown resin obtained by the addition of petrolic ether to a solution which had been oxidized for 22 days, with the following results.

Weight of solvent 10.089 gm

Weights of substance	0.0366 gm	0.0160 gm	0.0144 gm
Δ	.069°	.101°	.129°
M	296	290	289

Average molecular weight 292.

It is difficult to reconcile this observation with that of Peachey and Leon, and the only reasonable explanation seems to be that their resin formed colloidal solutions in benzene and chloroform. The resins are much more readily soluble in ketones than in benzene, but they appear to be very soluble in chloroform. This molecular weight is of the same order of magnitude as that abtained by Kirchhof (27) for his product from the oxidation with H_2SO_4. His product had a molecular weight of 320.

All the solid resins, soluble in acetone, have a strong reducing action on Fehling's solution on boiling, and reduce Tollen's reagent with difficulty on standing for a few minutes. With phenylhydrazine, gummy products, similar to the original substances are obtained. No crystalline products are obtained. Purification of the gummy products was a difficult and uncertain thing, and nothing beyond a qualitative test for nitrogen was done. Attempts to prepare oximes were a failure.

The resins which had separated out from the xylene solution at the end of 18 days were placed in a canvas bag, extracted with acetone and dried in vacuo at 100°C. Part of the mixture was soluble in caustic alkalis and ammonia. Following Peachey and Leon, this part was extracted by boiling with ammonia, and after acidifying with dilute H_2SO_4 and drying the precipitate, a brown resin was obtained. This substance was insoluble in most ordinary organic solvents but soluble in formic, acetic, and propionic acids. Peachey and Leon did not describe their substance C as being soluble in these acids. The acetic acid solution of the resin may be diluted to a large volume with water without precipitation but the addition of a very small amount of a base or of an electrolyte causes instantaneous precipitation.

By the relative rate of sulution in acetic acid, the resin was separated in to two fractions, and each analysed. This resin will be called resin X.

The more soluble fraction A, gave the following values.

0.0858 gm gave 0.1720 gm CO_2 and 0.0583 gm H_2O.

% C 54.67 % H 7.55.

The less soluble fraction, B, gave the values

0.0952 gm gave 0.2043 gm CO_2 and 0.0685 gm H_2O.

% C 58.52 % H 7.98.

It is evident that resin X also represents a mixture of resins. The values given by Peachey and Leon for their substance C were C 62.21% - H 7.53%.

The ready solubility of the resin above in ammonia, indicated an acid nature , and part of fraction B was converted into its barium salt. Analysis of this salt gave a barium content considerably higher than would fit in with the oxygen content of the substance, and, as there was not enough material available to repeat the analysis, it was not confirmed. The substance reduces Fehling's solution, and reacts with phenylhydrazine and semi-carbazide. With the former it gives a yellow amorphous substance, and with the latter a brownish yellow substance, also amorphous. These substances had no definite melting point. Acetic acid was the only available medium for determining the molecular weight of the substance, and as that medium was found to give abnormally low values with the resins (values of 40 to 50 being obtained in one case), the molecular weight was not established.

The portion of the original mixture of resins insoluble in ammonia was a brittle black substance when dry, and was insoluble in all organic solvents. It will be called Resin X_1.

Analysis -

0.1085 gm gave 0.2509 gm CO_2 and 0.0760 gm H_2O.

% C 63.07 % H 7.78.

This agrees fairly well with Peachey and Leon's insoluble substance D which gave values of C 63.19% - H 8.29%. Their observation, that prolonged boiling with formic acid attacked some of the substance, dissolving it, was confirmed by the author, and it was shown that the substance in the formic acid solution was aldehydic, by its reducing action off Fehling's solution.

Oxidation in Saturated Paraffin Solvent

At a temperature of 97 - 101°C, after 12 days passage of air through the solution, a large amount of a dark brown resin separated which was insoluble in all organic solvents. This resin was extracted with benzene and dried at 100°. When dry it was a black, brittle, inert solid, similar to Resin X, above.

Analysis -

0.1011 gm gave 0.2519 gm CO_2 and 0.0737 gm H_2O.

% C 67.96 % H 8.10.

This substance will be referred to as Resin K.

By carrying out the oxidation at a temperature of 130°, at the end of a day, a large amount of resin had separated out, and the remaining solution was almost colorless. After extracting thoroughly with benzene, and drying, the substance was a brown, brittle resin, insoluble in all organic solvents and chemically inert.

Analysis of two different preparations -

1. 0.1002 gm gave 0.2607 gm CO_2 and 0.0776 gm H_2O.
2. 0.2010 gm gave 0.5284 gm CO_2 and 0.1498 gm H_2O.

	1	2	For $(C_5H_8O)_x$
% C	70.95	71.69	71.42
% H	8.60	8.27	9.52

It will be seen that the hydrogen values are too low for

$(C_5H_8O)_x$. This substance will be referred to as Resin S. .

Laevulinic Aldehyde in Oxidized Rubber.

Ever since Harries established the fact that laevulinic aldehyde was one of the chief products of the action of ozone on caoutchouc, there have been attempts to establish evidence of its formation in the oxidation by means of atmospheric oxygen. The belief that this substance was formed during oxidation was strengthened by the fact that aqueous extracts of resinified rubber gave the pyrrol test which is charcateristic for gamma diketones, and, although it has never been identified, Gorter even went so far as to assume that it was associated with tackiness in rubber.

A sample of resinified rubber, of unknown history, which had been exposed for a number of years, was extracted with water in a siphon extractor, the filtered solution treated with phenylhydrazine acetate according to Harries and then with a few drops of HCl. A large amount of precipitate separated out, and this was washed with water, dried and dissolved in hot alcohol. From the solution there was deposited only a very small amount of a pale yellow crystalline substance, which, after recrystallizing three times from alcohol, melted at 194 - 5°(uncorr.). The melting point of Harries' phenyl methyl dihydropyridazine was 197°. It is probable, then, that a very small amount of laevulinic aldehyde was present in the resinified rubber. Many other samples of oxidized rubber were tested for the substance after having been exposed to the air for periods varying between 1 and 18 months, some being soaked in ammoniacal copper acetate solution after extraction of the resin, and some being merely extracted. In no case was there any laevulinic aldehyde formed, although in all cases the aqueous extract contained a substance which gave the pyrrol reaction, and which gave a gummy phenylhydrazone which could not be crystallized from any solvent. It appears, then, that laevulinic aldehyde is one of the final oxidation products of caoutchouc, and, even on complete oxidation, is only formed in small amounts, unless, of course, volatilization balances the rate of formation.

Carbon Dioxide Evolved during Oxidation.

Peachey and Leon found that there was always a certain amount of CO_2 given off during the oxidation of caoutchouc. This varied somewhat in amount, but was found to approximate that corresponding to 1/4 of a carbon atom per $C_{10}H_{16}$. The formation of CO_2 was investigated by the present author, with the idea of determining the point in the reaction at which the CO_2 was evolved, and, if possible, the substances involved. The apparatus is shown in Figure I.

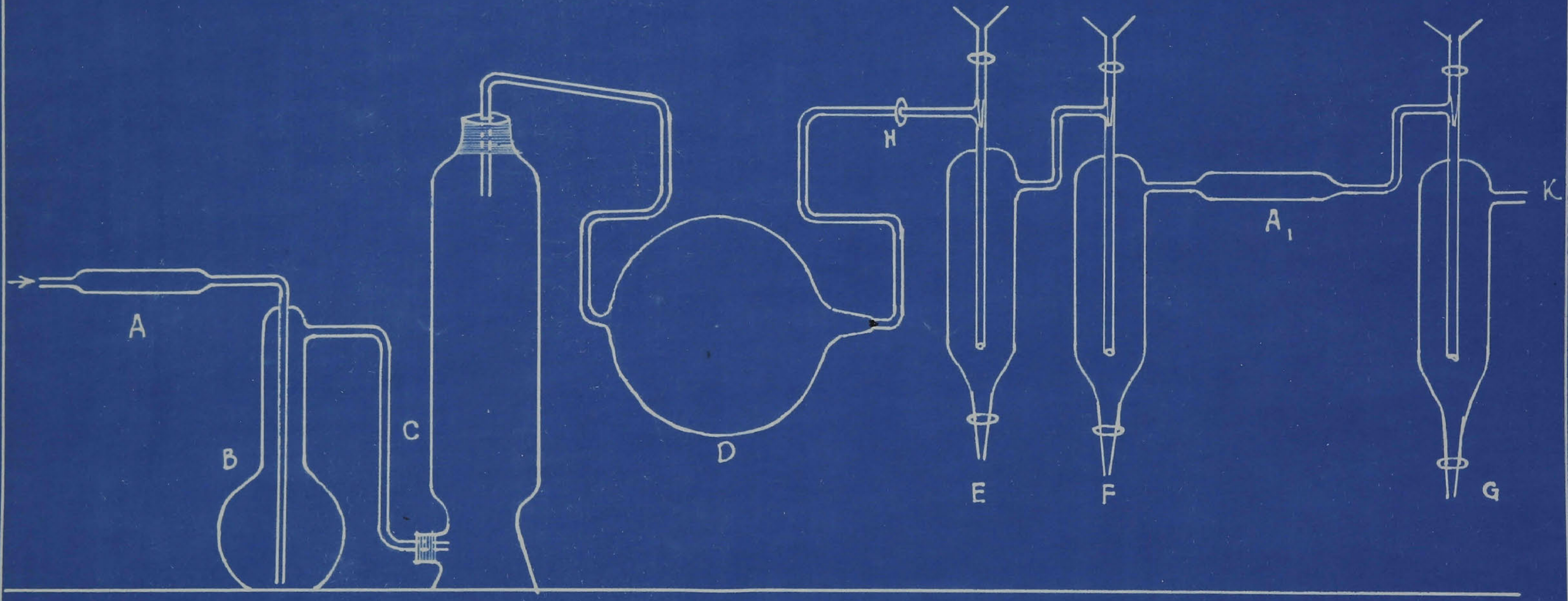
A and A_1 were filled with yellow HgO (28) to convert CO to CO_2.

B and E contained H_2SO_4.

C was filled with soda lime.

F and G contained a solution of $Ba(OH)_2$. These vessels

Fig. I



could be drained, washed and re-filled without disturbing the apparatus.

Thin films of extracted rubber were deposited from their chloroform solutions, by evaporation of the solvent in vacuo, on the inside of flask D, which was then sealed inside of a small oven heated by means of an electric plate. Sulphuric acid was run into E, purified air sent through the apparatus for a few minutes, and F and G washed out with water free from CO_2. The tap H was then closed, and the $Ba(OH)_2$ solution filtered into F and G with the aid of a gentle suction at K. A small calcium chloride tube filled with soda lime was attached at K. The oven was then brought to the temperature of 80° and a gentle current of air forced through the apparatus. In no case was any turbidity noticed in the $Ba(OH)_2$ solution in F until after 10 - 12 hours, when a gradual evolution of CO_2 began. The product was almost altogether soluble in acetone, and was a clear, hard resin. No CO was detected by a turbidity in G.

Two different samples of the resinous oxidation products were then used in place of rubber itself, being deposited on the inside of the flask D from their acetone solutions. The whole apparatus was filled with nitrogen at first, then heated to the required temperature. In both cases evolution of CO_2 was shown by a turbidity in F within 10 or 15 minutes after starting a current of air through the apparatus. No CO was detected. This shows that the CO_2 formed in the oxidation of caoutchouc is confined to the oxidation of the resinous products.

Observations on the Behaviour of Caoutchouc toward Solvents.

It has long been known that rubber, on treatment with suitable solvents, swells gradually to form a stiff gel, which, on standing, breaks down to a limpid solution. Heat, and the action of ultraviolet light accelerate the reduction of viscosity. If precipitated from a solution which is still viscous, the caoutchouc coagulates almost instantaneously, but if the solution has stood for a month or so, or has been heated, especially if the concentration is not more than 2% to 3%, the coagulation is slower, and the substance separates in an oily form. On removing the solvent, however, the elastic material is obtained again.

The author found that on heating a 2% solution in benzene in a sealed tube at 140° for about 5 hours with nitrogen, and precipitating the product with alcohol, a soft, tacky, transparent substance was obtained which precipitated very slowly, and which was very soluble in ether. On long standing this substance became elastic, but did not approach the toughness of caoutchouc itself. Part of the original solution was allowed to stand for a day with finely divided charcoal in suspension, and then filtered. The filtrate was clear and colorless and, examined under the ultra-microscope, showed no colloidal particles. The original solution had many colloidal particles, which appeared to be all suspensoids, and also gave the Tyndall effect. These suspensoid particles were probably all particles of protein and inorganic matter.

A 2% solution which had stood for over a year at room temperature ina full, tightly-stoppered bottle, was found to be entirely free from colloidal particles, the protein and inorganic matter having all settled to the bottom. The clear solution was decanted off and treated with alcohol, when the dissolved material separated out very slowly as an oily substance. This seemed to be identical with the substance obtained on heating to 140°, and became somewhat elastic on standing for several days.

One analysis gave the figures

0.1182 gm gave 0.3811 gm CO_2 and 0.1264 gm H_2O.

% C 87.93 % H 11.87.

$C_{10}H_{16}$ requires . . % C ~~87.93~~ 88.24 % H ~~11.87~~ 11.76.

This product is evidently the "oily" form referred to by Harries (29) but it is extremely doubtful whether this substance is identical with caoutchouc, as the elastic product cannot be compared with caoutchouc in tensile strength, even on long standing in vacuo.

A number of attempts to free a solution of unchanged caoutchouc from suspended protein by means of charcoal were unsuccessful, as the latter seemed to be peptized and filtration was rendered impossible; neither did centrifuging free the solution from the finely divided material.

In one exceptional case, on treating 2 grams of extracted rubber with 100 c.c. of benzene, and allowing to stand undisturbed for about 3 weeks, well-defined threads of protein had separated out from the solution. By filtering through asbestos fibre, then a large number of times through one, two, and three thicknesses of filter paper, a solution was obtained which showed practically no opalescence. Optical examination showed, however, that some suspended particles were present, and these could not be removed by filtration. The product gave no test for nitrogen, so the particles were probably finely divided iorganic matter. After precipitation, and removal of the solvent in vacuo at 100°, a colorless, transparent, elastic substance was obtained which swelled in solvents but did not go into solution.

Several other samples of precipitated caoutchouc from which the solvent had been completely removed, also became insoluble. This is what Harries (30) calls the ''insoluble'' form. Combustion showed a small amount of ash. The best analysis gave the figures,

0.1111 gm gave 0.3555 gm CO_2 and 0.1179 gm H_2O and 0.0004 g Ash.

If we deduct the weight of ash from the sample, the composition will be C 87.58% - H 11.83%.

The carbon-hydrogen ratio is 10 to 16.21.

The fact that the presence of small amounts of solvent have a considerable effect on the solubility of caoutchouc was further illustrated by heating two samples of precipitated rubber at 110° for 8 hours, one sample in a sealed tube with nitrogen, and the other in a high vacuum. The sample in the sealed tube, after standing for a day, was quite readily soluble, while the other had become quite insoluble.

Another sample of precipitated rubber containing benzene, on exhausting for 5 days in a high vacuum at room temperature, also became insoluble.

The Influence of the Resin Content on the Solubility of Rubber.

As Harries has pointed out, precipitated rubber, on standing, becomes insoluble, and it has just been shown that complete removal of solvent causes insolubility.

A solution of unextracted rubber, which was evaporated to dryness in vacuo and heated in vacuo at 100° for about 8 hours, then allowed to stand for two days, was found to be quite as readily soluble as the ordinary crepe sheet. A sample of a solution of exhaustively extracted rubber, given similar treatment, yielded a product which was almost insoluble.

A 2% solution of rubber to which had been added an amount of crude acetone extract, sufficient to increase the percentage of resin to 20% of the weight of caoutchouc, was allowed to stand for about two weeks, when the solution had become quite limpid. On evaporating to dryness in vacuo, as above, and heating in vacuo at 100° for 8 hours, the product was rather soft, and showed far less elasticity than the original sample of crepe. The substance, on treatment with caoutchouc solvents, went into solution rapidly on stirring, with no noticeable swelling.

On examining* this mixture of caoutchouc and resin under the ultramicroscope, it was found to consist of large, closely-packed globules, evidently of caoutchouc, embedded in an external phase of resin, and around each globule was noticed a film of fine suspenoid particles. On the addition of solvent, the globules swelled rapidly, fused into one another and, if there was sufficient solvent present, passed into a homogeneous solution, with the suspensoid particles showing rapid Brownian movement. On observing such a solution during evaporation, no marked change took place until nearly all of the solvent had evaporated, when the globules slowly took form again, with the films of suspensoid particles around each one. Finally, the whole reverted to the original solid emulsion.

This evidently means that caoutchouc is not very soluble in some of the constituents of the resin, and that when the volatile solvent evaporates, the caoutchouc separates out of the gradually concentrating solution. However, from the remarkable difference in solubility of the mixture from that of purified caoutchouc, it is evident that some of the constituents of the resin are soluble in caoutchouc. This

* This examination was made in the laboratory, and under the direction of Professor F. E. Lloyd.

is actually the case, as Whitby and Dolid have shown that the acetone extract of rubber contains higher unsaturated acids, and these are quite soluble in caoutchouc. It is quite obvious, then, that the resin content of rubber has a great influence on the solubility (31).

Harries has observed that by rolling rubber on hot mills for some time, it is rendered more soluble. The present author has found that the reverse is true in the case of thoroughly extracted rubber, it becoming more difficultly soluble. Evidently the influence of the resin is an important factor here also.

The Solubility of the Oily Oxidation Products in Caoutchouc.

As would be expected, the oily oxidation products are very soluble in caoutchouc. The small amount of these products necessary to transform extracted rubber into a soft, sticky mass is quite remarkable. About 10% by weight of Substance F was rubbed into the surface of a sheet of extracted crepe, in which it was readily dissolved, and after standing for two days, the whole had become soft and sticky, losing some of its original elasticity. Heated in vacuo for 2 hours at 100° caused almost complete loss of elasticity, the whole being transformed into a plastic, sticky mass. This material was much more readily soluble than the original crepe, and swelled very little before dissolving. This explains Schridowitz' (32) observation in regard to the low viscosities of solutions of tacky rubber.

Unextracted crepe absorbed the oxidation product more slowly.

The Molecular Weight of Caoutchouc.

A small sample of exhaustively extracted plantation crepe was ex~~tract~~hausted in a high vacuum to remove all traces of acetone, then dissolved in a weighed quantity of pure benzene. After standing for a week, part of the solution was heated in a sealed tube at 100° for 2 hours with nitrogen, to ensure complete solution. Before sealing the tube the solution was frozen in CO_2 and ether to prevent volatilization of benzene. The freezing point of this solution was then compared with that of pure benzene.

Weight of solvent 25.180[illegible] gm. Weight of caoutchouc 0.4812 gm.
Δ . . . . .017° M . . . . . . 5529.

If we deduct 2½% from the weight of caoutchouc to allow for protein and ash, we get the value, M = 5667.

A similar solution which had stood for 3 weeks at ordinary temperature gave the foll~~we~~owing results,

Weight of solvent 14.895 gm. Weight of caoutchouc 0.2652 gm.
Δ . . . . .017° M . . . . . . 5176.

Correcting, as above, we obtain the value, M = 5306.

The error in the above procedure would be considerable, but the two values are at least of the same order of magnitude.

By taking solutions which have not stood long enough for the caoutchouc to become completely dissolved, almost any value above 6000 may be obtained, depending on the degree of solution.

The values given above are of the same order of magnitude as that obtained by Gladstone and Hibbert (33), who give the value of 6000.

Iodine Values of Caoutchouc and its Oxidation Products.

The iodine values were determined by the Hübl method, ~~using the —— modification~~. In all cases the solution was allowed to stand 16 - 20 hours before titrating with sodium thiosulphate. Instead of using the usual 10 c.c. of CCl_4 to dissolve the substance, it was found necessary to use as much as 60 - 75 c.c. in the case of caoutchouc and the earlier oxidation products to prevent separation on the addition of the alcoholic solution. Addition of the alcoholic solution was accompanied by shaking to prevent precipitation of the substance under investigation. A very large excess of the Hübl solution was used in each case to ensure complete absorption. In the case of caoutchouc itself, the solution of extracted rubber was allowed to stand 2 days exposed to sunlight to ensure complete dispersion, before the determination was carried out.

(Results over page.)

77.05 c.c. thiosulphate = 40 c.c. iodine solution.

1.0 c.c. '' = 0.~~0212~~ .01212 gm I_2.

Substance		Weight	I_2 Solution	$Na_2S_2O_3$	Iodine No.
Extr'd Rubber	#1	0.1746	40 c.c.	33.4 c.c.	303
	#2	.1745	40	32.9	307
Subst. A	#1	.1952	40	29.3	297
	#2	.1847	40	32.4	293
Subst. A_1	#1	.1862	40	28.9	313
	#2	.1731	40	33.0	309
Subst. B	#1	.1880	40	31.8	292
	#2	.1913	40	31.3	290

The value for A is probably low as a small amount would not go into solution. If we deduct from the weight of the extracted rubber 2.5% for the protein and ash, we obtain the values 311 and 315 for caoutchouc. The theoretical value is 373. The Wij's solution was also tried for caoutchouc but gave a much lower value than did the Hübl solution.

35 c.c. ICl solution = 77.8 c.c. thiosulphate.

Sample	ICl in HOAc	Thiosulphate	Iodine No.
0.1514	35 c.c.	44.6	266

With new solutions, the following values were obtained for other oxidation products.

(Results over page)

40 c.c. Hübl solution = 78.4 c.c. thiosulphate

1 c.c. thiosulphate = 0.01211 gm I_2.

Substance		Weight	Iodine Solution	Thiosulphate	Iodine No.
C	#1	0.2713 gm	40 c.c.	14.8 c.c.	284
	#2	.2469	40	19.6	288
C_1	#1	.2347	40	23.1	285
	#2	.2621	40	17.45	282
D	#1	.2345	40	24.15	280
	#2	.2606	40	18.5	278
E	#1	.2225	50	48.0	272
	#2	.2433	50	42.75	275
F	#1	.2626	50	38.7	273
	#2	.2810	50	38.4	278
G	#1	.2822	50	57.0	176
	#2	.2438	50	62.1	178

Part III - Theoretical.

The Physical Properties of Caoutchouc
and its Oxidation Products.

It has been observed in the case of caoutchouc itself, and also in the cases of A, B, and C, that complete removal of solvent and other impurities causes insolubility. When we say that a substance is soluble we mean that the attraction of solvent molecules for solute molecules is greater than the attraction of solute molecules for one amother. If the substance is insoluble, the reverse holds true. The most reasonable interpretation of the insolubility of the above substances is that the removal of foreign substances allows the molecular attractive forces, which act over very small distances, to come into full play, and consequently, on later treatment with solvents, these forces cannot be overcome. The caoutchouc imbibes solvent and swells, but does not go into solution, so it seems evident that the attractive forces between caoutchouc molecules, when allowed to come into unrestricted play, are greater than the attractive forces between them and the molecules of any solvent. Thus, caoutchouc, once freed from impurities, is insoluble.

When caoutchouc is formed in the plant, it is ~~found~~ formed in solution in the caoutchouc soluble matter; when it is coagulated from the latex it still retains, dissolved in it, some other plant products. Crude rubber is a solid emulsion, the internal phase of which consists of caoutchouc globules in which are dissolved certain caoutchouc soluble constituents, the external phase consisting of substances which are insoluble in caoutchouc. On account of the solid solution of caoutchouc being very concentrated, the molecular attractive forces come into play to a certain extent, but not to the full extent; consequently, solvents are able to dissolve the substance, although there is some difficulty in overcoming these forces, and the gel which forms breaks down only slowly.

When a thoroughly dispersed solution of crude rubber is evaporated to dryness, there remains an emulsion essentially the same as the original crude rubber, but when an excess of resin is introduced, the caoutchouc is in a more dilute solution in the caoutchouc soluble constituents, hence solution in an ordinary solvent takes place much more readily and without the customary swelling.

The fact that some of the oxidation products of caoutchouc became insoluble and elastic on complete removal of solvent, and also that the original solutions were non-colloidal when freed from suspended protein, suggested to the author that the latter was probably true of solutions of caoutchouc itself. Although it was found to be impossible to get a solution of unchanged caoutchouc free from colloidal particles, these particles appeared under the ultramicroscope to be all suspensoids, so it is almost certain that it can be obtained in true solution. Thus caoutchouc offers a striking example of the close relationship between the so-called ''colloids'' and ''crystalloids''. Hitherto it has been considered to be one of the outstanding examples of colloidal substances.

Harries classifies caoutchouc as a typical dispersoid and emulsoid in the following words :'' Der Kautschuk ist ein typisches Dispersoid, und zwar ein Emulsoid. Die Emulsoide unterscheiden sich von den Suspensoiden dadurch, dass ihre Viscosität in Dispersionsmitteln bei steigenden Prozentgehalt sehr stark wäehst.'' It is quite true that this rapid rise in viscosity with increasing concentration applies to caoutchouc, but only if we are considering the process of solution. If we take a dilute solution which has stood a sufficient time for the caoutchouc to become completely dissolved,and concentrate it by evaporation, we do not get any rapid rise in viscosity as the concentration increases. On the contrary, the solution may be evaporated to a thick, syrupy liquid containing about 50% of caoutchouc. This shows that abnormally high viscosity is attendant only on the initial stages of solution, while the attractive forces within the caoutchouc are only gradually being overcome.

Harries' observation that rubber was rendered more soluble by rolling on hot mills was interpreted by him as indicating that the caoutchouc had become depolymerised. Depolymerisation might explain such a change in solubility, but it seems rather unnecessary to employ a speculative theory to explain facts which require only the application of common sense. The mechanical and thermal agitation applied would naturally work up the solid emulsion into a finer state of dispersion and the attendant ease of solution would simply be analagous to that caused by powdering of a crystalline solid. Thoroughly extracted rubber, as has been shown, becomes less soluble on milling, probably due to the compression of the caoutchouc into a more closely packed and continuous mass.

To use Pickles words, ''depolymerisation'' is a ''vague and unnecessary conception'' which has been so loosely employed by various chemists as to render it altogether meaningless. No evidence has been advanced which necessitates the introduction of such a conception and the term simply serves as a subterfuge for those who desire to evade the simple facts and make them seem complicated.

If Harries' conception of depolymerisation of complex aggregates of large rings were correct, all the oxidation products obtained by the present author would be expected to have a very much lower molecular weight than caoutchouc itself, and this is not the case. There is a gradual reduction of molecular weight as the complex molecule is broken down, and this shows conclusively that there is no such thing as depolymerisation, as Harries represents it. Hence, the '' Kolloidnebenvalenzen'' of Harries, and the ''kolloiden Hemmungen'' of Schmitz must be relegated to the chemical refuse heap.

Oxidation and Tackiness.

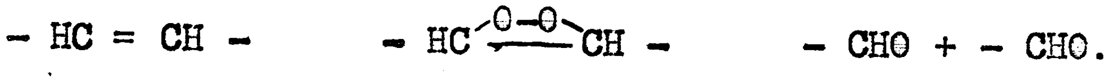
Various theories have been advanced from time to time to account for the tackiness of degraded rubber. Bertrand (34) explained this phenomenon by assuming isomerization of the unsaturated hydrocarbon, the sticky product being isomeric with the original elastic ~~product.~~ substance. Later, Whitby (35) suggested the possibility of enzyme action being the cause of the change. Spence (36) showed that analyses of sound and tacky rubber gave identical results and Schridowitz (37) showed that the visocsity of solutions of tacky rubber was lower than that of solutions of sound rubber. The two latter investigators believed the change to be due to a difference in the state of aggregation. Gorter (38), however, showed that conditions favouring oxidation caused tackiness, and that 0.6% by weight of absorbed oxygen was sufficient to bring about this result. He believed that laevulinic aldehyde was formed in the process, although he was unable to isolate it. Kirchhof (39) found that extracted rubber was more readily oxidised than unextracted, and also that it became tacky more rapidly, thus confirming Gorter's contention that the two processes were connected.

The existence of a large number of oily oxidation products such as those described above readily explains the tackiness of oxidized rubber, and shows, beyond any possible doubt, that oxidation is the cause of the phenomenon. The change of color through yellow to reddish-brown before final resinification is also readily understood, as the color of the oily substances passes towards red as the molecular weight decreases. At first sight it would seem strange that such a small amount of oxygen as that found by Gorter could cause tackiness, as the oxygen content of the lowest oxidation product isolated was approximately 2.5%. When, however, we consider that oxidation takes place only at the surface of the rubber, and also the extraordinary solvent properties these oily products have for caoutchouc, the thing becomes quite intelligible. When, as indicated above, 10% by weight of substance F dissolved in extracted crepe, will cause a complete loss of elasticity, the whole being transformed into a soft, sticky mass, the reason for Spence's failure to notice any difference in the analyses of sound and tacky rubber, becomes quite evident. The lower viscosities found by Schridowitz are also easily understood, as in the case of tacky rubber, the caoutchouc is already in solution, and addition of a solvent merely dilutes this solution. The initial difficulty in overcoming the molecular attractive forces is already partially overcome, and the substance passes into solution more rapidly and completely.

The Mechanism of the Oxidation of Caoutchouc.

Wo. Ostwald (40) was the first to suggest that the oxidation of caoutchouc was a true autoxidation. This view has been shared by various other investigators, and Peachey (41) and others have obtained tests for peroxides in oxidized rubber. However, there has hitherto been advanced no definite evidence tracing the progressive break-down of the complex molecule; neither has any explanation been offered of the obvious lack of agreement ~~between~~ amongst the results obtained by various investigators who studied the resinous oxidation products. Boswell indicated the existence of earlier oxidation products, but he did not show that any of his products were homogeneous, nor did he obtain any molecular weight determinations.

Taking into consideration the facts that all the products obtained were aldehydic, that the carbon-hydrogen ratio of 10 - 16 is maintained through at least 10 stages of oxidation, and that there is a gradual decrease in the molecular weight of the products as the oxidation proceeds, there seems to be only one possible explanation of the course of the reaction: That is, that peroxides are formed first, and these break down into aldehydes in the following manner,



$$- HC = CH - \qquad - HC\overset{O-O}{\frown}CH - \qquad - CHO + - CHO.$$

The application of this mechanism to the oxidation of caoutchouc explains the gradual division and subdivision of the complex unsaturated molecule. In view of the difficulties encountered in obtaining re~~a~~liable molecular weights for these substances it would be presumptious to attempt to trace the exact course of the reaction; however, it seems probable that the earlier stages of oxidation are accompanied by the elimination of a molecule of solid resin, probably of molecular weight approximating 300, while in later stages larger units may be split off, such as substance D, with a molecular weight of 1745. This is evidenced in the marked drop in molecular weight noted in substance C_1, which appears at about the same stage in the oxidation. The detection of petrolic ether insoluble material, even as early as the first stage of oxidation, supports the view that the earlier stages are accompanied by elimination of one of these units of low molecular weight.

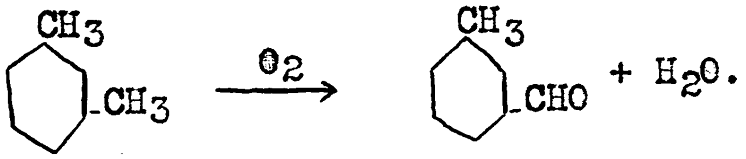
The oxygen content of the first and other oxidation products is greater than that required by the addition of oxygen to one double bond, and the subsequent scission of the molecule at that point. This would appear at first sight to be a weak point in the arguments being advanced. There are, however, other possibilities besides scission which may account for the decomposition of the peroxides. According to the theory of autoxidation developed by Engler and Weissberg (42), peroxides of unsaturated substances may act as autoxidator to another oxidizable substance, or to other molecules of the original unsaturated substance, giving up half of their oxygen in the process. An example of this type of reaction is in the employment of organic peroxides such as benzoyl hydroperoxide in the oxidation of ethylenic compounds

$$>C=C< + C_6H_5CO\cdot O\cdot OH \qquad >C\overset{O}{-}C< + C_6H_5COOH.$$

Thus, in the oxidation of caoutchouc, there are probably two courses which the reaction may pursue, subsequent to the formation of peroxides. First, the peroxide grouping may give up part of its oxygen to other molecules, or other parts of the same molecule, or second, the peroxide may split up into two aldehyde groupings.

Although much work has been done on the mechanism of autoxidation processes, the present state of our knowledge on that subject leaves much to be desired, and the above must be regarded merely as a suggestion as to what actually takes place.

All the solid resins, on analysis, gave values for hydrogen which were too low to correspond to a carbon-hydrogen ratio of 10 to 16, and the hydrogen content of these substances gradually decreased as oxidation proceeded. This is probably due to the same type of reaction noted in the oxidation of the xylene solvent



This explains the formation of considerable amounts of water in the later stages of oxidation. This type of reaction might also apply to the oxidation of methylene groups to carbonyl groups,

$$-CH_2- + O_2 \longrightarrow -C{=}O + H_2O,$$

but in view of later arguments to be advanced, it seems preferable to assume that the oxidation of methyl groups is at least predominant.

The insoluble and inert substance D, obtained by Peachey and Leon, which is probably identical with resin X_1, described above, was assumed by them to be isomeric with substance B, which had the same composition. It would be remarkable, though, if simple isomerization could effect such a tremendous change in physical and chemical properties. A much more reasonable interpretation would be that their substance B, on account of the multiplication of aldehyde graups, condensed to an aldehyde resin, which would be expected to be insoluble and chemically inert. Prolonged boiling with formic acid would merely regenerate some of the original aldehyde.

On carrying out the oxidation in a paraffin solvent, the tendency to form insoluble and inert resins manifested itself at an earlier stage in the oxidation. The product was similar in properties to resin X_1, but had considerably lower oxygen content. As would be anticipated, the use of a higher temperature (130°) further increased this tendency to condense, and the product contained a still lower amount of oxygen. At the latter temperature this tendency was remarkable, there being obtained practically a quantitative yield of a brown, inert resin at the end of one day.

It has been pointed out that all the soluble resinous oxidation products are aldehydic, and that they are slowly dissolved by caustic alkalis. This latter fact would appear to indicate the presence of carboxyl groups. It has been found, though, that these substances do not form salts with the metals, and this fact, in conjunction with the fact that the substances are not soluble in aqueous ammonia, seems to contradict this. It is probable that they are merely alkali soluble aldehydes.

Resin X, above, appeared to consist of a mixture of acidic substances, as it was readily soluble in aqueous ammonia, and formed salts. These substances are probably formed by the oxidation of aldehyde groups to carboxyl groups.

Oxidation and Vulcanization.

Two main theories have been advanced to explain the action of sulphur on caoutchouc, a process knwon technically as vulcanization. Weber (43) prepared a substance corresponding to the composition $(C_{10}H_{16}S_2)_x$, by vulcanizing rubber at 120 - 130°, and several other investigators have reported this same substance. Recently, Whitby and Jane (44) have made a study of this substance, advancing strong evidence of it being a definite substance. Weber also believed that there existed a sulphur compound containing 2.5% of sulphur, basing his view on the fact that the most important technical preparation contains about that amount. Then, without advancing any further experimental proof, he assumed that there existed a series of sulphur compounds ranging in composition from $C_{200}H_{320}S_2$ to $C_{200}H_{320}S_{40}$. In reference to this idea, Porritt (45) justly says, ''Such views of the matter are no longer of much importance.''

In 1910 Wo. Ostwald (46) proposed his adsorption theory of vulcanization, his main arguments being that there had been advanced no experimental evidence in favour of Weber's series of sulphur compounds, and that the evidence on record regarding the compound $(C_{10}H_{16}S_2)_x$ was not satisfactory. He discarded the theory of chemical combination and advanced the theory that the sulphur was adsorbed by the caoutchouc.

In 1913 Ostromisslenski (47) published a new interpretation of the process of vulcanization, combining the two older theories. In his opinion the process proceeded in two stages, first, the formation of a small amount of the compound $(C_{10}H_{16}S_2)_x$, and second, the adsorption of this compound by the caoutchouc.

The close relationship between sulphur and oxygen in the periodic classification of the elements gives reason to assume that their action on caoutchouc would be analagous. It has been shown above that the only reasonable interpretation of the action of oxygen is based on the assumption that peroxides are formed first. Granted this, it would be quite justifiable to assume that the action of sulphur was accompanied by the production of sulphur analogues of this class of compounds. Thus, if the action of sulphur parallels that of oxygen, a series of sulphur compounds would be formed, analagous to the oxidation products described above. The insolubility and elasticity of some of the earlier oxidation products offers some analogy to the vulcanized products. The most striking analogy, though, is in the formation of an oxidation product, Resin S, corresponding to the sulphur compound $(C_{10}H_{16}S_2)_x$. This substance was obtained by oxidizing at 130° in solution. Whitby and Jane treated with sulphur in solution at 140°. It will be noted that resin S contains somewhat less hydrogen than is required by $(C_{10}H_{16}S_2)_x$. If a corresponding reduction of hydrogen took place during the treatment with sulphur, H_2S would be eliminated instead of H_2O. It was actually found by Whitby and Jane that H_2S was always given off toward the end of the reaction and this has been noted by other investigators also. None of the present theories of vulcanization are able to explain this fact. If, then, the action of sulphur proceeds in a manner analogous to that of oxygen, the end product would be a thio-aldehyde resin, and we should expect it to have properties similar to the aldehyde resin obtained as the end product of the oxidation. This also is actually the case, as they are both brittle, inert resins, insoluble in all organic solvents.

To test further this analogy between oxidation and vulcanization it would be very interesting to study the action of sulphur at a lower temperature and for a longer time, to determine whether the lower temperature would allow the action of sulphur to proceed further before condensation took place.

The Constitution of Caoutchouc

Although it would be a comparatively easy matter to build a new structure for caoutchouc on the experimental evidence above, it is not the intention of the writer to enter in the race after fantastic formulae. It is frankly admitted that the evidence is hopelessly inadequate, and it would be presumptuous to propose a formula without first getting some evidence on the structure of the oxidation products. Even such evidence would have to be carefully weighed, as there are so many possibilities of re-arrangement during the many stages of the reaction. For example, the tremendous drop in iodine value shown in substance G would seem to indicate re-arrangement into a complex polycyclic substance. The present research has shown the inadequacy of most of the structures already proposed, but has contributed very little to our knowledge of the intimate structure of the complex caoutchouc molecule. However, the writer feels that it may be claimed that solid foundations have been laid for a new field of research, and that the evidence has been set forth in a perfectly impartial manner.

The iodine values obtained for caoutchouc and its oxidation products are so obviously out of accord with other work on the additive capacity of caoutchouc that their value as an argument for the constitution of caoutchouc is a matter of serious doubt. The hydrogenation experiments of Pummerer and Burkard, together with the gradual break-down of the molecule recorded above, seem to indicate that the open chain structure is the only one which can be seriously considered.

If we consider very briefly the structures proposed by Harries, Kirchhof, and Boswell, we shall see that none of these is capable of interpretating the experimental facts.

Harries structure implies a depolymerization of the complex aggregates into simple ring structures before the action of ozone on the double bonds takes place. If this is true for ozone, it ought certainly to be true for molecular oxygen but there has been no evidence obtained in support of this idea. Again, the series of oily oxidation products described above do not show simple enough relationships to be interpreted by Harries' structure.

Kirchhof's structure fails to interpret any of the evidence submitted above. Leaving out of the question the analyses of rubber, which is impure caoutchouc, there have been described 10 oxidation products which give carbon-hydrogen ratios varying between the narrow limits of 10 to 15.8 and 10 to 16.14. These slight deviations from the ratio 10 to 16 are well within the limits of experimental error, and in no case was there any indication of a ratio of 10 to 17. If this ratio existed in caoutchouc itself, there would have to be an elimination of water at the first stage of the reaction, and in no case was this found to be true, although there were considerable amounts formed in later stages.

The impossibility of Boswell's formula is obvious when we consider the high iodine values obtained for caoutchouc and its oxidation products. Again, his structure requires 9 oxidation stages having the carbon-hydrogen ratio of 10 to 16, the last being a brittle resin. There have been described above 10 oily oxidation products which have the above carbon-hydrogen ratio, and in addition it has been shown that there are a large number of solid resins formed.

As has been mentioned, the open chain structure seems to be the only one capable of interpreting all the known facts. If we accept this type of structure, the gradual subdivision of the complex molecule through scission of the intermediate peroxides, is readily understood. As the percentage of oxygen in the products is greater than that required by the addition of oxygen to one double bond and subsequent scission, we must further assume that the peroxides give up some of their oxygen to other molecules, or other parts of the same molecule. In regard to the arrangement of atoms in the open chain structure, it seems that Pickles' formula is the only one capable of interpreting the action of ozone on caoutchouc.

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Summary.

1. The various theories of the constitution of caoutchouc, together with the experimental evidence on which they are based, have been reviewed and criticized.
2. A series of 10 oxidation products of caoutchouc have been described, and the existence of many more indicated.
3. The molecular weight of caoutchouc has been shown to be over 5500.
4. The caoutchouc molecule has been shown to be non-colloidal.
5. Various experiments have been carried out on the physical behaviours of caoutchouc and simple explanations have been offered for most of these.
6. Reasons have been given for discarding the meaningless terms "depolymerization" and "Kolloidnebenvalenzen" .
7. Unquestionable proof of the cause of tackiness in rubber has been advanced.
8. A new mechanism has been suggested for the oxidation of caoutchouc by molecular oxygen.
9. An analogy has been drawn between oxidation and vulcanization, and a new interpretation of the mechanism of the latter process has been offered.
10. The theories of the constitution of caoutchouc, advanced by Harries, Kirchhof, and Boswell, have been shown to be inadequate to explain the facts set forth in the present paper, and the advantages of the open chain structure have been indicated.