48. *The Oxidation of Caoutchouc, Gutta-percha, and Balata with Hydrogen Peroxide.*

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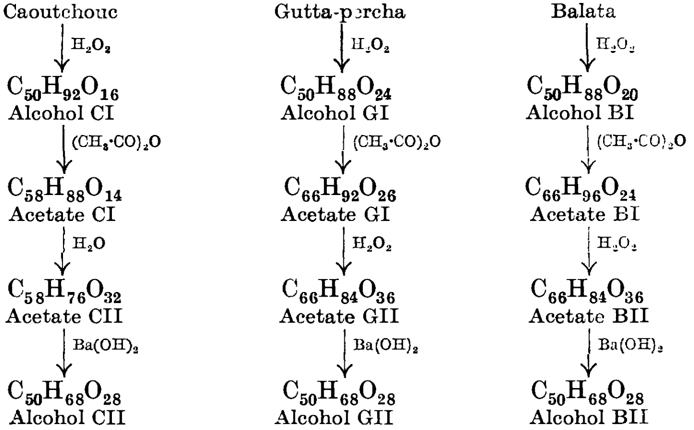
THE behaviour of caoutchouc towards hydrogen peroxide was studied first by Boswell, McLaughlin, and Parker (*Trans. Roy. Soc. Can.*, 1922, **16**, 27) and more recently by Robertson and Mair (*J. Soc. Chem. Ind.*, 1927, **46**, 41T).

The earlier workers, using a solution of caoutchouc in carbon tetrachloride, isolated a compound $C_{30}H_{48}O$ which they found to absorb atmospheric oxygen and yield another compound $C_{25}H_{40}O_2$. The later workers adopted a modification of the usual method of hydrogen peroxide oxidation of terpene hydrocarbons and employed a chloroform solution of caoutchouc, to which glacial acetic acid was added. They obtained a product, alcoholic in character, of the empirical formula $C_{59}H_{102}O_{16}$. The present work was commenced with the object of extending the latter work to include gutta-percha and balata. Certain changes were introduced and new avenues of investigation opened up, and it was thought desirable to extend the scope of the work to include caoutchouc so that each of the three substances caoutchouc, gutta-percha, and balata and corresponding derivatives of them might be submitted to as nearly as possible identical reaction conditions.

Since all the products were non-crystalline solids which decomposed on distillation, even under reduced pressure, it was almost impossible to obtain a complete separation from resinous materials once these were formed. Therefore, every effort was made to reduce to a minimum the risk of the formation of such undesirable by-products. Polymerisation took place very readily, even when solutions of the products were warmed to temperatures above 50°, and all operations were carried out at temperatures not exceeding 40° to avoid this difficulty. There was little difference in the behaviour of the various products towards solvents and this increased the difficulty of their purification.

The main results of the work have been embodied in the accompanying diagram. In order to obtain a general idea of the relationship existing throughout the whole series the empirical formulæ which are suggested for the various products have been reduced to a common unit, C_{50}, the lowest one consistent with the analyses of the semicarbazones and acid salts to be described later. The discrepancies noticeable in some cases between actual and calculated analyses are only to be expected, because no criterion is available to guarantee the absolute purity of any of the products.



Caoutchouc.

Caoutchouc, in chloroform solution to which glacial acetic acid had been added, was oxidised with 100 vol. hydrogen peroxide and yielded a colourless amorphous compound, alcoholic in character, approximating, after reduction to a C_{50} basis, to $C_{50}H_{92}O_{16}$. It was still unsaturated to bromine and to dilute alkaline permanganate, did not possess acidic or reducing properties, and was thought to be an alcohol corresponding to the usual products of hydrogen peroxide oxidation in the terpene series. Estimation by the method of Tschugaev and Zerewitinov (*Ber.*, 1902, **35**, 3912; 1907, **40**, 2023) indicated that all the oxygen was present as hydroxyl. The compound was therefore $C_{50}H_{76}(OH)_{16}$ and was probably produced from caoutchouc by simple addition of hydroxyl groups to the unsaturated linkages of the parent molecule. Accurate determination of its molecular weight by the cryoscopic method was impossible and values obtained by the Rast method, using camphor or menthol as solvent, varied considerably and were of no use in fixing the actual molecular weight : camphor gave values in the neighbourhood of 1000, and with menthol as solvent values from 600—1000, varying with concentration, were obtained.

The unsaturation as determined by measuring the absorption of bromine by the method of Gladstone and Hibbert (J., 1888, **53**, 679) was greater than that required for a compound of the type C_nH_{2n}. Possibly this was due to some oxidising action of the bromine. No characteristic derivative of this alcohol could be obtained, owing to the impossibility of separating the main product in each case from resinous by-products.

By oxidation of alcohol CI with chromic acid, a substance, aldehyde CI, was obtained having pronounced aldehydic properties. The semicarbazone obtained from it gave the analytical values required for the formula $C_{50}H_{88}O_{16}(CN_3H_3)_2$—indicating the presence in the aldehyde of two CHO groups per C_{50} and, consequently, the presence, in alcohol CI, of two $CH_2{\cdot}OH$ groups per C_{50}.

Further oxidation of aldehyde CI by means of dilute nitric acid yielded an acid, the silver salt of which had a silver content of 17·78% in fair agreement with the calculated silver content for $C_{48}H_{86}O_{14}(CO_2Ag)_2$, namely, 18·15%.

From these facts the formula for alcohol CI on the C_{50} basis would be $C_{48}H_{72}(OH)_{14}(CH_2{\cdot}OH)_2$.

Alcohol CI was treated with acetic anhydride in the presence of anhydrous sodium acetate, and it was found that the product did not give analytical results in agreement with those calculated for the acetate of alcohol CI. This new product, acetate CI, was hydrolysed with baryta to alcohol CIA, which, in turn, was oxidised with chromic acid to aldehyde CII; the last-mentioned product, on further oxidation with atmospheric oxygen, yielded acid CII. The lead salt of acid CII contained 18·9% of lead and indicated that, if the salt were normal, the acid would be dibasic and of molecular weight 890. It is on this evidence that the C_{50} basis for the series was chosen.

Alcohol CIA, mentioned above, possessed four hydroxyl groups per $C_{50}H_{80}O_{10}$ and, since it yielded a dialdehyde (CII), two of these must have been present as primary alcoholic groups, giving $C_{48}H_{72}O_6(OH)_2(CH_2{\cdot}OH)_2$. Aldehyde CII would then be

$$C_{48}H_{72}O_6(OH)_2(CHO)_2,$$

yielding the semicarbazone $C_{50}H_{76}O_{10}(CN_3H_3)_2$, and acid CII would be $C_{48}H_{74}O_8(CO_2H)_2$, giving the lead salt $C_{48}H_{74}O_8(CO_2)_2Pb$.

Since alcohol CIA, $C_{50}H_{76}O_6(OH)_4$, was derived, by hydrolysis, from acetate CI, the latter compound must have been

$$C_{50}H_{76}O_6(O{\cdot}CO{\cdot}CH_3)_4.$$

Now, acetate CI was derived from alcohol CI, $C_{50}H_{76}(OH)_{16}$, so it would appear that, under the influence of the acetic anhydride, loss of the elements of water had accompanied acetylation of several of the hydroxyl groups.

Acetate CI was still unsaturated and, on further treatment with 100 vol. hydrogen peroxide, yielded acetate CII, $C_{58}H_{76}O_{32}$, containing free hydroxyl groups in addition to the acetoxy-groups of the original acetate. Alcohol CII, $C_{50}H_{56}O_{16}(OH)_{12}$, was produced by the action of aqueous baryta on acetate CII, which was then assigned the formula $C_{50}H_{56}O_{16}(OH)_8(O{\cdot}CO{\cdot}CH_3)_4$. Acetate CII and alcohol CII were both saturated to bromine and therefore represent the final stage of the oxidation process.

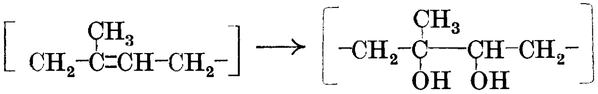
The following table summarises the preceding observations :

$$\begin{tikzcd}
 & \begin{matrix} C_{50}H_{76}(OH)_{16} \\ \text{Alcohol CI} \end{matrix} \arrow[r] \arrow[dl] & \begin{matrix} C_{48}H_{86}O_{14}(CHO)_2 \\ \text{Aldehyde CI} \end{matrix} \arrow[d] \\
\begin{matrix} C_{50}H_{76}O_6(O{\cdot}CO{\cdot}CH_3)_4 \\ \text{Acetate CI} \end{matrix} \arrow[d] \arrow[dr] & & \begin{matrix} C_{48}H_{86}O_{14}(CO_2H)_2 \\ \text{Acid CI} \end{matrix} \\
\begin{matrix} C_{50}H_{56}O_{16}(OH)_8(O{\cdot}CO{\cdot}CH_3)_4 \\ \text{Acetate CII} \end{matrix} \arrow[d] & \begin{matrix} C_{50}H_{76}O_6(OH)_4 \\ \text{Alcohol CIA} \end{matrix} \arrow[r] & \begin{matrix} C_{48}H_{74}O_8(CHO)_2 \\ \text{Aldehyde CII} \end{matrix} \arrow[d] \\
\begin{matrix} C_{50}H_{56}O_{16}(OH)_{12} \\ \text{Alcohol CII} \end{matrix} & & \begin{matrix} C_{48}H_{74}O_8(CO_2H)_2 \\ \text{Acid CII} \end{matrix}
\end{tikzcd}$$

It is suggested that the changes recorded above have been brought about by the addition of hydroxyl groups to double bonds under the influence of hydrogen peroxide, and subsequent removal of the elements of water through the action of acetic anhydride. There is no evidence of extensive degradation of the hydrocarbon molecule involving loss of carbon, the proportion of acidic products formed during the oxidations being very small. In this respect the action of hydrogen peroxide on caoutchouc differs materially from that of neutral or alkaline potassium permanganate. In the latter case there is evidence of extensive degradation, as shown by the formation of substantial amounts of lævulic and oxalic acids. In addition, the proportion of carbon liberated as carbon dioxide corresponds approximately to the oxidation of only 0·5% of the total carbon of the hydrocarbon.

No attempt has been made to distinguish between the cyclic and open-chain formulæ in interpreting the experimental results. The C_nH_{2n} form has been used throughout, since, on the whole, it agrees best with the values obtained for the unsaturation of the various products. The C_{50} basis on which the empirical formulæ have been calculated represents the minimum unit within which all the oxidation products can be included, and permits of their arrangement according to a definite scheme. It is of course obvious that a great number of alternative empirical formulæ could be assigned to any one product in dealing with such large molecular weights.

Taking the accepted unit of the caoutchouc molecule, oxidation with hydrogen peroxide might be expected to yield a glycol as follows :



$$\left[CH_2-\overset{CH_3}{C}=CH-CH_2-\right] \longrightarrow \left[-CH_2-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_2-\right]$$

Removal of the elements of water might take place in several ways. If two adjacent hydroxyl groups were involved, the result would be an outside ether ring, whereas, if two hydroxyls on opposite sides of the molecule were concerned, an inner ether ring would be formed. Finally, elimination of water between a hydroxyl group and the hydrogen of an adjacent methylene group would give rise to a new double bond. Since the observed loss of water does not lead to an increase in unsaturation, as would occur in this case, the double linkages thus formed must rearrange to give a ring system inside the molecule. Oxide formation seems most probable, since the methylene groups are themselves apparently involved in a further oxidation.

Between acetate CI and acetate CII there is a considerable replacement of hydrogen by oxygen. This is evident from a consideration of the corresponding alcohols.

Alcohol CIA has the empirical formula $C_{50}H_{76}O_6(OH)_4$ and has an unsaturation equal to four double bonds. Addition of hydrogen peroxide (to its acetyl derivative) should give a saturated alcohol $C_{50}H_{76}O_6(OH)_{12}$ and this should be identical with alcohol CII, the end product of the oxidation series. Alcohol CII, however, has the empirical formula $C_{50}H_{56}O_{16}(OH)_{12}$. There has therefore been replacement of hydrogen by oxygen to the extent of twenty atoms, and in this reaction the methylene groups must be involved.

Gutta-percha.

Gutta-percha was treated in a manner similar to that described for caoutchouc and under as nearly as possible identical reaction conditions. The results are incorporated in the following table, in which all the formulæ have been reduced to the same basis as that adopted for caoutchouc, namely, C_{50}.

$$\begin{tikzcd}
 & \begin{array}{c} C_{50}H_{68}O_4(OH)_{20} \\ \text{Alcohol GI} \end{array} \arrow[r] \arrow[dl] & \begin{array}{c} C_{48}H_{82}O_{22}(CHO)_2 \\ \text{Aldehyde GI} \end{array} \arrow[d] \\
\begin{array}{c} C_{50}H_{68}O_{10}(O{\cdot}CO{\cdot}CH_3)_8 \\ \text{Acetate GI} \end{array} \arrow[d] \arrow[dr] & & \begin{array}{c} C_{48}H_{82}O_{22}(CO_2H)_2 \\ \text{Acid GI} \end{array} \\
\begin{array}{c} C_{50}H_{56}O_{16}(OH)_4(O{\cdot}CO{\cdot}CH_3)_8 \\ \text{Acetate GII} \end{array} \arrow[d] & \begin{array}{c} C_{50}H_{68}O_{10}(OH)_8 \\ \text{Alcohol GIA} \end{array} \arrow[r] & \begin{array}{c} C_{48}H_{70}O_{16}(CHO)_2 \\ \text{Aldehyde GII} \end{array} \arrow[d] \\
\begin{array}{c} C_{50}H_{56}O_{16}(OH)_{12} \\ \text{Alcohol GII} \end{array} & & \begin{array}{c} C_{48}H_{70}O_{16}(CO_2H)_2 \\ \text{Acid GII} \end{array}
\end{tikzcd}$$

The products were very similar to those obtained from caoutchouc. They also seem to have been produced by a series of reactions involving the addition of hydroxyl groups, followed by the removal of the elements of water. The gutta-percha hydrocarbon, however, seems to be more readily attacked by hydrogen peroxide than is caoutchouc, the larger proportion of oxygen in the primary product, alcohol GI, being probably due to this. It would also appear that the replacement of hydrogen by oxygen, already noted in the case of caoutchouc, has occurred in the first stage of the gutta-percha oxidation, since the alcohol formed by addition of hydroxyl to the hydrocarbon, and corresponding in unsaturation to alcohol GI, should be $C_{50}H_{80}(OH)_{16}$ instead of $C_{50}H_{68}O_4(OH)_{20}$.

Balata.

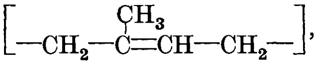
A similar series of reactions was carried out on balata, and a similar series of products isolated. Each of the balata products seemed to bear a closer relationship to the corresponding gutta-percha products than to those from caoutchouc. Again alcohol BI gave an analysis indicating an initial replacement of hydrogen by oxygen as in alcohol GI. The results are summarised below.

$$\begin{tikzcd}
 & \begin{array}{c} C_{50}H_{72}O_4(OH)_{16} \\ \text{Alcohol BI} \end{array} \arrow[r] \arrow[dl] & \begin{array}{c} C_{48}H_{82}O_{18}(CHO)_2 \\ \text{Aldehyde BI} \end{array} \arrow[d] \\
\begin{array}{c} C_{50}H_{72}O_8(O{\cdot}CO{\cdot}CH_3)_8 \\ \text{Acetate BI} \end{array} \arrow[d] \arrow[dr] & & \begin{array}{c} C_{48}H_{82}O_{18}(CO_2H)_2 \\ \text{Acid BI} \end{array} \\
\begin{array}{c} C_{50}H_{56}O_{16}(OH)_4(O{\cdot}CO{\cdot}CH_3)_8 \\ \text{Acetate BII} \end{array} \arrow[d] & \begin{array}{c} C_{50}H_{72}O_8(OH)_8 \\ \text{Alcohol BIA} \end{array} \arrow[r] & \begin{array}{c} C_{48}H_{74}O_{14}(CHO)_2 \\ \text{Aldehyde BII} \end{array} \arrow[d] \\
\begin{array}{c} C_{50}H_{56}O_{16}(OH)_{12} \\ \text{Alcohol BII} \end{array} & & \begin{array}{c} C_{48}H_{74}O_{14}(CO_2H)_2 \\ \text{Acid BII} \end{array}
\end{tikzcd}$$

It will be seen that the end product, alcohol II, in each of the three series has been assigned the same empirical formula, the analytical results being sufficiently in agreement to justify this conclusion. In the absence of other data it cannot be said that these alcohols are identical, but a close similarity in structure seems probable.

The preceding results show that it is possible to obtain an oxidation series of corresponding terms for the three hydrocarbons caoutchouc, gutta-percha, and balata. The physical properties of the products indicate that the oxidation is accompanied by more or less extensive depolymerisation.

Caoutchouc, gutta-percha, and balata may be regarded as condensation products of isoprene, an undetermined number of isoprene molecules condensing to give a cyclic or open-chain hydrocarbon with approximately one half of the initial unsaturation of the isoprene molecules involved. Further aggregation of the condensed isoprene molecules takes place through partial valences to give the caoutchouc, gutta-percha, or balata complex. These complexes can be partly broken down by suitable solvents, presumably as a result of solvation. On this basis the treatment of caoutchouc, etc., with oxidising agents should cause depolymerisation by saturation of the available double bonds, with consequent disappearance of the secondary valencies. Should the complex aggregate be of different dimensions in the three hydrocarbons, oxidation would be expected to give different intermediate products owing to the varying number of partial valencies involved in each case. The preceding results seem to justify this view, the close resemblance between the final oxidation products being probably due to complete saturation of the double bonds of the fundamental unit produced by the initial isoprene condensation. This view of the mechanism of oxidation is borne out by the observation that the process must be carried out in stages, it being found impossible to secure complete saturation of the hydrocarbons by a single oxidation process. It should be noted, as regards the intermediate oxidation products, that although the end-point of the first stage of oxidation of the hydrocarbons was an arbitrary one, it was reached in each case by an identical procedure and provides a reasonable basis for comparison.

If the suggestion put forward that the later stages of oxidation involve not only addition of hydroxyl to the double bonds of  $\left[-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-\right]$, but also oxidation of the methylene groups, is correct, the direct addition of hydroxyl to caoutchouc in the first stage of the oxidation, without replacement of hydrogen by oxygen as occurs in BI and GI, and the occurrence of the latter action in the second stage of the caoutchouc oxidation, would indicate that the reaction has further to go with caoutchouc to reach the point of saturation represented by the fully oxidised fundamental unit. The molecular complexity of the caoutchouc hydrocarbon is therefore apparently greater than that of the gutta-percha or balata hydrocarbon, the last two being of a similar order of complexity.

From the experimental results it appears that the minimum complex unit of all three hydrocarbons contains ten isoprene residues, or some multiple of this number. From the general behaviour of the oxidation products, themselves undoubtedly of high molecular weight, it seems probable that the minimum complex unit of the hydrocarbons contains substantially more than ten isoprene residues.

The proportion of carbon dioxide evolved during the first stage of the oxidations varies with the hydrocarbon concerned, being least with caoutchouc and greatest with balata. Assuming that its formation in each case is the result of a similar reaction, the minimum complex unit of caoutchouc is the largest, consisting of at least forty isoprene residues. This supports the conclusion, drawn from the results in the oxidation series, as to the relative complexity of the three hydrocarbons.

EXPERIMENTAL.

Purification of Raw Materials.—The caoutchouc, prepared from crêpe which was in the form of thin sheets of a pale yellow colour, was purified by Harries' standard method, consisting in extraction with acetone in a Soxhlet apparatus, followed by dissolution of the hydrocarbon in benzene, and reprecipitation of the caoutchouc from the filtered solution by means of alcohol.

The gutta-percha and balata hydrocarbons were purified by a different method. To 20—25 g. of the crude shredded material were added 400—500 c.c. of boiling petroleum (b. p. 60—80°) and the mixture was kept at 40° until the insoluble material had settled. On cooling, the hydrocarbon settled out from the solution and was separated easily from the residue, insoluble in hot or cold petroleum, and from the resins, soluble even in the cold solvent. The precipitated hydrocarbon was submitted to several similar treatments, fresh petroleum being used each time and kaolin added, when necessary, to facilitate settling of the suspended matter. The final products were colourless solids of a leather-like consistency, transparent in hot alcohol, and readily oxidised on exposure to the air, becoming brown and friable.

Action of 100-*Vol. Hydrogen Peroxide on the Hydrocarbons.*—The method adopted for the oxidation was that used by Robertson and Mair (*J. Soc. Chem. Ind.*, 1927, **46**, 41T), a solution of the hydrocarbon in chloroform and glacial acetic acid being treated with 100-vol. hydrogen peroxide. In the earlier oxidations the proportions of reagents employed by the earlier workers were used, but products which varied a good deal on analysis were obtained.

The final reaction mixture was: 25 g. of the hydrocarbon, 350 c.c. of chloroform, 250 c.c. of glacial acetic acid, and 55 c.c. of 100-vol. hydrogen peroxide. The hydrocarbon was dissolved in the chloroform, and the hydrogen peroxide added with shaking. Precipitation of part of the hydrocarbon occurred. The mixture was kept at 40° until homogeneous. The products were extracted with chloroform, the combined extracts washed with dilute sodium carbonate solution and water and dried over anhydrous sodium sulphate, and the chloroform removed under reduced pressure below 40°. The residue, a pale yellow glassy solid, was freed from any unattacked hydrocarbon by solution in alcohol, decantation from insoluble hydrocarbon, and removal of the solvent under reduced pressure. The product was obtained finally in a workable form by slow dropping of an acetone solution into a mechanically stirred solution of sodium chloride.

In some cases the hydrogen peroxide oxidation followed an irregular course, giving products of abnormal composition, due apparently to partial polymerisation. Measurements of the unsaturation were adopted as a guide to the course of the reaction, products giving abnormal values being rejected. The products studied were those giving the maximum observed unsaturation. Those having lower values were assumed to have undergone partial cyclisation.

In the initial stages of the reaction carbon dioxide was evolved in varying amounts, the maximum yield observed, in the case of caoutchouc, being equivalent to the oxidation of 0·5% of the carbon of caoutchouc, corresponding to the oxidation of one carbon atom per C_{200}. In the oxidation of gutta-percha and balata the largest yields of carbon dioxide measured were equivalent to 1·0% and 1·4%, respectively, of the carbon of the parent substances, corresponding to the oxidation of one carbon atom per C_{100} and C_{70} respectively.

The yields of the oxidation products being almost quantitative, no special effort was made to extract any acid products from the reaction mixture, containing, as it did, such a large proportion of acetic acid.

The Oxidation Products.—The three products were odourless, colourless, amorphous solids, insoluble in water, light petroleum, carbon tetrachloride, and carbon disulphide, sparingly soluble in benzene and ether, and very soluble in methyl and ethyl alcohol, acetone, chloroform, ethyl acetate, acetic acid, and pyridine. They were neutral in character and did not possess reducing properties, but were unsaturated to bromine and to dilute alkaline permanganate solution. On distillation in a vacuum they decomposed, giving dark oily distillates.

Ultimate analysis of the oxidation products gave the following results:

Caoutchouc. Found: C, 62·6, 62·9; H, 9·9, 9·7 ($C_{50}H_{92}O_{16}$ requires C, 63·3; H, 9·7%).

Gutta-percha. Found: C, 55·6, 55·3; H, 8·2, 8·2 ($C_{50}H_{88}O_{24}$ requires C, 55·9; H, 8·2%).

Balata. Found: C, 57·6, 57·6; H, 8·6, 8·5 ($C_{50}H_{88}O_{20}$ requires C, 59·5; H, 8·7%).

The hydroxyl contents of the alcohols and their unsaturations, determined by the methods mentioned on pp. 387 and 388, were as follows (the unsaturations are expressed in g. of bromine per 100 g. of oxidation product).

Oxidation product.	Hydroxyl content. Found, %.	Hydroxyl content. Calc., %.	Unsaturation. Found, %.	Unsaturation. Calc., %.
Caoutchouc	29·6, 29·0	28·7	85·0, 85·7	67·3
Gutta-percha	32·2, 32·0	31·7	44·9, 44·8	29·8
Balata	25·8, 25·7	27·0	47·0, 46·8	31·7

The considerable discrepancy in each case between the unsaturation found and that calculated from the empirical formula corresponds actually to almost exactly one additional double bond per C_{50}. Whether this irregularity is due to oxidation by the bromine or to rupture of the ring system cannot be decided, since none of the brominated oxidation products was sufficiently stable to permit of its isolation and analysis.

Action of Chromic Acid on the Alcohols.—The above alcohols, failing to yield a satisfactory derivative, were treated with chromium trioxide in glacial acetic acid solution. The reaction mixtures used were as follows:

	Caoutchouc.		*Gutta-percha and Balata.*
A	10 g. alcohol CI. 80 c.c. glacial acetic acid.	A	10 g. alcohol GI or BI. 80 c.c. glacial acetic acid.
B	1·4 g. chromium trioxide. 40 c.c. glacial acetic acid.	B	1·2 g. chromium trioxide. 40 c.c. glacial acetic acid.

Solution A, to which a few drops of water were added, was cooled in a freezing mixture and mechanically stirred, and solution B, also cooled, was added drop by drop. Rapid mixing of the reagents caused the formation of resinous acids. The reaction was completed at room temperature over-night, the mixture was then thrown into water, and the acid just neutralised with sodium carbonate. A white solid which separated was extracted repeatedly with ether. the combined extracts being washed with water and dried over anhydrous sodium sulphate. Removal of the solvent under reduced pressure left a colourless glassy solid, which was taken up again in acetone and reprecipitated with sodium chloride solution.

The three products, in appearance, were practically identical. They were colourless amorphous solids, insoluble in water, benzene, and light petroleum, sparingly soluble in ether, and very soluble in methyl and ethyl alcohols, acetone, chloroform, and acetic acid. They reacted with ammoniacal silver oxide, Fehling's solution, and Schiff's reagent. The sodium bisulphite compound of each was obtained only after several weeks' exposure to the reagent, the semicarbazone after about a week. In each case it was a colourless, odourless, amorphous solid, insoluble in water, benzene, toluene, ether, and carbon tetrachloride, sparingly soluble in chloroform, and very soluble in methyl and ethyl alcohols, acetone, and in ethyl acetate. Found for the semicarbazones: (caoutchouc) C, 58·1, 58·0; H, 8·9, 8·8; N, 7·8, 7·8 ($C_{52}H_{94}O_{16}N_6$ requires C, 59·0; H, 8·9; N, 7·9%); (gutta-percha) C, 52·6, 52·1; H, 7·6, 7·7; N, 7·1, 7·0 ($C_{52}H_{90}O_{24}N_6$ requires C, 52·8; H, 7·6; N, 7·1%); (balata) C, 56·0, 55·8; H, 7·8, 7·9; N, 7·5, 7·4 ($C_{52}H_{90}O_{20}N_6$ requires C, 55·8; H, 7·9; N, 7·5%).

Action of Nitric Acid on the Aldehydes.—The aldehyde was left in contact with dilute nitric acid (5 c.c., *d* 1·42, in 15 c.c. of water) for 4 days at the ordinary temperature. The acid product was extracted by means of ether from the reddish solution.

The three products were fawn-coloured granular solids, insoluble in water, benzene, toluene, and light petroleum, soluble in ether, methyl and ethyl alcohols, acetone, and in dilute solutions of sodium carbonate and caustic alkali. They did not contain nitrogen, but, when a more concentrated acid was used, the products were dark brown and nitrogen-containing. When the reaction mixture was heated, a resinous mass, nitrogen-containing and acidic, was obtained.

Only the silver salts were obtained and these decomposed readily. Found: (caoutchouc) Ag, 17·86, 17·68 [$C_{48}H_{86}O_{14}(CO_2Ag)_2$ requires Ag, 18·15%]; (gutta-percha) Ag, 16·32, 16·27 [$C_{48}H_{82}O_{22}(CO_2Ag)_2$ requires Ag, 16·44%]; (balata) Ag, 17·02, 16·94 [$C_{48}H_{82}O_{18}(CO_2Ag)_2$ requires Ag, 17·28%].

Action of Acetic Anhydride upon the Alcohols.—Each of the alcohols was treated with acetic anhydride in presence of fused sodium acetate for 3 hours at 30°. When the reaction mixture was poured into water, the product was precipitated as a yellowish paste, which was taken up in acetone and reprecipitated several times by means of sodium chloride solution.

The products were colourless, odourless, amorphous solids, insoluble in water, benzene, toluene, carbon tetrachloride, and light petroleum, and soluble in ether, methyl and ethyl alcohols, chloroform, acetone, ethyl acetate, and pyridine. Found : (caoutchouc) C, 68·5, 68·7 ; H, 8·7, 8·4 ($C_{58}H_{88}O_{14}$ requires C, 69·0 ; H, 8·7%) ; (gutta-percha) C, 61·4, 60·9 ; H, 7·0, 7·1 ($C_{66}H_{92}O_{26}$ requires C, 60·9 ; H, 7·1%) ; (balata) C, 61·8, 62·0 ; H, 7·3, 7·4 ($C_{66}H_{96}O_{24}$ requires C, 62·2 ; H, 7·5%).

The acetyl content of each was determined by Perkin's method, and the unsaturation by the usual method :

	Acetyl content.		Unsaturation.	
Acetate.	Found, %.	Calc., %.	Found, %.	Calc., %.
Caoutchouc	19·6, 18·9	17·1	64·8, 64·7	63·5
Gutta-percha	25·9, 25·3	26·4	24·7, 24·8	24·6
Balata	26·4, 26·3	27·0	25·4, 25·3	25·3

Hydrolysis of the Acetates.—This was effected by treatment with aqueous baryta for several hours at 30° and was possible only on a small scale, as, when larger amounts were used, the hydrolysis was difficult to control. The resulting alcohols were purified by repeated fractional precipitation from ethyl acetate solution by means of ether, in which solvent the alcohols were less soluble than the corresponding acetates. The purest specimens were colourless. Found : (caoutchouc) C, 70·8, 71·2 ; H, 9·6, 9·4 ($C_{50}H_{80}O_{10}$ requires C, 71·4; H, 9·5%); (gutta-percha) C, 60·8, 61·3; H, 7·8, 7·6 ($C_{50}H_{74}O_{18}$ requires C, 62·2 ; H, 7·9%) ; (balata) C, 63·5, 64·2 ; H, 8·4, 8·4 ($C_{50}H_{80}O_{16}$ requires C, 64·1 ; H, 8·5%).

	Hydroxyl content.		Unsaturation.	
Alcohol.	Found, %.	Calc., %.	Found, %.	Calc., %.
Caoutchouc	8·3, 8·6	8·1	76·5, 76·8	76·2
Gutta-percha	13·4, 13·0	14·1	31·3, 31·5	33·2
Balata	14·2, 14·3	14·5	33·6, 33·5	34·2

Oxidation of the Alcohols.—Chromium trioxide in glacial acetic acid solution was used, as before, to oxidise the new alcohols. The three products were colourless amorphous solids, insoluble in water, benzene, and light petroleum, sparingly soluble in ether, and very soluble in alcohol, acetone, chloroform, and acetic acid. They all gave the usual tests for an aldehyde group. From alcoholic extracts, semicarbazones were prepared in the usual way. These were amorphous solids, colourless and without odour. They were insoluble in water, ether, and the hydrocarbon solvents and were very soluble in alcohol and acetone. Found : (caoutchouc) C, 64·8, 65·0; H, 8·7, 8·7; N (Kjeldahl), 8·8, 8·8 ($C_{52}H_{82}O_{10}N_6$ requires C, 65·7; H, 8·6; N, 8·8%); (gutta-percha) C, 58·4, 58·6; H, 7·1, 7·1; N, 7·7, 7·7 ($C_{52}H_{78}O_{18}N_6$ requires C, 58·1; H, 7·3; N, 7·8%); (balata) C, 60·2, 60·0; H, 7·7, 7·7; N, 8·0, 7·9 ($C_{52}H_{82}O_{16}N_6$ requires C, 59·6; H, 7·8; N, 8·0%).

Oxidation of the Aldehydes.—The products resulting from the treatment of the above aldehydes with dilute nitric acid were not acidic and contained a fair proportion of nitrogen. By drawing a current of air through an alcoholic solution of the aldehyde at 40°, an acid product was obtained. Removal of the solvent from an ethereal extract of the reddish solution left a reddish syrup which was to a large extent soluble in dilute sodium carbonate solution. A brown gelatinous precipitate was formed on acidification of the alkaline solution. The acid was taken up several times in dilute aqueous sodium carbonate, the solution filtered, and the product reprecipitated by addition of acid. The filtered, washed, and dried product was a brown friable solid.

The three acids were insoluble in water, benzene, toluene, and light petroleum, soluble in ether, methyl and ethyl alcohols, acetone, and in dilute sodium carbonate and caustic alkali solutions. The silver and lead salts were obtained, but only the latter were suited to analysis, as the former gave varying results even when the determinations were made in diffused artificial light. Found: (caoutchouc) Pb, 19·0, 18·8 [$C_{48}H_{74}O_8(CO_2)_2Pb$ requires Pb, 19·3%]; (gutta-percha) Pb, 17·2, 17·1 [$C_{48}H_{70}O_{16}(CO_2)_2Pb$ requires Pb, 17·3%]; (balata) Pb, 17·6, 17·5 [$C_{48}H_{74}O_{14}(CO_2)_2Pb$ requires Pb, 17·7%].

Action of Hydrogen Peroxide on the Acetates.—The acetates were still unsaturated and were oxidised further with 100-vol. hydrogen peroxide. The method and procedure were similar to those employed in the oxidation of the hydrocarbons, save that there was no necessity to use chloroform as solvent, since the acetates were soluble in glacial acetic acid.

The new products, which were purified by fractional precipitation from alcoholic solution with ether, in which the original acetates were the more soluble, were colourless amorphous solids, insoluble in water, benzene, toluene, carbon tetrachloride, and light petroleum, sparingly soluble in ether, and very soluble in methyl and ethyl alcohols, acetone, chloroform, and ethyl acetate. They were saturated, non-acidic and non-reducing, and decomposed on distillation, yielding dark oily distillates. They contained hydroxy- as well as acetoxy-groups, but no alcoholic derivatives suitable for characterisation were obtained. Treatment with methyl sulphate and caustic alkali at a low temperature did not effect methylation, and when the temperature was raised resinification occurred. Found: (caoutchouc) C, 54·0, 54·2; H, 5·9, 5·9 ($C_{58}H_{76}O_{32}$ requires C, 54·2; H, 5·9%); (gutta-percha) C, 54·4, 54·8; H, 5·7, 5·7 ($C_{66}H_{84}O_{36}$ requires C, 54·5; H, 5·8%); (balata) C, 54·6, 54·4; H, 5·7, 5·7 ($C_{66}H_{84}O_{36}$ requires C, 54·5; H, 5·8%).

	Acetyl content.		Hydroxyl content.	
Acetate II.	Found, %.	Calc., %.	Found, %.	Calc., %.
Caoutchouc	16·2, 15·9	13·4	10·7, 10·7	10·6
Gutta-percha	23·0, 22·9	23·7	4·5, 4·5	4·7
Balata	23·0, 22·8	23·7	4·5, 4·5	4·7

Hydrolysis of the New Acetates.—This was effected by treatment for several hours at 40° with aqueous baryta. The alcohols thus produced resembled the parent acetates very closely and considerable difficulty was experienced in obtaining a workable method of separation. By continued fractional precipitation from alcoholic solution with ether, three products, very closely resembling one another, were obtained. They were colourless amorphous solids, similar in solubilities to the parent acetates, and were saturated in character. Found: (caoutchouc) C, 53·3, 53·3; H, 6·2, 6·1; OH, 17·0, 17·7; (gutta-percha) C, 53·3, 52·7; H, 6·1, 6·1; OH, 18·4, 18·5; (balata) C, 53·8, 53·3; H, 6·0, 6·0; OH, 18·1, 18·0 ($C_{50}H_{68}O_{28}$ requires C, 53·7; H, 6·1; OH, 18·3%).

These substances were treated with chromium trioxide in glacial acetic acid solution, in the manner previously described, but no trace of an aldehydic or ketonic product could be obtained. Treatment with Beckmann's mixture (potassium dichromate and sulphuric acid) yielded products of high molecular weight, devoid of acidic or reducing properties, together with a small amount of an acid substance of a resinous nature.

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