J.R.R.I.M. Communication 273.

# STUDIES IN HEVEA RUBBER

## Part V

## Oxygenated and Low Molecular Fractions in Fresh Rubber.

By

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**The presence in rubber of oxygenated low molecular constituents with molecular weights (estimated from intrinsic viscosity) below 100,000 and oxygen contents in the range 0.3% to over 1%, indicated by previous work in Europe and in the East, has been confirmed, even when latex is collected and treated under conditions excluding access of air.**

**The oxygenated fractions are soft plastic rubbers which on hydrolysis undergo change into viscous gums of similar intrinsic viscosity to the corresponding unhydrolysed substances, but with reduced oxygen contents. Both the original oxygenated fractions and their hydrolysis products contain active hydrogen which, if present in hydroxyl or carboxyl groups, corresponds to an appreciable proportion of the oxygen contents.**

The precise analytical work of Midgley, Henne, Shepard and Renoll(1) showed that rubber hydrocarbon purified by fractional precipitation in the absence of air contained a small proportion of combined oxygen (0.04%), half of which appeared to be hydroxylic. Later, Roberts(2) isolated from fresh rubber in the East a fraction designated "caoutchol" containing two or three units per cent of oxygen which appeared to be present in the form of an ester of a lightly hydroxylated polyprene of relatively low molecular weight. No precautions were, however, taken to guard against autoxidation, and Kraay and Altman(3) showed that increased exposure to air in Roberts' separative procedure substantially increased the proportion of material isolated in the "caoutchol" fraction, and, furthermore, when the separation was conducted in an atmosphere of nitrogen the amount of the "caoutchol" fraction was reduced somewhat, although it did not become zero. Kraay and Altman did not, however, state whether their material was chemically, or even physically, identical with that of Roberts.

During some experiments on fractionation of rubber by a dissolution technique the present author with Dr. E. H. Farmer(4) isolated oxygen-containing fractions

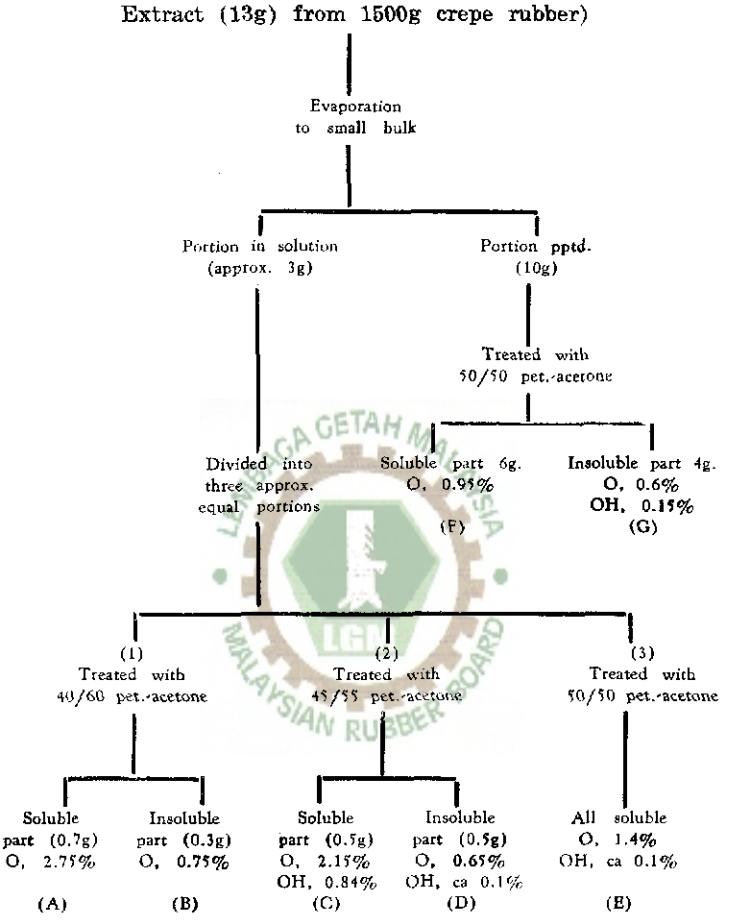
from crepe rubber, from dried latex film, and from rubber latex shipped to England in sealed containers after preservation with sodium pentachlorophenate in the East.

## Properties of oxygenated low-molecular fractions extracted in England

Table I shows a separative procedure applied to a low-molecular product originally extracted from 1500g. of acetone-extracted crepe rubber between the limits of 48/52 to 52/48 petroleum (40-60°)—acetone in the apparatus of Michael(4).

Table I

*Sub-fractionation of a low-molecular fraction of crepe rubber.*




The oxygen contents in the above table were differences between 100% and the totals of C, H (ash contents being generally small).

Hydroxyl contents were determined by the method of Bolland(5).

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This sub-fractionation thus yielded components progressively lower in oxygen content when the original extract was allowed to diffuse into solvent mixtures progressively richer in petroleum. The combined oxygen appeared to be present in these fractions partly in non-hydroxylic form, suggesting that the fractions might be chemically similar to "caoutchol" even though physically they were quite different, being soft, sticky plastic materials with little or no rubberlike elasticity. The chemical similarity to caoutchol suggested the desirability of applying a hydrolytic treatment, and small samples were accordingly sealed under vacuum in tubes containing (per g. of sample), benzene (20 ml.) and 0.2N alcoholic potassium hydroxide (2 ml.), after degassing the solvents, and heated for 4 hours at 60°. The contents of the tubes were then centrifuged to remove a precipitated gelatinous substance and the clarified solutions were greatly diluted with ether and washed free from alkali. (Larger amounts of material were hydrolysed under reflux in a stream of nitrogen at the boiling point of the solvent mixture). Soluble neutral products of hydrolysis isolated from these solutions ranged from cold-flowing yellow viscous gums with no rubberlike properties to soft sticky rubbers, according to the oxygen contents of the fractions before hydrolysis (Table II). The insoluble matter separated by centrifuging was also insoluble in a wide range of solvents, but when treated with acetic acid in a benzene-alcohol medium its acidic constituent was liberated and remained in solution, enabling inorganic salts to be removed by washing. A sample of this material, isolated in England from a sample of "caoutchol" prepared in Malaya in 1941 ([6]), and representing 11% of the original material, was a crumb-like acidic substance of considerable molecular weight which could only be brought into solution in mixtures of benzene and alcohol (Found: C, 84.8; H, 11.9; iodine value 180; equiv. *ca.* 1000; $[\eta]$ 0.24 in benzene + 15% methanol). The composition of a silver salt (Found: Ag, 9.5%) prepared from the sodium salt of the acidic material was in agreement with the observed oxygen-content (calc., 3.1%) and equivalent (calc., 1020) of the free acid. (It follows that the acidic component must have been of considerable molecular magnitude since the acid was obtained in 11% yield, yet the hydroxyl content (0.2%) calculated from the active hydrogen in the corresponding neutral component was so small as to give but few points of attachment of acidic material).

The active hydrogen contents of the samples before and after hydrolysis indicated that the hydroxyl content of the unhydrolysed material must have been present in the acidic constituent, possibly in free carboxyl groups (a small "acid value" of rubber has been reported(7) ). With this assumption the above data are consistent with the hydrolytic fission of an ester group involving a hydroxyl group in the polyisoprene chain and a high molecular carboxylic acid.

Table II

*Hydrolysis products of some oxygenated fractions examined in England.*

| Fraction | Oxygen and active hydrogen contents | | | |
|---|---|---|---|---|
| | Before hydrolysis | | After hydrolysis | |
| | 0% | active H% | 0% | active H% |
| A, table I .. | 2.75 | .017 | 0.7 | .017 |
| C, " " .. | 2.15 | .049 | 1.0 | .049 |
| E, " " .. | 1.4 | .006 | 0.9 | .012 |
| G, " " .. | 0.6 | .009 | 0.3 | .012 |
| "Caoutchol" .. | 2.5 | .028 | 0.7 | .013 |

## Properties of oxygenated low molecular fractions extracted in Malaya

Owing to the difficulty of maintaining stocks of petroleum in a peroxide free condition in the tropics, the benzene-alcohol azeotrope of composition 65.2% benzene by volume and b.p. 68.24° has been used for extraction of low molecular fractions in Malaya. The mixture becomes a solvent for rubber at temperatures above 50°, but at 20° it extracts only non-rubber constituents, consequently, a progressive increase of extraction temperature between these limits provides a convenient method of extracting fractions of progressively increasing molecular weight.

The extraction apparatus used in Malaya was similar to that of Michael(4), but it was found more convenient to replace the glass bottle by an aluminium container in which the rubber could be distributed over a series of baffle-plates, so rendering extraction more efficient by preventing the rubber from massing together at the bottom of the apparatus. For temperature control the aluminium container was placed in a thermostat. In order to ensure in at least one instance that the rubber sample was as representative as possible of that leaving the tree, latex was collected in a bottle, in which an atmosphere of nitrogen was maintained, while nitrogen was also blown over the tapping cut which was bridged by paper secured to the tree with adhesive tape. Latices were coagulated by pouring into acetone in a shallow tray and the resulting sheets were consolidated, rolled thin, extracted with acetone in the aluminium container of the extraction apparatus and finally freed from acetone by evacuation into a high-vacuum system while being contained in a large desiccator. (Acetone extraction was omitted in the first sample examined, and the fractions were themselves individually acetone-extracted).

Table III shows the properties of some low-molecular fractions isolated in Malaya, including sub-fractions obtained by benzene-methanol fractionation of some of the primary fractions. Most of the fractions contained more oxygen* than could be accounted for by their ash-contents.

(The oxygen-contents were determined by Dr. W. T. Chambers using a modification(8) of the Unterzaucher method).

For an absolute determination of the oxygen content it was clearly most desirable to obtain relatively ash free fractions comparable to those isolated from crepe rubber in England, but washing and machining of the rubber prepared as above was not permissible owing to the risk of oxidative degradation and there were strong practical objections to purifying the latex since treatment with ammonia, necessary for preservation of the latex during purification, is known to reduce the oxygen-content and alter the character of low molecular fractions in a manner similar to that brought about by hydrolysis(4). An alternative method of soap-displacement purification at pH 7-8 using latex preserved with sodium pentachlorphenate and buffered with phosphates gave fractions with even larger ash contents than unpurified (but acetone-extracted) rubber, doubtless due to formation of calcium and magnesium soaps which were soluble in the benzene-alcohol azeotrope but were insoluble in acetone.

* The fractions were shown to be free from peroxidic oxygen by the method of Bolland(9). No peroxidic oxygen has been observed in fresh latex, and after conversion into smoked sheet the peroxidic oxygen content does not exceed 30 parts per million.

**Table III**

*Low-molecular fractions of fresh Hevea rubber.*

| Rubber | Tem. of extraction | % fraction in rubber | Analysis | | | | | [η] |
|---|---|---|---|---|---|---|---|---|
| | | | C% | H% | O% | N% | ash % | |
| Rubber not acetone-extracted .. | 30° .. | .04 | — | — | — | — | — | .18 |
| | | .06 | 84.0 | 11.85 | 1.9 | .07 | 2.45 | .24 |
| | | .10 | 84.5 | 11.85 | 2.2 | .05 | 1.1 | .31 |
| | | .17 | 82.8 | 11.7 | 2.7 | .07 | 2.45 | .40 |
| | | .18 | 86.5 | 11.9 | 1.1 | — | 0.9 | .61 |
| | | .34 | 85.7 | 11.8 | 0.65 | — | 1.45 | .69 |
| | | .44 | 86.1 | 11.7 | 1.1 | — | 0.9 | .70 |
| | | .52 | 85.7 | 11.9 | 1.2 | — | 0.9 | .72 |
| | 37° .. | .50 | 87.1 | 11.8 | 0.6 | — | 0.5 | .96 |
| | | .19 | 86.4 | 11.65 | 1.1 | — | 0.85 | 1.10 |
| | 42° .. | .38 | 86.65 | 11.8 | 0.8 | — | 0.7 | 1.7 |
| | 48° .. | .85 | 87.4 | 11.8 | 0.5 | — | 0.1 | 2.8 |
| Latex of tree 3, collected under nitrogen .. | 35° .. | 1.5 | 87.3 | 11.85 | 0.47 | 0.05 | 0.15 | .52 |
| | | 2.2 | 87.4 | 11.8 | 0.40 | — | 0.15 | .69 |
| | 40° .. | 1.8 | 87.4 | 11.9 | 0.30 | — | nil | 1.07 |
| Latex of soft trees (Group A) | 30° .. | 0.25 | 74.0 | 10.7 | 9.0 | — | 7.0 | .14 |
| | | 3.4 | 87.1 | 11.8 | 0.9 | — | 0.4 | .60 |
| Latex of soft trees (Group A) | 35° .. | 0.2 | — | — | — | — | — | — |
| | | 1.0 | 86.4 | 11.8 | 1.0 | 0.06 | 0.85 | .41 |
| | | 1.1 | 87.8 | 11.9 | 0.46 | — | 0.15 | .82 |
| | | 0.4 | 87.5 | 11.9 | 0.47 | — | 0.25 | 1.25 |
| | 40° .. | 0.9 | 87.7 | 11.8 | 0.35 | — | 0.2 | 1.10 |
| Latex of hard trees (Group G) | 35° .. | 0.35 | 73.0 | 10.55 | 8.95 | — | 7.4 | 0.19 |
| | | 1.75 | 86.9 | 11.9 | 0.8 | 0.04 | 0.8 | 0.67 |
| | | 1.25 | 87.6 | 11.75 | 0.53 | — | 0.3 | 0.86 |
| | 40° .. | 1.2 | 87.4 | 11.8 | 0.25 | — | 0.1 | 1.26 |

After hydrolysis the oxygenated fractions exhibited the same general characteristics as those examined in England. The very pronounced change in the physical nature of the material—from soft plastic rubber to viscous gum—was not accompanied by any marked change in intrinsic viscosity (Table IV).

Table IV

*Hydrolysis of three oxygenated fractions isolated in Malaya.*

| | [η] | Analysis | | | | |
|---|---|---|---|---|---|---|
| | | C | H | O | ash | active H |
| Before hydrolysis .. | .60 | 87.1 | 11.8 | 0.9 | 0.4 | .0153 |
| After „ * .. | .47 | 87.55 | 11.9 | 0.4 | 0.2 | .0124 |
| Before hydrolysis .. | .69 | 87.4 | 11.8 | 0.4 | 0.15 | .006 |
| After „ * .. | .59 | 87.6 | 11.9 | 0.3 | 0.2 | .006 |
| Before hydrolysis .. | .41 | 86.4 | 11.8 | 1.1 | 0.85 | .0159 |
| After „ * .. | .39 | 87.7 | 11.85 | 0.42 | 0.1 | .0147 |

* Neutral products of hydrolysis.

The extraction method, while convenient for obtaining relatively large quantities of low molecular material, does not quantitatively extract any given intrinsic viscosity range owing to consolidation of the rubber on the baffle-plates in the mixed solvent. It is not therefore possible with the diffusion method to make reliable comparisons of the relative amounts of any particular fraction in different rubbers.

**Isolation of low-molecular fractions by precipitation**

In the fractionations described in Part III, small proportions of low molecular fractions in a large volume of solvent remained after precipitation of the bulk of the rubber, and the isolation of these fractions involved considerable risk of degradation. When the major part of the rubber content was precipitated from fairly concentrated solutions the task of isolating the remaining low-molecular material was simplified and it has been demonstrated in Part III that a typical oxygenated low-

molecular fraction could be isolated without degradation by this procedure. This confirmed that the character of fractions isolated by the extraction (diffusion) method was not changed by heating the solution of the extract at the boiling point of the solvent mixture.

Two low molecular fractions were also isolated by means of the carbon tetrachloride-acetone mixtures used by Roberts(2). These were again no different from the fractions obtained by extraction; the soft tree group (A) yielded 9.1% of a soft plastic rubber with intrinsic viscosity 0.7 (Found: C, 87.2; H, 11.9; ash 0.1; O, 0.65%) and the hard tree group (G) yielded 2.2% of a similar product with intrinsic viscosity 0.77 (Found: C, 85.8; H, 11.65; ash 0.6; O, 1.6%). The difference in yield is probably significant.

## Summary and Conclusions

Fresh Hevea latex, even when collected under conditions excluding access of air as far as possible, yields rubbers from which small proportions of fractions of low molecular weight can be isolated by either diffusion or precipitation methods. These fractions contain combined oxygen in excess of that which can be accounted for in combination with mineral-containing impurities the presence of which is revealed by an appreciable ash content when the fractions are ignited. The oxygen content decreases as the intrinsic viscosity of the fractions increases, and when the intrinsic viscosity is greater than unity (estimated molecular weight above 100,000) the amount of combined oxygen is 0.3% or less. On the assumption that the mineral content is mainly due to metallic salts of carboxylic acids, the oxygen combined with the hydrocarbon in fractions of intrinsic viscosity 0.75 (estimated molecular weight *ca.* 50,000) is *ca.* 0.5% rising to a little over 1% in fractions with intrinsic viscosity below 0.5 (estimated molecular weight below 30,000).

The oxygenated fractions contain active hydrogen corresponding to 30-50% of the combined oxygen if the active hydrogen is present in hydroxyl groups, and to most if not all of the combined oxygen if it is present in carboxyl groups.

Hydrolysis of oxygenated fractions yields as major products neutral viscous gums which have intrinsic viscosities little different from those of the parent

substances. The oxygen content is reducd on hydrolysis but the active hydrogen content is not significantly changed. In the neutral products of hydrolysis the active hydrogen is believed to be present in hydroxyl groups corresponding to points of attachment of an acidic component of considerable molecular magnitude which is also liberated on hydrolysis.

Preciptitation methods are of more promise than diffusion methods for quantitative separation of low molecular fractions, although the latter methods are of advantage when a considerable amount of low molecular material is required.

It is further proposed to study the variation in the proportion of oxygenated components between trees, and also the effect of processing and storage on the proportion of oxygenated material present.

## Acknowledgments

The author acknowledges the assistance of Dr. W. T. Chambers (B.R.P.R.A.) for the microanalyses recorded in this paper, which forms part of the programme of fundamental research undertaken by the Boards of the British Rubber Producers' Research Association and the Rubber Research Institute of Malaya.

The author particularly desires to record his appreciation of the co-operation of Mr. M. W. Philpott, Head of the Chemical Division of the Rubber Research Institute.

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