

#### 41. *The Caoutchol Component of Natural Rubber : A Correction.*

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It has proved impossible to isolate from rubber or latex as available in this country materials having the characteristic properties of caoutchol and caoutchene (cf. Roberts, J., 1938, 215, 219) as prepared in the East. Samples of these materials prepared in Malaya have, however, been examined in England by the author and his colleagues. It is reaffirmed that caoutchol is a naturally occurring, oxygenated constituent of rubber, quite distinct from artificially oxidised rubbers, but in the light of the evidence now discussed it is necessary to withdraw the original suggestions (*a*) that the elasticity of rubber is derived essentially from that of its minor constituent caoutchol, and (*b*) that caoutchol has a molecular formula  $C_{80}H_{130}(OH)_2$ .

THE author recently described a method (J., 1938, 215, 219), developed in Malaya, for separating natural rubber into two main fractions, one containing amongst other things a hydrocarbon which was called "caoutchene," and the other including an oxygenated material which constitutes some 2—5% of natural rubber. The latter, which was named "caoutchol," was described as a non-tacky, freely soluble, highly elastic substance for which the formula  $C_{80}H_{130}(OH)_2$  was suggested. "Caoutchene," constituting 87—91% of total rubber and isolated only in a crude state, was described as being tacky, of low tensile strength, and as giving solutions of notably low viscosity, and its elongation under tension was stated not to exceed 200%. It was further suggested that the elasticity of rubber was derived essentially from its minor constituent "caoutchol."

The author has now been able to re-examine the material in collaboration with his colleagues on the staff of the British Rubber Producers' Research Association. Fresh facts have been brought to light, both here and elsewhere, in consequence of which it has been found necessary to amend or withdraw the suggestions originally put forward. Nevertheless it is emphasised that "caoutchol" is a naturally occurring material of real interest, quite distinct from artificially oxidised rubbers.

A critical comment by Kraay and Altman (*Arch. Rubbercultuur*, 1938, 22, 231) claims to show that "caoutchol" is an oxidation product of "caoutchene," first, because increased access of oxygen gave increased yields of the "caoutchol" fraction, and secondly, because further amounts of the "caoutchol" fraction could be obtained by resubmitting the precipitated "caoutchene" to the fractionation procedure. Unfortunately, however, the authors made no attempt to characterise the material contained in the "caoutchol" fractions. They did not attempt to show that it was, in fact, "caoutchol," and not "caoutchol" together with, for example, the somewhat differently constituted oxidation products of the rubber hydrocarbon. Their conclusion, therefore, cannot be accepted as valid.

A further communication, by Haefele and McColm (J., 1939, 676), pointed out that, if care were taken to exclude air, the removal of caoutchol from rubber did not lead to tackiness and loss of elasticity in

the residual crude hydrocarbon. Their evidence, though strong, unfortunately suffers from lack of quantitative data.

Their observation is, however, supported independently by Gee and Treloar (*Trans. Inst. Rubber Ind.*, 1940, **16**, 197), who have shown that fractions of purified rubber hydrocarbon obtained by removal of gummy oxygenated material from natural rubber are still highly elastic and similar in physical properties to total crepe rubber. Moreover, it has been shown by Treloar (*Trans. Faraday Soc.*, 1940, **36**, 538) that it is not necessary to postulate a two-phase system in order to account for the elasticity of natural rubber, and that such elasticity is essentially a property of the long-chain molecules of which rubber is composed. In the light of these publications the author now withdraws his suggestion that the elasticity of rubber is derived essentially from that of its minor constituent "caoutchol."

The author's claim that "caoutchol" purified by hydrolysis is a chemical individual with a formula approximating to  $C_{80}H_{130}(OH)_2$  must be withdrawn in the light of the following new evidence, for details of which the author is indebted to the workers named.

(1) "Caoutchol," whether hydrolysed or not, can be fractionated. Dr. G. F. Bloomfield, employing the technique previously applied to rubber (Bloomfield and Farmer, *Trans. Inst. Rubber Ind.*, 1940, **16**, 69), has obtained the following fractions:

Type of caoutchol.	Light petroleum-acetone at 20°.	% dissolved.	Average mol. weight.	Oxygen content, %.
Hydrolysed	50/50 extract A	47	45,000	0.15
	50/50 extract B	16	—	0.1
	55/45 extract	23	93,000	1.6
	Residue (insoluble in light petroleum or in petroleum-acetone)	10	—	6.2
Unhydrolysed	50/50	29.2	20,000	3.95
	52/48	14.6	—	1.3
	55/45	16.4	53,000	0.9
	60/40	32.2	70,000	1.05

(2) The molecular weight, as determined by Dr. G. Gee, does not agree with the molecular weight required by the formula. Molecular weights of four different samples determined by viscosity methods already described (*Trans. Faraday Soc.*, 1940, **36**, 1162) were 43,000, 47,000, 50,000, and 57,000. The molecular weights of the last two, determined osmotically, were 51,000 and 54,000. These high values cannot be ascribed to association, since the specific viscosity of the first sample in benzene was shown to be almost independent of temperature.

(3) The analytical evidence, by Dr. W. T. Chambers and Dr. F. Hilton, does not point unequivocally to the formula suggested [Found: C, 85.7, 86.5, 86.1, 85.3; H, 11.7, 12.0, 11.8, 11.2; OH (cf. Bolland, *Trans. Inst. Rubber Ind.*, 1941, **17**, 267), 0.48. Calc. for  $C_{80}H_{130}(OH)_2$ : C, 85.4; H, 11.8; OH, 3.0%].

Nevertheless, as has already been stated, "caoutchol" is a naturally occurring material of considerable interest, differing markedly in physical properties from any artificially oxidised rubber which has been examined in these laboratories. In the first place, Dr. L. R. G. Treloar has shown that, in spite of its low molecular weight, "caoutchol" possesses mechanical properties approximating much more closely to those of total rubber than to those of a degraded rubber of approximately the same molecular weight. Using the methods already applied to rubber (*loc. cit.*; *Trans. Faraday Soc.*, 1941, **37**, 84), Treloar has shown:

- That the maximum elongation of "caoutchol" is 700% at 25°.
- That the tensions are only 20—40% lower than those of crepe rubber at corresponding elongations.
- That the plastic flow at 25° is relatively small, being not more than 6% of the elastic elongation (the corresponding figure for crepe rubber is 2%).
- That crystallisation of caoutchol commences at 400% elongation and that its birefringence rises to 60 Na wave-lengths per mm. at breaking point. The latter figure is about half the maximum observed with crepe rubber at the same elongation.

In contrast with this, both a rubber hydrocarbon and an artificially oxidised rubber of similar molecular weight (60,000) were observed to be merely sticky gums, without appreciable strength or elasticity. The possession of good rubber-like properties by the low-molecular "caoutchol" is thought to indicate a stronger cohesion between the molecules than occurs in the rubber hydrocarbon, at least at certain points in their length.

Furthermore, Dr. G. A. Jeffrey, over a period of time, has examined the X-ray diffraction patterns of a number of samples of "caoutchol" prepared in Malaya. He finds that, when stretched, all the samples give a well-defined fibre diagram identical with that of stretched rubber, but that in the unstretched state they show a diffraction pattern having a narrower halo than that of unstretched rubber and two or more distinct Debye-Scherrer rings. On freezing at 0.5° for several days, "caoutchol" does

not give the powder diagram characteristic of frozen rubber. A summary of his observations on unstretched "caoutchol" is included in the following table of mean values for the glancing angles of the diffraction maxima. Figures in parentheses indicate the number of observations.

"Caoutchol."			"Oxide" fraction of Bloomfield and Farmer.		
Diffuse halo	8° 30'—10° 0'	(4)	Diffuse halo	8° 30'—9° 48'	(3)
Ring 1	10° 46'	(4)	Ring 1	10° 41'	(3)
Ring 2	12° 3'	(4)	Ring 2	11° 58'	(2)
Ring 3	13° 36'	(2)			
Ring 4	17° 53'	(1)			
Ring 5	19° 4'	(2)			
Ring 6	20° 19'	(1)			
Ring 7	21° 43'	(1)			

The series of rings for "caoutchol" is quite distinct from that of frozen raw rubber and indicates a higher degree of regularity than is possessed by amorphous rubber. The precise nature of this structural regularity is not at present known. The rings are completely absent from the photographs of all artificially oxidised rubbers so far examined, but a halo and two rings have been observed in *X*-ray photographs of the "oxide" fraction separable from natural rubber by the technique of Bloomfield and Farmer (*loc. cit.*). Data for the latter are included in the above table, from which it is seen that the photographs resemble those of "caoutchol" in the size of the halo and the position of the rings. They were, however, much less distinct and showed more general diffused scattering. The "oxide" fraction, unlike "caoutchol," is an inelastic gum. T. C. Roberts (*Nature*, 1938, **141**, 834) has reported the existence of sharp rings in the *X*-ray diffraction pattern of unstretched "caoutchol." Her unpublished data have been examined by Dr. G. A. Jeffrey, who states that they are not significantly different from his own and that he therefore cannot support the suggestions made by her in the publication above referred to.

A sample of "caoutchene" received from Malaya was found by Dr. G. Gee to have a molecular weight of approximately 140,000. Dr. G. A. Jeffrey found that this sample gave *X*-ray data identical with those given by rubber, *i.e.*, the same amorphous pattern when unstretched, the same fibre diagram on stretching, the same crystalline powder ring pattern when frozen. No systematic study of its mechanical behaviour has been undertaken, but its relatively poor elastic properties and its molecular weight, combined with the *X*-ray data, indicate clearly that it is merely a degraded rubber.

The above conclusions are based on evidence obtained from specimens of "caoutchol" and "caoutchene" sent to this country from Malaya. It should be stated that it was found necessary to work with such samples because it has proved impossible to prepare in England materials having all the properties of those prepared in the East.

The above work has been carried out as part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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