

41. *The Chemistry of Natural Rubber.* Part I. The Isolation of the Constituents.*

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Finality of outlook has not yet been reached on many aspects of rubber science. Opposing views are held on the most fundamental phenomena, such as the elasticity of rubber and its behaviour on exposure to air and light, and even its elementary composition and its molecular weight are still subjects of discussion. Until now no single comprehensive process has existed for the separation of natural rubber into its constituents, and it was felt that the development of such a process might throw light on some at least of the debated points.

The material hitherto regarded as the rubber hydrocarbon consists of two constituents—caoutchene and caoutchol (see following paper)—each of which lacks certain fundamental properties of natural rubber. Other points established are (a) the existence of two new minor non-hydrocarbon constituents, (b) the separation of the phosphatic material into two contrasted fractions, and (c) the failure to separate completely the major nitrogenous constituent and the rubber hydrocarbon.

Quantitative analyses based on the process are proving of value in approaching the problems of the variability of latex and of rubber, the effect of preservation on latex, and latex metabolism.

It is generally accepted that the solid matter which constitutes 30—50% of the latex of *Hevea brasiliensis* (the source of almost the whole of the raw rubber of commerce) consists essentially of the rubber hydrocarbon (~ 90%) together with small and varying amounts of mineral phosphates, sugars, quebrachitol (*l*-methylinositol), fatty acids, sterols, and nitrogenous matter including protein. Raw rubber and the various concentrated latices of commerce contain all these constituents, but owing to their modes of preparation they contain in general a more or less reduced amount of water-soluble matter, *viz.*, phosphates, sugars, quebrachitol, and nitrogenous matter.

Many detailed investigations of individual constituents have been reported, but there is in general use for the examination of latex or of rubber no method which involves the isolation of the constituents in the forms in which they occur in the raw product. In this respect no advance has been made on the work of Faraday, who (*Quart. J. Sci.*, 1826,

* A brief account of preliminary work on this subject has already been published (Roberts, *J. Rub. Res. Inst. Malaya*, 1936, 7, 46).

21, 19) reported the quantitative isolation of the constituents of a rubber-bearing latex from Mexico.

Present practice is to indicate the composition of rubber in terms of its content of "resin" (acetone extract), "sugars" (reducing power of water extract), ash, "protein" (nitrogen content $\times 6.25$), and "hydrocarbon" (the elastic residue). This has led to preconceptions on the part of many workers in this field. The nature of the substances responsible for the reducing power of the water extract of rubber is not yet well established, and attempts to isolate a protein have met with only partial success. Further, the current view that the essential rubber "substance"—the above elastic residue—is a hydrocarbon, is not well founded. The precise analytical data of Midgley, Henne, Shepard, and Renoll (*J. Amer. Chem. Soc.*, 1935, **57**, 2318) have shown that the elastic constituent of rubber contains a small but definite amount of hydroxylic oxygen.

In developing the present method for the isolation of the constituents, a departure has been made from current practice. Whereas it is customary to remove non-hydrocarbon material from rubber by extraction processes, the primary separation is now effected by treating a solution of rubber in such a way that the purely organic non-hydrocarbon constituents are retained in solution on removal of the hydrocarbon and the mineral-containing constituents by precipitation. To this end, the rubber is dispersed in an approved mixture of carbon tetrachloride and acetone, and the dispersion is treated with a further quantity of acetone (see scheme).

There is a two-fold reason for the use of the mixed dispersing agent: first, it expedites the notoriously slow process of dispersion of rubber by taking advantage of the fact that addition of acetone to such dispersions markedly reduces their viscosity; secondly, it exploits a possibility which does not appear to have been appreciated hitherto, that this reduction of viscosity may be due to a breakdown of the micellar structure of dispersed rubber in presence of acetone. If such a breakdown takes place, the rubber in the mixed dispersing agent will approach more closely to a true unimolecular state than in a simple solvent.

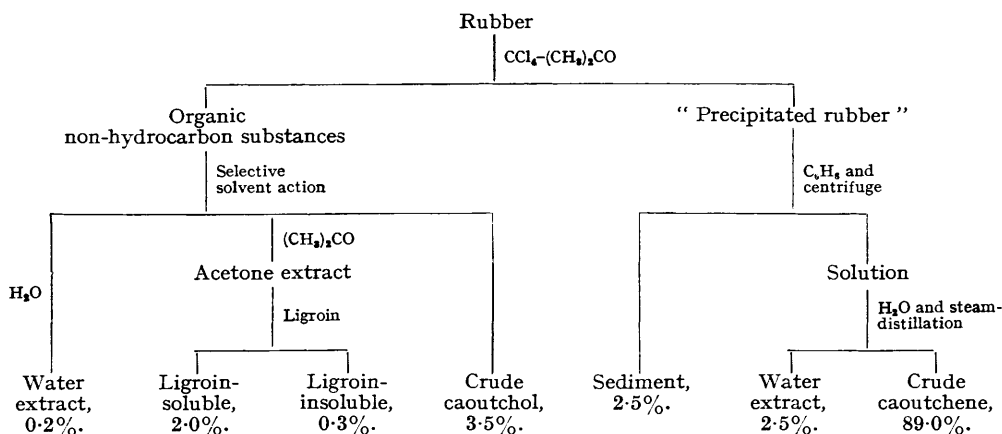
The principle employed in the further treatment of both the organic non-hydrocarbon material and the "precipitated rubber" (the mixture of hydrocarbon and mineral-containing constituents will be thus referred to) is to submit each to treatment by physical, as opposed to chemical, means until the ultimate constituents of the raw material are obtained.

For this purpose the organic non-hydrocarbon material is treated by selective solvent action (see scheme). First, by means of water, a small amount of a hitherto undetected organic material containing nitrogen is removed. The acetone-soluble portion of the remainder is further separable into ligroin-soluble and ligroin-insoluble portions. Preliminary work shows that the former consists essentially of a group of substances hitherto isolated from the "acetone extract" of rubber, which has been examined in some detail by Bruson, Sebrell, and Vogt (*Ind. Eng. Chem.*, 1927, **19**, 1187) and by Whitby, Dolid, and Yorston (*J.*, 1926, 1448). The ligroin-insoluble material, on the other hand, has not previously been detected. The portion of the organic non-hydrocarbon matter remaining after these extractions has novel characteristics. It is an elastic substance which comprises 2—5% of the solid matter of raw rubber, but differs from rubber in that it readily dissolves in ether to give clear solutions having a very low viscosity. For reasons which appear in the ensuing paper, this new substance has been named "crude caoutchol."

The above non-hydrocarbon constituents all burn without ash. Further, they contain only very small amounts of nitrogen and quebrachitol and give no evidence of the presence of the free reducing sugars frequently stated to be present in rubber. The inference is that practically the whole of the quebrachitol, mineral and nitrogenous matter, and sugars of the original rubber is retained by the "precipitated rubber."

The effect of the removal of the new constituent caoutchol is immediately seen in the properties of the "precipitated rubber," which is characterised by its lack of tensile strength and by the remarkably low viscosity of its solutions in the usual rubber solvents. These properties have been utilised for the removal of further non-hydrocarbon materials

(see scheme). Thus the viscosity of a 3—4% solution of the "precipitated rubber" in benzene is sufficiently low for undissolved non-hydrocarbon material to be removed from



Scheme illustrating the separation of the constituents of *Hevea* rubber.

The constituents occupying the lowest line appear to be the ultimate ones separable by usual physical processes. The figures represent typical amounts of each, and are expressed as percentages of the total solid matter of latex.

it by centrifugal action. Further, the non-hydrocarbon material retained by the mobile solution after this treatment may be quantitatively removed in water by the procedure described below. The sediment and the water-extractable material so obtained together comprise the substances hitherto known as the "serum solids" of latex or as the water-soluble matter of rubber, but this is the first occasion on which a separation of this matter into two well-defined fractions has been effected.

The non-hygroscopic, water-soluble sediment and the hygroscopic water extract together contain only about one-fourth of the total nitrogen of rubber (unpublished results), the major portion of which therefore remains associated with the residual rubber. The point is now emphasised that all attempts to separate the latter quantitatively into a nitrogenous constituent and a pure hydrocarbon have completely failed. The nature of the retained nitrogenous matter remains obscure. It is proposed to call the nitrogen-containing residue "crude caoutchene," and to reserve the name "caoutchene" for the pure hydrocarbon. Crude caoutchene is remarkable in that it is notably deficient in toughness and elasticity, properties hitherto regarded as fundamental attributes of the essential rubber substance.

With a view to determining the effect of a variety of factors on the composition of latex and of rubber, the separation of rubber into the above seven constituents has been placed on a quantitative basis. The table summarises the results of typical analyses of the total solid matter of latex and of a high-grade crêpe rubber.

Components of primary separation.	Constituent.	Item No.	Per cent. of total solids.		
			I, Latex.	II, Crêpe.	
Organic non-hydrocarbon material	Water extract	1	0.28	0.03	
	Acetone extract :	(i) Ligroin-insol.	2	0.27	0.14
		(ii) Ligroin-sol.	3	2.37	1.75
		Crude caoutchol	4	4.71	3.23
"Precipitated rubber"	Sediment	5	2.75	0.01	
	Water extract	6	2.12	0.24	
	Crude caoutchene	7	87.02	94.04	
	Total	—	99.52	99.44	

The newly discovered material caoutchol is seen to be the major non-hydrocarbon constituent of rubber.

The percentage of non-hydrocarbon matter for the above typical specimen of *Hevea* latex (col. I) is higher than that usually reported in spite of the absence of the usual item

“protein,” which is now included under crude caoutchene. Comparison of cols. I and II shows that the water-soluble matter (items 1, 5, and 6) is largely removed in the preparation of crêpe rubber. The differences between the other pairs of figures are not unusual for a biological fluid.

EXPERIMENTAL.

The finely divided, dried sample of rubber (30 g.) is added to a mixture of carbon tetrachloride (700 c.c.) and acetone (450 c.c.). The mixture is stirred intermittently until a homogeneous, opalescent and relatively mobile dispersion results, usually in 2—4 hours, but the mixture is kept in subdued light for 24 hours to allow time for the break-down of the micellar structure. A further 450 c.c. of acetone are then added while the mixture is agitated. The crude caoutchene together with phosphatic matter is quantitatively precipitated in fine white flakes, which slowly coalesce. After the mixture has been kept for 24 hours in subdued light, the supernatant, clear, pale yellow solution is decanted, and the “precipitated rubber” is washed first with 50 c.c. of a mixture of carbon tetrachloride (7 vols.) and acetone (9 vols.) and finally with acetone (50 c.c.). The combined solution and washings are distilled to small bulk and the remaining solvent is removed on a water-bath. The residue consists of the organic non-hydrocarbon constituents.

Treatment of the Organic Non-hydrocarbon Constituents.—Water extraction. The oily, dark-coloured material is extracted three or four times with small quantities of water, and the resulting pale yellow, slightly opalescent extract is dried on the water-bath. The product (approximately 0.2% of the total solid matter of latex) frequently includes as impurity a small amount of quebrachitol, which may be removed by treating the product with ethyl alcohol, in which quebrachitol is insoluble. The purified material is a viscous yellow oil which slowly deposits crystals.

Acetone extraction. The material remaining after the water extraction is stirred vigorously several times with warm acetone until all acetone-soluble material has been dissolved. Acetone is removed from the extract on the water-bath and the residue is resolved with ligroin.

The ligroin solution, dried to constant weight, yields a very viscous, dark red oil (1.5—2.5% of the rubber), which comprises the bulk of the acetone-soluble material. It slowly deposits crystals, and preliminary investigation of its hydrolytic products shows it to consist essentially of a complex of aliphatic acids, complex alcoholic substances, and a glucoside, together with small amounts of unidentified terpenic material. A small amount of a water-soluble, odorous, sulphur-containing substance is also present.

The ligroin-insoluble matter, constituting approximately 0.3% of the rubber, appears to consist of unsaturated higher aliphatic acids combined with an unidentified water-soluble substance.

The acetone-insoluble residue, dried on the water-bath, varies somewhat in texture from sample to sample, but is in general a transparent, brown, plastic solid possessing a high degree of elasticity and constituting 2—5% of rubber. It contains a small amount of sulphur. It dissolves rapidly in rubber solvents and in ether, giving very mobile and almost clear solutions, but is insoluble in alcohol. It is a crude form of the substance caoutchol described in the ensuing paper.

Treatment of the “Precipitated Rubber.”—The washed “precipitated rubber” (cf. above) is rolled to a thin sheet on a mill and allowed to dry by evaporation in subdued light at room temperature (24 hours). A solution of the material (10 g.) in benzene (300 c.c.) is kept in a centrifuge for 30 minutes at 2000 r.p.m., and the supernatant, clear yellow solution is then decanted. The sediment, representing approximately 2.5% of the total solid matter of latex, is carefully washed with small quantities of benzene and may be weighed. It is a white, non-hygroscopic powder which is essentially soluble in water, although it is liable to be contaminated with traces of rubber and also with any fine dirt (earth, bark scrap, etc.) which was present in the original specimen. Latex is as a matter of routine purified by sieving, but the nature of the liquid permits of the removal only of coarser impurities by this method.

The benzene solution, together with the washings, is treated with water (1000 c.c.) in a 2-l. flask. The mixture, shaken to an emulsion, is distilled with steam. A clear liquid and a spongy white mass remain in the flask. After decantation of the liquid, the residue is rinsed several times with water, and the liquid expressible from it is added to the main bulk, which, after being concentrated on a hot-plate, is finally dried to constant weight on the water-bath. The pleasantly odorous, clear brown, vitreous product, representing approximately 2.5% of

the total solid matter of latex, is highly hygroscopic and forms large crystalline plates in contact with moist air.

The washed spongy mass is passed through a rolling mill before being dried in a vacuum over sulphuric acid. The tacky, very feebly elastic product retains the bulk of the nitrogen of the original material [Found: N (original rubber), 0.55%; N (residue), 0.42%]. It constitutes about 89% of the total solid matter of latex. A description of the material, which is named crude cautchene, and an account of unavailing attempts to remove further non-hydrocarbon matter from it will be found in the ensuing paper.

Notes.—(1) Benzene may take the place of carbon tetrachloride in the initial stage of the process, but the acetone, owing to its highly specific action, is not replaceable by other common precipitants for rubber, such as alcohol. When benzene is used, the above proportions of solvent and precipitant require modification.

(2) The process has been carefully examined, particularly with respect to the possibility of oxidative or other changes in the constituents. No evidence of such changes has been obtained.

(3) The process lends itself to the analysis of any of the forms of raw rubber commonly met with, *viz.*, crêpe, smoked sheet, crumb, powder, or liquid latex. The last is conveniently prepared for analysis by spreading it in a thin film on plate-glass and drying it at 50—55° in a dark chamber. Analyses of latices and rubbers, the preparation of which has involved special chemical or other treatment, naturally present additional features. These will be reported elsewhere.

(4) Carbon tetrachloride is readily recoverable from the process by treating the distilled carbon tetrachloride-acetone mixture twice with large volumes of water.

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