

THE CONSTITUENTS OF HEVEA LATEX

PART IV

THE EFFECT OF AMMONIATION ON LATEX

BY

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It is widely recognised that the preservation of Hevea latex with ammonia produces profound changes, but up to the present time investigation of the ammoniated product has been very largely restricted to observations of its physical properties—viscosity, surface-tension, electrical conductivity, hydrogen ion-concentration, and so on (1).

There are two reasons for the lack of chemical studies. In the first place, the absence of a method for the isolation of the individual constituents, has rendered it impossible to correlate differences in the physical properties of latex with changes in any particular constituent; in the second place, fresh latex is, in the nature of things, not available in the laboratories of North America and Europe, with the consequence that comparison of the characteristics of fresh and preserved specimens *of the same latex* is not possible there. The first point has now been met by the development of the method of analysis described in Part I of this series (2), and the second, by applying the method to the study of ammoniated latex in one of the countries of production. An exhaustive comparative study of fresh and ammoniated latices from the point of view of acetone-extract, acid-value, surface-tension, viscosity and stability is now being made in these laboratories by Dr. E. Rhodes. This investigation should prove complementary to the present work.

Latex preserved by addition of 0.7 per cent. by weight of gaseous ammonia may be prepared for analysis in almost the same way as fresh latex. Owing to the reduced viscosity of the treated material, a volume of only 50 cc. (instead of 100 cc. as for fresh latex) is distributed over each of the plate-glass frames preparatory to drying as usual. A slight modification of the analytical procedure is necessitated by the lowered solubility of rubber from ammoniated latex. The dispersion of the dried material in the carbon tetrachloride-acetone mixture is incomplete in the period of 24 hours which amply suffices for the total solid matter of fresh latex, and in order to ensure complete removal of

soluble non-hydrocarbon constituents by the dispersing medium, the mixture is kept before further treatment for a period of days depending on the age of the latex. Even so, the ammoniated product, though finely disintegrated, remains on occasion incompletely dispersed.

Ammoniated latices examined have been of two types—ammoniated estate latices which had been stored for some months in metal drums treated internally to prevent discoloration of the latex, and laboratory specimens kept in glass vessels after ammoniation. The latter thus differed from the former in being exposed to the action of light. No evidence has, however, appeared that diffuse daylight itself has any effect on the latex constituents. Only with the laboratory specimens has it been possible to compare analyses with those of the same latex before preservation. Typical results are summarised in the Table below. In all the preserved samples the ammonia-content was approximately 0.7 per cent. by weight of the latex.

Ammoniation produces such extensive changes in the majority of the constituents that the usual nomenclature becomes inapplicable, and it has been necessary to describe the materials isolated in more general terms. Thus the “fatty acid complex” is in the present connection called “ligroin-soluble matter;” crude caoutchouc becomes “acetone-insoluble non-caoutchouc matter” and the phosphate complex, “water-soluble matter.” The major constituent, isolable in a less pure form than from fresh latex, is called the “crude hydrocarbon.”

Quantitative changes resulting from ammoniation do not appear to have any particular significance in the case of “ammonium salt,” “ester” and ligroin-soluble matter. The increase in amount of acetone-insoluble non-caoutchouc matter and the decrease in amount of water-soluble matter are however notable, and have been repeatedly observed.

The only constituents which are not profoundly changed qualitatively by ammoniation are the two minor ones, “ammonium salt” and “ester.”

The *fatty acid complex* of fresh latex, composed of a considerable number of alcoholic and acidic substances in chemical combination, is extensively hydrolysed under the conditions of ammoniation, and is isolable as a corresponding ligroin-soluble mixture of the individual constituents of the original complex, *viz.*, alcohols, aliphatic acids, glucoside and terpenic material. This has been established by comparing the behaviour of the two types of ligroin-soluble matter under the action of alcoholic caustic soda.

TABLE

Constituent	Laboratory Specimens			Commercial Latex. Ammoniated 18 months
	Fresh	Ammoniated (No. of weeks in brackets)		
" Ammonium Salt " ...	0.09	0.09	(8)	0.42
+ " Ester "	0.30	0.36	(4)	
		0.24	(14)	
Ligroin-soluble matter .	1.13	1.12	(8)	1.41
	1.76	1.81	(8)	
		1.73	(18)	
Acetone-insoluble	2.54	7.25	(8)	7.42
non-caoutchouc matter .	3.10	7.07	(18)	
Water-soluble matter	5.58	3.93	(4)	3.22
		3.53	(8)	
		3.22	(18)	

The *phosphate complex* suffers a similar change. The naturally-occurring material contains, among other things, mineral phosphates, a reducing sugar and quebrachitol, but owing to their state of combination, it does not give characteristic reactions for these components. The corresponding "water-soluble matter" from ammoniated latex, on the other hand, gives reactions for all three.

The *crude caoutchol* of fresh latex is in general an elastic body; the corresponding "acetone-insoluble" component of ammoniated latex however is invariably a highly viscous fluid, extremely tacky and possessing no elasticity.

The *hydrocarbon* constituent also undergoes a fundamental change during ammoniation. The hydrocarbon isolated from ammoniated latex showed a much greater resistance to solvent action than either raw rubber or the hydrocarbon from fresh latex.

The above extensive changes in the character of the major constituents of latex under the action of dilute aqueous ammonia are effected within a period of eight weeks, and will thus be far advanced before ammoniated latex reaches the consumer.

The most critical changes from the point of view of the properties of rubber are undoubtedly those involving the caoutchol and the hydrocarbon constituents. Specimens of these materials, isolated from fresh latex in their naturally-occurring forms, have

accordingly been independently subjected to the action of dilute aqueous ammonia, with a view to elucidating the nature of the changes.

Crude caoutchol (20 g.) isolated from 2 litres of fresh latex, was added in the form of a thin sheet to distilled water (2 litres) containing 0.7 per cent. by weight of ammonia, and the mixture was kept for eight weeks, with intermittent shaking. In this way the concentrations and storage period for typical commercial ammoniated latex were closely imitated. At the end of the period, the aqueous liquor remained clear, but had become yellow. From it was isolated a small amount of a complex mixture of organic acids, including the sulphur-containing constituent of crude caoutchol mentioned in Part I (2). It is concluded that dilute ammonia exerts a hydrolytic action on crude caoutchol. The insoluble portion of the reaction mixture had during eight weeks become opaque, cream-coloured and spongy by absorption of the medium. After being washed with water, milled, and dried *in vacuo*, it was a tough, translucent material *insoluble in ether and only very slowly dissolved by the usual rubber solvents*—behaviour very different from that of the untreated substance. Caoutchol so modified will necessarily be retained by the hydrocarbon on analysis. The change is apparently one of polymerisation.

The hydrocarbon from fresh latex, treated in a manner similar to the above, likewise became a soft opaque mass, but no portion of it was dissolved by the ammoniacal medium. The washed product, milled to a thin sheet and dried *in vacuo*, was a tacky, light-brown material which was only slightly dissolved in 3-4 hours by the usual rubber solvents. The undissolved portion slowly swelled in the solvents, but even after 24 hours it remained largely undissolved by benzene, carbon bisulphide, ether and ligroin. A higher degree of dispersion was observed in chloroform, carbon tetrachloride and toluene, but in these media also, solution was incomplete. The untreated hydrocarbon on the other hand dissolves readily with but little swelling. It is suggested that the soluble portion of the treated hydrocarbon is a disaggregated form, which, being more soluble than the normal form, is retained by the carbon tetrachloride—acetone mixture during the analysis and appears as the “acetone-insoluble matter” in place of caoutchol. The insoluble portion, which constitutes the bulk of the treated product, appears to be a polymer of the naturally-occurring hydrocarbon.

These relationships throw light on the apparent loss of water-soluble matter indicated in the Table. The procedure which suffices for the quantitative removal of water-soluble matter from the total solids of fresh latex, is inefficient when applied to the

ammoniated product. An appreciable amount of inorganic matter is retained, along with modified caoutchol, by the "crude hydrocarbon," and may be readily detected as ash.

Summary

(i) Comparative analyses of fresh and ammoniated latices have been made, and the constituents investigated.

(ii) The changes effected by ammoniation are profound, and are far advanced in a period of eight weeks. The minor constituents "ammonium salt" and "ester" are alone inappreciably affected.

(iii) The fatty acid and the phosphate complexes of fresh latex undergo extensive hydrolysis within eight weeks of ammoniation, and part of the inorganic matter is firmly retained by the modified hydrocarbon. (See (v) below.)

(iv) The crude caoutchol of fresh latex is replaced by an increased amount of a viscous fluid which is thought to consist of a disaggregated portion of the hydrocarbon. Caoutchol itself, treated with dilute aqueous ammonia, becomes relatively insoluble, and is presumably retained on analysis by the remainder of the hydrocarbon.

(v) The hydrocarbon of fresh latex is replaced by an ash-containing material which has a marked resistance to solvent action. This latter property is due not only to retention of the modified caoutchol (iv above), but also to modification (? polymerisation) of the hydrocarbon itself by the action of the ammonia.

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