385. *The Chemistry of Natural Rubber. Part III. The Effect of Ammoniation on the Latex of* Hevea brasiliensis.*

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The constituents of latex preserved with ammonia are isolated by a modification of the method described in Part I (this vol., p. 215) and compared with those of fresh latex. It is shown that during ammoniation the bulk of the solid matter of latex, including the crude hydrocarbon, is profoundly changed within 8 weeks (a minimum storage period for most of the latex of commerce). A preliminary study of the chemical nature of the more important of these changes is described.

The bulk of the liquid latex of commerce is protected against putrefaction by addition of 0·7—1·5% of ammonia. It is widely recognised that latex is profoundly affected by this procedure, but little insight has hitherto been obtained into the chemistry of the changes. The problem has now been approached by applying to latex before and after preservation with ammonia the method of analysis described in Part I (this vol., p. 215).

Ammoniated latex which has been kept under representative conditions of storage for periods of 8 weeks to 18 months in general differs in composition from fresh latex in the manner shown in the table. The quantitative findings for ammoniated latex, however, vary appreciably with the time of storage and with the ammonia content. The analysis recorded was made on latex containing 0·7% of ammonia after 18 weeks' storage.

Fraction.	No.	Fresh latex. %.	Fresh latex. Description.	Same latex ammoniated. %.	Same latex ammoniated. Description.
A. CCl_4/Me_2CO-sol. matter :					
Water extract	1	0·2	Cryst.	0·2	Oily
Acetone extr. (i) Ligroin-insol.	2	0·1	Cryst.	0·2	Oily cryst.
(ii) Ligroin-sol.	3	1·7	Oily cryst.	1·8	Non-cryst. oil
Residue *	4	3·1	Elastic solid	7·1	Viscid fluid
B. " Precipitated rubber " :					
Sediment	5	2·7	Cryst.	2·1	Cryst.
Water extract	6	2·9	Vitreous	1·1	Vitreous
Crude caoutchene	7	—	Soluble	—	Rel. insol.

* The name crude caoutchol applied to this fraction in Part I is not applicable in the case of ammoniated latex (see below).

Two major quantitative changes resulting from ammoniation are apparent : the increase in amount of the residue (fraction 4) and the decreased amounts of the water-soluble fractions 5 and 6.

Qualitative changes in the constituents as a result of ammoniation are extensive except in the minor fractions 1 and 2.

The fractions 3, 5, and 6 are isolable from fresh latex as crystalline, readily hydrolysable " complexes " comprising a considerable number of individual substances. The corresponding fractions of ammoniated latex consist essentially of the same materials in a more or less hydrolysed condition. Detailed examination of these hydrolytic changes necessarily awaits a more complete knowledge of the ultimate chemical components of latex than is now available.

There can be little doubt that these changes affect the properties of rubber derived from ammoniated latex, but more significant from this point of view are the changes undergone by caoutchol and caoutchene. The elastic crude caoutchol (fraction 4) of fresh latex disappears upon ammoniation, and its place is taken by a viscid fluid which further differs from crude caoutchol in retaining nitrogenous matter. The crude hydrocarbon constituent (7) is isolated from ammoniated latex in a relatively insoluble form which retains an appreciable amount of inorganic matter. The procedure which effects a quantitative removal of mineral-containing matter (fractions 5 and 6) from the " precipitated rubber " of fresh latex (*loc. cit.*, p. 218) is clearly not efficient when applied to the modified material.

* Preliminary work on this subject has been reported elsewhere (*J. Rubber Res. Inst. Malaya*, 1938, **8**, 192).

Elementary analysis of the impure fractions 4 and 7 of the modified material could not be expected to throw any light on the nature of the changes, and the problem has therefore been approached by examining the behaviour of the corresponding constituents of fresh latex, namely, crude caoutchol and crude caoutchene, under the action of dilute aqueous ammonia. Under this treatment crude caoutchol, which is normally very soluble in the usual rubber solvents, becomes relatively insoluble. Caoutchol so modified would necessarily be retained by the hydrocarbon fraction (7) during the above analysis. Crude caoutchene from fresh latex undergoes a complex change in contact with dilute aqueous ammonia. Solubility evidence indicates that a small portion of it is disaggregated, and the major portion reaches a higher degree of association than is found in the naturally occurring product. The same change doubtless takes place in ammoniated latex, with the consequence that the disaggregated portion, in virtue of its increased solubility, appears, together with associated nitrogenous matter, as the residue (4). The diminution in solubility of the main hydrocarbon fraction is intensified by the presence therein of the modified caoutchol; the observed retention of some mineral-containing matter by this mixture under the conditions of analysis is readily understood.

Experimental.

The differing characteristics of fresh and ammoniated latex and of certain of their constituents make necessary the use of somehat different analytical procedures in the two cases.

Analysis of Fresh Latex.—The latex (100 g.), the total solid content of which is determined, is evenly distributed over a sheet of plate glass approximately 50 cm. square and is dried at 45—50° (1—2 hours). The resulting film is added in strips to a mixture of carbon tetrachloride (14 vols.) and acetone (9 vols.) (115 c.c. of mixture for each 3 g. of dried film) and is kept in subdued light with occasional stirring for 24 hours. The homogeneous dispersion is then treated with a volume of acetone equal to that already used (45 c.c. for each 3 g. of dried film). The further procedure is as described in Part I (*loc. cit.*, p. 218).

Analysis of Ammoniated Latex.—The viscosity of ammoniated latex is low relative to that of fresh latex, and it is convenient to dry 100 g. of the liquid by distributing 50 g. on each of two plate-glass sheets 50 cm. square.

The dried film from ammoniated latex does not form a homogeneous dispersion in the carbon tetrachloride–acetone reagent. To ensure complete extraction of soluble matter from the dried film, the mixture is kept with occasional stirring for at least 48 hours before being treated with the precipitant. The remaining procedure is in general as usual; but the diminished solubility of the main hydrocarbon fraction of ammoniated latex may render the isolation of the sediment from the " precipitated rubber " by centrifugation impracticable. In this event the dispersion of the " precipitated rubber " in benzene is immediately subjected to the treatment with water. The water-soluble sediment and the water extract will thus be isolated as a single fraction (5 + 6. See Table).

The ammoniated latices examined had been stored either in the dark (metal drums) or in diffuse daylight (glass vessels). Neither diffuse daylight nor the type of container has been observed to affect the results of analysis.

Observations on the Constituents.—*Fraction* 1. Isolated from ammoniated latex, this material is completely soluble in ethyl alcohol and is therefore free from quebrachitol, but is otherwise indistinguishable from the corresponding fraction of fresh latex.

Fraction 2. Changes produced by ammoniation are of minor interest and have not yet been studied.

Fraction 3. The material isolated from fresh latex readily crystallises when kept (see *J. Rubber Res. Inst. Malaya*, 1938, **8**, 181) and is an ester-complex which is readily hydrolysed by alcoholic potassium hydroxide but not by cold dilute aqueous alkali. The corresponding material from ammoniated latex is an oil, uncrystallisable at room temperature. Extraction of the oil with light petroleum in presence of cold dilute aqueous alkali separates it into acidic and alcoholic fractions, the investigation of which is in progress.

Fraction 4. This elastic, hydrolysable constituent of fresh latex (crude caoutchol; *loc. cit.*, p. 224) is ash- and nitrogen-free. The corresponding viscid fraction of ammoniated latex is ash- and quebrachitol-free, but contains nitrogen (Found : N, 0·3%). It gives no evidence of being saponified when heated for 1 hour with 1% aqueous sodium hydroxide.

Crude caoutchol (20 g.), isolated from 2 l. of fresh latex, was added in the form of a thin sheet to water (2 l.) containing 0·7% by weight of ammonia, and the mixture was kept for 8 weeks with intermittent shaking. In this way the concentrations and storage period for typical ammoniated latex were closely imitated. At the end of the period the aqueous liquor was pale yellow and almost clear, and frothed when shaken. 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 II (this vol., p. 224). The insoluble portion of the reaction mixture was opaque, cream-coloured, and spongy. Washed, passed through the closed rolls of a mill, and dried in a vacuum, it was a highly elastic, tough, yellow substance, insoluble in ether and only very slowly dissolved by the usual rubber solvents.

Fractions 5 *and* 6. These mineral-containing fractions of fresh latex, after being heated for 30 minutes with 3N-sulphuric acid, both give normal positive reactions with ammoniacal silver nitrate, Fehling's solution, and ammonium molybdate. The untreated materials, on the other hand, do not reduce Fehling's solution and do not give normal reactions with ammoniacal silver nitrate or with ammonium molybdate. Both materials contain small amounts of nitrogenous matter (ninhydrin) (Found for fraction 5 : N, 0·5; for fraction 6 : N, 3·5%). Fractions 5 and 6 of fresh latex thus consist of " complexes " comprising reducing substances, nitrogenous matter and mineral phosphates (for the cations of latex, see Rae, *Analyst*, 1928, **53**, 330). The corresponding untreated fractions of ammoniated latex give normal positive reactions with the above reagents.

Fraction 7 (*crude caoutchene*). Isolated from fresh latex, this material is readily soluble in the usual rubber solvents and is virtually ash-free. The corresponding material from ammoniated latex burns with an appreciable ash and is difficultly and incompletely soluble. Both forms retain the bulk of the nitrogenous matter of latex (Found for caoutchene of fresh latex : N, 0·4; for caoutchene of the same latex after 4 weeks' ammoniation : N, 0·4%).

Crude caoutchene from fresh latex was treated with dilute aqueous ammonia in the same manner as crude caoutchol (see above). After 8 weeks the ammoniacal liquor contained only a negligible amount of dissolved solid matter. The caoutchene, after being washed, sheeted, and dried in a vacuum, was obtained as a tacky, light brown product, a portion of which was readily dissolved in 3—4 hours by the usual rubber solvents. The decanted clear solutions contained small amounts of viscid, semi-fluid material. The major, undissolved portion slowly swelled in the solvents, but remained to a large extent undissolved by benzene, carbon disulphide, ether and ligroin even after 24 hours. A higher degree of dispersion was observed in chloroform, carbon tetrachloride, and toluene, but in these media also, solution was incomplete in 24 hours.

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