

42. *The Chemistry of Natural Rubber. Part II, Caoutchene and Caoutchol and the Intermolecular Structure of Rubber.*

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The two components of the material hitherto regarded as the rubber "substance" (cf. preceding paper) are described.

Crude caoutchene, the major component, comprises 95—98% of this material, and consists essentially of a typical polyterpene, caoutchene. It is tacky and only feebly elastic. With it is very intimately associated a small amount of unidentified nitrogenous matter. Molecular-weight evidence indicates that *caoutchene* is an octaterpene, $C_{80}H_{128}$, the molecules of which are considerably associated at room temperature.

Crude caoutchol, constituting 2—5% of the former rubber "substance," consists of an alcohol, *caoutchol* (~97%), in combination with complex unidentified acidic material (2—3%) which contains sulphur. The evidence suggests that caoutchol is a dihydrate, $C_{80}H_{130}(OH)_2$, of caoutchene. The alcohol freshly purified by hydrolysis is a tough non-tacky substance which resembles rubber in being highly elastic, but differs from it in dissolving freely in ether to clear mobile solutions. The molecules of the freshly prepared substance are appreciably associated at room temperature.

The influence of caoutchol on the physical properties of plantation rubber is discussed. Evidence from viscosity measurements and other considerations in support of a two-phase intermolecular theory is adduced.

Two views of the nature of purified rubber are widely current—one, that it is composed of very large, open-chain hydrocarbon molecules having a molecular weight of the order of 100,000 (Staudinger and collaborators, 1920—1937. For a summary, see Staudinger, *Trans. Inst. Rub. Ind.*, 1934, **10**, 263); the other, that it consists of micellar aggregates of relatively small hydrocarbon molecules having a molecular weight of 1100—1600 (Pummerer, *Ber.*, 1927, **60**, 2167; 1928, **61**, 1591; 1929, **62**, 2628). The first is based primarily on consideration of the viscosity of rubber solutions, and the second on cryoscopic molecular-weight determinations of rubber in camphor and similar solvents.

Neither view provides a basis for a convincing explanation of the remarkable degree of elasticity of raw rubber. Midgley, Henne, Shepard, and Renoll (*J. Amer. Chem. Soc.*, 1935, **57**, 2318) on the basis of analytical evidence have advanced the further view that the rubber molecule contains a hydroxyl group and has a minimum molecular weight of 40,000.

New light is thrown on the subject by the separation of the supposed rubber "substance" into two constituents (see preceding paper), crude caoutchene and crude caoutchol (95—98% and 5—2% respectively of the former rubber "substance").

Caoutchene.—Crude caoutchene, the tacky, feebly elastic material which constitutes 87—91% of the total solid matter of *Hevea* latex, consists preponderantly of carbon and hydrogen (~ 99%) together with small amounts of nitrogen, sulphur, and oxygen (~ 1%). Attempts to remove nitrogenous matter have proved unavailing. Midgley, Henne, and Renoll (*J. Amer. Chem. Soc.*, 1931, **53**, 2733) have, however, isolated from rubber by fractional precipitation at the critical temperature a small amount of nitrogen-free material, and it is therefore inadmissible to conclude that nitrogen is a component of the rubber molecule. It is accordingly assumed that crude caoutchene consists of a hydrocarbon in intimate association with an unidentified nitrogenous constituent. Analytical and molecular-weight evidence indicates that the hydrocarbon is an octaterpene, $C_{80}H_{128}$, to be called *caoutchene*. It is noteworthy that the nitrogen content of crude caoutchene from numerous specimens of fresh latex has remained practically constant ($0.42 \pm 0.05\%$) over a period of months. The nitrogen content of crude caoutchene from other sources is discussed in the experimental section. Two points have been established concerning the nature of this nitrogenous matter: (1) the nitrogen is, at least in part, of amide type; (2) the relative amounts of nitrogen, oxygen, and sulphur are similar to those found in typical proteins.

Crude caoutchene is not a pure substance, but it may readily be shown that, since the amount of nitrogenous constituent present is very small, variation of its carbon/hydrogen ratio within quite wide limits will not cause a material divergence of the carbon/hydrogen ratio found for *crude* caoutchene from that of *pure* caoutchene. Any divergence will be inappreciable if the nitrogenous constituent is protein, the average carbon/hydrogen ratio for which (10/15.7) is very close to that of the terpenes (10/16). In other words, the carbon and hydrogen values found for crude caoutchene may fairly be taken as representing those of the hydrocarbon constituent. Thus from typical findings of C, 87.1; H, 11.8% for crude caoutchene, C, 88.1; H, 11.9% may be calculated for the hydrocarbon constituent, figures which are in good agreement with those required for $(C_5H_8)_x$, viz., C, 88.2; H, 11.8%. In this connection attention is drawn to the remarkably close physical resemblance between caoutchene as now obtained and the synthetic polyterpene, polymyrcene, of undetermined molecular weight, which is also a tacky mass (Harries, *Ber.*, 1902, **35**, 3264).

The molecular weight of crude caoutchene in melting camphor lies between 990 and 1170 ($C_{80}H_{128}$ requires 1088). Objections to the Rast method on the grounds that the high temperature involves decomposition of the rubber have been refuted elsewhere (Pummerer, Andriessen, and Gündel, *Ber.*, 1929, **62**, 2628), but it may also be mentioned that repeated cooling and remelting of a camphor solution of crude caoutchene produces no change in the melting point. Further, the molecular weight now observed is much lower than that of 3400 reported by Staudinger and Bondy (*Annalen*, 1929, **468**, 1) for rubber heated in solution at a considerably higher temperature, viz., 206°. Crude caoutchene undoubtedly exists in a considerably associated state at room temperature. The viscosity of its solutions, though of a different order from that of identical solutions of raw rubber (see Table, p. 221), is nevertheless considerable, and it has proved impossible to determine its molecular weight in benzene. Carothers and collaborators have shown (*J. Amer. Chem. Soc.*, 1930, **52**, 5279) that the intermolecular cohesive forces in paraffin hydrocarbons having a molecular weight of about 1000 approach the strength of the intramolecular C—C link. It is therefore to be expected that caoutchene should exist in a very strongly associated state.

Caoutchol.—Crude caoutchol is composed of an alcohol *caoutchol* (97—98%) in

combination with a small amount of a complex mixture of unidentified aliphatic acids (2—3%). In view of the experimental evidence, and because of the close relationship of caoutchol to caoutchene, the alcohol is considered to be the octaterpene dihydrate $C_{80}H_{130}(OH)_2$. It is nitrogen-free, but contains in addition to the above acids a variable and very small amount of an acidic sulphur-containing substance which has not yet been identified. Pure caoutchol prepared by hydrolysis of the crude product exists in the unimolecular form in melting camphor. Viscosity and benzene freezing-point observations indicate a considerable degree of association of its molecules in solution at room temperature.

Caoutchol contains 2.8% by weight of oxygen. Raw rubber, containing 2—5% of caoutchol, may therefore, after being freed from its other non-hydrocarbon constituents, contain as little as 0.05% of oxygen. This figure is in excellent agreement with that of 0.04—0.05% arrived at by Midgley, Henne, Shepard, and Renoll (*loc. cit.*) from a consideration of the results of analyses of rubber itself. This amount is so small as to evade detection by ordinary analytical technique. In any case, the prevailing belief that the rubber hydrocarbon is readily oxidised under atmospheric conditions has led the majority of investigators to regard oxygen found in purified rubber as having been adventitiously acquired.

The basis of the view of the physical nature of rubber now to be discussed is the remarkable degree of elasticity displayed by caoutchol, which, when freshly prepared, is as highly extensible as raw rubber itself. In view of its relatively low molecular weight (1124), this phenomenon must apparently be attributed to association of the molecules of the substance by means of their hydroxyl groups. A substance composed of long molecules associated in this way would inevitably form a complex network which might be expected to show the observed characteristics. It has been mentioned above that caoutchene, the major constituent of rubber, is relatively feebly elastic, exhibiting rather the highly viscous nature to be anticipated in a polyterpene. It is therefore suggested that the elasticity of raw rubber is essentially that of the minor constituent caoutchol, which in virtue of its own state of association and of its power of forming further associated links between its hydroxyl groups and the residual affinity of the caoutchene molecules, acts as a binding material which imparts its own elasticity to the entire mass.

A two-phase theory of the nature of rubber, similar in outline to the above, has been put forward by Fessenden (*J. Franklin Inst.*, 1896, **142**, 187; cf. Whitby, "Plantation Rubber and the Testing of Rubber," p. 257) from theoretical considerations, and a similar view of the structure of muscle has been advanced by Meyer and Picken (*Proc. Roy. Soc.*, 1937, *B*, **124**, 29).

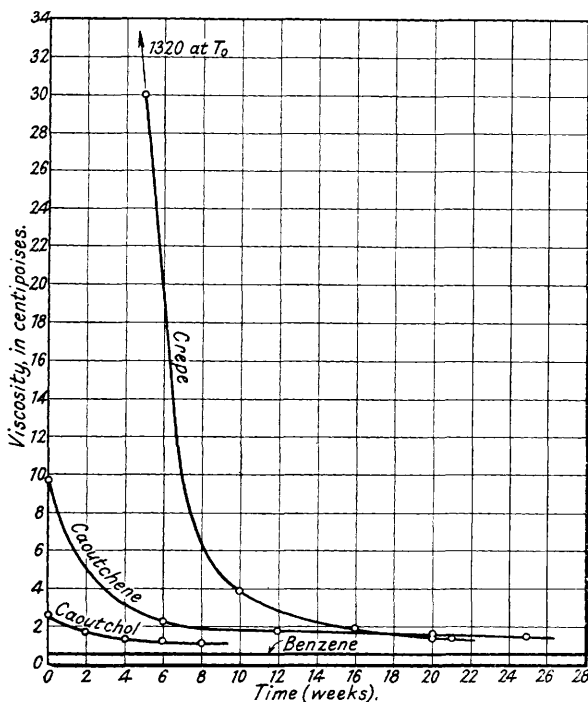
The elasticity of certain synthetic rubber substitutes may not be explained on the above basis, and is presumably due to the enormously high degree of polymerisation of their thread-like molecules. These would, by becoming entangled, impart to the material a matted structure which would resist deformation.

The two-phase intermolecular theory receives strong support from the following considerations. The viscosity measurements of contrasted specimens of rubber in freshly prepared solutions at the same concentration fall into two groups, one having viscosities of at least 1000 centipoises, the other of at most 100 centipoises (Table).

Specimen.	Viscosity of 3.8% soln. in benzene.
Latex total solids	6300 centipoises
" " acetone-extracted	4100 "
Pale crêpe rubber	1320 "
Pale crêpe acetone-extracted	1040 "
" Precipitated rubber " (cf. Part I)	15—100 "
Crude caoutchene	10—30 "
Caoutchol	2—4 "

All the specimens which contain caoutchol are in the former group, and the latter consists of those from which caoutchol has been removed. The low figure for caoutchol is noteworthy.

Further, the initial very high viscosity of a solution of crêpe rubber when kept in a closed vessel in diffuse daylight rapidly approaches a low value similar to that reached by caoutchol-free rubber solutions and by caoutchol solutions under the same conditions (Figure). When kept in the dark, however, solutions of raw rubber retain their intermolecular structure: during 20 weeks, the viscosity of a 3.8% benzene solution of crêpe rubber fell only from 1320 to 920 centipoises. Staudinger considers (*Trans. Inst. Rubber Ind.*, 1934, 10, 276) that the fall in viscosity in light is due to disruption of the rubber molecule by traces of atmospheric oxygen, but because of the magnitude of the effect now recorded and of the cryoscopic evidence discussed above, the writer prefers to regard it as due to a lowering of the degree of association. Further, crêpe rubber contains the naturally occurring non-hydrocarbon constituents which are well known to protect the hydrocarbon from oxidation. Evidence in favour of the disaggregation of rubber



Changes of Viscosity of 3.8% Solutions in Benzene of Crêpe Rubber, Caoutchène and Caoutchol in Diffuse Daylight.

without oxidation has been advanced by others (for a summary, see Fisher, *Chem. Reviews*, 1930, 7, 70). Additional support for this view is provided by the observation that crude caoutchène may be liquefied under conditions which preclude either oxidation or dissociation of its molecule (see Experimental).

The vital rôle of caoutchol in imparting elasticity to plantation rubber is further indicated by the parallel behaviour of caoutchol and of rubber under the action of heat. Caoutchol, which is tough at room temperature, is soft and plastic at 50–60° and is a viscous fluid at 100°. Correspondingly, rubber, which retains considerable elasticity at 45°, is preponderantly plastic at 70° (Hauser, Rosbaud, and Schmidt, *Kautschuk*, 1928, 4, 12; Memmler, "Handbuch der Kautschukwissenschaft," p. 655). Further, the X-ray diffraction pattern produced by stretched rubber in virtue of its elasticity vanishes under diverse conditions between 40° and 90° (von Susich, *Naturwiss.*, 1930, 18, 915; Pummerer and von Susich, *Kautschuk*, 1931, 7, 117). It is suggested that this temperature range is determined by the fact that caoutchol loses its elasticity within the same range. The diffraction of X-rays by caoutchène and caoutchol is now being investigated in this laboratory.

The action of caoutchol on caoutchene is apparently highly specific, but other substances also have a marked effect on the physical nature of caoutchene. Thus the "precipitated rubber" (preceding paper), which consists of crude caoutchene together with the bulk of the water-soluble matter of latex or rubber, though it resembles crude caoutchene in being readily soluble and only slightly elastic, is tougher and less self-adhesive. It has also been observed that a film consisting of the total solid matter of latex is mechanically much stronger than raw plantation rubber, from which practically all water-soluble matter has been removed. Crude caoutchene in the wet state is also tough and non-tacky. The presence of certain non-elastic materials therefore appears to impart toughness to caoutchene, without, however, appreciably increasing its elasticity. One may compare the analogous action of small amounts of divinylbenzene in changing the character of polystyrene (Staudinger, *Ber.*, 1935, 68, 1618).

The highly specific rôle of acetone in permitting the separation of caoutchol and caoutchene may be explained on the above view of the nature of rubber. It is suggested that the presence of a certain limited amount of acetone in a rubber dispersion causes a redistribution of co-ordinate links, links between the carbonyl-oxygen of acetone and the hydroxyl group of caoutchol being formed preferentially to those between molecules of caoutchol and caoutchene which normally persist in a dispersion. In this way the usual intermolecular structure of a dispersion is destroyed and the viscosity undergoes the observed reduction. In other words, the caoutchol is in a sense "solvated" by the acetone, and it ceases to maintain the intermolecular structure of the dispersed rubber, which is thus free to dissolve. Carefully regulated addition of more acetone quantitatively precipitates caoutchene (and the attendant insoluble inorganic matter) while the "solvated" caoutchol remains dissolved. In this way the resolution of the essential rubber "substance," which has so long eluded investigators, is effected. Still further addition of acetone will reduce the concentration of carbon tetrachloride (or other rubber-dispersing medium) to the point at which it can no longer hold caoutchol in solution, and the caoutchol, somewhat more soluble than caoutchene, will then be precipitated.

EXPERIMENTAL.

Crude Caoutchene.—Several of the physical characteristics of the material described by this name in the preceding paper have been mentioned in the foregoing. The material varies considerably in texture according to the previous history of the specimen, that obtained from fresh latex being more tacky (less highly associated) than that from plantation rubber. Additional data are: (a) Crude caoutchene has no definite melting point. When maintained at 100° under reduced pressure for 1—2 hours, it changes to a pale brown highly viscous liquid without increase in weight. When heated at 100° in air, it slowly oxidises (Found: Increase in weight after 24 and 48 hours at 100° in air, 0.32 and 3.30% respectively). This reaction will be discussed more fully in a later communication. (b) It is extensible without rupture by only 100—200% and shows very poor elastic recovery. It has proved impracticable (see next paragraph) to purify the material further, and it has therefore been brought to analysis in the crude state [Found, *e.g.*: C, 87.0; H, 11.8; N, 0.5; S, 0.1; O (by diff.), 0.6; *M* (Rast), 1050, 1109 ± 60. Whence may be deduced for pure caoutchene (cf. discussion above): C, 88.0; H, 11.9%. (C₅H₈)₁₆ requires C, 88.2; H, 11.8%; *M*, 1088]. Within the limits of error of the determinations, the oxygen content is equivalent to the nitrogen content. The analysis is typical of those obtained for crude caoutchene from fresh latex and from plantation rubber.

The Nitrogenous Constituent.—It has been mentioned above that a quantitative separation of caoutchene and the major portion of the nitrogenous matter of rubber has not been effected. This is the more remarkable in that crude caoutchene dissolves readily and almost without swelling in the usual rubber solvents and in ether to give solutions which are remarkably mobile and in some cases water-clear. The ethereal solution is opalescent, but prolonged centrifuging of both the ethereal and the benzene solution failed to remove any undissolved matter. Solutions of crude caoutchene were kept for 6 months in diffuse daylight, until their viscosity approached that of the solvent itself (Figure). Such solutions gave no evidence of the separation of insoluble matter (Found for dissolved matter: N, before exposure, 0.4; after 6 months' exposure, 0.4%). A further unsuccessful attempt to remove nitrogenous

matter from crude caoutchene involved prolonged continuous extraction of a benzene solution with 90% formic acid (Found for extracted caoutchene: N, 0.38%). It has been shown by Wilkins (*Science*, 1937, **85**, 526) that this reagent quantitatively removes the protein from dried grasses. Low values for the nitrogen content of crude caoutchene have been observed only for specimens prepared from the dried solids of creamed latices (Found: N, 0.3, 0.1, 0.3, 0.1, 0.1, 0.2% for the products of various processes). The creaming of latex involves a partial separation of the larger and the smaller globules, the latter tending to remain in the serum. The above results therefore indicate that the smaller latex globules contain a higher concentration of the nitrogenous constituent than the larger. Other "low-nitrogen rubbers" of commerce do not come into consideration in this connection, since they are prepared by treatments designed to remove nitrogen chemically.

Caoutchol.—Crude caoutchol (10 g.), isolated from the organic non-hydrocarbon matter of rubber as described in the preceding paper, is heated under reflux for 1 hour with 1% aqueous caustic soda (200 c.c.). The cooled product is filtered off (a coarse, hardened paper is advisable), and the residue washed with water on the filter.

(a) The residue. For complete removal of alkali, the product should be repeatedly passed through the closed rolls of a mill fitted with a water spray. It is thus obtained as a thin, elastic, opaque sheet which may be dried in a vacuum over sulphuric acid in 24 hours. The resulting substance, *caoutchol*, is transparent, pale brown, and non-self-adhesive, and is extensible by at least 700% with immediate recovery to only 100% extension [Found: C, 85.3, 85.2, 85.4; H, 11.8, 11.8, 11.7; *M* (Rast), 1085, 1116, 1192; mean, 1131. $C_{80}H_{130}(OH)_2$ requires C, 85.3; H, 11.8%; *M*, 1125]. It has not a definite m. p., but softens progressively up to 100°, at which temperature it is a highly viscous, deep yellow fluid. In this condition it slowly oxidises in air (Found: Increase in weight after 24 and 48 hours at 100°, 0.29 and 2.07% respectively). It also slowly softens and oxidises in moist air at room temperature (28—32°). These reactions are being further investigated. Depressions of the freezing point of benzene solutions of caoutchol were measurable, but are probably of doubtful significance (cf. the discussion of a similar phenomenon by Pummerer, Andriessen, and Gündel, *Ber.*, 1929, **62**, 2628, in connection with raw rubber) (Found: *M*, 3200, 7000, 1608, 3216). The Menzies-Wright method was not applicable owing to the tendency of solutions to froth when boiling.

Caoutchol (1.6 g.) in benzene (20 c.c.) was heated under reflux for 30 minutes with acetic anhydride (4 c.c.). After removal of benzene, the product was treated with hot water and with hot alcohol to yield a brown tacky substance, *caoutchol diacetate* [Found: C, 83.6, 83.8; H, 11.6, 11.1; *M* (Rast), 1227 ± 70 . $C_{80}H_{130}(O-CO-CH_3)_2$ requires C, 83.3; H, 11.3%; *M*, 1208].

(b) The filtrate. The faintly opalescent liquid resulting after removal of caoutchol was acidified with sulphuric acid. A strong mercaptan-like odour was detected and a flocculent buff-coloured solid separated. The latter, collected, dried, and weighed, constituted 2—3% of the crude caoutchol. It appears to be a complex mixture of carboxylic acids. The sulphur-containing substance is retained in the aqueous filtrate, which has been shown to contain a small amount of a highly reactive substance. Further investigation is proceeding.

Viscosity measurements were made in the Höppler research instrument at 26—29°.

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