

## The Coagulation of Latex.

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WHILE engaged during the latter part of 1896 in studying the functions of latex, my attention was frequently called to its spontaneous coagulation when in contact with the air.

De Bary describes the phenomenon as follows<sup>1</sup>:—‘As soon as latex comes in contact with the air, and still more quickly on treatment with water, alcohol, ether, or acids, coagula appear in the hitherto apparently homogeneous clear fluid itself, and independently of the aggregation of the insoluble bodies described by Mohl (Bot. Zeit. 1843, No. 33). The coagula collect together and separate with the insoluble bodies from the clear fluid. These phenomena of coagulation which appear under the action of so various agencies point especially to a complicated composition of the fluid, and deserve further investigation.’

An examination of the subject was therefore commenced with the small quantities of latex obtainable from plants grown for the purpose in the Cambridge Botanical Gardens. The results obtained were of some interest, and accordingly the experiments were continued, together with other researches

<sup>1</sup> De Bary, Comp. Anat. of Phanerogams and Ferns, p. 184.

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on a larger scale, in Mexico, Brazil, and the West Indian Islands.

Rubber-yielding plants which always have laticiferous cells, were for the most part chosen on account of the ease with which large quantities of latex could be obtained, and because the various processes used in the preparation of crude rubber seemed likely to throw some light upon the subject.

A microscopic examination of any one of these latices shows that its milky appearance is due to the presence of innumerable small granules of caoutchouc, which in themselves are soft and sticky, for they readily cohere to form a small mass of rubber if the cover-glass is lightly rubbed on the slide.

Some of the processes employed to prepare this rubber may be described here.

In the preparation of Pará rubber, a thin layer of the latex of *Hevea brasiliensis* (Muell. Arg.) or other species of *Hevea*, is exposed to the action of the smoke of burning 'urucuri' nuts (*Attalea excelsa*, Mart.); coagulation is immediately brought about, resulting in the formation of a soft, curdy mass of rubber, which on drying becomes tough and elastic.

The same process is now being applied with good results to the preparation of Ceará rubber from the latex of *Manihot Glaziovii* (Muell. Arg.).

The usually accepted explanation of this is that the water contained in the latex is simply evaporated off<sup>1</sup>; but as the coagulation is brought about in so short a time, and moreover as there is no loss of weight on its occurrence, this is obviously incorrect.

On passing the smoke of the burning *Attalea* nuts through a condenser, condensation occurs and two layers of liquid are found in the receiver, one colourless and limpid, the other dark brown and oily. If these are separated by means of a pipette, or with a moistened filter paper, and analyzed, the former is found to consist mainly of acetic acid, and the latter of creosote and traces of pyridine derivatives.

<sup>1</sup> Ernst, Trinidad Bulletin, vol. iii. p. 235.

On adding acetic acid to the crude latex of *Hevea* coagulation occurs immediately. This process of smoking the latex may then be classed with those mentioned by De Bary under the heading of treatment with acids. As other examples, the preparation of Lagos rubber from the latex of *Ficus Vogelii* (Miq.), in which case lime-juice is added<sup>1</sup>, and Helfer's process of adding acetic acid to the latex of *Artocarpus Chaplasha* (Roxb.)<sup>2</sup>, may be quoted.

It is worthy of note that the latex of *Hevea brasiliensis* is in itself alkaline, and that the addition of a solution of ammonia preserves it indefinitely from spontaneous coagulation. The addition of alkalies bring about coagulation, however, in the latex of *Castilloa elastica*. In Mexico and Nicaragua, where this tree abounds, a decoction is made of the stems of the Moonflower, *Ipomoea bona-nox* (*Calonictyon speciosum* [Choisy]), and added to the latex<sup>3</sup>. The alkaline properties of this extract are well known to the native Indians, who frequently employ it in the manufacture of soap. The latex has an acid reaction towards litmus-paper, and the addition of acids does not cause coagulation.

Another method of clotting latex is to add an excess of common salt. This method is almost invariably applied in the case of *Hancornia speciosa* (Gomez) to produce the 'mangabeira' rubber. It is also reported to have been employed at times to coagulate the latex of species of *Hevea* and *Manihot Glaziovii* (Muell. Arg.).

Coagulation may also be brought about by boiling the latex, as, for example, in the preparation of 'balata' from *Mimusops globosa* (Gaertn.) in Venezuela and Trinidad.

There are several other methods in general use besides the few that have been quoted, and many others have been suggested from time to time<sup>4</sup>.

<sup>1</sup> Kew Bulletin, 1890, Art. 142, p. 89.

<sup>2</sup> Watt's Dict. Economic Products of India, vol. iv. p. 343.

<sup>3</sup> Belt, Naturalist in Nicaragua, p. 33.

<sup>4</sup> For a complete account see *Le Caoutchouc et la Gutta-percha*, Seeligman, Lamy, and Falconnet, Paris 1896.

As the rubber exists in particles in the latex, it seemed possible that the centrifugal method of separation might be adopted in examining the phenomena of coagulation. A modified form of the ordinary centrifugal milk-tester was therefore designed capable of being rotated some 6,000 times per minute.

The latex was taken directly from the trees, strained through wire-gauze to remove any pieces of bark, and then, if very thick, diluted to about the consistency of thin cream. The first experiments were made with the latex of *Castilloa elastica*. After centrifugalizing for from three to four minutes, the rubber-particles completely separated as a thick, creamy, white layer, from the deep brown solution containing tannic acid in which they had been suspended. This layer was taken off, shaken with an excess of water to thoroughly wash it, and again separated. The separated particles were then shaken with water so as to form an emulsion, and alkalis were added. No coagulation now occurred, even though the mixture was allowed to stand for several days. The particles could however be brought into a solid mass by pressure, by gently heating, or by drying off the water with a porous tile.

So prepared, the rubber formed a pure white mass, without any trace of its usually characteristic smell. On exposure to the air for several days the surface gradually became brown, probably owing to oxidation.

The percentage of rubber in the latex was estimated at the same time by separating 50 c.c. The weight of the dry substance was 12.5 grammes, which, as the specific gravity of *Castilloa elastica* latex is practically 1.0, gives a yield of 25 per cent.

On treating the latex of *Hevea brasiliensis* in the same way for a slightly longer time a similar separation occurred. The same purely physical means as those employed in the case of the separated *Castilloa* rubber-particles caused them to coalesce to form a solid mass, while the addition of acetic acid and the action of the smoke of burning urucuri nuts had no effect.

The yield of rubber, estimated as before, was from 28 to 30 %. The latex of *Manihot Glaziovii* also separated readily and gave results completely parallel with those mentioned above. This latex is interesting, as it is readily clotted by churning. A soft spongy clot is formed in a few minutes containing in its meshes the greater part of the solution in which the rubber-particles were suspended. If this clot is cut into slices while still soft, and pressed between sugar-cane crushers, or in a heavy press, the bulk of the solution is extracted and a fairly pure rubber is found. On drying it does not give off the putrid smell characteristic of the ordinary Ceará 'scrap.'

Other latices can also be clotted by churning, but the process is a long one.

The latex of *Hancornia speciosa* and of *Mimusops globosa* gave similar results on centrifugalizing. In the case of the latter the pink colouring-matter which characterizes 'balata' was found to have separated as a thin layer at the bottom of the tubes.

*Artocarpus incisa* (Linn.) contains a very viscous latex employed by the Brazilians as a bird-lime or as a substitute for glue. When diluted and centrifugalized it separates readily, giving a creamy white layer which dries to a resinous mass somewhat resembling gutta-percha. At the ordinary temperature this is quite hard and brittle, but if the temperature is raised slightly it becomes plastic, and at the temperature of boiling water it is soft and excessively sticky. The substance is soluble in carbon bi-sulphide, and insoluble in alcohol and water.

*Urostigma gamelleira* (Miq.<sup>1</sup>) yields a similar substance of a chocolate-brown colour.

We thus see that the mere action of centrifugal force effects the separation of rubber; and from the failure of the processes usually employed, involving the use of chemical reagents, to bring about the clotting of the separated and washed rubber-particles, we must infer that no chemical change occurs in the

<sup>1</sup> Mart. Fl. Bras. 4. 1. 93, *Ficus doliarum* of Mart. Sys. Mat. Med. Bras. p. 88.

rubber itself, and that the cause of coagulation must be looked for in the medium in which they are suspended.

From our knowledge of the constitution of latex it is evident that the proteids are the most likely substances to cause this when treated with acids, alkalies, excess of salt, &c., and when boiled.

Unfortunately few latices have as yet been examined for their proteid constituents, chiefly on account of the difficulty of obtaining them in their natural condition in European laboratories, owing to their coagulating and undergoing decomposition during the journey from the tropics<sup>1</sup>. The investigations so far made prove the presence of albumin, globulin, albumose, and peptone in several rubber-yielding latices<sup>2</sup>. In the clear solution left after separation of the rubber-particles the xanthoproteic reaction always showed the presence of proteid matters, but under the circumstances it was impossible to identify them.

Now albumins are characterized by the coagulation of their solutions on heating, especially in the presence of dilute acids, and globulins by their ready precipitation with the salt-solution and their coagulation on heating.

Thus when the latex of *Hevea brasiliensis* is held in the smoke of the burning urucuri nuts, the albumin it contains<sup>3</sup> is clotted by the action of heat in the presence of dilute acetic acid.

The globulin of *Manihot Glaziovii* latex coagulates on heating when the temperature rises to 74–76° C.<sup>4</sup>

The acid latex of *Castilloa elastica* contains an acid albumin, which on neutralization forms a gelatinous precipitate.

These coagula on forming gather up the rubber-particles (and probably starch-grains also, in the case of starch-containing latices) in the same way as the white-of-egg gathers

<sup>1</sup> This does not apply to the latex of *Mimusops Globosa*, or *Hancornia speciosa*, both of which may be kept for months without undergoing any change.

<sup>2</sup> J. R. Green, Proc. Roy. Soc. 1886, p. 28.

<sup>3</sup> Faraday—see *Le Caoutchouc et la Gutta-percha*.

<sup>4</sup> J. R. Green, *ibid*.

up particles in suspension when clotted for the purpose of clearing jellies. We may even push the old analogy of blood and latex further, and compare the formation of a rubber-clot, in many cases, to the formation of a blood-clot, the rubber-particles being bound together by coagulated proteids in the same way as the blood-corpuscles are bound together by fibrin. In this case, however, we must remember that the rubber-particles, owing to their being sticky bodies unprotected by any external film, as *e.g.* the fat-particles of milk are, are capable of aggregating together of their own accord to form a solid mass.

Rubber then, as now prepared, contains among other substances proteid matters. To these must be ascribed the well-known 'fermentative change' which causes a considerable loss by converting the solid blocks of rubber into a foul-smelling spongy substance. In the Pará rubber the creosote, absorbed from the smoke of the burning nuts, acts as an antiseptic and prevents this proteid decomposition<sup>1</sup>.

To test for the coagulated proteids is not an easy matter; continued boiling with a concentrated solution of caustic potash will however extract small quantities of alkali-albumin. 'Balata' gives good results most readily. On extraction with caustic potash a flocculent precipitate is obtained, which is readily soluble in dilute nitric acid, and is reprecipitated on the addition of alkalies. Boiling precipitates it either in acid or alkaline solutions, and it gives no precipitate with acetic acid and potassium ferro-cyanide. The proteid is thus identical with the albumose described by Green from the latex of *Mimusops globosa*.

<sup>1</sup> Cf. the smoking of fish &c. for preserving purposes.

