

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. XI. CONSTITUENTS OF THE MILLED RUBBER HYDROCARBON

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL

RECEIVED APRIL 22, 1932

PUBLISHED AUGUST 5, 1932

The tenth paper of this series¹ has shown that *unmilled* pale crepe rubber contains a single "sol" component, which constitutes more than one-half of the specimen, and a continuous series of undefined "sol" portions amounting to about 20% of the specimen. These results have been obtained by a fractional precipitation from a benzene-alcohol mixture.

The same method of investigation has now been applied to *thoroughly milled* pale crepe rubber, and the present paper shows that the whole specimen is made up of a continuous series of undefined "sol" components, in undefined proportions.

Procedure.—Pale crepe rubber was milled for one hour on cold rolls. A 250-g. specimen was dissolved in benzene, and fractionated into primary cuts, by the method described.¹ Although the principle of fractionation remained unchanged, minor experimental details were altered, as follows.

Milled rubber is much more soluble in a given benzene-alcohol mixture than unmilled rubber. To illustrate: the s. p. p.'s¹ of the rubber specimen used, before and after milling, were 35.4 and 27.7°, respectively. Consequently, in order to be able to carry out the fractionation at a convenient temperature, *viz.*, about 40°, the solvent was made richer in alcohol than previously reported. In all cases, the length of time allowed for separation was extended to fourteen hours. Chilling out was accomplished by letting the solutions stand (under vacuum) in a refrigerator at about -10° for six hours. Since the fractions obtained from milled rubber did not precipitate sharply from an alcohol-benzene mixture, the experimental precipitation point could not be duplicated closer than ±0.2°.

Table I shows the results of the primary fractionation.

TABLE I
PRIMARY FRACTIONATION OF 250 G. OF MILLED CREPE RUBBER

| Fractions | Amounts, g. | Standard precipitation point (s. p. p.) in degrees | % based on 233.4 g. | |
|----------------|-------------|--|---------------------|--------|
| A ₀ | 36.4 | 23.2 | 15.6 | } 81.2 |
| A ₁ | 66.4 | 23.4 | 28.4 | |
| A ₂ | 68.5 | 24.3 | 29.3 | |
| A ₃ | 30.3 | 24.9 | 13.0 | |
| A ₄ | 24.5 | 24.9 | 10.5 | |
| B | 7.3 | Not obtained | 3.1 | |
| Total | 233.4 | | 99.9 | |
| Losses | 16.6 | | | |

Fractions A₁ to B inclusive were obtained by the previously described method of operation.

¹ Midgley, Henne and Renoll, *THIS JOURNAL*, **54**, 3343 (1932).

Fraction A₀ was found in the supernatant liquid remaining after the separation of A₁, in the following manner: the liquid was cooled to -10° and kept at that temperature until the lower half of the mixture (containing the rubber and benzene) had frozen. The upper half containing the so-called "resins" was decanted, and the rubber was precipitated from the benzene of the lower half with acetone.

The reported losses include an estimated amount of 12.5 g. of "resins," soluble in alcohol. Hence the actual losses amount only to 4 g., *viz.*, about 1.5%.

The tabulated results appear on the chart, where the percentages of rubber are plotted against the s. p. p. They are represented by the solid line. The length of the abscissa measures the size of fractions A₀ to A₄ inclusive. The s. p. p. of fraction B could not be determined, because it was insoluble. It was extracted with boiling benzene for several days, but the solvent removed only 1.1 g. of rubber. This B fraction was a nearly white, fibrous mass with a nitrogen content of 9.4%.

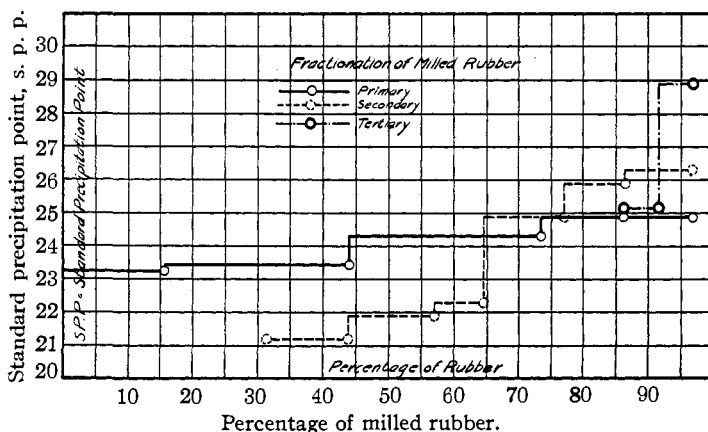


Fig. 1.—Fractionation of milled rubber.

Each of the primary cuts from A₁ to A₄, (*viz.*, 81.2% of the rubber recovered) was refractionated. A₃ and A₄ were combined because they had the

TABLE II
SECONDARY FRACTIONATION OF FRACTIONS A₁ TO A₄, *viz.*, 81.2% OF THE RUBBER RECOVERED

| Fractions | Amount, g. | S. p. p. in degrees | % based on 81.2% = 189.7 g. | |
|-----------------------|------------|---------------------|-----------------------------|------|
| A ₁ | Top | 28.6 | 21.2 | 12.2 |
| | Bottom | 27.2 | 24.9 | 11.6 |
| A ₂ | Top | 31.4 | 21.9 | 13.4 |
| | Bottom | 24.5 | 25.9 | 10.5 |
| A ₃₋₄ | Top | 17.9 | 22.3 | 7.7 |
| | Bottom | 23.7 | 26.3 | 10.2 |
| Total recovered | 153.3 | | 65.6 | |
| Remaining in solution | 36.4 | | 15.6 | |
| Total | 189.7 | | 81.2 | |

same s. p. p. The refractionation was carried out at 50°; the results appear in Table II, and on the diagram.

The 36.4 g. of rubber remaining in solution could have been recovered in the manner used for A₀, in the primary fractionation; but this was considered superfluous for the present research.

The tables and diagram show that there is no indication of a single component, present in large proportion.

The fraction called "A₃₋₄ bottom," in Table II was then refractionated, to give the results shown in Table III.

TABLE III
TERTIARY FRACTIONATION OF A₃₋₄

| Fractions | Amount, g. | S. p. p. in degrees | % based on 10.2% fractionated |
|------------------------|------------|------------------------|----------------------------------|
| A ₃₋₄ { Top | 9.5 | 25.1 | 4.7 |
| { Bottom | 11.3 | 28.9 | 5.5 |
| Total | 20.8 | | 10.2 |

The efficiency of the separation method is illustrated as follows: a 10-g. specimen (s. p. p. 35°) obtained from *unmilled* rubber and a 10-g. sample (s. p. p. 28.9°) obtained from the fraction called [A₃₋₄, bottom], in Table III, were dissolved in the same batch of benzene, and separated by fractional precipitation. A single fractionation yielded 11.5 g. of s. p. p. 34.9° and 85. g. of s. p. p. 28.5°. This experiment demonstrates that the fractionation method separates with ease individual components.

The appearance of the various cuts was as follows. The fractions with low s. p. p. were almost colorless, transparent and very tacky. The higher s. p. p. fractions were less tacky, and they were yellow; in spite of the color, they did not have the appearance of oxidized rubber.

Conclusion.—Fractional precipitation shows that *milled* rubber is constituted of a continuous series of undefined components. Milling degrades the components of *unmilled* rubber into materials of lower s. p. p. without producing a single predominating component.

Summary

The composition of *milled* rubber has been investigated by a method based on fractional precipitation from a benzene-alcohol mixture. This has shown that milled rubber is made of a continuous series of undefined components, without a single predominating individual. The same method had previously shown that one single individual constituted more than one-half of unground rubber.