

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

NATURAL AND SYNTHETIC RUBBER. VII. FRACTIONAL PRECIPITATION OF NATURAL RUBBER

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Crude rubber is an indeterminate mixture of several substances. The constituents of the mixture can be classified as "resins," soluble in acetone, rubber hydrocarbon (C_6H_8) $_n$, soluble in benzene and insoluble "proteins."

The so-called "resins" are conveniently removed by a Soxhlet extraction with acetone. This treatment leaves behind a mixture of the rubber hydrocarbons and the "proteins." The latter can be separated by a variety of methods, which are well summarized by Fisher.¹ However, none is entirely satisfactory, because the methods based on a physical property effect only an imperfect separation, while chemical methods injure one or both constituents.

This paper presents a method of separation based on the progressive precipitation of natural rubber from a mixture of alcohol and benzene by slow cooling. Within certain limits, a system containing definite amounts of natural rubber, benzene and alcohol is homogeneous above a definite temperature, its critical temperature of solution. This critical point is best determined by allowing a hot mixture of rubber, alcohol and benzene to cool and reading the temperature at which a sudden increase of turbidity occurs. The determination can be duplicated within 0.3°.

When a mixture of rubber, alcohol and benzene is heated to a temperature higher than its critical point, until it has become completely clear, and is then allowed to cool to a temperature about 1° below its critical point, a certain amount of gel collects at the bottom of the container, while the supernatant liquid becomes transparent. The gel is a mixture of rubber and nearly all of the "protein." The supernatant liquid contains rubber practically free of "protein"; it can be decanted and yields its rubber content upon cooling or by alcohol addition. If a very pure hydrocarbon is desired, the procedure is repeated.

To systematize the preparation of nitrogen-free rubber, the diagrams given in Figs. 1, 2 and 3 have been experimentally determined. The procedure used was the customary one for the determination of critical temperatures of solution. Figure 1 refers to crude crepe rubber, alcohol and benzene; Fig. 2 refers to pure rubber hydrocarbon, alcohol and benzene; and Fig. 3 refers to synthetic rubber (sodium rubber), alcohol and benzene. The diagrams show that the isotherms have generally the same trend; they are located farther to the right in Fig. 3 than in Fig. 2, and in Fig. 2 than in Fig. 1.

¹ H. L. Fisher, *Chem. Reviews*, 7, 51 (1930); *J. Chem. Education*, 8, 7 (1931).

The use of the diagrams is almost self-evident. A system containing 2.0% of natural rubber, 23.1% of alcohol and 74.9% of benzene is found to have a critical temperature of 43.0°. Such a system is represented by the circle *A* on Fig. 1. When this system is kept at 43.0°, it separates into two phases. The gel phase precipitates; it is a mixture of rubber hydrocarbon, "protein" and solvent, with a ratio benzene-alcohol larger than that of the system taken as a whole. The supernatant liquid contains

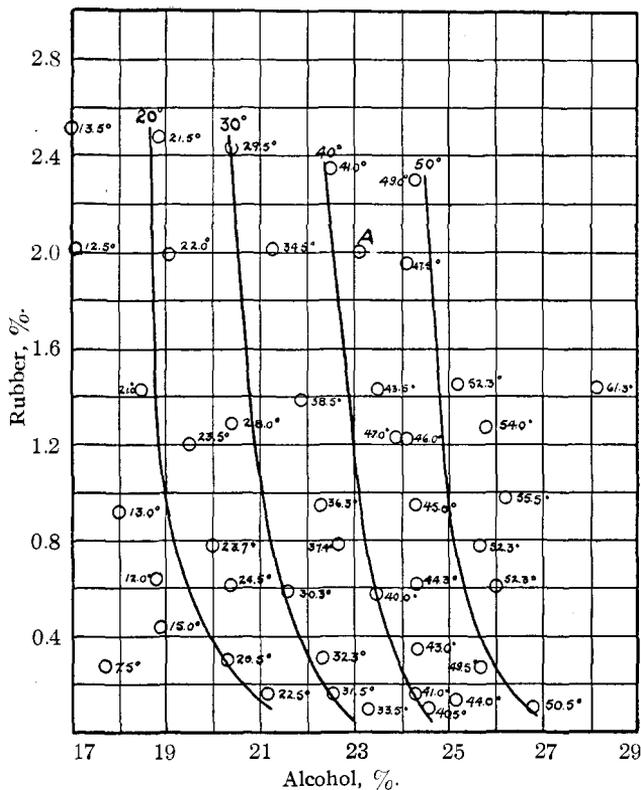


Fig. 1.

rubber practically free of nitrogenous matter, dissolved in benzene-alcohol, and in this liquid the ratio benzene-alcohol is smaller than in the system taken as a whole. The composition of the supernatant liquid is represented by the circle *B*, on Fig. 2; it corresponds to 0.55% of nitrogen-free rubber, 30.7% of alcohol and 68.75% of benzene. When such a system is cooled to 41°, it becomes heterogeneous and when it is cooled to 35°, it retains less than 0.1% of dissolved rubber.

Experimental Procedure

Two hundred and fifty grams of crepe rubber with a nitrogen content of 0.25% was dissolved in 808 g. of benzene, heated to about 50°. A hot mixture of 4500 cc. of

absolute alcohol and 1400 cc. of benzene was added slowly, with constant stirring, until complete solution was obtained. The critical temperature, determined on a 50-cc. sample, was 43.0°. The mixture was then held at 42.0° in a thermostat, for one hour. At the end of this period, the mixture was no longer homogeneous, but consisted of a completely settled gel phase and a clear supernatant liquid. This liquid was decanted, then cooled in an ice-bath, and yielded 52.9 g. of rubber hydrocarbon, hereafter designated as A₁. After removal of the A₁ rubber, the liquid was warmed and poured back on the gel phase. By warming and stirring, the gel phase was caused to dissolve, and a clear solution was then obtained. A sample of this solution exhibited a critical point of 43.5°. Consequently, the solution was placed in a thermostat regulated at 42.5° for one hour, and the above procedure was repeated. This time 30.5 g. of rubber hydrocarbon was obtained, called A₂ hereafter. Two repetitions of these operations yielded fractions A₃ and A₄.

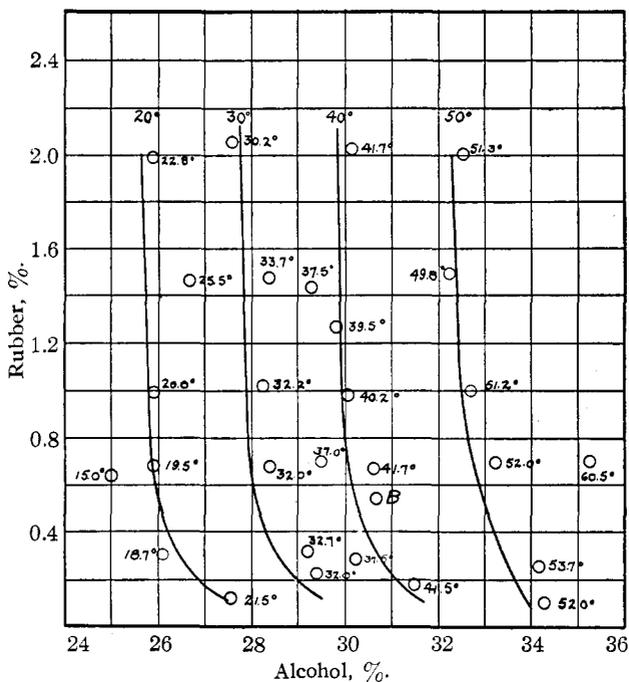


Fig. 2.

After the fraction A₄ had been collected, it was found that the gel phase would no longer dissolve completely in the alcohol-benzene mixture, even when the solvent was brought to its boiling point. Consequently, the insoluble matter was separated from the solvent; the solvent, upon cooling, yielded a fraction called A₅. Finally, the insoluble matter was extracted in a Soxhlet extractor with benzene. The material obtained from the benzene was called A₆, while the insoluble matter was called B. The various fractions were then analyzed for nitrogen. They were decomposed according to the usual Kjeldahl procedure.² After the addition of alkali, three 50 cc. portions were

² Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1927, Vol. II, p. 1593.

distilled, nesslerized, and compared with a set of standard tubes. Blanks were run on all reagents; ammonia-free water was used throughout. Fraction B was decomposed by the usual Kjeldahl method, but the distillate was received in standardized hydrochloric acid, whose excess was titrated with standard sodium hydroxide.

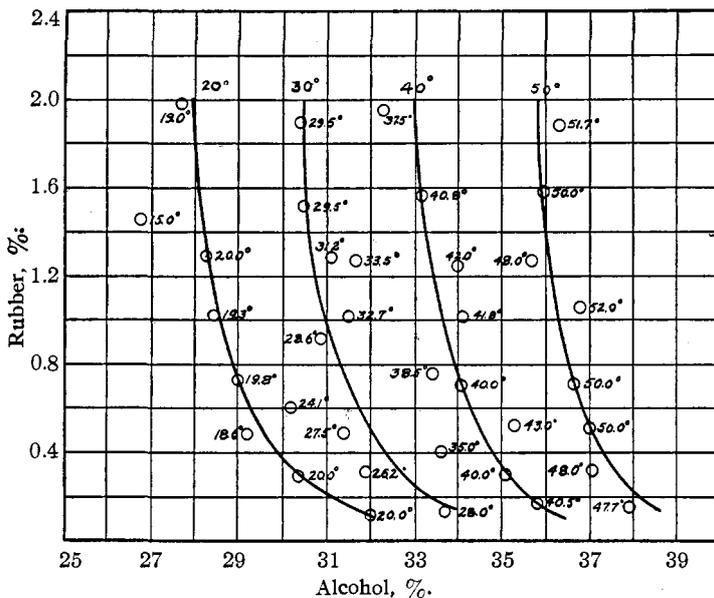


Fig. 3.

Table I summarizes the amounts of each fraction obtained, their critical temperature in the mixture alcohol-benzene described, and their nitrogen contents, by weight.

TABLE I

	FIRST FRACTIONATION						B
	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	
Grams	52.9	30.5	26.6	23.6	24.8	38.9	11.6
Crit. temp.	43.0	43.5	44.0	44.7	45.5
Nitrogen, %	0.026	0.033	0.044	0.125	0.142	0.160	4.21

After the first fractionation was completed, fractions A₁, A₂ and A₃ were combined, dissolved in a mixture of alcohol-benzene, and the whole procedure was repeated. Five successive fractions were thus obtained, as during the first fractionation, and they were analyzed for nitrogen. The results are reported in Table II.

TABLE II

	SECOND FRACTIONATION				
	A ₁₋₁	A ₁₋₂	A ₁₋₃	A ₁₋₄	A ₁₋₅
Grams	28.1	17.1	13.8	16.0	6.4
Nitrogen, %	0.000	0.021	0.028	0.048	0.100

Fractions A_2-2 , A_2-3 and A_2-4 were combined, dissolved in alcohol-benzene, and refractionated as previously. The results were as shown in Table III.

TABLE III
THIRD FRACTIONATION³

	A_2-1^a	A_2-2	A_2-3
Grams	20.8	6.1	7.8
Nitrogen, %	0.000	0.011	0.015

^a The carbon and hydrogen contents of Fraction A_2-1 were determined by micro-combustion. Calcd.: C, 88.17; H, 11.83. Found: C, 88.28, 88.32; H, 11.74, 11.74. This indicates the complete absence of oxygen.

The rubber hydrocarbon obtained by cooling the supernatant liquid has, so far, been referred to as "nitrogen-free rubber." When freshly prepared, this material bears a strong resemblance to the so-called " α -rubber" of Pummerer⁴ and it probably contains little if any " β -rubber." During the course of the fractionation, the " β -rubber" seems to concentrate in the fractions rich in protein.

Summary

Temperature-concentration diagrams are given of the systems natural rubber-alcohol-benzene, pure rubber-alcohol-benzene and synthetic rubber-alcohol-benzene. A method based on these diagrams is given for the separation of nitrogen-free rubber hydrocarbon by fractional precipitation of natural rubber from a mixture of alcohol and benzene.

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³ A point of interest in the behavior of the rubber hydrocarbon was discovered in the course of this fractionation. For example when A_2-2 was dissolved in benzene and precipitated with acetone, only 14.1 g. was recovered. The other 3 g. remained in the turbid solution, irrespective of the amount of acetone added. The addition of water, however, caused precipitation. Likewise, the addition of a small amount of acetic acid would cause precipitation, seemingly at a different *PH*. The residual three grams recovered by the addition of water was nitrogen-free.

⁴ H. L. Fisher, *Chem. Reviews*, **7**, 65 (1930).