

calcium chloride as a catalyst. The extent of reaction was determined by titrating the hydrogen chloride evolved, and the mixtures of butenes were analyzed by determining for their bromides, the densities and the reaction rates with potassium iodide in methanol.

In the absence of a catalyst, the decompositions of 1-chlorobutane at 550° and of 2-chlorobutane at 500° are homogeneous gaseous reactions. 1-Chlorobutane gave only 1-butene, but 2-chlorobutane gave a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene. The composition of the product from 2-chlorobutane was the same at 450, 500 and 550°.

In the presence of the catalyst at 450°, both chlorobutanes gave mixtures of all three butenes, there being relatively little 1-butene, however.

It is unknown whether the butenes rearranged in contact with the catalyst, or whether the catalyst caused the reaction to go in such a way that principally the 2-butenes were formed directly from the chlorobutanes.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]
**NATURAL AND SYNTHETIC RUBBER. X. CONSTITUENTS OF
THE RUBBER HYDROCARBON**

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

RECEIVED APRIL 6, 1932

PUBLISHED AUGUST 5, 1932

It has been shown in the seventh paper of this series,¹ that nitrogen-free rubber hydrocarbon can be prepared by fractional precipitation of natural rubber from a mixture of alcohol and benzene. This fractionation method is now applied to the rubber hydrocarbon itself to determine whether it is a single individual or a mixture of various components, and, in the last event, to isolate these constituents.

Some criterion is needed to follow the progress of any fractionation. The measurement of a well-defined physical property is best. In the present research, use is made of a standardized precipitation point (abbreviated to s. p. p. in the text), which is defined as follows. The standard precipitation point of a rubber specimen is the temperature at which a sudden increase of turbidity occurs in a slowly cooled solution of 0.85% rubber, 28.55% absolute alcohol and 70.60% benzene. The manner in which the s. p. p. is determined is described in the experimental part of this paper.

Procedure

Two hundred and fifty grams of crepe rubber was dissolved in benzene and fractionated into primary cuts. The method of fractionation was a duplication of that reported in the seventh paper. The technique, however, was improved to prevent alteration of the specimen by light or oxygen. The flasks containing the rubber solu-

¹ Midgley, Henne and Renoll, *THIS JOURNAL*, **53**, 2733 (1931).

tions were always completely covered with black cloth, frequently evacuated and filled with carbon dioxide. The solvents were removed by suction at room temperature. The rubber samples were stored in a bed of solid carbon dioxide. They were allowed to reach room temperature and exposed to atmospheric oxygen only during the short time required to take a sample for s. p. p. determinations.

Table I reports the results of this primary fractionation.

TABLE I
PRIMARY FRACTIONATION OF 250 G. OF CREPE RUBBER

Fractions	Amount, g.	Standard precipitation point (s. p. p.)	% based on 233.6 g.	
A ₁	44.8	33.0°	19.2	} 81.5%
A ₂	38.8	33.0°	16.6	
A ₃	46.5	34.9°	19.9	
A ₄	28.2	35.0°	12.1	
A ₅	31.9	35.3°	13.7	
B	43.4	Not obtained	18.6	
Total	233.6		100.1%	
Loss	16.4			

The loss of rubber during this separation amounts to 6.6% of the original 250-g. sample. This 16.4-g. loss includes an estimated amount of 12.5 g. of so-called "resins."

The tabulated results are shown on the chart, where the percentages are plotted against the s. p. p. They are represented by the solid line; the length of the horizontal lines measures the size of the fractions from

TABLE II
SECONDARY FRACTIONATION OF FRACTIONS A₁ TO A₅, *viz.*, 81.6% OF THE RUBBER HYDROCARBON

Fractions	Amounts, g.	S. p. p.	% based on 190.2 g. = 81.5%
A ₁ Top ^a	11.0	32.1	5.4
Bottom ^a	29.8	34.2	14.7
A ₂ Top	9.8	32.5	4.8
Bottom	24.2	34.2	11.9
A ₃ Top	6.7	31.2	3.3
Bottom	30.7	34.8	15.1
A ₄ Top	4.2	31.2	2.1
Bottom	19.7	35.0	9.7
A ₅ Top	3.8	31.5	1.9
Bottom	25.7	35.1	12.6
Total	165.6		81.5
Loss	24.6		

The losses are almost entirely due to sampling for s. p. p. determinations.

^a "Bottom" is the rubber which settles out from a benzene-alcohol mixture held at 1° below its precipitation point. "Top" is the rubber chilled out from the supernatant liquid.

A₁ to A₅, in percentage of recovered rubber. Fraction B could not be shown on the chart since its s. p. p. could not be determined. It amounted to 18.6% of the total, and consequently the curve on the chart stops short of 100% by this amount, viz., at 81.4%.

Each of the primary cuts, from A₁ to A₅ inclusive, amounting to 81.5% of the rubber recovered, was then resubjected to the same fractionation method. The only experimental detail altered was the lengthening of the time allowed for complete separation to fourteen hours. The results are given in Table II. These results appear on the chart.

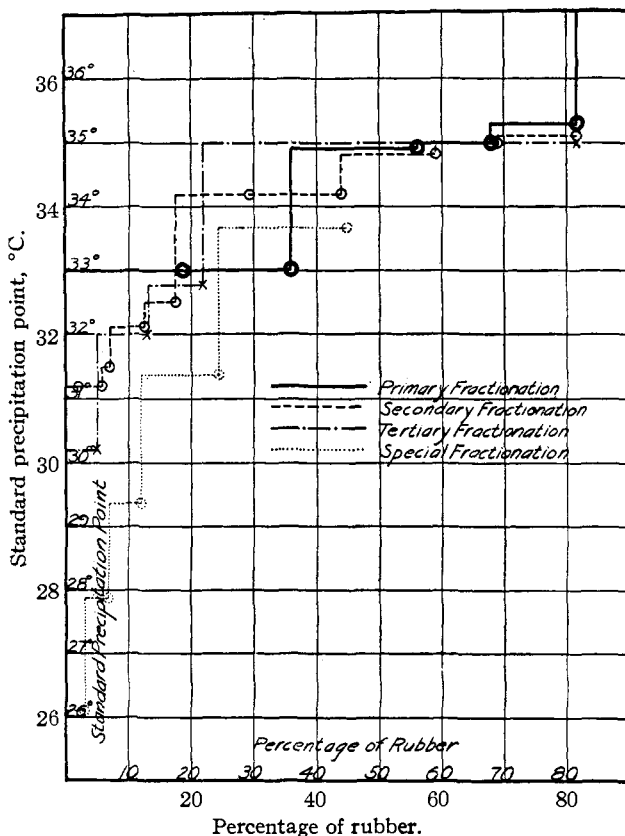


Fig. 1.

A third fractionation was then accomplished as follows. Cuts with an s. p. p. lower than 33° were put together, while cuts with an s. p. p. higher than 33° were united. The two fractions thus formed were separately fractionated as for the secondary fractionation, and the results shown in Table III were obtained. These results appear on the chart.

The third fractionation is only slightly better than the second one.

TABLE III

TERTIARY FRACTIONATION OF FRACTIONS A₁ TO A₆, OR 81.6% OF RUBBER HYDROCARBON

Fractions		Amounts, g.	S. p. p.	% based on 190.2 g. = 81.5%
Sum of tops	Top	8.5	30.2	4.7
	Bottom	15.7	32.8	8.8
Sum of bottoms	Top	14.4	32.0	8.1
	Bottom	107.3	35.0	59.9
Total		145.9		81.5
Loss		19.7		

The losses are almost entirely due to sampling.

It indicates that more than 50% of the initial material is no longer fractionated, *viz.*, the cut with an s. p. p. of 35°.

Since small amounts of the lower fractions were lost by solubility in the alcohol-benzene mixture, it was decided to investigate this lower portion by a somewhat modified technique.

A solution containing two hundred and fifty grams of crepe rubber was prepared and therefrom fractions A₁ and A₂ were obtained as before. After discarding the remainder of the rubber, these two fractions, A₁ and A₂, were redissolved in their original solvent, thus avoiding the loss of portions which were so soluble in the alcohol-benzene mixture that they could not be completely precipitated by chilling. These combined fractions were then treated by a procedure identical to the primary fractionation, and a fraction B₁ collected and stored. The supernatant liquid was then chilled. This precipitated some more rubber; one-half of the chilled liquid was then decanted and discarded. The chilled precipitate was then redissolved by warming in the retained half of the liquid. The whole procedure was repeated to give fractions B₂, B₃, etc. The results of this special fractionation are listed in Table IV and represented on the diagram.

TABLE IV

SPECIAL FRACTIONATION

Fractions	Amounts, g.	S. p. p.	% based on a total of 233 g. as 100%
B ₁	48.4	33.7	20.7
B ₂	29.2	31.4	12.5
B ₃	12.0	29.4	5.1
B ₄	9.4	27.9	4.0
B ₅	6.5	26.1	2.8

Results.—The diagram and the tables show that the present procedure separated a single component, characterized by an s. p. p. of 35.0%. The amount of this component exceeded 55% of the original rubber. A quantity of less than 20% of the original rubber was separated as a less soluble fraction, and was not investigated further; it probably still con-

tained an appreciable amount of the component s. p. p. 35°. The highly soluble part of the rubber, amounting to about 25%, was fractionated; it failed to reveal the presence of an important constituent, except more of the component s. p. p. 35°.

There was quite a difference in appearance between the high and low s. p. p. fractions. The rubber of s. p. p. 35.0° was very tough, non-tacky, and somewhat opaque. The lower fractions were soft, but white in color, showing no apparent signs of oxidation. The insoluble portion was yellow, in its fresh state, and darkened on standing. It had little elasticity and resembled horn more than rubber.

Conclusion.—It is therefore concluded that the original rubber specimen consisted of, (1) a soluble portion containing several individuals and totaling more than 20% of the specimen, (2) a single soluble component present in excess of 50% of the total, and (3) an insoluble portion amounting to less than 20% of the total.

Discussion.—The origin of the more soluble portions of rubber is obscure. Staudinger² suggests the possibility of forming such a portion by partial oxidation of the original molecule. Since precautions were taken to avoid oxidation during the course of the fractionation, it is suggested that the more soluble fractions were generated during the washing and sheeting of the original coagulate.

The present results bear a definite relation to two controversial points.

(1) Staudinger² has advanced the view that rubber is made up of a series of polymer homologs of many different lengths. It is now shown that though such a series may exist, to a limited extent, in the more soluble portions of rubber, the main constituent is one definite polymer.

(2) It is generally felt that in order to obtain a good grade of soft rubber goods, a two-phase system is required, implying that both sol and gel rubber should be present. Sol rubber, separated from gel, has been satisfactorily vulcanized, but the completeness of the separation was questioned. It is now found that pure sol rubber of s. p. p. 35° does give a satisfactorily vulcanized material (500% elongation and 4100 lb. tensile strength). That this sol rubber is of high purity is practically certain.

Experimental

Determination of the Standard Precipitation Point.—A 1.288-g. sample of the rubber (free from solvent) is placed in a 250-cc. Erlenmeyer flask. One hundred cc. of C. P. benzene is added. The flask is set away in the dark, under carbon dioxide, until complete solution is obtained. To this solution, warmed to about 50°, is added a hot mixture of 27 cc. of benzene and 56 cc. of absolute alcohol, and the whole is stirred and intermittently warmed until entirely clear. A calibrated thermometer reading tenth degrees is placed in it and it is allowed to cool. When the mixture becomes suddenly turbid, the temperature is read. This is the experimental precipitation point. It is

² Staudinger and Bondy, *Ann.*, [2] 488, 153 (1931).

reproducible to $\pm 0.1^\circ$. After checking the point, the flask is equipped with a bent tube carrying a water jacket on its downward branch. This branch delivers into a 250-cc. receiver cooled in ice; the receiver is in turn connected to a second one cooled in a mixture of carbonic snow and acetone, to ensure the recovery of all solvents during distillation. Atmospheric moisture is kept out of the system by means of a calcium chloride tube. While passing a slow stream of purified carbon dioxide through the system, the solvents are distilled with a steam-bath. The distillate is weighed, and its refractive index is measured in a Pulfrich refractometer, at 20.0° . From a previously constructed curve, the composition of the distillate is read. The rubber sample is weighed as soon as the distillation is finished, and its increase in weight, regarded as benzene, is added to the amount of benzene in the distillate. The percentages of alcohol and benzene are thus determined with accuracy; they can be duplicated to 0.1%. By means of the chart, Fig. 2, paper VII, the experimental precipitation point is then corrected to standard conditions, *viz.*, 28.55% alcohol and 0.85% rubber. This is the s. p. p. Including experimental errors and corrections, the s. p. p. determination is correct within $\pm 0.2^\circ$.

Summary

1. Fractional precipitation has been used to determine and isolate the constituents of the rubber hydrocarbon.
2. A "standard precipitation point" has been devised and its use advanced as a physical constant of rubber.
3. The presence of a single component, amounting to more than 50% and characterized by a standard precipitation point of 35° , has been demonstrated.
4. The presence of highly soluble portions, of indeterminate s. p. p., has been shown.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

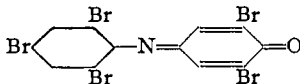
THE OXIDATION OF SYMMETRICAL TRIBROMOANILINE BY CHROMIC ANHYDRIDE IN ACID SOLUTION. II. MECHANISM¹

BY W. H. HUNTER AND CARYL SLY

RECEIVED APRIL 11, 1932

PUBLISHED AUGUST 5, 1932

In some unpublished work performed in this Laboratory by A. G. Mayers (now deceased), it was found that symmetrical tribromoaniline, dissolved in a mixture of acetic and dilute sulfuric acids, on oxidation with chromic anhydride gave a compound with the molecular formula $C_{12}H_4ONBr$, and the structural formula



¹ Abstracted from a thesis submitted by Caryl Sly to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.