

## THE COMPARISON OF VARIOUS CRUDE RUBBERS.\*

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The nature of the work outlined in this paper is merely a continuation and, perhaps, also a supplement in some parts of what others have done on crude rubber. Although much attention in rubber chemistry at the present time is being given toward obtaining a synthetic rubber that may equal raw rubber in quality, yet it would not be amiss to publish this paper as an aid to what the properties of a rubber are, towards obtaining a synthetic gum or rubber.

Rubber has been known in Europe since the days of Columbus. However, no investigation of rubber was undertaken until about the beginning of the nineteenth century. It is generally obtained from the process of coagulation of the latex contained in the laticiferous system of various species of tropical trees and shrubs.

Rubber, chemically, belongs to the class of hydrocarbons and is polyprene having the empirical formula  $(C_{10}H_{16})_x$ . The formula  $(C_{10}H_{16})_x$  gives an idea of the complexity of the molecule of rubber.

There are three sources of rubber:

## I. WILD RUBBER. II. PLANTATION RUBBER. III. SYNTHETIC RUBBER.

I. *WILD RUBBER*.—This comes from South and Central America, Asia, Africa and Australia. Their chief botanical orders are:

- (a) *Euphorbiaceæ*—*Hevea braziliensis* being the most important genus.
- (b) *Apocynaceæ*—Mostly African plants.
- (c) *Urticaceæ*—Tropical Asia, Mexico, South and Central America.
- (d) *Compositæ*—Shrubs being grown scientifically in California and South Arizona, called Guayule-Rubber.

II. *PLANTATION RUBBER*.—This is obtained from Ceylon, Dutch East Indies, Federated Malay States, Pacific Islands and Borneo. The tree *Hevea Braziliensis* is the tree grown exclusively in these regions.

III. *SYNTHETIC RUBBER*.—This has been the dream of many rubber chemists. It has been made by various means. During the World War, Germany made synthetic rubber, but it was not very good, due to its becoming rapidly oxidized. There are two setbacks against synthetic rubber coming on the market at present, *viz.*, its high cost of manufacture, and its poor grade compared with a good natural rubber.

At about the beginning of the nineteenth century, chemists became interested in rubber and its uses. The first problem in rubber confronting chemists at that time was its constitution. About 1860, G. Williams (1) isolated isoprene, the active constituent of rubber, and stated that isoprene could be polymerized to rubber. Williams' (1) view regarding the polymerization of isoprene was supported by Bourchardat (2) and Tilden, in 1882.

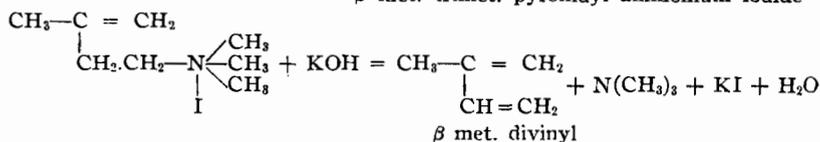
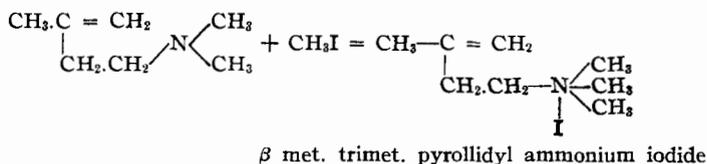
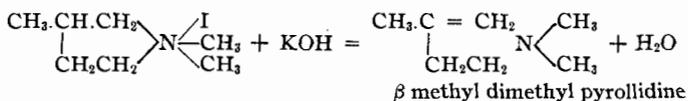
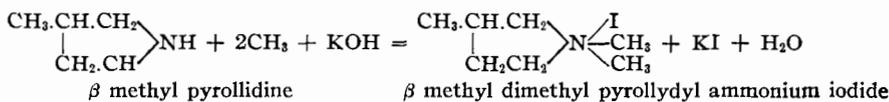
These earlier workers obtained isoprene by the destructive distillation of crude rubber. Hlasiwetz (3) in 1876 had obtained isoprene by the pyrolysis of turpentine. Weber (4) in 1894 also isolated isoprene from rubber, and he also did much toward forming a system of analysis for rubber.

Tilden (5) was about the first chemist to give isoprene the constitutional formula of  $CH_2=C(CH_3)-CH=CH_2$ ,  $\beta$  methyl isothylene (beta methyl divinyl). Euler (6) was able to produce  $\beta$  methyl divinyl synthetically and he showed it to be identical

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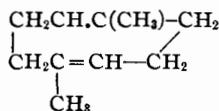
with isoprene. Euler's experiments were based on the reactions published by Ciamiciani and Magnagni. (7) Ciamiciani and Magnagni prepared divinyl from dimethyl pyrrolidyl ammonium iodide on treating it with potassium hydroxide. Euler transformed the beta methyl pyrrolidine into beta methyl divinyl as follows:



The following is the yield generally obtained by the earlier workers when working on rubber:

Isoprene	6.20%
Dipentene	46.20%
Higher boiling oils	43.80%
Carbonized residue	1.90%
Loss and mineral matter	1.90%
Total	100.00%

Harries (8) obtained by ozonizing natural Heves rubber, levulinic acid, and levulinic aldehyde. He concluded from these results that Heves rubber is a polymer of the di-isoprene 1-5 dimethyl cyclo octadiene 1.5.



The group  $\text{CH}_2\text{---C} = \text{CH}\text{---CH}_2\text{---}$  is the real unit which polymerizes to ring



complexes an unknown number of times. Advantage of this unsaturation is taken in the analysis of rubber, by the formation of addition products of bromine and chlorine.

Ostromislenski (9) describes his method of obtaining "rubber." He polymerized isoprene containing amylene or similar olefins, producing a sticky and soft rubber.

The samples of rubber used in this work are from Dutch East India plantations. They are:

1. Ribbed smoked sheets.
2. Rolled brown crepe, rolled back.
3. Thin pale crepe.
4. Standard clean thin brown crepe.
5. Rolled Ceylon sheets.

These samples were received through the courtesy of the Murbas Trading Co., New York City. When received, the rubbers were kept in a dark cool place so as to avoid oxidation and tackiness.

#### EXAMINATION.

Following is the order of examination of the rubber samples:

##### 1. *Chemical analysis.*

- |                      |                      |
|----------------------|----------------------|
| (a) Specific gravity | (d) Mineral matter   |
| (b) Moisture content | (e) Insoluble matter |
| (c) Resins           | (f) Rubber           |

2. *Effect of exposure of the rubber samples to ultraviolet rays for 48 hours.*
3. *Viscosity of the solutions of these rubbers in C<sub>6</sub>H<sub>6</sub>.*

#### DESCRIPTION OF THE EXPERIMENTS AND RESULTS.

(a) The specific gravity of the rubber samples is determined by means of the pycnometer at 15° C.

(b) Moisture content is determined by drying a weighed sample in a vacuum desiccator over H<sub>2</sub>SO<sub>4</sub>, until a constant weight of the sample is obtained.

(c) Resins are determined by taking one gram of the finely cut rubber and extracting with C.P. acetone for six hours. The best means of extraction is by using a Wiley condenser and tube. A Gooch crucible containing the finely cut rubber is attached to the condenser. The condenser is slipped into the Wiley glass tube, the whole being warmed over a hot water- or steam-bath. At the end of six hours' extraction the samples are dried in a hot-air oven for one hour, then allowed to cool one-half hour in a desiccator and are weighed.

(d) The mineral matter is obtained by taking the dried and weighed extracted rubber and igniting over a low Bunsen burner until all the carbon is driven off, after cooling, the ash is weighed.

(e) Insoluble matter is determined by taking one gram of finely cut rubber, and dissolving in 100 cc. of benzene. After shaking vigorously to help solution, the mixture is filtered through a weighed coarse filter paper. The residue on the filter paper is dried for one hour in an air oven at about 80° C. The residue is cooled for one-half hour and weighed, the difference being the amount of insoluble matter. In this case the rubber solutions were kept in a dark cool place for one week shaken about 10 minutes every day. This insures solution.

(f) The rubber content is generally determined by difference. This method of finding rubber consists in subtracting the sum of the figures obtained for moisture, resins and insoluble matter (insoluble matters contain the ash), from the total. Another method which has found use for the determination of rubber is to take the soluble matter (in the determination of the insoluble matter) and evaporate the solvent. The residue on evaporation is considered as rubber. This method may be inaccurate, because of proteins being present.

A. *Specific Gravities at 15° C.*

1. Ribbed smoked sheets	0.917
2. Rolled brown crepe, rolled back	0.915
3. Thin pale crepe	0.901
4. Standard thin brown crepe	0.899
5. Rolled Ceylon crepe	0.917

All the following figures are in percentage.

B. *Moisture Content.*

1	2	3	4	5
0.14	0.26	0.22	0.47	0.31

C. *Acetone Extract (by difference)*

1	2	3	4	5
2.55	1.60	1.98	2.64	2.44

*Acetone Extract (by weight).*

1	2	3	4	5
2.89	2.00	2.40	2.69	1.98

*Average*

1	2	3	4	5
2.72	1.80	2.19	2.67	2.11

D. *Mineral Matter.*

1	2	3	4	5
0.34	0.83	0.18	0.55	0.56

E. *Insoluble Matter.*

1	2	3	4	5
4.00	4.48	4.28	4.72	4.56

F. *Rubber (by difference).*

1	2	3	4	5
93.31	93.66	93.52	92.17	92.89

## EXPOSURE OF RUBBER TO ULTRAVIOLET RAYS.

A piece of each sample about 10 cm. long, 4 cm. wide and 1 cm. thick was taken and exposed to ultraviolet light for 48 hours. The distance between the source of ultraviolet light and the samples was twelve inches. On examining the exposed surface of the samples after 4 hours a slight tackiness was noticed. This tackiness increased with the time of exposure. At the end of 48 hours the rubber samples were examined again. The ultraviolet rays had penetrated some of the rubber samples about 4 cm. showing that ultraviolet had a powerful action on rubber. Some of the samples were also "cracked," *i. e.*, they were full of small holes. This condition present in ultraviolet exposed rubber is one of depolymerization. On standing a while these rubber samples lost their elasticity.

*Results of Exposure 48 hours.*

- 1—Tacky. U. V. penetrated the rubber. Still flexible.
- 2—Very tacky. Was cracked. U. V. penetrated about 4 mm.
- 3—Cracked and penetrated by U. V. 2 mm. Dark yellow due to tackiness.
- 4—Not very tacky, was cracked and also slightly discolored on under sides.
- 5—Not tacky, quite resilient.

Two theories have been given regarding the cause of tackiness and cracking in crude rubber. One theory considers the rubber as oxidized while the other holds

that the rubber is depolymerized. The latter theory is concerned with the physical degradation of the rubber molecule.

Gorter claims that tackiness is due to an autoxidation of rubber. He also believes another cause is the change of degree of dispersion of the colloid. Spence, Schidrowitz and Whitby consider the tackiness of rubber as due to polymerization.

G. Bernstein (10) claims that there is first a depolymerization, and afterwards an oxidation due to the ozone formed in the air around ultraviolet lamps.

The theory of depolymerization, regarding crude rubbers exposed to ultraviolet light seems to be more accepted since Henri (11) in 1913 showed that when raw rubber in quartz vacuum tubes is exposed to ultraviolet rays, tackiness results.

#### VISCOSITY OF RUBBER SOLUTIONS.

The question of viscosity has been one of considerable interest to many workers. It has been held among various workers that a correlation between viscosity and the grade of rubber may be made. Viscosity at the present time is considered important due to the correlation between this factor and the nerve and strength of the rubber. The viscosity or viscous stress of the rubber solution has been taken as an index of the shearing stress of the strained elastic soluble rubber.

Schidrowitz and Goldsbrough, (12) Van Heurn, (13) and Van Rossen (14) have done much regarding the technique of measuring the viscosities of rubber solutions. Attempts were made to find some relationship between the viscosity of rubber solutions and their vulcanization properties. Schidrowitz (15) drew a curve through the value of the viscosity of the solvent at concentrations of  $X, X/2, X/4\%$  ( $X =$  about 1). The two latter concentrations being obtained from the former by dilution. Then a tangent is drawn to the curve at a concentration of about 1%. This method although good in itself depends upon the personal equation.

Abernethy (16) uses the falling sphere method for determining the viscosity of rubber solutions. By using Stoke's law as a basis, he shows various figures for rubber solutions from 5 to 15%. In working with lower than 5% solutions the Ostwald viscosimeter is used. The drop-ball method seems to be promising in use.

The viscosity measurements are generally made in a benzene solution of rubber at 20° C. using the Ostwald viscosimeter. Viscosities of rubber solutions in chlorinated solvents are about twice the viscosity of the solvents of the same concentration in gasoline or benzene, but, after heating, all kinds of rubber solutions have about the same viscosity, cf. Kirchoff (17). A 10% solution of raw para-rubber in amyl acetate is fluid enough to filter through ordinary filter paper. Acetone is soluble in rubber to the extent of about 17%. Rubber may be precipitated from benzene or either solutions by the addition of alcohol or acetone. A good solvent for rubber is tetralin (tetrahydronaphthalene).

#### PRACTICAL WORK.

A simple method for the determination of viscosity of rubber solutions in benzene has been tried. The ordinary pipette was used in these viscosity determinations. A 1% solution of each sample was tried. These solutions were made up, were well shaken and were kept in a dark place for one week in order to effect solution, and to prevent oxidation. In order to obtain sufficient values for making graphs of the rubber solutions a number of viscosity determinations were run on each sample.

The pipettes used had a two-mm. bore at the outlet end and the same length of stem. Pipettes of various sizes were used so that sufficient numerical values may be obtained by which graphs can be drawn, and a better idea obtained regarding the particular solution. The viscosity of benzene was also taken as a comparison. The logarithms of the number of seconds were taken also to determine what type of graph is given by the logarithm of these values.

Following are the results obtained:

No. 1.			No. 2.		
Cc.	Time in seconds.	Logs. of seconds.	Cc.	Time in seconds.	Logs. of seconds.
10	6.87	0.813	10	4.16	0.619
25	19.87	1.298	25	15.66	1.195
45	35.76	1.5536	45	34.50	1.5390
90	78.00	1.8928	100	76.66	1.8851
100	86.00	1.9399			

No. 3.			No. 4.		
Cc.	Time in seconds.	Logs. of seconds.	Cc.	Time in seconds.	Logs. of seconds.
10	5.95	0.775	5	3.3	0.519
25	20.90	1.31	10	5.0	0.699
50	49.83	1.6969	25	19.0	1.2789
90	89.70	1.9524	50	42.80	1.6319
			90	76.98	1.8860

No. 5.			Benzene.		
Cc.	Time in seconds.	Logs. of seconds.	Cc.	Time in seconds.	Logs. of seconds.
5	3.87	0.588	10	2.83	0.4510
10	5.27	0.723	25	10.00	1.0000
25	19.76	1.2958	50	23.90	1.3780
30	28.90	1.4599	75	35.85	1.5549
90	86.94	1.9392	100	47.80	1.6795

It will be noticed in the graphs that the values for the rubber solutions are represented by straight lines. From 0 to 5 cc. it will be noticed that there is a slight curvature for each sample. In some cases, the values at certain points are away from the path of the straight line. This discrepancy may be due to: inaccuracy of the pipette, inaccuracy of the graph paper, or the personal equation in obtaining the results of viscosity.

The values of the logarithms show interesting results. The graphs of these logarithms trace the sides of a parabolic curve and intersect some point on the straight line. In the case of benzene the viscosity averages about half that of the rubber samples. The logarithm curve in this case does not intersect the straight line within 100 cc., but if more than 100 cc. were used in determining the viscosity of benzene, there would be a point common to both lines.

In dealing with the values of the logarithms it may be said that the accuracy on the graphs is to the second place to the right of the decimal.

#### CONCLUSIONS.

##### 1. *Chemical Analysis.*

In discussing the results obtained in the chemical analysis it will be seen that

the specific gravities, with the exception of number four come within the values found by other workers for plantation rubber, *viz.*, 0.91–0.94.

The results of the extract by difference of the samples as shown do not all agree with the findings of acetone, extract by weight. There is an average difference of about 0.4 with the exception of number four. The latter findings are considered more correct since the results of acetone extract by difference most likely are affected, when the extracted rubbers are dried in a hot air oven, for one hour at 100° C.

The insoluble matter in each case appears somewhat high. This is due to the fact that benzene does not completely dissolve the rubber. The rubber content, as determined by difference, averages up to about 93% which amount comes well within the requirements of a good plantation rubber.

### 2. *Exposure to Ultraviolet.*

In the case of exposure to ultraviolet rays, it may be said that most rubbers are penetrated by them. These rubbers were attacked to the extent of producing tackiness and cracking (holes). When those exposed rubbers are stretched they tear and break, indicating thereby the loss of elasticity.

On taking some of the exposed rubber and rolling between the fingers a tacky spherical mass is formed. It has no resiliency and can be put into any shape without returning to its former shape.

The ultraviolet ray machine used in these experiments is the A. C. type Mercury Arc, manufactured by the Hanovia Chemical Company. The use of u. v. arcs in rubber chemistry has opened a broad field. Who knows but that it may be the medium of obtaining a suitable synthetic rubber?

### 3. *Viscosities.*

A 1% solution of the finely ground rubber was made up in benzene and kept one week before using. The values obtained indicate that they trace a straight line on graph paper, but the logarithms of these values trace the side of a parabola, and intersect at some point common to both lines.

It is possible, by finding some relationship between the equation of the straight line and that of the parabola that an index may be obtained regarding crude rubbers.

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