

## GENERAL SESSION

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### PRESIDENT'S ADDRESS

## THE STORY OF SYNTHETIC RUBBER

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Members of The Indiana Academy of Science, ladies and gentlemen, and dear friends: The Story of Synthetic Rubber, a fascinating chapter in chemical history, is a story which goes back three quarters of a century. While time and circumstances do not permit a detailed résumé of all the facts, it will suffice, I trust, to trace the story very briefly, mentioning in approximate chronological order the sequence of some of the more important events that ultimately led to the discovery and commercial development of the newest synthetic rubber, Duprene.

Record of the formation of synthetic rubber-like substances goes back to 1860, when Greville Williams (English) first destructively distilled rubber, yielding, in part, what we now know to be isoprene. Williams noted that when the pyrolysis products were allowed to polymerize and partially oxidize, an elastic rubber-like mass was obtained. In one respect this can hardly be considered a synthesis of rubber since the isoprene required had been obtained by breaking down natural rubber. This early work indicated, however, that isoprene could be polymerized to yield a form of synthetic rubber. It was only natural that so important a discovery should stimulate general scientific interest; consequently, studies on the pyrolysis of rubber and the polymerization of isoprene were soon undertaken in various European laboratories.

Nineteen years after Williams' classical contribution Bouchardat (French) published his researches on isoprene polymerization in which analysis of his polymers indicated that they were of the formula  $(C_5H_8)_n$  while isoprene itself is the simple  $S_2H_4$  unit, written structurally by the organic chemist as



Evidence was thus obtained that the synthetic rubber was a direct polymer of isoprene. The polymerization of isoprene was also studied by Tilden (English) who showed that the polymerization could be effected under the action of nitrosyl chloride (1882) and later (1892) spontaneously under the action of light and air. It might be mentioned that Tilden's work deserves special merit because his was a real synthesis in this regard: he had obtained his isoprene by cracking turpentine vapour in a red hot tube. Previous investigators had only resynthesized rubber from the pyrogenic decomposition products of natural rubber. The

cracking of turpentine, although used by Tilden, was not discovered by him, but by Hlasiwetz in 1876.

When Harries (German) undertook the study of synthetic rubber at the beginning of the present century, one of his first publications was a destructive criticism of previous work. Harries claimed that he was unable to repeat the previous work of Bouchardat and Tilden. Opinions have since been expressed that the fault was more with Harries than with previous workers. Certain other contributions might be cited: Kondakov (Russian) showed (1889-90) that other isoprene-like hydrocarbons could be polymerized to rubber-like materials and thereby greatly broadened the field of research. In 1909, Hoffman (German) discovered that heat alone will convert isoprene into the rubber polymer.

Another interesting angle of the synthetic rubber problem, namely, that of the ultimate molecular configuration of natural and synthetic rubbers, has been studied by such well-known authorities as Staudinger (German) and our well-known American contemporary, Thomas Midgley, and his co-workers.

In August of 1910, Matthews (English) observed that sodium metal will catalyze the isoprene polymerization. At this time the synthetic rubber problem acquired a possible commercial significance. Matthews, working for a British firm, had worked out a means of obtaining fusel oil on a fairly larger scale and obtaining isoprene therefrom. The butyl alcohol in the fusel oil was converted to butyl chloride and this chlorinated to a mixture of dichlorobutanes. Hydrogen chloride was removed from these chlorides in some manner such as by passing the dichloro compounds over heated soda-lime. In this way, butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ) was obtained which could be polymerized to a butadiene rubber. This was accomplished by allowing it to stand in contact with sodium metal for a period ranging from a few hours to more than as many weeks. A patent on the process was applied for on October 25, 1910. It is interesting to note that on December 12, 1910 (less than two months later) the Elberfeld Farbenfabriken applied for a somewhat similar patent in Germany on the basis of claims made by Harries. It was stated by Harries that he had noted the effect of sodium on isoprene while attempting to distill isoprene from it. While this may have been so, Matthews enjoyed undoubted priority of publication and the controversy ended in his favor. Anyone following the synthetic rubber problem through the chemical literature will find many examples of such disagreeable controversies among pioneers in the field. Arguments and counter-arguments may be found in the published literature, sometimes over only technicalities of phraseology.

The first fifty years of synthetic rubber research, then, had brought out the following facts: isoprene and butadiene (compounds containing the carbon nucleus  $-\text{C}=\text{C}-\text{C}=\text{C}-$ ) can be polymerized under the action of various catalytic agents to yield resilient, elastic substances resembling natural rubber. While this information is of the highest scientific importance, its practical value had not been as significant, because isoprene and butadiene are expensive and difficult to obtain in quantity, and because the rubbers produced from these compounds are inferior to natural rubber.

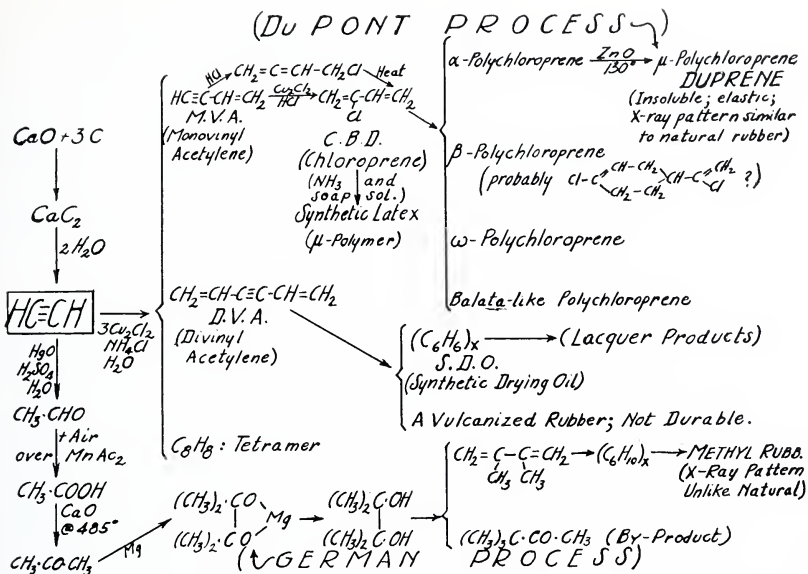


Table 1. Flow Sheet of Rubber Processes with Intermediates.

Probably the next significant page in the problem of synthetic rubber was written with the development in Germany of what has been variously called the "Carbide," "Pinacol," or "Methyl Rubber" process.

Like Duprene, Methyl Rubber was made from acetylene as the starting material. Without going into a great deal of technical detail, the steps involved in the synthesis may be enumerated as follows: conversion of the acetylene to acetaldehyde by hydration with water, oxidation of the aldehyde to acetic acid followed by conversion to acetone and thence by reduction to pinacol. Dehydration of the pinacol yielded, in part, dimethyl butadiene known also as methyl isoprene and written structurally as



This process is lengthy and too expensive for practical use except as a drastic emergency measure. The chemical relationship between butadiene, isoprene, and dimethyl butadiene is exemplified by the similarity of their molecular nuclei.

When Germany was shut off from the natural rubber market at the opening of the World War, she was practically forced to turn to synthetic rubber as a substitute. Such a crisis really brought out the inferiorities of the known synthetic rubbers and showed how generally previous conclusions had been over-emphasized. When it came actually to fabricating rubber articles from synthetic preparations, it was found that butadiene rubber was brittle when acid-polymerized, isoprene rubber was sticky and lacked tensile strength. Both products were even worse when sodium-polymerized. The Methyl Rubber, when polymerized by heat, was also unpromising—it could not be readily vulcanized, and

it oxidized too easily. In all cases, the polymerization required many days for completion. It was found, however, that the addition of certain organic bases such as aldehyde ammonia and piperidine derivatives exhibited a beneficial effect when incorporated in the synthetic rubber.

Other improvements came about which made the usage of Methyl Rubber at least possible, and, in May of 1918, the output of Methyl Rubber was about 150,000 kilograms per month. The Baeyer plant in Germany had a capacity of about 150 tons of Methyl Rubber per month at the close of the War. Of this, about 30 tons were used monthly as hard rubber for battery jars, etc.

When the synthetic material was mixed with about 20 per cent of reclaimed rubber the product was fairly satisfactory. The former alone gave quite an inelastic material, though this was improved by adding various oils. The use of dimethyl aniline in this respect was eventually generally adopted because of its preservative action. The synthetic rubber was not good enough for the manufacture of inner tubes for pneumatic tires. For this reason the Germans had to resort to the use of solid tires which were made from the synthetically prepared rubber.

While the methyl rubber process was abandoned at the close of the War, owing to its general impracticability, acetylene is nevertheless a logical starting point in rubber synthesis because of its comparatively low price and because of its chemical reactivity due to a high degree of unsaturation. The chemistry of acetylene led the way to Duprene. In 1906, while experimenting with acetylene it was noticed that a reaction occurred when this gas was passed into a solution of copper and alkali metal chlorides. The product was not isolated but was definitely believed to be a gas as its odor was extremely noticeable and yet no solid or liquid was isolated. Experimentation was continued at frequent intervals for the next fourteen years, until finally means were found to increase the concentration of the catalyst mixture by substituting ammonium chloride for the alkali metal chlorides and by altering its acidity to increase the rate and extent of acetylene absorption. To our surprise an oil was formed along with the gas previously noted. Scarcely more than a year later, it was proven that this oil is divinyl acetylene—a compound having a degree of unsaturation even greater than isoprene, butadiene, or dimethyl butadiene. Our interest was further stimulated in 1923 when treatment of divinyl acetylene with sulphur dichloride produced an elastic substance resembling natural rubber, though too plastic for practical use.

While delivering a paper at the Organic Symposium in Rochester, New York, in 1925, I had occasion to mention incidentally some of these acetylene experiments. The E. I. DuPont de Nemours and Company became interested in the work, and arrangements were made whereby this concern might take over the commercial development of these materials. To our mutual disappointment, different specimens of the divinyl acetylene products did not retain their elasticity for comparable lengths of time, and means to correct this fault were not immediately found. Meanwhile, however, the gas which had been noted as early as 1906 was being investigated in the Jackson Laboratories of the Du Pont Corporation. As had been anticipated this gas proved to be mon-

ovinyl acetylene,  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ , and, like divinyl acetylene, it was formed directly by acetylene polymerization.

Monovinyl acetylene is somewhat like isoprene and its homologs in that it contains a four carbon atom nucleus and has two points of unsaturation. It was subsequently found that the elements of hydrogen chloride may be added to the triple bond of monovinyl acetylene and that the use of cuprous chloride as a catalyst made possible almost a theoretical yield of chlorobutadiene,  $\text{CH}_2=\text{CH}-\text{C}=\text{CH}_2$ .



Inspection of the structural formulas previously mentioned shows a close molecular similarity between this compound and isoprene—the only difference being that chlorobutadiene contains an atom of chlorine in place the methyl group,  $-\text{CH}_3$ , in isoprene. Because of this close structural similarity the synthetic material was named "Chloroprene." On standing for a few days chloroprene spontaneously polymerizes to a stiff, plastic substance which can be vulcanized by merely heating to  $114^\circ\text{C}$ . for five minutes to form an elastic, non tacky, tough material—a *synthetic rubber*. This new rubber was given the trade name, "Duprene." Thus ended in success a problem that had occupied the minds of organic chemists for seventy-five years.

The Duprene rubber is particularly interesting because of its many virtues over natural rubber. Its resistance to gasoline, kerosene, oils, air, ozone, acids, alkalis, etc., opens up many entirely new fields of rubber technology. It can be used to better advantage for nearly all the purposes that natural rubber serves, as also for hundreds of uses to which natural rubber is unequal to adapt itself. In general, one may say that it is a better product than natural rubber. Although somewhat more expensive, thousands of pounds are being made in the Du Pont Duprene Plants. Chloroprene may be emulsified in an ammoniacal soap solution to produce a milky liquid resembling natural latex in appearance and application. Another fact of great interest to the chemist is that a sheet of Duprene stretched 500 per cent gives an X-ray diffraction pattern which closely resembles that of natural rubber under the same stress. This shows that the three dimensional structures of the synthetic and natural rubber are very similar. Furthermore, Duprene is economically practical. The United States need never worry that a national crisis will forbid or seriously hinder the fabrication of rubber goods.

Upon this memorable occasion, the fiftieth anniversary of the founding of The Indiana Academy of Science, we may be pardoned in feeling highly honored and extremely happy that an Indiana laboratory should have had the distinction of contributing to the final solution of a most practical and perplexing scientific problem.