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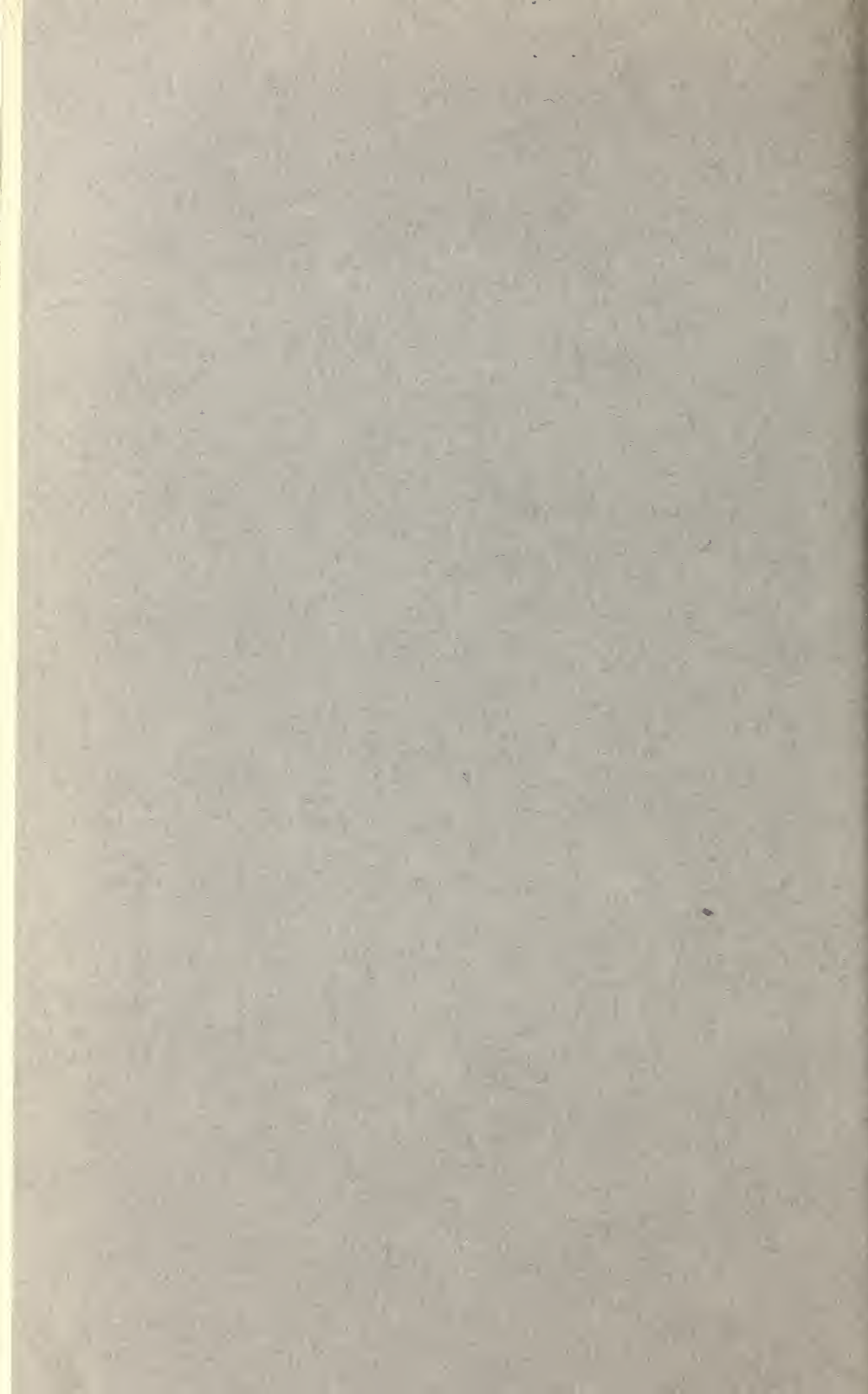
SYNTHETIC RUBBERS
A REVIEW OF THEIR COMPOSITIONS,
PROPERTIES, AND USES

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**SYNTHETIC RUBBERS: A REVIEW OF THEIR
COMPOSITIONS, PROPERTIES, AND USES**

By Lawrence A. Wood

[Issued June 25, 1940]



UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1940

PREFACE

The production of synthetic rubber on a commercial scale in the United States and abroad has increased very greatly in recent years. The increasing use of synthetic rubber in this country has been due entirely to its superiority over the natural product for many applications. In some other countries it has been developed as a substitute for natural rubber as a measure of national economic self-sufficiency. Consequently, there has been a growing interest in the development of synthetic rubber in America. In response to frequent requests for information, this Circular has been prepared at the National Bureau of Standards to furnish a comprehensive summary and a complete bibliography of the literature regarding the different varieties of modern synthetic rubber.

LYMAN J. BRIGGS, *Director.*

SYNTHETIC RUBBERS: A REVIEW OF THEIR COMPOSITIONS, PROPERTIES, AND USES

By Lawrence A. Wood

ABSTRACT

Twenty-nine commercial varieties of synthetic rubber are classified as (1) chloroprene polymers, (2) butadiene polymers (including co-polymers), (3) organic polysulfides, (4) isobutene polymers, (5) plasticized vinyl chloride polymers, and (6) dimethylbutadiene polymers. Familiar examples of each of these types are, respectively, (1) Neoprene, (2) the German Buna rubbers, (3) Thiokol, (4) Vistanex, (5) Koroseal, and (6) "methyl rubber." Since the last type is chiefly of historical interest, it is treated only briefly. For each of the first five types a brief discussion is presented concerning the raw materials used, the chemical reactions of manufacture, and the general conditions of polymerization or condensation. There is also some discussion of compounding and vulcanization, and of the properties and uses of the product. Published data on the different types are summarized in comparative tables of values of density, refractive index, identity period along the fiber axis, swelling in liquids, tensile strength, and permeability. The reported values of dielectric constant, power factor, and resistivity are also given. In Germany and Russia synthetic rubber is used to displace natural rubber in all its applications; in other countries, especially the United States, only those applications where natural rubber is notably deficient are of present importance. Synthetic rubbers show outstanding superiorities to natural rubber in resistance to the effects of liquids, especially petroleum products, and in resistance to deterioration by light, heat, ozone, and oxygen. These superiorities offset the higher cost of the synthetic materials, which is in most cases at least three or four times that of natural rubber. A bibliography of over 200 references covers the literature of the decade 1930-40.

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I. INTRODUCTION

Synthetic rubber has been the dream of many during the century which has passed since Faraday first determined the carbon-hydrogen ratio in natural rubber, but it has completed only about a decade of

commercial success. Every year of the past 10 has seen an increase in the quantity produced, the number of varieties available, and the number of applications.

The aims in various countries have been different and the development has proceeded in different directions. The most active research has been carried on in Germany, Russia, and the United States. There has been relatively little collection and intercomparison of the rather limited data on the physical properties of the different varieties of synthetic rubber. Scientific articles have been largely devoted to descriptions of single varieties or to discussions of limited phases of the work with respect to one variety. The present paper represents an attempt to make a summary of the facts regarding the different varieties, an intercomparison of some of their properties, as reported in previous publications, and to present a fairly complete bibliography of the modern literature on the subject of synthetic rubber. Because of the relatively short time during which the different varieties of synthetic rubber have been available, the data concerning them have been reported almost entirely by observers in the laboratories of companies each interested in the manufacture and sale of a particular variety. In almost every case, therefore, the figures necessarily lack independent confirmation.

The development of synthetic materials to replace those of vegetable or animal origin has been a matter of frequent occurrence. Many examples can be cited, beginning with alizarin and indigo and continuing with dyes, fertilizers, drugs, and vitamins. Usually the development follows a fairly well-defined pattern, consisting of (1) scientific research on the analysis of the natural product leading to an exact knowledge of the chemical constitution and structure, (2) the evolution of methods for the duplication of the substance from cheap raw materials, and (3) the commercial production of the synthetic product at a price low enough to compete with and even to displace the natural product. In most cases the synthetic product is chemically and physically the same as the natural product and is not an improvement, unless the absence of impurities or nonessential ingredients can be considered an improvement.

Although 30 years ago the expectation was general that the development of synthetic rubber would follow this course, it has not done so, since serious difficulties were encountered with each of the three steps of the typical pattern of development. Consequently, scientific workers engaged in much research which now seems fruitless. The belief that the development should follow the customary pattern, as outlined, has given rise to many popular misconceptions as to the present status of synthetic rubber.

Scientific research on natural rubber has yielded much information, but even today it cannot be said that the structure of rubber is known in the sense that the structures of most substances of lower molecular weight are known. Our knowledge, though incomplete, is probably sufficient to enable us to say that no process has yet been found by which it is possible to produce a material possessing both the chemical constitution and the physical properties of natural rubber. Finally, the cost of the synthetic products which most nearly approach natural rubber in character is far above the present price of natural rubber. In view of these facts the whole approach to the problem has been revised. It seems now to be recognized that the desirable physical

properties of rubber are not necessarily closely related to its chemical constitution, and since, in almost all its uses, its physical properties are of first importance, the effort to duplicate the chemical constitution of natural rubber has been abandoned.

In recent years the very meaning of the term "synthetic rubber" seems to have changed to agree with the change in the point of view. Thirty years ago, the term meant a synthetic material physically and chemically indistinguishable from natural rubber (except possibly for the absence of impurities). Since no material has been produced which fits this definition, the term has come to mean to most people a synthetic material possessing the approximate physical properties of natural rubber [224].¹ Several authors [4, 18, 19, 21, 225] have attempted to express such a definition in more exact terms. Others, following the older definition, have hesitated to use the phrase "synthetic rubber" and have taken refuge in the more indirect expressions "synthetic rubberlike material," "elastic synthetic," and "rubber substitute." Perhaps the most satisfactory solution would be the adoption of some single word such as "elastomer," as suggested by Fisher [7], but as yet no such word has met with general acceptance. The term "synthetic rubber" has been used so widely that it would probably be difficult to displace it.

The economic factors involved in the production of synthetic rubber have changed considerably in the past 30 years. The growth of plantation rubber in the Far East has reduced the price of natural rubber from the maximum of about \$3 a pound in 1910 to less than 20 cents a pound in 1940. The cheapest commercial synthetic rubber still costs about twice as much as the natural product. Nevertheless, in recent years certain countries, notably Germany and Russia, insisting upon economic self-sufficiency, have considered a high price paid within the country to be of little importance as compared with expenditures in foreign currency for natural rubber. Self-sufficiency in wartime, of course, has also been a factor of paramount interest to these governments [14, 125].

These economic and political factors have influenced the scientific objectives and development in the different countries. In Germany and Russia the primary aim appears to have been to duplicate, or nearly duplicate, the properties of natural rubber as cheaply as possible and any improvement in qualities seems to have been of only incidental or secondary importance. In the United States, on the contrary, the primary aim has been to produce a product superior to natural rubber in some respect, the cost being a matter of secondary importance. In a free world market, only a superior synthetic rubber can justify a higher price. Whether or not in the future the other countries, including the United States, will be moved by considerations of self-sufficiency to follow Germany and Russia remains to be seen. Up to the present time, such considerations have not played much part in the development of synthetic rubber in these countries.

II. VARIETIES OF SYNTHETIC RUBBER

In conformity with the trend already mentioned, the term "synthetic rubber" in this paper will be taken to mean merely a synthetic

¹ Numbers in brackets refer to the literature references given in the bibliography, section XI.

substance which has physical properties resembling those of natural rubber; that is, it can be stretched a considerable amount, let us say to an elongation of at least 300 percent, and when released will quickly and forcibly retract to substantially its original dimensions. About 30 varieties of synthetic rubber are listed in table 1 under the trade names used by the manufacturers. Of these, some are practically identical and some are very closely related to others. They have been classified in six general types according to chemical composition; the discussion in the present paper follows this classification. The chemical constitution of almost all of the varieties in table 1, together with that of natural rubber, is shown in table 2.

TABLE 1.—Varieties of synthetic rubber

Name	Type	Remarks	Reference	Manufacturer	Country of origin
Buna 85.....	Butadiene polymer..	Molecular weight about 85,000.	[128]	I. G. Farbenindustrie.	Germany.
Buna 115.....do.....	Molecular weight about 115,000.	[128]do.....	Do.
Buna N ¹	Butadiene co-polymer.	Co-polymer with acrylonitrile; now called Perbunan.	[128]do.....	Do.
Buna S.....do.....	Co-polymer with styrene.	[128]do.....	Do.
Buna SS.....do.....	Co-polymer with styrene — higher styrene content than Buna S.	[129]do.....	Do.
Duprene ¹	Chloroprene polymer.	Now called Neoprene.	[60]	E. I. duPont de Nemours & Co., Inc.	United States.
Ethanite.....	Organic polysulfide..	Similar to Thiokol A.	[171, 182]	Belgian Cracking Co.	Belgium.
Flamenol.....	Plasticized vinyl chloride polymer.	General Electric Co.	United States.
Ker.....	Butadiene polymer.	[126]	Stomil Co.	Poland.
Korogel.....	Plasticized vinyl chloride polymer.	Highly plasticized Koroseal.	[210]	B. F. Goodrich Co.	United States.
Koroseal.....do.....	[212]do.....	Do.
Levulkan ¹	Butadiene co-polymer.	Now called Buna SS.	[129]	I. G. Farbenindustrie.	Germany.
Methyl rubber B.	Dimethylbutadiene polymer.	Sodium used as catalyst.	[33]	Bayer & Co. 1915-18.	Do.
Methyl rubber H.do.....	Cold polymerization.	[33]do.....	Do.
Methyl rubber W.do.....	Hot polymerization.	[33]do.....	Do.
Neoprene.....	Chloroprene polymer.	[60]	E. I. duPont de Nemours & Co., Inc.	United States.
Mustone.....do.....	[20]	Umeno Institute.	Japan.
Oppanol.....	Isobutene polymer	[203]	I. G. Farbenindustrie.	Germany.
Perbunan.....	Butadiene co-polymer.	Co-polymer with acrylonitrile.	[128]do.....	Do.
Perbunan Extra.do.....	Co-polymer with acrylonitrile—higher nitrile content than Perbunan.	[128]do.....	Do.
Perduren.....	Organic polysulfide.	[183]do.....	Do.
Resinit ¹do.....	[109]do.....	Russia.
SKA.....	Butadiene polymer..	From petroleum ..	[116]do.....	Do.
SKB.....do.....	From alcohol.....	[109]do.....	Do.
Sovprene.....	Chloroprene polymer	[63]do.....	Do.
Thiokol.....	Organic polysulfide..	[180]	Thiokol Corporation.	United States.
Thionite.....do.....	[172]do.....	Japan.
Vistanex.....	Isobutene polymer	[206]	Standard Oil Co.	United States.
Vulcplas.....	Organic polysulfide..	[176]	Imperial Chemical Industries.	England.

¹ This term is now commercially obsolete.

In common with natural rubber, all types of synthetic rubber consist of atomic chains of very great length—giant molecules as they are sometimes called—built up by the repetition, usually thousands of times, of some unit configuration. In all but the last two cases shown in table 2, the long chains are built up by the polymerization, or linking together, of the molecules of liquids. In the process of formation of the polymer from the liquid monomer, in each case the double bond attached to a carbon atom at the end of the molecule opens to form the necessary valence bond for attachment to the next unit. The organic polysulfide rubbers, which are illustrated by the last two types in table 2, possess long chains formed not by polymerization, but by condensation. The atoms at the ends of two different molecules combine with each other, thus leaving the remaining radicals free to combine, and forming long chains by the repetition of the process [180]. In none of the different varieties of synthetic rubber has the nature of the terminal group of the chain been definitely established. It comprises only a very small fraction of the total material and may be different in different chains of the same material.

The production of synthetic rubbers involves two steps—the manufacture of the monomer, and the polymerization or condensation reaction. The first step usually follows fairly common and well-understood reactions; the second step is much more empirical and less understood, but usually involves the use of a catalyst and the control of temperature and pressure.

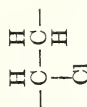
One of the most important improvements during the past few years has been the adoption, in many cases, of polymerization in emulsion. The monomer is emulsified in a liquid, usually water, and the product is a suspension similar to the latex of natural rubber. Another important advance was the discovery and development of co-polymerization. This is a process involving the simultaneous polymerization of two or more liquids and yielding a product in which a single chain contains units of both configurations. The co-polymers of butadiene with styrene and of butadiene with acrylonitrile are the best-known examples.

Prolonged research [28] has failed to locate a cheap source of supply for the manufacture of isoprene, or to produce from it a polymer with physical properties close to those of natural rubber. Consequently, efforts in these directions have been almost completely abandoned, and all the commercial synthetic rubbers differ chemically from natural rubber. Between 1915 and 1918 the Bayer plant in Germany produced about 2,500 tons of rubber from dimethylbutadiene [33]. The product, called "methyl rubber," has not, since then, retained any commercial importance. With these exceptions and possibly a few others, all the materials shown in tables 1 and 2 are at present in commercial production, although some are produced in very limited quantities. From the diversity of chemical constitutions shown by the examples in table 2, one may conclude that the physical properties ordinarily associated with rubber are not limited to one group of related chemical compounds and that there are probably many more undiscovered types of synthetic rubber.

TABLE 2.—*Chemical structures of different varieties of synthetic rubber*

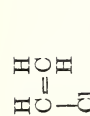
NOTES.—The bonds between carbon and hydrogen are not indicated. The structural formulas are not intended to give any indications regarding stereo-isomerism. Fuller [37] has recently suggested a ring structure in the organic polysulfides.

SIMPLE POLYMERS	
Monomer	Unit of polymer
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{C}=\text{C}-\text{C}=\text{C} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{1,3-butadiene} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{Buna 85, Buna 115, SKA,} \\ \text{SKB, or Ker} \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{C}=\text{C}-\text{C}=\text{C} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{Isoprene (2-methyl-1,3-butadiene)} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{Natural rubber} \end{array}$
$\begin{array}{c} \text{CH}_3\text{CH}_3 \\ \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{C}=\text{C}-\text{C}=\text{C} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{2,3-dimethyl-1,3-butadiene} \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH}_3 \\ \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{Methyl rubber} \end{array}$
$\begin{array}{c} \text{Cl} \\ \\ \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{C}=\text{C}-\text{C}=\text{C} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{Chloroprene (2-chloro-1,3-butadiene)} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{Neoprene, Sovprene, or Mustone} \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} \quad \text{H} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{H} \\ \text{Isobutene (2-methyl-1-propene)} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \\ \text{Vistanex, Oppanol} \end{array}$

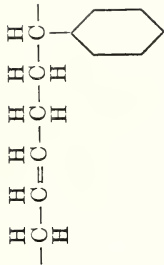


Plasticized materials:
Koroscal, Korogel, or Flamenol

CO-POLYMERS

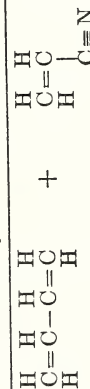


Vinyl chloride



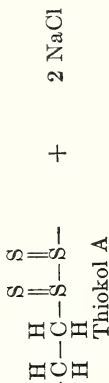
Buna S or Buna SS

Butadiene + styrene (vinylbenzene)



Butadiene + acrylonitrile (vinyl cyanide)

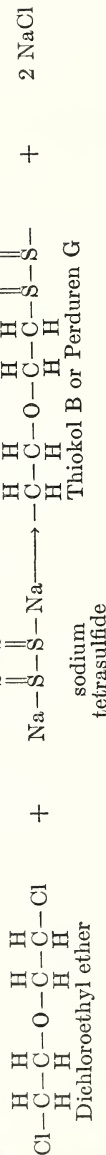
ORGANIC POLYSULFIDES



Thiokol A

sodium tetrasulfide

Ethylene dichloride (1,2-dichloroethane)



Thiokol B or Perduren G

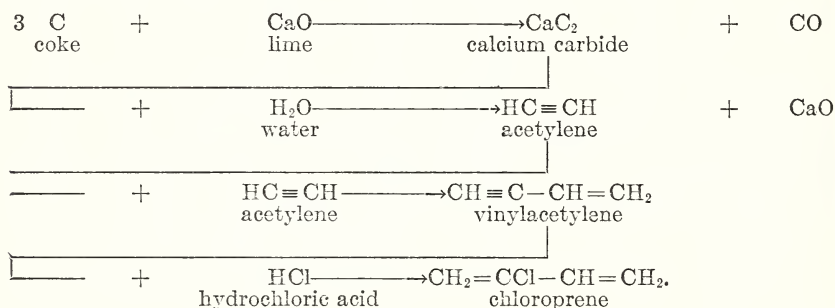
sodium tetrasulfide

Dichloroethyl ether

III. CHLOROPRENE POLYMERS

The preparation and properties of the chloroprene polymers have been described quite extensively in the scientific literature. Neoprene, formerly called Duprene, is the leading representative of this type and is widely used in the United States and in England. The Russian chloroprene polymer is called Sovprene [63].

The chemical reactions [60, 71] involved in the manufacture of chloroprene are indicated by the following equations:



Chloroprene polymerizes much more rapidly than butadiene and, with a few unimportant exceptions, somewhat more rapidly than any of the derivatives of butadiene [73]. If the polymer is removed when polymerization is about one-third complete it is found to possess quite different mechanical properties from those of the completely polymerized material [60]. The former product, the α -polymer, resembles unvulcanized rubber while the latter, the μ -polymer, resembles vulcanized rubber. The commercial varieties of Neoprene correspond to the α -polymer, and are made by the polymerization of chloroprene under different conditions. Neoprene G, for example, is an emulsion polymer [89]. A very small amount of a stabilizing material, commonly phenyl- β -naphthylamine, is usually added to Neoprene after polymerization [64, 93]. The stabilizer prevents continued polymerization, or more particularly cross-linking or cyclization, which would cause a stiffening of the Neoprene during storage. Plasticizers are frequently added in small amounts for the purpose of enabling the material to be processed more conveniently with the usual rubber machinery [83].

When Neoprene is heated, it undergoes a permanent change in physical properties similar to that involved in the vulcanization of rubber. The chloroprene polymers are unique among rubbers, synthetic or natural, in that this process can occur without the addition of other materials. In commercial practice, however, it is found more desirable to add a number of compounding ingredients. Several of the metallic oxides [83, 88], such as magnesium oxide, zinc oxide, and litharge, function as vulcanizing agents, rather than sulfur, which, when used, acts as an accelerator. Many of the organic accelerators used with natural rubber are not effective with Neoprene, but catechol and some similar substances are said to be promising substitutes

[86, 90]. The addition of carbon black, which is usually found desirable, makes a stiffer compound, but, contrary to its effect with natural rubber, it does not increase the tensile strength. It has not been found possible to vulcanize Neoprene to a state corresponding to ebonite, or hard rubber. Compounding materials are mixed with Neoprene by means of the usual rubber machinery, but its behavior on milling is somewhat different. Neoprene *E* and the types previously produced appear to be unaffected by mastication, the softening which occurs being caused merely by the elevation of temperature. The newer types *G*, *GW*, and *GN* may be substantially softened by mastication [93].

IV. BUTADIENE POLYMERS

Butadiene, either alone or in combination with other substances, is the source of almost all the synthetic rubber manufactured in Europe. Butadiene, a gas at temperatures above -5°C , is being manufactured by a number of different methods. One method [133] involves the pyrolysis ("cracking") of petroleum, especially the higher-boiling constituents. Under the proper conditions the process yields butadiene directly. The crude butadiene is then subjected to purification. This process is used in the manufacture of the Russian rubber called "SKA" [116], and it is reported to be the one which the Standard Oil Co. is planning to use in the United States for the manufacture of a rubber similar to Perbunan [112, 113, 117]. A dehydrogenation of some of the lower-boiling constituents of petroleum has also been described, but not yet put into commercial practice [134, 135].

In another important method, alcohol is converted into butadiene by a reaction [130] indicated by the following equation:

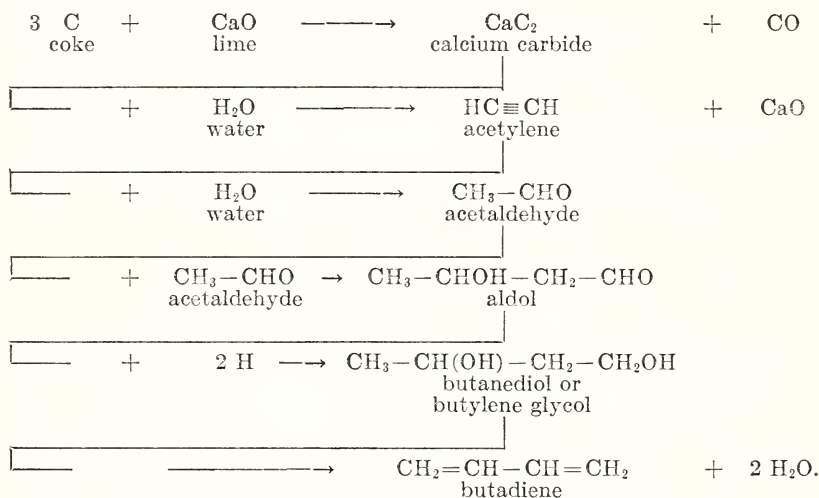


The butadiene used in the manufacture of the Russian rubber SKB is prepared in this manner from alcohol obtained by the fermentation of grain or potatoes [109, 114, 131].

The polymerization of an impure material yields a product of low molecular weight, presumably because the formation of long chains is interrupted by the impurity. It is very difficult to obtain butadiene of high purity from petroleum products, especially when they are the products of cracking operations, or from agricultural products, particularly when they are obtained by fermentation. This fact is one of the major causes of difficulty and expense in the manufacture of butadiene from these sources.

One possible process for the manufacture of butadiene from acetylene is similar to that already given for the manufacture of chloroprene except for the substitution of hydrogen for hydrochloric acid in the last step. However, the reactions of the process [123,140] actually

used most extensively in Germany are indicated by the following equations:



Although long, the process is said to be free from side reactions and to yield butadiene of high purity.

The first reaction is carried out in a furnace for which large amounts of electric energy are required [110]. The cost of the electric energy is probably one of the largest items in the whole process. In another process reported to be in use in Germany the acetylene is said to be extracted from coke-oven gases.

For the products known as Buna 85, Buna 115, SKA, and SKB, polymerization of butadiene is carried out with metallic sodium as the catalyst. Emulsion polymerization is used for Buna S and Perbunan. The co-polymers Buna S and Perbunan contain 20 to 40 percent of styrene [139] or acrylonitrile [138], respectively. Polymerization, in addition to the formation of the long chains, leads to a certain amount of cross-linking, or cyclization. The continuation of cyclization during storage of the raw material is prevented by the addition of a very small amount of a stabilizer, phenyl- β -naphthylamine being almost always used [128].

Buna S and Perbunan, in the uncompound state, are somewhat stiffer than natural rubber, and they behave somewhat differently during processing on the usual rubber machinery. Heating Buna S to a temperature of 130° to 150° C for 1 or 2 hours in the presence of air, produces a temporary change known as thermal oxidative softening, which is of very considerable importance in the technology of this material [142]. Since such a treatment is not effective with Perbunan, various softeners are usually added to facilitate processing.

Vulcanization of the butadiene polymers is carried out with sulfur as the vulcanizing agent, together with zinc oxide and organic accelerators. With sufficient sulfur, compounds of the ebonite type can be made [157]. In these respects the butadiene polymers are similar to natural rubber and differ from Neoprene. The ebonite made from the Buna rubber is said to soften at a higher temperature than that made from natural rubber [147].

V. ORGANIC POLYSULFIDES

The condensation reactions of organic dihalides with sodium tetrasulfide indicated by the equations shown at the end of table 2 are typical of a large number of reactions [180, 183] for obtaining substances which, although bearing no chemical relation to natural rubber, conform to the definition of synthetic rubber already given. Certain products of this type are given the trade name Thiokol in the United States, and Perduren in Germany. In each unit of these compounds, two sulfur atoms are part of the main chain, while the two others are attached to them and are not part of the main chain. If the latter two sulfur atoms are removed by chemical means [180], Thiokol A yields an inextensible product, but Thiokol B yields material which is still extensible and is sold as Thiokol D [183]. Perduren G is similar to Thiokol B, while Perduren H is formed by the reaction of di(chloroethyl) formaldehyde acetal with sodium tetrasulfide [31, 183]. Perduren L is a mixture of Perduren and Perbunan. A Japanese product, Thionite, is obtained from the reaction of ethylene diglycoside with sodium tetrasulfide [172]. Vulcaplas is an organic polysulfide made in England by the reaction of glycerol dichlorohydrin with sodium tetrasulfide or similar sulfides [176]. The raw materials from which many of the polysulfide rubbers are made are relatively cheap. The sodium tetrasulfide is obtained from the reaction of caustic soda and sulfur; the organic dichlorides are produced from common organic compounds and chlorine. The chlorine is obtained from salt and many of the organic compounds can be obtained from natural gas.

The polysulfide rubbers can be vulcanized, like Neoprene, with the metallic oxides as vulcanizing agents and sulfur as an accelerator. The chemical reaction must be of a type somewhat different from that in the vulcanization of natural rubber, where there is a decrease in the number of double bonds in the long-chain molecules; for the polysulfide rubbers an oxidation with the evolution of water and an increase in chain length has been suggested [180]. Fillers are usually required for the development of satisfactory tensile strength. Carbon black is most frequently employed for this purpose.

The polysulfide rubbers, particularly Thiokol A, are by far the most resistant of the synthetic rubbers to the effects of liquids. Their chief disadvantages are a rather strong, unpleasant odor and some deficiency in mechanical properties. The odor has, however, been considerably reduced and rendered less objectionable in some of the newer varieties, and practically eliminated in others. Cold flow is a mechanical deficiency which can be reduced somewhat by increase of the amount of filler or by mixture with other types of rubber, natural or synthetic. Thiokol A is recommended for use only at temperatures between -10°C and $+70^{\circ}\text{C}$, but many of the other types are serviceable from about -40°C to $+80^{\circ}\text{C}$ [190].

VI. ISOBUTENE POLYMERS

The polymerization of isobutene, a hydrocarbon obtainable from petroleum, gives a synthetic rubber which was developed in Germany under the name Oppanol [203]. Further research has continued in the United States, where the product is sold under the name Vistanex

[206]. The polymerization is conducted at low temperatures with substances like boron fluoride or aluminum chloride as catalysts, and is extremely rapid, often being completed in a fraction of a second [200, 207]. The molecular weight of the product is controlled by the temperature at which polymerization occurs. For a temperature of -10°C , the molecular weight, as measured by the Staudinger viscosity method, is about 10,000; for a temperature of -95°C , about 250,000. Isobutene polymers with molecular weights as high as 400,000 can be prepared in this manner [206].

Since the vulcanization of natural rubber is usually thought to be connected with a chemical reaction involving double bonds in the long-chain molecules, it is not surprising to note the failure of all attempts [206] to vulcanize isobutene polymers, which contain no double bonds.

Some writers [21, 128] prefer to use vulcanizability as one of the criteria for the classification of a material as a synthetic rubber. Consequently, contrary to the practice of the present paper, they do not include among synthetic rubbers the isobutene polymers, or the plasticized vinyl chloride polymers, discussed in the following section. Isobutene polymers maintain their elastic properties at temperatures as low as -50°C and as high as $+100^{\circ}\text{C}$ [32, 194, 204].

VII. PLASTICIZED VINYL CHLORIDE POLYMERS

Polymerized vinyl chloride is ordinarily obtained as an amorphous white powder, but by the application of pressure can be converted at 120°C into a transparent brittle solid, possessing a very small extensibility [219]. By itself it is not rubberlike; it has been found, however, that by the addition of a suitable liquid it may be plasticized to give an extensible material with an increase in the ultimate elongation up to about 500 percent [212]. The amount of tricresyl phosphate, the plasticizer most commonly employed, may be as high as 60 percent of the total. In the United States, Koroseal and Flamenol are the most widely used varieties of plasticized vinyl chloride polymers. The vinyl chloride polymers, like the isobutene polymers, contain no double bonds, as can be seen in table 2. Similarly, no method for their vulcanization has been discovered. No increase in tensile strength has been found when fillers are mixed with plasticized vinyl chloride polymers [212]. Since a reversible softening of the material occurs when it is heated, service temperatures above 77°C are not recommended [215].

Fuoss [219] has given an equation for the calculation of the specific volume, V , in cm^3/g , of mixtures of polymerized vinyl chloride and tricresyl phosphate. His equation is equivalent to

$$V=0.706+0.155P,$$

where P is the weight of tricresyl phosphate expressed as a fraction of the total. A mixture of 40 percent of tricresyl phosphate with polymerized vinyl chloride was found [217] to have a specific heat of 0.417 cal/g between 28° and 59°C and a thermal conductivity of $1.42 \pm 0.07 \times 10^{-3} \text{ j} \cdot \text{sec}^{-1} \cdot \text{cm}^{-1} \cdot \text{deg}^{-1}$ at temperatures between 50° and 100°C .

VIII. COMPARISON OF PROPERTIES

1. DENSITIES

Values of the densities of a number of different varieties of synthetic rubber are shown in table 3. The temperature of the observation was seldom specified but may be presumed to have been between 20° and 25° C. It will be noted, as might be expected, that the varieties consisting of hydrocarbons possess the lowest densities, while the varieties containing chlorine, namely Neoprene and Koroseal, and those containing sulfur, namely, the Thiokols and Perdurens, have higher densities.

TABLE 3.—Densities of unvulcanized materials

Material	Density	Reference
	<i>g/cm³</i>	
Natural rubber.....	0.911	[223]
μ -Polymer of chloroprene.....	1.23	[60]
Neoprene.....	1.25	[93]
Perbunan.....	.96	[128]
Perbunan Extra.....	.97	[128]
Methyl rubber (20° C).....	.9292	[33]
Thiokol A.....	1.60	[190]
Thiokol D.....	1.34	[190]
Thiokol DX.....	1.39	[190]
Thiokol F.....	1.38	[190]
Perduren G.....	1.68	[31]
Perduren H.....	1.56	[31]
Perduren L.....	1.17	[31]
Vistanex HM (25° C).....	.9125	[202]
Vinyl chloride polymer containing 0% plasticizer.....	1.42	[219]
Vinyl chloride polymer containing 30% plasticizer.....	1.33	[219]
Vinyl chloride polymer containing 60% plasticizer.....	1.25	[219]

2. REFRACTIVE INDICES

The values of refractive index which have been reported are shown in table 4.

TABLE 4.—Refractive indices of unvulcanized materials

Material	Temperature	<i>n_D</i>	Reference
	<i>° C</i>		
Natural rubber.....	25	1.5190	[227]
μ -Polymer of chloroprene.....	20	1.5512	[60]
Neoprene.....	25	1.5580	[51]
Do.....	30	1.5562	[51]
Perbunan.....	25	1.5213	[51]
Do.....	30	1.5198	[51]
Methyl rubber.....	20	1.525	[33]
Vistanex HM.....	25	1.5089	[209]
Do.....	10	1.5131	[209]
<i>Components of plasticized vinyl chloride polymers:</i>			
Vinyl chloride polymer (unplasticized).....	40	1.565	[219]
Tricresyl phosphate (plasticizer).....	40	1.5494	[219]

3. IDENTITY PERIODS ALONG THE FIBER AXES

The X-ray patterns obtained when many of the varieties of synthetic rubber are stretched indicate the existence of a fiber structure

during stress. Identity periods along the fiber axes have been reported, in angstrom units, as follows:

Natural rubber.....	8.20 A [226].
μ -Polymer of chloroprene.....	4.81 A [60, 73, 75].
Thiokol A.....	4.32 or 8.64 A [37, 38].
Oppanol.....	18.50 A [196].
Vistanex.....	18.63 A [199].
Vinyl chloride polymer (un- plasticized).....	5.0 A [37].

4. ELECTRICAL PROPERTIES

The published data on the electrical properties of the various varieties of synthetic rubber are rather incomplete. The presence of polar groups—chlorine in Neoprene and Koroseal, and the nitrile group in Perbunan—is responsible for relatively high values of conductivity and dielectric constant in the types mentioned. The following values have been observed [102] at 28° C and are said to be representative of Neoprene compounds containing only enough added ingredients to insure proper vulcanization: dielectric constant at 1,000 c/s, 7.5; power factor at 1,000 c/s, 300×10^{-4} ; and d-c conductivity, 10^{-12} mho·cm⁻¹. The electrical properties of Buna 85, Buna 115, and Buna S are nearly alike. Values reported [156] for a temperature of 20° C are dielectric constant at 50 c/s, 2.9; power factor at 50 c/s, 7×10^{-4} ; and conductivity, 10^{-15} — 10^{-14} mho·cm⁻¹. Perbunan, with its polar nitrile group, has a dielectric constant of the order of 15 and a conductivity of 10^{-7} — 10^{-6} mho·cm⁻¹ [158].

The same author [153] has more recently reported values for Buna S and Buna SS at 20° C as: dielectric constant at 50 c/s, 4.3 to 4.7; and power factor at 50 c/s, 170×10^{-4} . In the same work the conductivity of Perbunan was given as between 10^{-10} and 10^{-8} mho·cm⁻¹. The dielectric constant of a Thiokol compound has been reported as 4.60 [58]. Scott [205] has made some electrical measurements on Vistanex at 25° C. The dielectric constant at 1,000 c/s and at 100,000 c/s was found to be 2.29. The power factor at 1,000 c/s was measured at 1.5×10^{-4} and at 100,000 c/s as 3.4×10^{-4} . The d-c conductivity 1 minute after the application of the potential was less than 20×10^{-18} mho·cm⁻¹. The electrical properties of vinyl chloride polymers, plasticized with tricresyl phosphate, have been the subject of extensive studies by Fuoss [216, 217, 218, 219] and by Davies and Busse [213]. The results obtained are too detailed and complex for summary here, but a few values selected from one paper [219], reporting measurements at 40° C, are given below.

Plasticizer	Dielectric constant		Direct-current conductivity
	60 c/s	1,000 c/s	
Percent			mho·cm ⁻¹
0.....	3.435	3.338	0.1×10^{-12}
30.....	7.56	5.72	2.8×10^{-12}
60.....	10.18	9.65	$323. \times 10^{-12}$

5. TENSILE STRENGTHS

The maximum reported values of the tensile strengths with the corresponding elongations for different kinds of synthetic rubber are

given in table 5. Since the data were necessarily obtained from a number of sources, the conditions of measurement may not have been strictly comparable in all cases. In some instances, the figures have been rounded off from those actually observed. The figures refer, respectively, to the unvulcanized material, to a vulcanized compound containing no fillers, and to a vulcanized compound containing approximately the optimum amount of carbon black for maximum tensile strength in each case.

TABLE 5.—Maximum tensile strengths and corresponding elongations

Material	Unvulcanized			Vulcanized pure-gum compound			Vulcanized carbon-black compound		
	Tensile strength	Elongation	Reference	Tensile strength	Elongation	Reference	Tensile strength	Elongation	Reference
	<i>kg/cm²</i>	<i>%</i>		<i>kg/cm²</i>	<i>%</i>		<i>kg/cm²</i>	<i>%</i>	
Natural rubber.....	25	1, 200	[228]	290	710	[33]	350	650	[33]
Neoprene.....	30	1, 100	[86]	300	820	[86]	290	700	[91]
Buna 85.....							175	600	[147]
Buna 115.....							200	700	[147]
Buna S.....							280	650	[147, 156]
Perbunan.....				150	900	[128]	320	600	[128]
Methyl rubber W.....				30	510	[33]	170	530	[33]
Methyl rubber H.....				90	240	[33]	160	300	[33]
Thiokol A.....							60	370	[183, 190]
Thiokol D.....	7	570	[179]	35	750	[190]	120	610	[179]
Vistanex MM (Oppanol B100).....	20	1, 000	[201]						
Vistanex HM (Oppanol B200).....	60	1, 000	[32, 201]	(a)	(a)		(a)	(a)	
Koroseal 0% plasticizer.....	400	2	[212]						
Koroseal 30% plasticizer.....	270	170	[212]						
Koroseal 60% plasticizer.....	70	500	[212]						

* Not vulcanizable.

A study of table 5 reveals a number of interesting facts. The major increase in tensile strength of natural rubber occurs on vulcanization; the effect of the addition of carbon black is to increase the tensile strength somewhat and to stiffen the rubber quite considerably. No synthetic rubber compounds have been made with tensile strengths exceeding those of the best carbon-black compounds of natural rubber. Neoprene shows no increase in tensile strength with the addition of carbon black, but undergoes a stiffening. Thiokol, very weak in the unvulcanized form, is markedly strengthened by vulcanization; by far the major increase in tensile strength, however, occurs on the addition of carbon black. Carbon black is also the major factor in obtaining high tensile strengths with Perbunan and the other types of Buna rubber, as well as with methyl rubber. Vistanex shows an increase of tensile strength with increasing molecular weight; the figures given are presumably for molecular weights of the order of 100,000 and 200,000, respectively. Koroseal is found to decrease in tensile strength and to increase in the corresponding elongation, as the amount of plasticizer is increased.

6. SUPERIORITIES OF SYNTHETIC RUBBERS TO NATURAL RUBBER

The higher cost of synthetic rubbers is offset in a number of cases by the superiority of some of their properties in comparison with those of natural rubber. Foremost among these properties at present is

resistance to the effects of liquids, particularly petroleum products. Table 6 presents the results of swelling measurements for natural and synthetic rubbers in a number of liquids in which the swelling of natural rubber is particularly large. The figures have, in some cases, been rounded off from those actually observed. Since the data were necessarily obtained from a number of sources, the values, like those for tensile strength, may not be strictly comparable in all cases. However, the figures suffice to give an idea of the orders of magnitude involved and an idea of the relative swelling of different types of synthetic rubber.

TABLE 6.—*Swelling of vulcanized compounds in liquids*

[Volume increase, in percent, after immersion for 8 weeks at room temperature]

Liquids	Natural rubber	Neoprene	Perbunan	Perbunan Extra	Thiokol A	Thiokol D	Thiokol DX, F
	%	%	%	%	%	%	%
Light gasoline (benzine).....	150		20	20	0		
Gasoline.....	230	8	40		0	3	3
Kerosine.....		60			0	2	2
Diesel oil.....	120		15	15			
Fuel oil.....					0	10	10
Lubricating oil.....		40	-4		0	1	1
Paraffin oil.....	140		3				
Transformer oil.....	150		5				
Acetone.....		25	110	100			9
Benzene.....	370	160	210	140	7	150	90
Carbon tetrachloride.....	670	160	220	120	0	40	30
Ethyl ether.....	130	50	50				
Linseed oil.....	100		20			1	1
Turpentine.....	300	90	50	30	0		
References.....	[156]	[96]	[31, 49, 156]	[31]	[190]	[190]	[190]

The first eight liquids are petroleum products, in the handling of which synthetic rubber has been found particularly useful. Unfortunately, the common names used for the liquids are insufficient to describe their chemical compositions, which may vary widely with place of origin and subsequent treatment. Since the swelling is determined largely by the chemical composition of the liquid, such a wide variation of values is obtained that the figures quoted for these products are less significant than those for the others. Neoprene, for example, may swell in different lubricating oils at 100° C as much as 120 percent or as little as 12 percent [95]. Correlation is found with a figure which represents to some extent the ratio of aliphatic to aromatic constituents in the oil.

For many uses loss of tensile strength on swelling is an even more serious factor than the actual swelling. Very little information on this subject has been published. Usually the tensile strength of a synthetic rubber shows less impairment than that of natural rubber, even when the amounts of swelling are not widely different. Synthetic compounds can be made which are greatly superior to natural rubber in that there is much less extraction of soluble material by liquids in contact with them.

The second important general superiority of many synthetic rubber compounds is their resistance to deterioration or aging under conditions which impair the utility of natural rubber. Some of these conditions are exposure to the oxygen of the atmosphere, to ozone from electric discharges, or to light, especially direct sunlight [102, 187] or

to high temperatures [102, 147, 162]. Flex-cracking can also be considerably reduced or eliminated in many cases [91, 128].

Since the usual deterioration of natural rubber is thought to be connected with an oxidation reaction involving the double bonds, it is not surprising to note the superiority, in this regard, of isobutene polymers [206] and plasticized vinyl chloride polymers [212], which contain no double bonds.

Synthetic rubber compounds can be made which show a greatly decreased permeability to liquids and gases as compared with natural rubber. Part of the advantage is due to the absence of proteins and other nonhydrocarbon constituents, and part to differences in structure. The diffusion constant for water is defined by Taylor, Herrmann, and Kemp [57] as the number of grams of water-vapor passing through 1 cm² of the material 1 cm thick in 1 hour under a differential pressure of 1 mm of mercury. The values which they found are as follows:

Soft vulcanized rubber.....	6.66 × 10 ⁻⁸ g.hr ⁻¹ .cm.cm ⁻² .(mm of mercury) ⁻¹ .
Ebonite.....	1.51 × 10 ⁻⁸ g.hr ⁻¹ .cm.cm ⁻² .(mm of mercury) ⁻¹ .
Neoprene, vulcanized.....	2.63 × 10 ⁻⁸ g.hr ⁻¹ .cm.cm ⁻² .(mm of mercury) ⁻¹ .
Thiokol A.....	0.22 × 10 ⁻⁸ g.hr ⁻¹ .cm.cm ⁻² .(mm of mercury) ⁻¹ .
Plasticized vinyl chloride polymer..	3.85 × 10 ⁻⁸ g.hr ⁻¹ .cm.cm ⁻² .(mm of mercury) ⁻¹ .

Roelig [153] has given corresponding figures for the Buna rubbers. Buna SS has a lower permeability than natural rubber, especially when the unvulcanized materials are compared.

The permeability to gases, of several types of synthetic rubber, has been measured by Sager and Sucher [99], by Sager [189], and by Barrer [44]. "Permeability" is defined by the former observers as the number of cubic centimeters per minute passing through a membrane 1 cm thick and 1 cm² in cross-sectional area, when it separates air at atmospheric pressure from the gas at a pressure of 30 mm of water above atmospheric. The mean values which they obtained for hydrogen at 25° C are as follows:

Rubber.....	24	× 10 ⁻⁶ cm ³ .min ⁻¹ .cm.cm ⁻² .
Neoprene.....	4.2	× 10 ⁻⁶ cm ³ .min ⁻¹ .cm.cm ⁻² .
Thiokol B.....	0.71	× 10 ⁻⁶ cm ³ .min ⁻¹ .cm.cm ⁻² .
Thiokol D.....	1.5	× 10 ⁻⁶ cm ³ .min ⁻¹ .cm.cm ⁻² .

Buna S, Buna 85, and Buna 115 possess about the same permeabilities to air as natural rubber does, but Perbunan vulcanizates show a permeability less than half as large [147, 153].

Since a very appreciable fraction of the weight of Neoprene and Koroseal consists of chlorine, these materials show a greater resistance to burning than natural rubber. They burn when a flame is applied, but combustion usually ceases when the flame is removed [91, 212].

Losses from abrasion measured in the laboratory are reported to be about the same for the best compounds of Buna 85 and Buna 115 as for a high-grade tire tread of natural rubber [147]. With Buna S, the abrasion is said to be about 25 percent less and with Perbunan about 40 percent less. The figures refer to a material containing no softener or plasticizer. With the addition of the plasticizers which are necessary for working the materials on ordinary rubber machinery, as is done in the manufacture of tires on a plant scale, the advantages in resistance to abrasion are considerably reduced. It is stated that road tests in which 40 test cars traveled about 750,000 miles showed losses from abrasion for tires of Buna S and Perbunan to be about 10

percent less and about 30 percent less, respectively, than for tires of natural rubber [161]. More recently the figure of 25 to 35 percent has been given as the result of a long series of road tests on tires of Buna S [128]. The other varieties of synthetic rubber are either inferior to natural rubber in resistance to abrasion, or only slightly superior.

The absorption of energy by synthetic rubber during repeated stresses is generally greater than that for natural rubber [84, 102, 103, 104, 154, 160]. This quality, a disadvantage under many conditions, especially where it may lead to overheating of the rubber as in tires, is desirable in cases where the rapid damping of vibrations is important.

As has been already mentioned, emulsion polymerization yields a latex similar to that of natural rubber. The latices of Neoprene [60, 105a, 106] and Buna S [164] contain particles which are smaller than those in the latex of natural rubber and are more nearly uniform in size. Furthermore, they contain no organic impurities subject to putrefaction through bacterial action. Consequently, they are often used where the penetration of the latex into fine pores is of importance or where decomposition must be avoided. The latex of Thiokol A contains particles larger than those of natural rubber [193].

The electrical properties of some types of synthetic rubber, notably Vistanex [205] and Buna S [153, 156], may be superior to those of natural rubber. The presence of polar groups, as already mentioned, is responsible for relatively high values of conductivity in Neoprene, Perbunan, and Koroseal. This property may sometimes be turned to advantage as for example in the dissipation of undesired static charges.

IX. APPLICATIONS OF SYNTHETIC RUBBER

The applications of synthetic rubbers, like those of natural rubber, are so many and varied that it is impossible to do more than list some of the general fields and to illustrate with a few specific examples. In general there are possibilities for the use of synthetic rubber in every application of natural rubber and in a number of additional fields from which natural rubber is barred by some of its deficiencies. No single type of synthetic rubber possesses outstanding advantages in all fields. However, for any given application it is usually possible to select a particular variety of synthetic rubber which excels natural rubber in some property of importance for that application. Possibly no individual synthetic rubber will ever have as wide a field of application as natural rubber, but collectively synthetic rubbers possess a marked advantage over natural rubber by reason of the diversity of properties which they afford.

The commercial applications of synthetic rubber throughout the world today are determined in part by considerations of national economy and in part by those of the inherent characteristics of the different varieties. More natural rubber is used in vehicle tires and tubes than in any other single field of application. Where considerations of national economy enter, notably in Germany and in Russia, synthetic rubber is used very extensively for this purpose. Elsewhere, however, its higher cost has thus far prevented anything more than experimental applications in this field, where the deficiencies of natural rubber are not particularly noticeable.

Buna S is at present the type of synthetic rubber in general use in Germany for tires, while Perbunan is generally reserved for those

uses where resistance to the effects of liquids is important [128]. There are several important factors dictating the choice of Buna S rather than Perbunan for tires. It is cheaper to produce, and plasticization with hot air is possible. In adhesive properties Buna S is superior to Perbunan, although still inferior to natural rubber. Natural rubber, because of its greater adhesiveness and smaller energy absorption, is sometimes used for the carcass of a tire in which Buna S is used for the tread. A direct bonding between the two, without the use of intermediate material, is possible, but direct bonding is impossible between Perbunan and natural rubber. The lack of sufficient adhesiveness leads to difficulties in building tires with a large number of plies without the use of natural rubber. The manufacture of 4-ply and 6-ply passenger car tires exclusively from Buna S is said to be on a satisfactory basis, but some problems connected with the manufacture of heavy truck tires apparently have not yet been completely solved [111, 128].

Each of the properties in which synthetic rubbers may be superior to natural rubber, as mentioned in the preceding section, suggests possible applications for the former. Resistance to the effects of liquids, particularly hydrocarbons, is responsible for the very extensive use of synthetic rubber in hose and tubing especially in the handling of petroleum products. In oil fields, refineries, tankers, filling stations, and in the automobile itself, petroleum products now usually pass through hose and tubing of synthetic rubber and into tanks which are sealed with it. Elsewhere in the automobile are many other parts which may come in contact with oil. More of them every year are being made of synthetic rubber or jacketed with it. The number of such parts at present on some cars is said to be as high as thirty or forty. For use in contact with oils, grease, fats, and many chemicals mountings for vibration absorption, conveyor belts, tires for industrial trucks, gaskets, and sealing devices are being made of synthetic rubber. Additional examples are shoe soles and heels, aprons, gloves, and similar articles for personal use under the same conditions. The relative stability of synthetic rubbers towards liquids is responsible for their increasing use in printers' rolls and blankets, engraving plates, and similar articles. Tubes for spraying equipment for paints and lacquers utilize synthetic rubber to advantage. Neoprene, Thiokol, and Koroseal are extensively used in these applications.

The electrical uses of synthetic rubber deserve special mention. As already noted, Vistanex, Buna S, and the numbered Bunas are the only varieties which show superiorities to natural rubber in respect to purely electrical properties. They are being used as insulation for wires and cables. For many uses, especially at low voltages, the other varieties, such as Neoprene, Thiokol, and Koroseal, may be used also for insulation. There is much wider application, however, of these other varieties as jackets over insulation of natural rubber. They are frequently used in this way to protect natural rubber from the effects of light, air, ozone, oils, and other deteriorating influences. In many types of cables, jackets of synthetic rubber are displacing the lead sheaths formerly used.

The properties of low permeability to gases and stability in direct sunlight have been responsible for the use of synthetic rubber in balloons, from small ones intended for meteorological observations to large passenger-carrying dirigibles. For example, the Goodyear

airship *Resolute*, used for sightseeing flights, is covered with fabric coated with Neoprene.

The impregnation of silk, cotton, and other fabrics with synthetic rubber of better aging qualities than the natural opens up a whole field of household and personal uses. A few examples of products of this type are umbrellas, raincoats, tablecloths, shower curtains, and garment bags. Koroseal, which can be obtained in an extremely wide variety of colors, is especially applicable in this field.

X. PRODUCTION FIGURES AND PRICES

The steady increase in production of each type of synthetic rubber has been accompanied in general by a decrease in price. Many types are still produced in such small quantities that an expanded scale of operations may yet bring drastic reductions in price. In Germany and Russia, the only foreign countries where significant amounts of synthetic rubber are being produced, political considerations enter into reports of production figures, and the controlled economy of these countries makes it almost impossible to compare costs with those elsewhere. Even when market prices are known the foreign exchange situation of these countries renders impossible a really significant calculation for the conversion of currencies.

In Germany a plant at Schkopau with a capacity of 25,000 tons a year began production in April 1939 [55]. Another at Huls, Westphalia, of the same capacity has been under construction, and is probably now in operation [3]. Recent Russian figures are not available, but estimates as high as 50,000 tons a year or more are not uncommon [115, 124].

Compared with these figures for the countries where synthetic rubber is used in tires, the production figures seem very small for the United States, where such is not the case. The total production of synthetic rubber of all types in the United States in 1939 probably did not exceed 2,500 tons. Frolich [8] has also recently made a similar estimate. Neoprene and Thiokol have been produced in far larger quantities than the other types.

The present market price of Neoprene is from 65 to 75 cents a pound, depending on the variety; that of Thiokol is from 35 to 60 cents a pound; that of Vistanex is from about 60 cents to a dollar a pound. Koroseal is not sold on the open market, but its price is estimated as being of the order of 50 or 60 cents a pound. The cost of the Buna rubbers has been stated to be less than four times the cost of the natural rubber [125]. Perbunan has been sold in the United States at about a dollar a pound, a figure in general agreement with this statement. The cost has probably been somewhat reduced by the recent very extensive expansion of production facilities already mentioned.

XI. BIBLIOGRAPHY

The bibliography cites with some degree of completeness the scientific literature of the decade 1930-1940, in which almost all the development of modern synthetic rubber has occurred. References to the patent literature are included only rarely. Brief summaries of almost 250 United States patents dealing with synthetic rubber have been given in a series of articles by Rossman [26]. The patents have also been discussed in some detail by Génin [10], Voge [32a],

Whitby and Katz [33], and Midgley [18]. The Russian literature, which includes at least one journal devoted exclusively to synthetic rubber, has not been exhaustively investigated, because the journals are not readily accessible, and most of the work has not had a great deal of influence outside of Russia. Sixteen references which have been found to be especially valuable or important are marked with an asterisk. Of the two books devoted exclusively to synthetic rubber the one by Schotz [28], published just before the beginning of the modern development of synthetic rubber, is chiefly of historical interest. The book by Naunton [19] includes much more recent information, and is particularly complete in its discussion of Neoprene.

I. GENERAL DISCUSSION, COVERING TWO OR MORE TYPES.

A. General survey

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