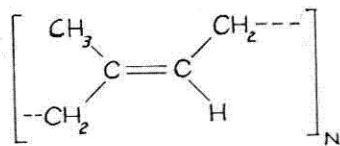




chains in which the unit  $C_5H_8$  is repeated many times. This process is known as linear polymerization, and the product is a linear polymer. Raw rubber is believed to be formed in nature by essentially this process; the chains of polyisoprene present are of variable length; the number of isoprene units per chain ranges up into the thousands. The structure of natural rubber may accordingly be represented as—



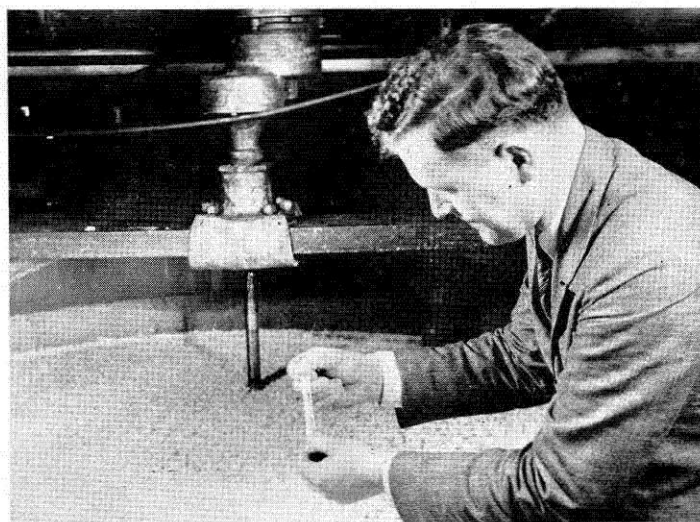
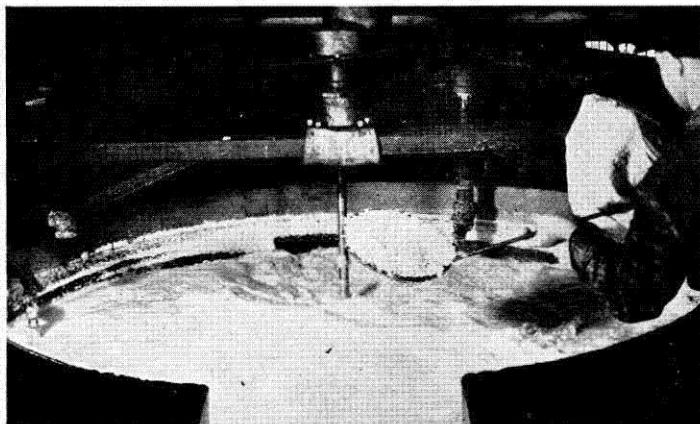
where N is a large number whose value varies from one chain to another.

The familiar elastic properties of natural rubber are due to the fact that these chains are flexible; they can bend by a process in which groups connected by a single bond rotate about that bond. In a piece of raw rubber most of the chains tend to be coiled rather than extended as straight as possible. When an attempt is made to stretch the rubber, the coiled chains may slip past one another, in which case the rubber is permanently deformed. The process occurs with natural rubber at temperatures not very far above room temperature; the rubber is then said to be plastic. Over a small range of temperature the chains in raw rubber instead of slipping past one another uncoil to some extent under an applied stress which is not too great, but are eager to return to their initial configuration when the stress is removed. Under these circumstances the rubber manifests its familiar and useful elastic properties.

The double bonds which still remain in polyisoprene are the most reactive parts of the molecule and are important for two reasons. In the process of vulcanization sulfur reacts with the double bonds and this reaction is believed to result in the formation of cross-links between the chains which tend to prevent the chains from slipping past one another. At any rate the result of vulcanization is to increase the tensile strength and the range of temperature over which rubber shows its useful elastic properties. Articles made of unvulcanized rubber are relatively useless; they become brittle in cold weather and plastic and tacky in warm water. If vulcanization is carried far enough with a large enough proportion of sulfur, the chains are so firmly bound together that the rubber becomes hard and relatively inextensible. The double bonds in polyisoprene are also the points at which the molecule is attacked by oxygen. Reaction with oxygen has results similar to those obtained by reaction with sulfur; the familiar embrittlement and cracking resulting from atmospheric deterioration of rubber is principally the result of attack by oxygen.

Besides being subject to attack by oxygen and other chemicals which react with the double bonds in polyisoprene, rubber is also subject to attack by solvents such as benzene, gasoline, petroleum oils, etc. The relatively small molecules of solvent are attracted to the polyisoprene chains by van der

Waals forces, just as the chains are attracted to each other. If the attraction between solvent molecules and isoprene chain is greater than the attraction between the chains themselves,



Courtesy of Chemical and Metallurgical Engineering.

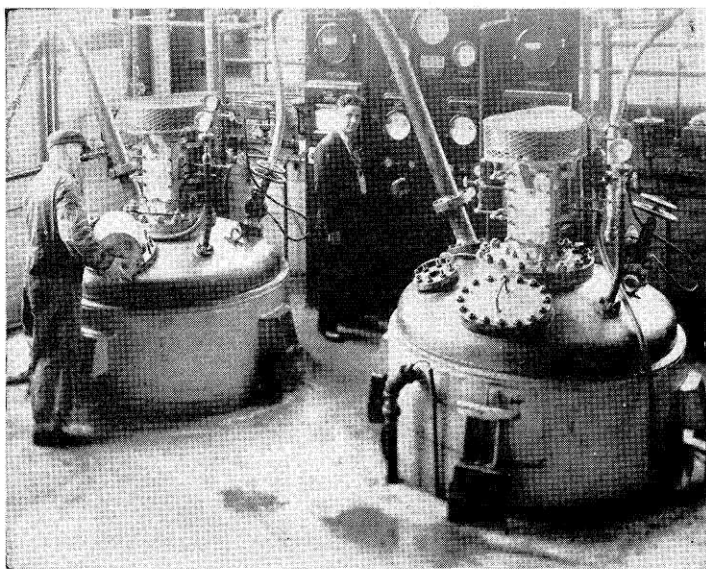
Vat of a solution of raw rubber after it has been coagulated showing close-up of a strainer full of curd-like particles. Curd rises to the top of the solution after the washing process.

solvent molecules squeeze in between the chains and cause the rubber to swell and become soft. Certain solvents when present in excess may even dissolve part or all of the rubber. The susceptibility to attack by solvents is decreased but not removed by vulcanization.

The most obvious course to follow in attempting to make synthetic rubber would be to make isoprene synthetically and to attempt to polymerize the isoprene to yield a product similar to natural rubber. Some synthetic rubber has been made this way in the past, but this method is not now of commercial importance because isoprene is relatively difficult and expensive to prepare, and its polymerization is relatively difficult to control. Modern methods for making synthetic rubber involve the synthesis of compounds which can be cheaply obtained from abundant raw materials and are capable of forming flexible linear polymers similar to polyisoprene. No synthetic rubber has been prepared so far which is quite the equal of natural rubber in flexibility and rebound, but several varieties of syn-

thetic rubber are superior to natural rubber in their resistance to attack by oxygen and other chemicals and to swelling by certain solvents.

It should be remarked that natural rubber, before it is made into useful articles such as tires and conveyor belts, is mixed or compounded with a variety of substances; sulfur for vulcanization, carbon black and other finely divided solids to increase resistance to abrasion, plasticizers to decrease brittleness at low temperatures, and other materials which, though



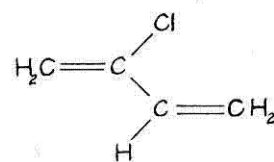
Courtesy of Chemical and Metallurgical Engineering.

**Butadiene and other ingredients which go into the production of synthetic rubber are polymerized in large steel vessels in which they are agitated and emulsified in a soap solution under pressure.**

present in small quantity, are extremely important; i.e. accelerators to speed up the vulcanization reaction and enable its closer control, and antioxidants to delay deterioration by oxygen. The proper kinds and proportions of these substances, the proper methods for incorporating them with the rubber, and the duration of and conditions in the final heating process in which vulcanization or curing is carried out—in a word, the ways in which all the operating variables must be controlled to produce a product of the desired properties—have been discovered empirically as the result of multitudinous experiments. For each type of synthetic rubber a similar program of time-consuming experimentation is required before optimum conditions for utilization of the rubber can be established. The use of synthetics is further complicated by the effect of variations in the conditions under which the raw materials are polymerized. Fortunately a considerable amount of experimental information is already available as a result of investigations carried out by the chemical and rubber industries in adapting synthetic rubber to special applications for which its superiority in certain properties enabled it to compete, in spite of higher price, with natural rubber.

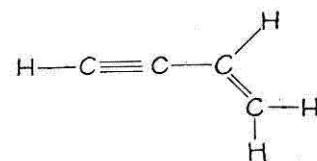
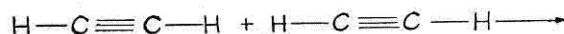
One of the first rubbers to become of commercial importance in this country was Neoprene, announced by duPont in

1932. Neoprene is a polymer of 2 chloro 1, 3 butadiene, whose structure is—

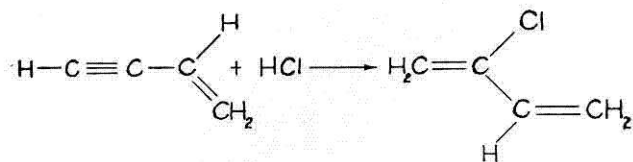


It will be noticed that this structure is identical with that of isoprene except for the replacement of the  $\text{CH}_3$  group by a chlorine atom.

The raw materials for neoprene are coke, lime, and hydrochloric acid. Coke and lime are heated in an electric furnace to produce calcium carbide which will react with water to produce acetylene. By means of a suitable catalyst acetylene is made to react with itself to produce vinyl acetylene, a gas.



This gas is swept rapidly through a mixture of hydrochloric acid and a cuprous chloride catalyst to produce chloroprene—

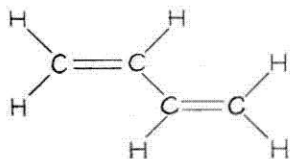


which polymerizes, under the influence of air as a catalyst, to produce a tough jelly, the so-called alpha polymer. The material may be stabilized in this form by the addition of diphenylguanidine and can then be compounded with other materials just as natural rubber can. The vulcanizing process can be carried out without sulfur, simply by heating with suitable catalysts, such as zinc chloride, aniline, or naphylamine.

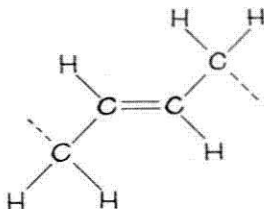
Several types of Neoprene rubber are produced. They are similar to natural rubber in mechanical properties, but excel natural rubber in resistance to oxidation and to chemical attack generally. They are much more resistant than natural rubber to swelling and dispersion by petroleum oils, though they are subject to swelling and solution in aromatic hydrocarbons such as benzene. Neoprene is satisfactory for many purposes for which ordinary rubber is not, for example, for gasoline lines and tanks. The price quoted in August, 1941, for Neoprene GN was sixty-five cents a pound as compared to twenty-three cents a pound for raw natural rubber. Yes, it is suitable for tire treads.

The principal products of the new production program will, however, be of the Buna type. This type derives its name

from butadiene and the symbol for sodium, Na. The reaction on which this name is based is the sodium-catalyzed polymerization of butadiene:



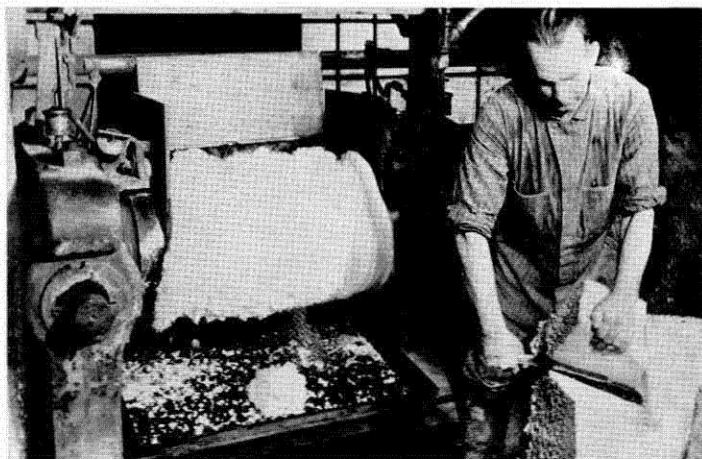
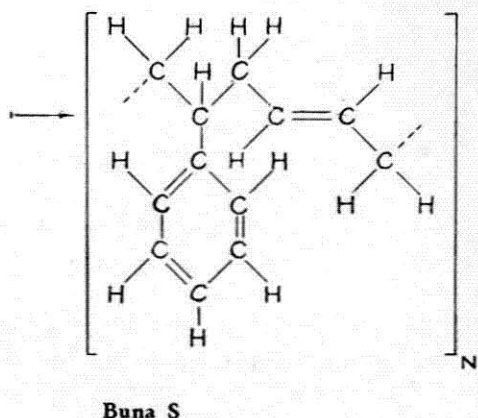
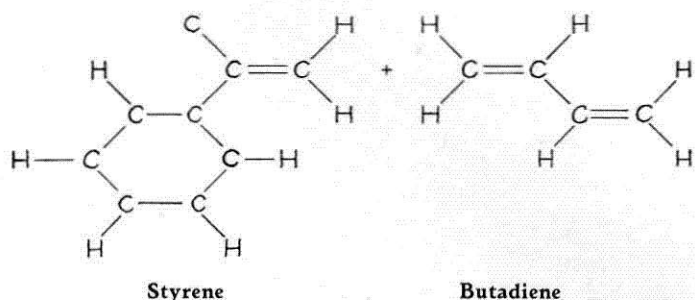
to produce long chains which are repetitions of the unit.



This structure occurs in the synthetic rubber known as Buna 85.

It has been found that a product of better mechanical properties and better resistance to solvents is obtained by polymerizing a mixture of butadiene and another unsaturated compound to produce linear copolymers in which the units which make up the chain are derived from both compounds.

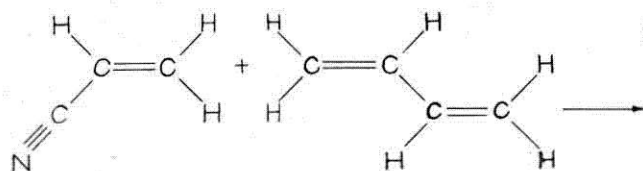
Thus the synthetic rubber known as Buna S is made by the catalytic polymerization of butadiene and styrene, according to a reaction which may be represented as follows:



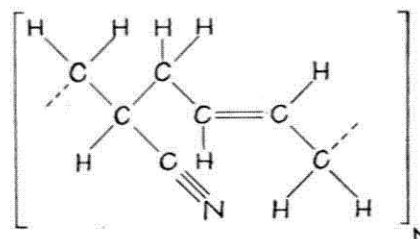
Courtesy of Chemical and Metallurgical Engineering.

Chunks of rubber, cut from the block in the foreground, are placed on a washmill where moisture is extracted and it is sheeted into thin sheets.

Likewise, the synthetic rubber known as Buna N, or Perbunan, is a copolymer of butadiene and acrylonitrile, prepared according to the reaction—



Acrylonitril



Perbunan

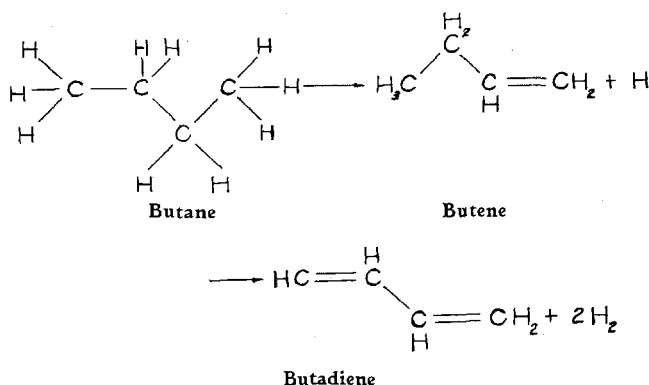
It is estimated that perhaps seventy per cent of the synthetic rubber program will be devoted to the production of the Buna copolymers. Under such names as Ameripol, Hycar, and Chemigum, this type of synthetic rubber has been on the American market for some time, and has been used for the production of conveyor belts, hose, gaskets, machinery mounts, and oil-resistant insulation. The Buna rubbers can be compounded and vulcanized in essentially the same way as natural rubber by the use of machinery of the type at present available in the rubber industry, though the details of the compounding procedure must be varied to fit the properties of the polymer being processed. One difficulty is that uncured Buna rubber is considerably stiffer and harder to work in the compounding mill than is natural rubber, and tends to overheat during compounding. If care is not used in the compounding,

(Continued on page 16)

(Continued from page 7)

the rubber gets hot enough to become partially depolymerized, and must be discarded. This is one of the principal problems with which the tire companies attempting to use synthetics in tires have had to contend. Buna tires have been in use in Germany for several years and have been successfully made in this country; in fact early in 1941 tires made of synthetic rubber of the Buna type were being produced by one company at the rate of 500 to 1000 a week. It is said that passenger-car tire treads which are at least equal and perhaps superior in durability to those made from natural rubber can already be made from Buna type synthetics, and the possible improvements which may result from variations in processing techniques, and in the proportion of butadiene in the copolymers have not yet been fully explored.

The butadiene required can be prepared in a variety of ways, but the most likely sources are butane from natural gas and butene from the gaseous products of cracking processes in petroleum refineries. The reaction involved is essentially the removal of hydrogen at high temperatures under the influence of a catalyst.



A mixture of products is obtained from which the butadiene can be extracted and purified. The operations are of a type with which the refiners of petroleum and the manufacturers of synthetic organic chemicals are familiar, and the supply of raw material for butadiene production is enormous. Styrene can be separated from the products obtained by cracking selected petroleum fractions or can be made from ethylene (a by-product of petroleum refining) and benzene by catalytic operations at high temperatures. The acrylonitrile can be made from ethylene, chlorine, water and sodium cyanide, or from acetylene and hydrocyanic acid. Considerable expansion in the facilities for making these compounds in reasonably pure form will be required for the production of synthetic rubber on a large scale, and this expansion is in progress.

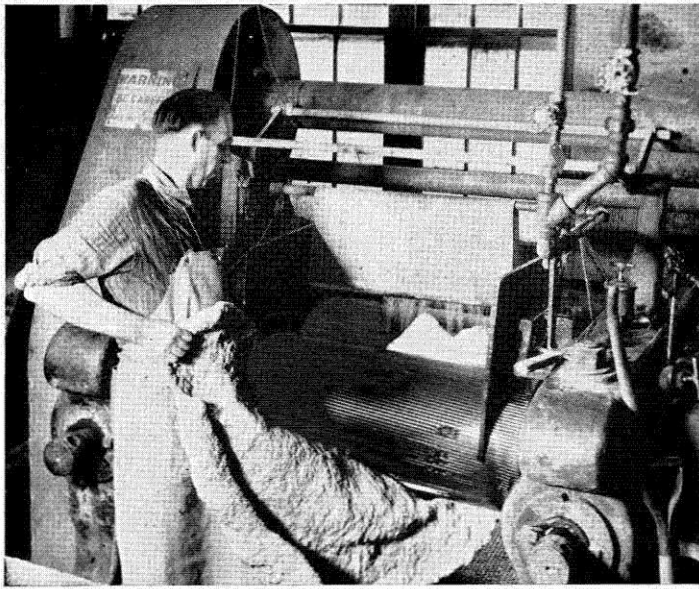
The preparation of the Buna copolymer itself is carried out by emulsifying butadiene and either styrene or acrylonitrile with water containing a suitable catalyst and agitating the mixture under suitable conditions of temperature and pressure. The reaction conditions must be closely controlled. The polymer separates out as a sort of synthetic latex, a creamy suspension of small particles of the polymer in the water. This latex can be coagulated by the addition of acids and processed like natural rubber.



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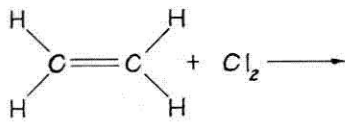


Courtesy of Chemical and Metallurgical Engineering.

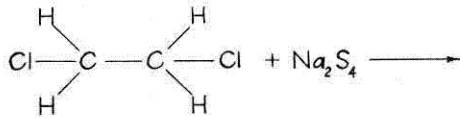
Mill man cutting a sheet of rubber so as to remove it from the wash mill.

It is estimated that when the methods for large scale processing have been stabilized Buna copolymer rubber can be made for perhaps thirty cents a pound, perhaps for as little as twenty cents. The cost of producing natural rubber in the far East in normal times ranges up to ten cents a pound, and the selling price of natural rubber in New York in recent years has ranged from three to twenty-seven cents a pound.

In addition to the Neoprenes and the Bunas there is a variety of synthetic rubber-like materials which are not so suitable as all-purpose substitutes for natural rubber, but are so superior to natural rubber for special purposes that even in normal times they compete successfully with natural rubber. For example there are the thiokols, made from unsaturated hydrocarbons, chlorine, and sodium sulfide according to reactions like the following:

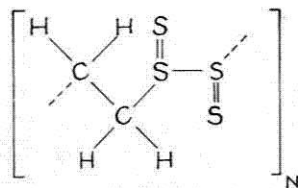


Ethylene Chlorine



Ethylene Dichloride

Sodium Tetrasulfide.



Thiokol

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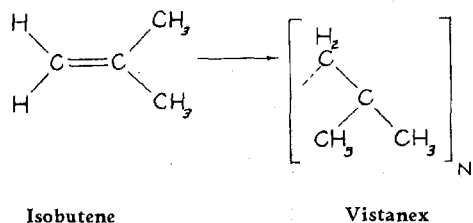
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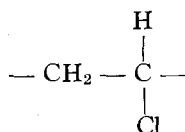
This type of rubber can be produced relatively cheaply and rapidly, is resistant to oxidation and to attack by many solvents, and is much less permeable to gases than is natural rubber.

Another type of synthetic rubber is obtained by polymerizing hydrocarbons containing a single double bond. Thus Vistanex is produced from isobutene obtained from petroleum:



The unit which recurs in this polymer contains no double bonds; hence the rubber cannot be vulcanized, but is more resistant to chemical attack than is natural rubber. A relatively recent development is Standard Oil's Butyl rubber, in which hydrocarbons containing a single double bond, such as isobutene, are copolymerized with a small proportion of hydrocarbons like butadiene, so that the resulting polymer contains occasional double bonds which permit vulcanization. The material after vulcanization should be highly resistant to oxidation and to chemical attack in general. Butyl rubber has interesting possibilities as a material for tire manufacture. It can be produced entirely from petroleum or natural gas, and the manufacturing operations are said to be relatively simple.

Still another synthetic rubber is prepared by polymerizing vinyl chloride; the group which recurs in this polymer is:



The long chains in this material attract one another so strongly that the pure polymer is an amorphous white powder with little apparent resemblance to rubber. By the incorporation of about thirty per cent of an appropriate plasticizer, i.e., a non volatile liquid, such as tricresyl phosphate, the relative motion of the chains is lubricated, so to speak, and a somewhat plastic rubber is obtained. Plasticized polyvinyl chloride is marketed in this country under the name of Koroseal, and finds many special applications in industry where its long flexing life and its high resistance to the attack of sunlight, oxygen, water and some oils make it superior to natural rubber.

Within each class of synthetic rubbers which we have mentioned great variations in the physical properties of the product can be obtained by variations in processing.

The contemplated intense development of the synthetic rubber industry may make available a great variety of types of

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rubber which are specifically adopted to duties which at present natural rubber has to be coaxed into doing. Apparently no synthetic rubber has yet been developed which is the equal of good natural rubber in all its mechanical properties, but rapid improvement is still going on. At any rate, there seems to be no good reason why we shouldn't be able to get enough rubber, natural, reclaimed, or synthetic, to run our war.

The following tables may be of interest in providing a condensed comparison of the properties of various types of rubber, and of the development of productive capacity in this country.

Prices Quoted for Rubber, August 1941. (per pound)

Natural	\$0.23	Thikol F	\$0.45
Neoprene GN	0.65	Vistanex	0.45
Buna S	0.60	Koroseal	0.60 (approx)
Buna N	0.70	Hycar	0.70
Perbunan			

U. S. Production of Synthetic Rubber (long tons)

	Neoprene	Buna	Polysulfide (Thiokols)	Butyl	Koroseal
1939	1,750		500		
1940	2,500	60	700		
1941	6,300	4,000	1,400		?
1942 (estd.)	19,000	70,000*	?	5,000	18,000

\*Very tentative and probably quite unreliable estimates of the productive capacity to be attained at the end of this year.

Comparisons of the Properties of Various Types of Vulcanized Rubber as produced in July, 1941  
 Courtesy of Chemical and Metallurgical Engineering.  
 E—Excellent, G—Good, F—Fair, P—Poor

	Natural Rubber	Neoprene	Thikol	Koroseal	Buna N Perbunan	Buna S Ameripol (Oil Resistant Type)
Resistance to tear and abrasion	E	G	P	E	E	E
Adhesion to Metals	E	E	F	F	E	E
Resistance to Ozone	P	E	E	E	F	F
Resistance to Acids and Alkalies	G	G	G	G	G	G
Resistance to Gas Diffusion	F	G	E	E	G	G
Elasticity and Rebound	E	G	P	F	G	F
Resistance to Corona Cracking	P	E	E	E	P	P
Flame Resistance	P	G	P	E	P	P
Resistance to Flex Cracking	G	G	F	E	G	G
Resistance to Flow	E	G-F	P	F-P	E	E
Freedom from Odor	G	F	P	E	F	F
Resistance to Swelling						
By aromatic Solvents	P	P	P	Shrinks	P	F
By lacquer Solvents	P	P	G	Shrinks	P	F
By gasoline or mineral oil	P	G	E	Shrinks	G-E	E
Stretchability Range	E	G	F	F	G	G
Resistance to checking in Sunlight	F	E	E	E	F	G

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