ADA060984

TECHNICAL REPORT
NATICK/TR-78/015

[illegible] ITS HISTORY AND APPLICATIONS

by

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April 1978

[illegible] and Materials Engineering Laboratory
CEMEL-183

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

⑲ REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

⑱ ~~1. REPORT NUMBER~~
NATICK/TR-78/019

2. GOVT ACCESSION NO.

~~3. RECIPIENT'S CATALOG NUMBER~~
⑨ Technical rept.

⑥ ~~4. TITLE (and Subtitle)~~
RUBBER, ITS HISTORY, PROPERTIES, AND APPLICATIONS,

~~5. TYPE OF REPORT & PERIOD COVERED~~

~~6. PERFORMING ORG.~~ REPORT NUMBER
⑭ CE/MEL-183

7. AUTHOR(s)
⑩ Angus/Wilson

~~8. CONTRACT OR GR~~ANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
US Army Natick Research & Development Command
ATTN: DRDNA-VMP
Natick, MA 01760

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
O&MA

11. CONTROLLING OFFICE NAME AND ADDRESS
US Army Natick Research & Development Command
ATTN: DRDNA-VMP
Natick, MA 01760

~~12. REPORT DATE~~
⑪ Jan[redacted] 78

13. NUMBER ~~OF PAGES~~
21

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
⑫ 23p.

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release:
distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

RUBBER	RUBBER HISTORY
NATURAL RUBBER	RUBBER PROPERTIES
SYNTHETIC RUBBER	RUBBER APPLICATIONS
RUBBER COMPOUNDING	RUBBER TEST METHODS

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Rubber, once only the product of a tree growing in South American jungles, became the prototypic material for a class of synthetic materials, all having the common properties of rubber elasticity. Members of the class vary markedly in structure and properties, and the inherent properties can be varied by compounding. Thus, the various rubbers and their compounds are suitable for a wide variety of applications. The specification of a rubber item utilizes test methods based on evaluations of various properties pertinent to the item.

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PREFACE

Rubber, its capabilities, and conversely its limitations, are often misunderstood by those not directly associated with it. It is in reality an intriguing class of materials with unique characteristics. Those characteristics define its nature and determine its uses. This report was prepared to provide information on the origins of rubber and an understanding of its potential applications.

The material was first presented as a lecture to a Naval Reserve Unit (VTU Research 0101), which met at the Massachusetts Institute of Technology in September 1977. Because members of the group were of varied educational backgrounds and training, the presentation was kept general and somewhat nontechnical in nature. Various reviewers of the paper remarked that these features would make it of general interest, especially to those concerned with the selection of materials in item design and, accordingly, this report was written.

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RUBBER, ITS HISTORY, PROPERTIES, AND APPLICATIONS

INTRODUCTION

Rubber was once regarded as a botanical curiosity, but later became one of the world's great natural commodities and the prototypic material from which a whole new class of synthetics would evolve. This report covers in narrative form its history, properties, and applications. It is intended to provide neither an in-depth technical review, nor a rubber selection guide (the choice of a rubber compound for a particular application is best left to the rubber technologist), but general information on the origin and development of an interesting and unique engineering material.

Consider for a moment the world of today without rubber. What form would personal transportation have assumed? Would it be limited to slow moving vehicles rolling on metal, plastic, or composition-rimmed wheels? Indeed, would plastics exist as they do today without the impetus provided by the polymerization research carried out on synthetic rubber? Perhaps air-cushioned vehicles would now be in wide use. Or, would the answer be in a population clustered even more than now in large cities, dependent, as they were in the beginning of this century, on railed transportation for land communication and commerce? How would aircraft take off and land? Perhaps vertical take-off craft would have commonly evolved from the early planes? How would liquids, slurries, and solids be transferred in industry? What would seal our valves and flanges? Indeed, how would we have erased our mistakes?

Imagination can roam over these and similar conjectures, and the problems in designing a technology equal to today's, without rubber. It follows from such considerations that rubber contributed greatly to the industrial revolution. It was a material available at the right time to fill a need. Would a synthetic material have been developed to fill that need without the existing example of natural rubber?

HISTORY

As important as rubber is in our present technology, the greater part of man's progress throughout history was made without it. While civilization moved on its tortuous way through the rise and fall of the great Egyptian, Greek, and Roman Empires; while Alexander marched across the face of the known world; while Europe evolved into a collection of separate and distinct countries; the use of bronze, iron, copper, the rare metals, glass, and woven fabrics of cotton, linen, and silk were known; but the existence of anything like rubber, was not imagined. Yet, during that long parade, rubber existed in over 2,000 species of trees and shrubs in various parts of the world; but it was to remain undiscovered by what was regarded as the civilized world until well into the second millenium of the Christian Era.

Although unknown by civilization, rubber had been discovered by the Indians of the Sub-American Continent as the product of a tree growing in the Amazon River basin and the tropical rain forests. The natives called the tree cahuchu, "the weeping wood" because of the milk-like substance that oozed from the bark -- the liquid now known as Latex. The word cahuchu became the root of the word for rubber in Italian, Spanish, German, and French. The English name "rubber" was bestowed by Joseph Priestly, the discoverer of oxygen, because it rubbed out pencil marks. Eventually it replaced a material previously used for that purpose -- dampened bread crumbs.

There is archeological evidence that rubber was known by the South Americans as early as the 6th century. Ruins of the Mayans in Yucatan revealed the existence of a game similar to basketball, played on a stone walled court, except that the rings, or goals, were vertical. The ball used was rubber, made from dried latex, and it is believed that it was the size of today's basketball, but solid. If so, it would have weighed about forty pounds. Either the Mayans were powerfully muscled, or they had found some means of making a hollow sphere from latex. The first knowledge of this strange new material by Europeans was from members of Columbus' second voyage (1493–1495), who reported that Haitian natives made bouncing balls from the dried liquid of a tree. In a book written in 1521, Pietro d'Anghiera described the incredible rebound of the material. In 1540, Pizarro, the Spanish conqueror of Peru, reported the use of latex to waterproof fabrics and clothing. The Spaniards, though cognizant of rubber and its uses by the natives, did very little to use the material. It remained for a Frenchman, M. de la Condamine, to provide the impetus that started rubber on its way as an article of commerce. He first came to Peru in 1735 as a member of a French Civil Survey Team. When that project was completed, he remained to explore by himself, traveling the full length of the Amazon (4,000 miles). He was fascinated by the use of rubber by the natives and sent back samples and descriptions of shoes, syringes, bottles, and of coated fabrics made by putting on successive layers of latex, and drying each over a fire. It was for this last use, and waterproof boots, that rubber found its first applications in Europe. The problem was the transportation of the rubber in a liquid form to Europe. The latex coagulated on standing, and could not last the long ocean voyage. LaCondamine reasoned that the latex should be dried in South America, shipped as a solid, and be re-dissolved in France for use. Latex, however, is an emulsion of solid rubber particles, and once the emulsion is broken, the particles coagulate into a mass and there is no way of reforming the original emulsion. A solvent was needed that would dissolve the rubber and allow it to be used as a liquid. In a search of the then available liquids, turpentine was found to be a solvent, and the first coating solutions, or cements, were made with it -- the materials becoming the forerunners of the solvent cement coatings used on fabrics today.

At this point however, rubber was not really widely used and was not widely known, except in the scientific community. It was regarded by some as defying the laws of gravity because of its great rebound and bounce.

In the early 1800's the fledgling rubber industry began its growth in England when Thomas Hancock discovered that naphtha, up until then a useless by-product of coal gas manufacture, was a better solvent than turpentine for rubber. As a result, the use of dissolved rubber as a water-proofing for fabrics increased, the cements being used by Hancock in England, MacIntosh in Scotland, and various entrepeneurs in the United States, mainly in New England. The really unique properties of natural rubber, its resilience, rebound, and elasticity, were largely ignored.

The new garments and the lesser number of items made of solid rubber, all suffered serious deficiencies. Near heat or on hot summer days, they became tacky, softened and sometimes collapsed. In cold weather they became brittle. On occasions the rubber turned "sour and rotten" and items made of it simply fell apart.

Around 1839, an impecunious New England inventor by the name of Charles Goodyear discovered, in Woburn, Massachusetts, that when rubber was mixed with sulfur and heated, a material with greatly improved properties resulted. The rubber became stronger and more durable, and it was no longer greatly affected by climatic temperature extremes.

Goodyear's discovery, which he named vulcanization, is often regarded as the result of a happy accident. Various accounts exist; one that a mixture of rubber and sulfur boiled over on his stove; another, that he had promised his wife to abandon his work on rubber, but in her temporary absence had resumed, only to have her return unexpectedly – whereupon, he tossed a piece of sulfur impregnated rubber into a hot oven until he could safely retrieve it. Whatever the circumstances, and what may be legend or fact, the result was a piece of charred rubber, crudely vulcanized or cured. Goodyear was astute enough to realize that the material was fundamentally changed and improved. He set about refining the process, and five years later obtained a US Patent. At about that time, Hancock obtained a British Patent on the method; but it is fairly well established that he had seen the American material, and the credit for the invention is Goodyear's.

Other patents followed from the Yankee inventor on processes for making rubber articles, but he had little interest in business and his finances were usually in disarray. He was in and out of prison for debt, and in fact, once set up his laboratory in his jail cell. In addition to his financial misfortunes, his patents were frequently ignored and infringement was common. In the late 1840's he brought suit against Horace Day, one of the more flagrant violators, and hired as his attorney, Daniel Webster. Mr. Webster won the case, but his fee was $25,000.

Goodyear lived a life regarded by some as unfortunate, filled with frustration and bad luck. He was certainly impractical, and his early obsessions with rubber, was regarded as the village eccentric. He fluctuated between the meanest of poverty and occasionally modest security. He still persevered and in 1868, while again in patent litigation in Washington, and in poor health, he received word that his daughter was dying in New Haven. He died in New York on his way to her bedside, and left behind debts of several hundred thousand dollars and a discovery that was the foundation of rubber technology.

In England, the diligent Mr. Hancock had made a thin solid rubber tire; and in 1888, J. B. Dunlop made a tube of natural rubber, inflated it with air, covered it with canvas nailed to a wooden disc, and filed a patent for "An Improvement in Tyres of Wheels for Bicycles, Tricycles and Other Road Cars" -- little did he know!

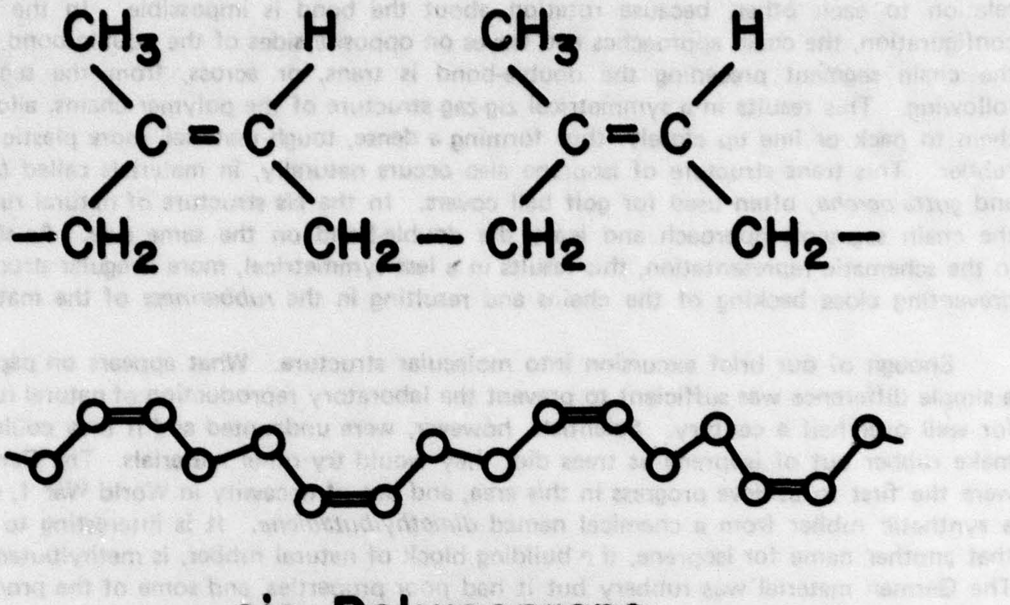
Meanwhile, the British had grown dissatisfied with having to obtain rubber from sources over which they had no control. In 1876, Mr. Henry Wickham arrived in England with some 70,000 seeds of the rubber trees of Brazil. They were planted in Kew Gardens, but sensitive to time and drying out, only about 2400 germinated. From these, and a subsequent set of seedlings, 2,000 plants were taken to Ceylon and less than 100 to Singapore, and from this latter small group a majority of the plantation trees in the world descended.

Although the idea of planting rubber trees on farms or plantations seems feasible now, it was not originally widely accepted. Henry Ridley, an early champion of the idea in the Far East, was largely ignored and became somewhat a Johnny Appleseed, or Rubberseed, giving seeds to anyone showing interest in planting them. His dedication earned him the name "Mad Ridley," but in later years his efforts were honored and, at the age of 99, Mr. Ridley received a medal from the Institution of the Rubber Industry. Perhaps longevity, at least, contributes to honor.

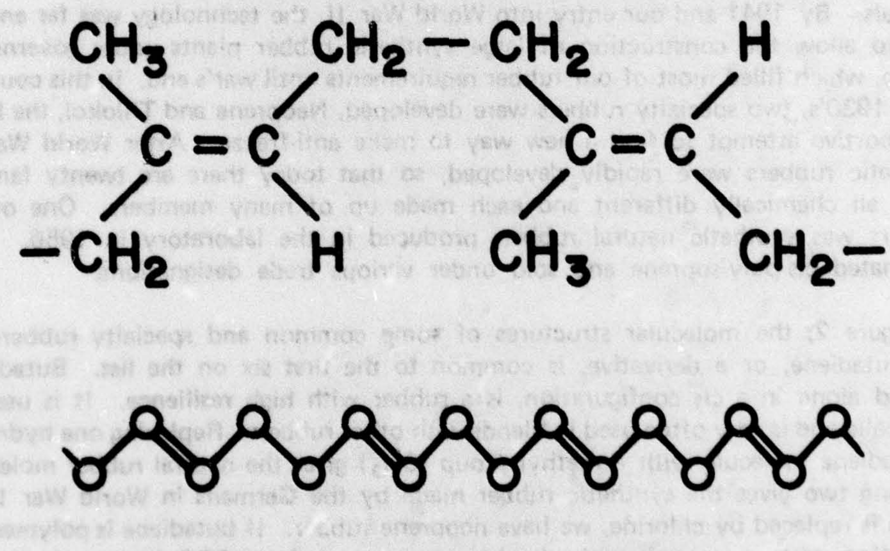
The establishment of plantations in Southeast Asia and Africa was fortuitous, because rubber trees were susceptible to a particularly virulent leaf blight in their South American homeland, and plantations there have generally been unsuccessful. There is now hope that this blight may be controllable through recent developments in aerial fogging.

With the source of rubber assured and controlled, and with the advent of the automobile in the first decade of the 20th century, the conditions for the growth of the rubber industry were at hand, with opportunities even greater than the pioneer manufacturers anticipated. In 1910, production of natural rubber was 100,000 long tons. By 1941, the entry of the United States into World War II, it was almost two million long tons, and the prediction for 1980 is between four and five million tons. Concurrent with the increases in production, progress was made in improving rubber products. The search for a cheap extender resulted in the discovery that the addition of lamp black improved the strength and wear of rubber, and it became the first of the reinforcing fillers and the reason so much rubber is black. Accelerators that shortened vulcanization from hours to minutes were developed, and antioxidants and antiozonants to retard the aging and cracking of rubber came into use.

While scientists and technologists were improving natural rubber through compounding, others wondered why the material made by the tree could not be made in the laboratory. By the late 1800's it was known that the building block of rubber was a chemical called *isoprene*. Natural rubber is a polymer (*poly* meaning many, *mer* meaning part -- thus, many parts), and in natural rubber the isoprene units are attached one to another to form long, convoluted, chainlike molecules. Attempts were made for decades to reproduce the structure synthetically. Although some rubber-like materials were made, natural rubber was not reproduced. One of the reasons was that the tree produces a structure known as *cis*, while the laboratory efforts produced a polymer that was largely of a structure known as *trans*. This is known as *isomerism*, and in Figure 1 is shown structurally for two isoprene units and schematically for four. It can be explained in this case if one thinks of each isoprene unit in the chain as being made up of four segments (carbon atoms). The first two segments are joined together by a single bond, which one might consider as a rod, about which each segment can freely rotate. The third and fourth units are likewise joined; but the second and third are joined by a double bond, which may be considered as two rods joining the segments, and the rest of the chain attached to them. On each side of the double-bond the segments are fixed in



cis-Polyisoprene



trans-Polyisoprene

STRUCTURES OF POLYISOPRENE

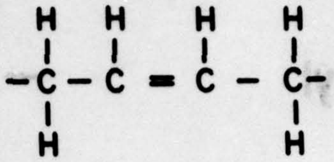
FIGURE I

relation to each other, because rotation about the bond is impossible. In the trans configuration, the chain approaches and leaves on opposite sides of the double bond, thus the chain segment preceding the double-bond is trans, or across, from the segment following. This results in a symmetrical zig-zag structure of the polymer chains, allowing them to pack or line up closely, thus forming a dense, tough material, more plastic than rubber. This trans structure of isoprene also occurs naturally, in materials called *balata* and *gutta-percha*, often used for golf ball covers. In the cis structure of natural rubber, the chain segments approach and leave the double-bond on the same side. As shown in the schematic representation, this results in a less symmetrical, more irregular structure, preventing close backing of the chains and resulting in the *rubberiness* of the material.

Enough of our brief excursion into molecular structure. What appears on paper as a simple difference was sufficient to prevent the laboratory reproduction of natural rubber for well over half a century. Scientists, however, were undaunted and if they could not make rubber out of isoprene as trees did, they would try other materials. The Germans were the first to achieve progress in this area, and out of necessity in World War I, made a synthetic rubber from a chemical named *dimethylbutadiene*. It is interesting to note that another name for isoprene, the building block of natural rubber, is methylbutadiene. The German material was rubbery but it had poor properties, and some of the processes used required months to make the product. Not too bad perhaps, when compared with a rubber tree, but intolerable in wartime. Their research continued, and in the 1930's they discovered two rubber copolymers; i.e., polymers made up of two materials. One of them contained butadiene and styrene and the other butadiene and acrylonitrile. The discoveries were noted in this country, and various companies initiated programs to develop the materials. By 1941 and our entry into World War II, the technology was far enough advanced to allow the construction of large synthetic rubber plants under government sponsorship, which filled most of our rubber requirements until war's end. In this country, during the 1930's, two specialty rubbers were developed, Neoprene and Thiokol, the latter from an abortive attempt to find a new way to make anti-freeze. After World War II, new synthetic rubbers were rapidly developed, so that today there are twenty families of rubber, all chemically different and each made up of many members. One of the new rubbers was synthetic natural rubber, produced in the laboratory in 1956. It is now designated cis-polyisoprene and sold under various trade designations.

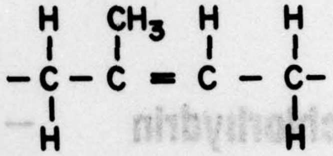
In Figure 2, the molecular structures of some common and specialty rubbers are shown. Butadiene, or a derivative, is common to the first six on the list. Butadiene, polymerized alone in a cis configuration, is a rubber with high resilience. It is used in solid golf balls and is very often used in blends with other rubbers. Replacing one hydrogen in the butadiene molecule with a methyl group (CH_3) gives the natural rubber molecule, and replacing two gives the synthetic rubber made by the Germans in World War I. If a hydrogen is replaced by chlorine, we have neoprene rubber. If butadiene is polymerized in conjunction with, or copolymerized with, styrene, we have SBR (styrene butadiene rubber), the most widely used of the synthetics and a major rubber component of passenger car tires. If it is copolymerized with acrylonitrile, we have NBR (nitrile butadiene rubber).

cis-Polybutadiene



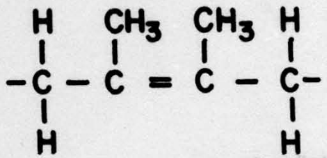
$-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$

Natural Rubber (cis-Polyisoprene)



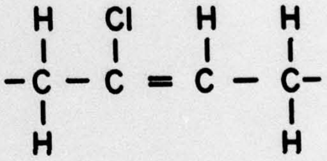
$-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$

Dimethylbutadiene



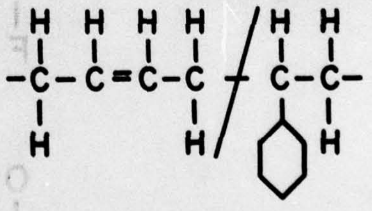
$-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=\overset{CH_3}{C}-\overset{H}{\underset{H}{C}}-$

Neoprene

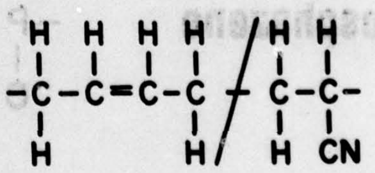


$-\overset{H}{\underset{H}{C}}-\overset{Cl}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$

SBR



NBR

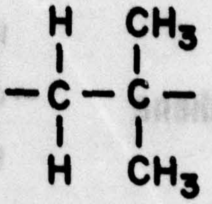


$-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}/\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CN}{C}}-$

STRUCTURAL FORMULAS OF VARIOUS RUBBERS

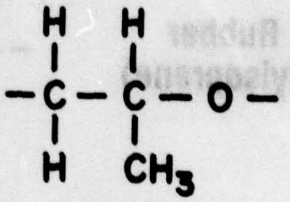
FIGURE 2

Butyl



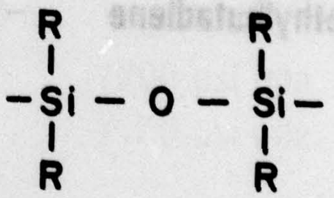
$-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-$

Epichlorhydrin



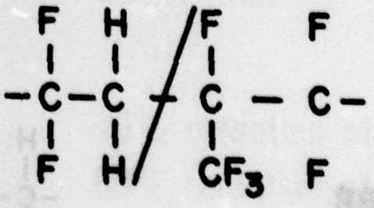
$-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-O-$

Silicone



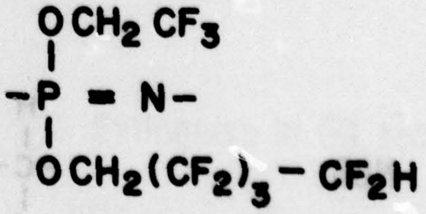
$-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-$

Fluorocarbon



$-\overset{F}{\underset{F}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-/-\overset{F}{\underset{CF_3}{\overset{|}{\underset{|}{C}}}}-\overset{F}{\underset{F}{C}}-$

Phosphazene



$-\overset{OCH_2CF_3}{\underset{OCH_2(CF_2)_3-CF_2H}{\overset{|}{\underset{|}{P}}}}=N-$

STRUCTURAL FORMULAS OF VARIOUS RUBBERS (continued)

There are, of course, as you can see from Figure 2, many other rubbers that are not based on butadiene. Each of these rubbers has several variations. For example, the SBR and NBR copolymers can have a variety of properties, depending on the ratio of butadiene to the other ingredient. This partial list represents many and varied structures. But, why so many rubbers? An analogous question might be: "Why so many metals?" Why do we use copper, zinc, tin, iron, silver, etc. or blends or alloys of them? Because, they all have different properties, and so it is with rubber.

Each kind of rubber has some inherent characteristic that makes it different from all others. For some applications, any of several kinds of rubber may be used. For instance, either natural rubber or SBR may be used in many items. Other applications require the use of a specific kind of rubber and in some cases, a specific type of that kind. For example, a silicone may be required for a high temperature use, or a fluorosilicone for high temperature use and exposure to lubricants. But, before going too far into looking at the common and specific properties of the rubber families, perhaps we should stop and define the term *rubber* itself. What is rubber? If we were to use Priestly's original nomenclature, rubber would be something capable of rubbing out pencil marks, and we are back to moist bread crumbs, and so much for that definition.

What then is rubber? From Figure 2 it is apparent that the various rubbers have different chemical structures and compositions. Yet, there must be something common in their behavior, some like property that would cause them to be grouped together under a common name. One property that quickly comes to mind is rebound, the ability of a natural rubber ball to bounce, for example; but a butyl rubber ball shows little rebound, scarcely more than that of a steel ball when both are dropped on a steel plate. Since rebound is not the property we are seeking, perhaps it is flexibility. True, flexibility is a common property, but it is not an identifying one. Rubber is often used for its flexibility, in hoses for example, but the property is not unique, and other materials such as plastic may be used. Rubber, in the simplest terms, is a material possessing rubbery elasticity. Or, to use a definition approved by ASTM, The American Society for Testing and Materials, "Rubber is a material that is capable of recovery from large deformation quickly and forcibly and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvents such as benzene, MEK, and ethanol toluene azeotrope.

A rubber in its modified state, free of diluents, retracts within one minute to less than 1.5 times its original length after being stretched at room temperature to twice its length and held one minute before release."[1]

What all this means is that rubber possesses a particular and specific type of elasticity called kinetic elasticity, and any material possessing it is defined by the property as a rubber. Kinetic, or rubbery elasticity,is not true or perfect elasticity -- the type possessed by some metals and other solids, provided they are not stretched beyond their elastic

[1] Glossary of Terms Relating to Rubber and Rubber Technology. American Society of Testing and Materials. STP 184, 1972.

limit, usually 1% or less. In true elasticity, the phenomenon is reversible and reproducible. That is, if a force is applied to compress or stretch a true elastic, it will deform some specific amount and return fully to its original dimensions when released. If the same force is reapplied, the material will deform again the same specific amount, and when released, will return again to its original dimensions. The kinetic elasticity of rubber is different in two distinguishing ways. It permits large extensions; for instance, some rubber items can be stretched 1000% without breaking. Secondly, when released, rubber will return to almost its original dimensions. The difference, or lack of complete recovery, may be so small as to be practically immeasurable or relatively large, depending on the amount and duration of the deformation and the physical properties of the rubber compound. If an equivalent force is now again applied to the rubber, it will deform to a value different from the first value obtained. Thus, rubber has a peculiar form of elasticity, but basically it is used because of its ability to recover rapidly from large deformations.

COMPOUNDING

The term *modified state* in the ASTM definition above refers to vulcanization, but rubber can also be modified by compounding. Goodyear's discovery that rubber could be advantageously changed by heating it with sulfur, by vulcanization, demonstrated that the properties of rubber could be varied by materials added to it -- and very often improved by the addition. Vulcanization with sulfur alone required several hours, and then it was found that the addition of metallic oxides, such as zinc or magnesium, to the sulfur cut that time, sometimes by half. The discovery and development of organic accelerators shortened the time further, and the addition of the zinc oxide to them further increased their efficiency. Now, curing can be accomplished in a few minutes.

Fatty acids, present in natural rubber in amounts of 1.2% to 1.5%, were also found to increase the efficiency of the acceleration used. So today, the basic curing system of many rubber compounds consists or rubber, sulfur, one or more organic accelerators, zinc oxide, and stearic acid (a material used in soaps and candles). These five components alone will make a high grade compound with many rubbers, natural for example, called a gum compound, but it will be relatively expensive because of its high rubber volume.

To extend rubber compounds and reduce their cost, various materials have been used -- the most common being carbon blacks, clays, and silicas. These are generally referred to as fillers and, next to the curing ingredients, are the most important. They may be either reinforcing or non-reinforcing. Reinforcing fillers actually improve the properties of rubber compounds, result in increased tensile strength and can improve tear strength and abrasion resistance, among other things. Since raw rubber is priced from 35¢ to $50.00 per pound, with one specialty rubber available in small quantities at $100.00 per pound, and since carbon black, for instance, is around 10¢ to 15¢ per pound and, in a compound, may outweigh the rubber used, the economic advantage for fillers becomes apparent and desirable, especially when it is accompanied by material improvement. Non-reinforcing fillers do not improve the strength properties of the compounds, but may change some properties such as hardness, and can improve processing characteristics. These fillers are even less expensive, calcium carbonate, for example, selling for 1¢ a pound; and high volume loadings may be used, especially in items where low price is considered more important than good properties.

In addition to these major categories, materials classified as antioxidants, antiozonants, plasticizers, softeners, tackifiers, coloring materials, flame retardants, blowing agents, and retarders are used. Many of their functions are described by their names, most of them concerned with the effect on the properties of the cured rubber. Some are added to improve fabrication, for instance, tackifiers, which are added to increase the tackiness of uncured rubber compounds used to make items by building up various pieces and sections, the tack being necessary to hold them together until further processing forces them together to form a cohesive unit prior to curing. It is a property important in the construction of tires and some footwear.

The selection of a rubber for a particular application is based on the basic properties inherent in the rubber, and on those properties that can be added by compounding. Table 1 shows some, not all, of the rubbers and the characteristics that make them unique or specialized.

The inherent properties of the various rubbers guide, or may mandate, the selection of a specific rubber for a specific use. Then, laboratory testing of various compounds of that rubber against a set of target properties may be carried out. After that, prototype items can be made from the most promising compound, or compounds, and tested in actual use in conjunction again with laboratory testing. The data thus obtained in many cases can be used to control the production of the items and to adequately describe them for specification purposes. Thus, the selection and testing of the right set of properties is necessary to provide items that perform satisfactorily in service; and this is true of both commercial and military items. A list of the properties commonly tested is shown in Table 2. The test methods commonly used are contained in the ASTM Book of Standards, or in Federal Test Method Standard No. 601, in which many test methods are now being converted to ASTM methods.

A buyer of rubber items in the industrial market may depend on previous acceptable performance in purchasing items from a manufacturer, often specifying a certain company's part number. The government, seeking more control over its purchases, generally relies on the use of a specification in which the item and its assembly are described, and the performance characteristics of the rubber are spelled out according to the properties involved, along with values considered acceptable and the test methods to be used to determine conformance. Some industries also use this method, notably the automobile firms. The specification test methods may be common or unique -- the latter found especially in military specifications. We have, for instance, low temperature requirements more stringent than those needed commercially, although these have been received with somewhat more understanding since the construction of the Alaskan Pipeline. Table 3 shows an example of a list of specification requirements, in this case for a fuel hose.

TABLE I

PROPERTIES OF VARIOUS RUBBERS

RUBBER	PROPERTY
Natural	Resilience, good strength low heat build-up, good low temperature flexibility.
SBR	Good strength, high heat build-up, fair low temperature flexibility.
Butyl	Good ozone & weather resistance, low gas permeation, energy absorber.
Neoprene	Good weather resistance, good strength, oil resistant.
NBR	Gasoline resistant, good strength, poor low temperature flexibility.
Silicones	Good heat resistance, good low temperature flexibility, poor strength and tear.
Fluorocarbons	Fuel, oil, heat, chemical resistance, very poor low temperature flexibility.
Phosphazene	Fuel, oil, chemical resistance, very good low temperature flexibility.

TABLE 2

ASTM RUBBER TEST METHODS

Tensile strength	D412
Elongation	D412
Modulus	D412
Hardness	D2240
Tear strength	D624
Compression set	D395
Tension set	D412
Volume Swell	D471
Ozone resistance	D518
Oven aging	D573
Brittle point	D2137
Low temp. torsional stiffness	D1053
Cut growth	D1052
Abrasion resistance	D1630

TABLE 3

REQUIREMENTS-MIL-H-10868, HOSE ASSEMBLY

PROPERTY	REQUIREMENT
Bursting strength	400 psi min.
Tensile strength	
tube	1200 psi min.
cover	1100 psi min.
Elongation at break	
tube & cover	200% min.
Aging, 70 hr./212°F	
tube & cover	75% retention of Tens. 60% retention of elong.
Volume swell in 70/30 isooctane/toluene	
Flammability	Extinguish in 60 sec.
Low temperature torsional modulus at -40°F	5 max.
Corrosion resistance	II max.

FABRICATION

The configuration and end use of a rubber item in most cases dictate the method used in its fabrication. The oldest technique is that of dipping from a rubber latex, the method used by the first fabricators -- the South American natives. In today's technology a form with the shape and details of the item desired is repeatedly dipped in compounded latex and dried. When the desired thickness has been achieved, the form with its dried latex coating is placed in an oven or autoclave for curing, cooled, and the finished article stripped from the dipping form. The technique is used for gloves, balloons, and other thin items. A variation of this is rotational casting where latex is poured inside a mold and gelled by use of heat or absorption of water. During the casting, the mold is rotated about several axes to provide an even disposition of rubber. Again, curing and stripping results in the finished article -- which in many cases may be a child's soft flexible toy.

Another liquid system uses compounded but uncured rubber dissolved in a suitable solvent to form a cement. A dipping procedure may also be used with this process to form desired articles, such as gloves, or the cement may be applied to fabrics in a continuous process to make water-impermeable materials used in tents, rainwear, tarpaulins, inflatable mattresses, boats, and similar coated fabric items.

Coatings can also be applied to fabrics by use of a calender, a machine consisting of multiple metal rolls through which compounded, uncured rubber is passed to form a continuous sheet. Simultaneous passage of the rubber and fabric results in a coating of the rubber on the fabric, which is subsequently cured. Calenders may also be used without fabric to make unsupported sheet such as matting or thicker figured or embossed material from which shoe soles, for instance, may be cut and cured.

Many rubber articles are made by molding. In this technique a slight excess of uncured rubber compound is placed in a heated mold and pressure is applied, squeezing the mass into the mold, with the excess exiting into flash channels. The mass is held there until cure is accomplished; the mold is opened and the finished articles removed, cooled, and trimmed. Various types of molds and techniques are used, including, in recent times, injection molding. A wide variety of articles are produced, including soles, heels, washers, gaskets, hand grips, grommets, mountings, toys, industrial tires, rolls, o-rings, and numerous others.

Long solid, hollow, or open structures with uniform cross sections are made by extrusion. In this process uncured rubber is fed into an extruder where it is caught by a travelling screw or ram and forced through a head and die of the proper configuration to give the desired shape. The lengths of extruded material are supported and cured. In the case of a hose, it may be supported on a rod-like mandrel during cure, or if the cross-sectional area will permit, it may be supported by internal air pressure. The extrusion technique is used for tubes, channels, edging, gasketing, and similar items.

Finally, items may be made by building them up from pieces cut from uncured rubber sheets or strips, generally prepared by extrusion or calendering, and may or may not be supported by fabric. The components are pieced together and pressed into each other, often over a form, and cured. The process is often used in the construction of rubber or rubber and fabric footwear, but is becoming unattractive because of the amount of hand labor required and its attendant high cost.

NEW DIRECTIONS

One of the most interesting recent developments in rubber is the discovery and growing use during the last decade of thermoplastic rubbers or TPR's. The materials are not thermosets as are most rubbers but true thermoplastics due to a peculiar and tailored molecular structure. The TPR's contain a rubber matrix of one polymer in which are embedded domains of a rigid thermoplastic polymer which acts as cross links. The result is a group of materials with many of the desirable properties of general purpose rubbers, but which will soften and flow with heat and cool back to their original rubbery properties. Thus, they can be handled like plastics in injection molding systems with all their desirable properties of rapidity, cost reduction, and reuse of scraps. The materials are not suitable for use in items that may be exposed to high temperatures, but can be used in many other items, shoe soles being one of the major applications.

A new class of speciality materials, the polyphosphazenes, have been developed by the US Army Materials and Mechanics Research Center in Watertown, Massachusetts through contracts with Horizons, Inc. of Cleveland, Ohio. Commercial development is now underway by the Firestone Tire and Rubber Co. The versatility of the polymerization used in the manufacture (based on discoveries of Dr. Harry Alcock at the Pennsylvania State University) permit a variety of polymers to be made, ranging from plastics to rubbers. The latter have a unique combination of properties including inherent fire resistance, fuel and oil resistance, and flexibility down to -55°C. Unfortunately, present prices are very high because of the materials used in their manufacture and, though likely to decrease with increased volume, will always be in the upper price ranges along with some other specialty rubbers.

While looking into the future is always risky, it is probably safe to predict a slowing down and end of the proliferation of synthetic rubbers that has moved along so rapidly since World War II. The changes now will probably be evolutionary with continuing improvements in the preparation and the properties of existing rubbers and in improved compounding materials. Hardly likely is the development of a universal rubber, one with all the good properties of the many rubber families -- a rubber with the fuel and chemical resistance of fluorocarbon rubbers, the low temperature flexibility and heat resistance of the silicones, the impermeability of butyl, the strength of urethanes, the resilience, building tack, and heat dissipation of natural rubber, all bound up in one material selling at the price of SBR -- possibly in some future day! But we can be sure that rubber as a class of materials will continue to grow and adapt to the changing needs of new technology, and that its own unique properties will enable it to perform where no other material will suffice.

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