THE CHEMISTRY OF RUBBER

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I. LATEX AND CRUDE RUBBER

1. Introduction

Everyone is familiar with the pictures of the *seringueiro* with his slender hatchet, in the heart of the Amazon jungle, cutting into the bark of the giant *Hevea*[1] *brasiliensis,* and of the typical coolie, carefully tapping descendants of the Amazon *Hevea* trees on the well-kept plantations in the Far East, both obtaining the milky fluid or latex that yields the crude rubber of commerce. Everyone is also familiar with the rise of Brazil as the dominating factor in the production of the world's supply of crude rubber, and with the wonderful growth of the plantation industry, until in 1913 it finally outstripped Brazil and gave to the world an ever increasing supply of rubber without which the great automotive industry could not have continued its remarkable development.

TABLE 1

Production of crude rubber in long tons (1a)

YEAR	PLANTATION	AMAZON VALLEY	OTHER	TOTAL	U. S. NET IMPORTS	RATIO IMPORTS/TOTAL	TONS OF RUBBER EXPORTED AS LATEX (CALCULATED ON BASIS OF 3 LBS. TO THE GALLON). NOT INCLUDED IN THE TOTAL
1904	4	26,750	27,136	53,890			
1910	10,916	37,938	45,096	93,950	42,254	0.45	
1911	17,501	35,970	40,584	94,055	41,901	0.44	
1912	33,306	41,619	39,351	114,276	55,979	0.49	
1913	53,644	35,659	30,820	120,123	52,025	0.43	
1914	74,567	33,001	15,585	123,173	62,266	0.51	
1915	116,370	34,610	19,846	170,826	99,011	0.58	
1916	161,842	30,997	21,250	214,089	117,611	0.55	
1917	221,452	33,461	23,227	278,140	179,255	0.64	
1918	181,061	22,303	16,320	219,684	143,386	0.65	
1919	348,990	32,726	18,015	399,731	238,407	0.60	
1920	305,106	23,216	13,672	341,994	249,520	0.73	
1921	277,516	17,164	6,938	301,618	179,736	0.60	
1922	379,520	19,542	7,336	406,398	296,394	0.73	
1923	380,271	16,765	11,683	408,719	301,527	0.74	2,124
1924	393,931	23,165	9,082	426,178	319,103	0.75	1,902
1925	478,428	25,298	13,797	517,523	385,596	0.75	5,028
1926	581,215	24,298	16,017	621,530	399,972	0.64	2,850
1927	562,059	28,782	15,633	606,474	403,493	0.67	2,160
1928	621,782	21,129	10,690	653,601	407,564	0.62	4,167
1929*	813,000	21,000	9,000	843,000	475,000	0.56	

* Estimated figures.

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[1] Pronounced Hēv-ea.

One is probably not so familiar with the fact that, whereas the plantations produced for the market only four tons of rubber in 1900, Brazil and the rest of the tropical world produced 54,000 tons; that in 1910 when the plantations produced 11,000 tons, Brazil was at its peak with 38,000 tons and the rest with 45,000 tons; and that in 1929, the plantations produced the enormous quantity of 813,000 tons, while Brazil and the rest produced only 30,000 tons altogether. Two-thirds of the total production is annually imported into the United States, and half of this finds its way to Akron, Ohio,—the great manufacturing center of the rubber world. Over three-quarters of the total production is made up into automobile tires and tubes.

TABLE 2

Estimated acreage of the estate and native rubber plantations (2)

	1922 ACRES	1927 ACRES	1928 ACRES
British Colonies:			
Malaya	2,268,000	2,632,000	2,714,000
Ceylon	443,000	499,000	534,000
India and Burma	126,000	147,000	167,000
North Borneo	59,000	93,000	288,000
Sarawak, etc.	81,000	113,000	
Total	2,977,000	3,484,000	3,703,000
Other Middle East:			
Dutch Estates	940,000	1,199,000	2,899,000
Dutch Natives	500,000	1,300,000	
Indo-China	83,000	137,000	250,000
Siam	30,000	43,000	150,000
Total	1,553,000	2,679,000	3,299,000
Rest of the World (Liberia, etc.)			65,000
Grand Total	4,530,000	6,163,000	7,067,000

The price of crude rubber has fluctuated much. It was around $3.00 a pound in the great rise of 1910 and dropped to 14 cents a pound during the slump of 1921–22. Now, it sells for 15–20 cents a pound. The great rubber industry of the United States manufactures annually goods valued at over a billion dollars ($1,225,077,114 in 1927).

Tables 1 and 2 show in greater detail the growth and the size of the plantation industry. You will note that the total area planted at the end of 1928 was 7,067,000 acres, which is equivalent to 11,040 square miles or 105 miles square. For the sake of comparison, it may be mentioned that this is equal to the combined areas of the states of New Jersey, Delaware and Rhode Island. Since the trees are generally planted on the average 225 to the acre (estates, 150, and natives, 300), the plantations contain approximately 1,575,000,000 trees, and about 70 per cent of them are bearing. At 380 lbs. an acre the total *potential* annual yield is almost 1,200,000 long tons of crude rubber. The relative decrease in the percentage of rubber imported into the United States in 1926–28 is due to the increased production and use of "reclaimed" rubber, which amounted to about 250,000 long tons in 1929.

2. Sources of crude rubber

Rubber is obtained from the milky exudations of trees, shrubs and vines, belonging to several large botanical families which grow chiefly in the tropical zone. Some of these families and their important genera are EUPHORBIACEAE, which includes the *Hevea, Manihot* and *Micandras;* URTICACEAE, the *Ficus* and *Castilloa;* APOCYNACEAE, the *Funtumia, Landolphia* (vine rubbers), and *Clitandra* (creepers); ASCLEPIADACEAE, the *Asclepias* (milk weeds); and COMPOSITAE, *Parthenium argentatum,* (the guayule shrub). The crude or raw rubbers obtained from these different sources vary in their physical and chemical properties, some being firm and strong and others soft and weak. They all contain a hydrocarbon $(C_5H_8)_x$, "resins," etc., and their properties depend largely upon the relative amounts of these substances. The plantation rubbers and "Fine Para" contain 90–93 per cent of the hydrocarbon and 2–4 per cent of "resin," whereas other varieties may contain as low as 25 per cent of the hydrocarbon and as high as 60 per cent of "resins." The raw rubbers are obtained by coagulation of the latex with dilute acetic or formic acid, or with salts such as alum, by heating in smoke ("Fine Para"), by "spontaneous" coagulation—caused by the formation of organic acids from bacterial action—and by evaporation on a drum or in a spray drier. Guayule rubber is obtained from the guayule shrub by crushing the woody stems and twigs and separating the woody portion by "water logging" it (3). On account of the importance and general use of plantation rubbers only such will be considered hereinafter unless mention is made otherwise.

3. *Latex* (4, 5, 6, 7, 8)

The latex is the milky fluid contained in microscopic tubes known as latex vessels which are found in all parts of the tree. It is under a certain turgor pressure and yet ordinarily there is no internal flow. For commerce it is obtained by tapping the trunk (9) where it is found in the cortex layer, the layer between the bark and the cambium layer. The cambium layer is very thin and lies between the cortex and the large woody inner section of the trunk, and it is through this layer that the sap travels up and down the tree. It is seen, therefore, that the latex is separate from the sap, and in fact is quite different from it. The usual method of tapping is to make an incision 1–1.5 mm. deep with a V- or U- shaped cutting tool along a slanting line three to four feet from the ground and extending one-third of the way around the trunk. This incision is then shaped in such a manner that the bottom of the V is below the bottom line of the incision, thus making a trough or channel in which the latex as it oozes out flows to the lower end, where a spout is placed to direct it into the collecting cup. The trees are tapped every other day by skilfully cutting out a very thin shaving along the lower side of the V-shaped channel. In this way the channel is lowered about one inch a month and about one foot of bark is therefore removed from the tapped section in the course of a year. The trees can be tapped when they are five to seven years old and for many years thereafter. The wounds heal and in after years the same sections can be tapped over again. The trees exhibit the phenomenon known as "wound response" and up to certain limits of tapping they give greater yields as time goes on. The latex flows for about an hour after tapping and an average tree yields about 15 cc. of latex at each tapping. Since the latex contains about 30 per cent of its weight of raw rubber, one tree gives approximately 900 grams (2 lbs.) a year. The trees grown under the new bud-grafting system (10) produce from two to three or more times this amount. In this system, buds from high-yielding trees are grafted to one-year-old seedlings in the nursery and subsequently transplanted to the field.

The latex upon microscopical examination is found to consist of numerous minute globules suspended in a watery solution. These globules are frequently pear-shaped, are 0.0005–0.003 mm. (0.5–3μ) in diameter, and exhibit the usual Brownian movement; and each one carries a negative electrical charge (11). According to Hauser (12), they consist of a viscid interior and a firm elastic membrane which when pierced allows the contents to ooze out. Protein and resins are probably adsorbed on the outer surface. von Weimarn (13) describes latex as a polydisperse system of isoaggregate particles with a general liquid-jelly consistency. He regards each particle as made up of smaller particles with a liquid-gelatinous interior, each one being surrounded by a layer of adsorbed protein and resins, and the larger pear-shaped particles as made up by the combination of other smaller particles of unequal size. For the most part, the isoaggregate particles are indistinguishable under the ultramicroscope. Addition of a coagulant causes the cessation of the Brownian movement, the globules coalesce and then form strings or clots (14). The globules in latex from the leaves and young twigs are smaller than those from the stems and trunk; the globules in latex from younger trees are smaller than those from older ones. The specific gravity of the fresh latex varies from 0.967 to 1.000, corresponding to 45 and to about 17 per cent of rubber respectively. So-called normal or average latex contains about 33 per cent of rubber and its specific gravity is approximately 0.983. Fresh latex is approximately neutral, its pH being 7.0–7.2 (15). In a few hours after tapping it diminishes to 6.6–6.9 and coagulation takes place. This acid condition, as already mentioned, is due to bacterial action. The amount of rubber in fresh latex varies considerably —from 15 to 60 per cent—but generally it is 20 to 45 per cent. It is highest at the beginning of a tapping period or after a rest period and also from trees well cared for; it is higher from trees tapped as mentioned above than from those "heavily" tapped, from shallow tapping than from deep tapping, and from the roots and trunk than from the twigs. Latex can best be preserved by the addition of 2–5 per cent of concentrated ammonium hydroxide; it can also be preserved with 0.5 per cent of formalin. Ammonium hydroxide lowers the viscosity of latex. Preserved *Hevea* latex "creams" on standing for several weeks (see also p. 59). Latices from the *Manihot* and *Castilloa* cream more readily, but they contain larger rubber globules.

TABLE 3

Substances in the latex and in coagulated rubber

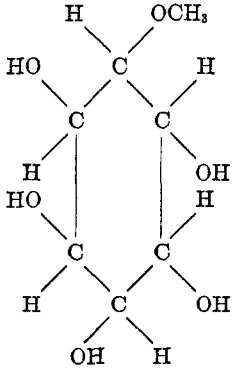
	IN THE LATEX	IN THE CRUDE RUBBER	PORTION OF ORIGINAL SUBSTANCES FOUND IN THE CRUDE RUBBER
	per cent	*per cent*	
Crude rubber	30.0	100.0	
Rubber hydrocarbon	28.0	92.0–94.0	
Total solids	33.0–34.0	98.8–99.7	$\frac{9}{10}$
Mineral substances (ash)	0.3–0.7	0.15–0.45	$\frac{1}{6}$
Components containing nitrogen (calculated as proteins: 6 × %N)	1.0–2.0	2.5–3.5	$\frac{2}{3}$
Components soluble in acetone ("resins")	2.0(?)	2.5–3.2	?
Quebrachitol	1.0–2.0	Trace	?
Reducing sugars	0.15–0.35	—	—

When *Hevea* latex is coagulated with dilute acetic acid (1 part of glacial acetic acid to 100 parts of dry rubber) and the coagulum passed between corrugated, uneven-speed rollers, in the presence of running water, there is obtained the familiar "pale crêpe" of commerce. Sodium bisulfite is added before coagulation to prevent the color formation from enzymic action. "Smoked sheet" is prepared by passing the coagulum between even-speed rollers to squeeze out the serum, and then drying the sheet in a smoke house. "L. S." rubber ("latex sprayed") is obtained by evaporation of the latex in a spray drier (16). It contains all the solids of the latex and is a very uniform and very tough product. Drying the latex on a heated revolving drum also gives a rubber containing all the solids in latex (Kerbosch process) (17).

Although acids coagulate latex, it is possible to make the latex definitely acid without coagulating it by adding certain protecting agents, such as the sodium salt of the reaction product obtained by condensing naphthalene and isopropyl alcohol in the presence of sulfuric acid (18). Acid latex has about the same viscosity as ammonia-preserved latex.

Table 3 gives an idea of the substances contained in the latex and in the coagulated rubber obtained therefrom.

The rubber hydrocarbon is apparently the same after coagulation as before. The protein is not necessary as a stabilizer because when it is removed the latex is still stable, and acid coagulates it as it does before (19) (20). The nature of the protein is not well understood, but it is probably a globulin. The proteins and their decomposition products remaining with the crude rubber act as accelerators of vulcanization and confer other important properties on the rubber. Analysis of the ash shows that it consists chiefly of sodium, potassium, calcium and magnesium phosphates and a small amount of sulfate and sometimes chloride. The quebrachitol ($C_6H_{11}O_5OCH_3$) is a methyl ether of inositol (a cyclic sugar) and is levo-rotatory. It has the following structure:



Some glucose is present among the small amount of reducing sugars, and traces of hydrogen cyanide and of acetaldehyde have also been found in latex. Other substances found in latex, and generally included in the "resins" obtained in the "acetone extract" of crude rubber are as follows (21) (22) (The figures given in parentheses represent the per cent present in crude rubber): Oleic and linoleic (1.3), and stearic (0.15) acids which comprise about one-half of the total weight of the extract; quebrachitol (1–2), a phytosterol (0.225), a phytosterol glucoside (0.175), two liquid sterols, $C_{27}H_{42}O_3$ (0.08) and $C_{20}H_{30}O$ (0.16), a sterol ester, $C_{17}H_{32}O_2 \cdot C_{27}H_{45}$ (0.075), *d*-valine (0.015), *n*-octadecyl alcohol, a ketone, $C_{15}H_{24}O$, and a hydrocarbon, $C_{15}H_{24}$. The fatty acids play an important part in the vulcanization of rubber especially in the presence of organic accelerators, because the oxides of zinc, lead, magnesium, etc., are converted into the corresponding organic salts which are soluble in the rubber (21) (23) (24) (25) (26). The liquid sterols are powerful, naturally-occurring antioxidants and are chiefly responsible for the preservation of crude rubber (22). The amount and nature of the acetone extract also affects the "working" properties of crude rubbers and their physical properties after vulcanization.

Crude rubber can be redispersed to form an artificial latex by milling into it a hydrophilic colloid, such as glue and certain clays, and then mixing in water (27). The artificial latex has properties very similar to those of natural latex and is finding interesting commercial applications. Reclaimed rubber can also be dispersed in the same general way (28).

4. Concentration and uses of latex

During the creaming process mentioned above, the rubber hydrocarbon becomes more concentrated in the upper layer just as the fat in milk becomes more concentrated in the cream. This concentration (of preserved latex) on long standing can also be carried on by centrifuging (29), and by the addition of certain hydrophilic creaming agents, such as Irish moss, gelatin, ammonium alginate, etc. (30). These creams, when separated, are found to contain upwards of 75 per cent of rubber hydrocarbon, and this high amount approaches the calculated maximum value for close packing of spherical particles (31). The creams are comparatively free from the water-soluble, non-rubber constituents of latex. Direct concentration of latex can be carried out by the addition of potassium hydroxide and other stabilizers such as potassium salicylate or fluoride, followed by evaporation under diminished pressure in a rotating drum (revertex process) (32). These creams and other concentrated latices are often almost butter-like in consistency, but can be readily diluted with water.

Latex is used commercially in the manufacture of tire web-cord fabric (33), gloves and inner tubes on porous forms by filtration (34), rubber-covered metal articles by electro-deposition (35), rubber articles of the outside shape of a porous form by electro-deposition (36), rubber impregnated mohair upholstery (37) and for backing the piles of rugs (38), special papers (39), etc.

Latex can be vulcanized by heating with alkali polysulfides (40).

5. Function of latex in the tree

The exact purpose of the latex is not definitely understood (41). It no doubt has some relation to the environment of the tree, that is, an ecological function (42). In some cases it may serve as a protective layer against insects, because it is known that where the latex vessels have been removed, the tree is attacked by borers. Latex occurs in some but not in all organs and therefore apparently has no indispensable function to perform for the continuance of the life of the plant; it has no influence on the development of sieve tubes nor can these be replaced by latex vessels (43). Latex contains organic materials provided by the assimilative and metabolic processes of the tree, and it may, therefore, have nutritive value. For example, it has been shown (44) that during the period of leaf-fall and new leaf-formation in March and April, "The yield per tree was very low. . . . . This variation in the amounts of rubber obtained agrees with the order of variation in the amounts of reserve starch in the bark and wood during the same months." Furthermore, in studies on the guayule shrub, Macallum (45) has found that the rubber content increases after cutting if preserved under proper conditions, increases under conditions that generally result in other plants in the storing up of starch, no reserve food in the form of starch being laid by, and decreases during periods of extensive growth.

It should be added that the chemical forerunner of the rubber hydrocarbon is not known and that the process of its conversion to rubber is still an open question.

6. The importance of vulcanization

A good quality of crude rubber is tough, strong, resilient, elastic, and resistant to abrasion (witness its use as crêpe rubber soles), but by means of vulcanization these qualities can be enhanced greatly and can be made to hold over a much greater range of temperature (46). Crude rubber becomes soft and sticky when heated even to 100°C., and, when cooled beyond a certain point, becomes stiff and horn-like. The early raincoats manufactured before vulcanization was discovered became useless in midsummer because they tended to "run" and stick, and in winter they became unyielding like a one-piece coat of armor. Vulcanization changes all this, increases immeasurably the varieties and grades of soft rubber articles, gives the rubber its capacity to hold the shape of the mold in which it is fashioned, makes it more insoluble in organic solvents and much less absorbent of water, and increases enormously its durability. As a specific example there may be mentioned the automobile tire. The tread has most remarkable resistance to abrasion, its resilience is noteworthy, and even at the high running temperatures in midsummer, 65–80°C. (47), it keeps these qualities and its shape unchanged.

II. THE RUBBER HYDROCARBON

1. Isolation and properties

The word "rubber" may mean the crude or raw rubber, or vulcanized articles made therefrom. The word itself comes from the use of crude rubber for rubbing out pencil marks. It was recorded in this meaning in 1770 by Priestley (48), and, according to a recent article by Speter (49), it was used even a little earlier by Nairne, a maker of mathematical instruments in London. The term "India-rubber" was given to it because of the fact that it was first brought to Europe from the land which Columbus and his contemporaries thought was India,—namely, the West Indies. The French word is "caoutchouc," and the German, "Kautschuk,"—both from the native words meaning "weeping tree" (*caa o-chu*). C. O. Weber, the "Father of the Chemistry of Rubber," used the word "polyprene" for the purified rubber hydrocarbon. This word was coined from polymer and isoprene. Some writers have used the French word for crude rubber, caoutchouc, to signify the purified rubber hydrocarbon, but its use leads to ambiguity. Since it is not known whether the rubber hydrocarbon consists of a single hydrocarbon or of a mixture of hydrocarbons, it seems best to speak of it simply as the rubber hydrocarbon.

Rubber owes its characteristic properties to its chief constituent—the rubber hydrocarbon (50). Although it has been isolated in a high state of purity, not all of its properties are well understood. Its strength, tackiness, stretch, rate of solubility (dispersibility), resilience, etc., vary with the kind and manner of physical treatment. Working it between the rolls of a rubber mill causes it to become plastic (putty-like) and at the same time to become weak, less extensible, less resilient, more tacky, more readily soluble, etc. Other methods of treatment, such as stirring in solution, and exposure to the action of light and of certain reagents, cause similar changes. This so-called "breaking down" or mastication (51) of the rubber is very important, because it is on account of this property that it is possible to mill into the rubber the necessary ingredients for vulcanization and for preparing the rubber for such an infinite variety of uses. Whether this change is entirely physical or chemical or both is not yet known. The chief constituent of rubber is, no doubt, a polymerized hydrocarbon with colloidal properties, and if it is depolymerized during the "breaking down," then there should be a corresponding increase in the chemical unsaturation per unit group. A. E. Gray and the writer (52) found, however, that, within the error of the method employed, there was no change in the unsaturation when rubber was milled for several hours in an atmosphere of carbon dioxide, although in air there was a decrease of about 2 per cent. However, if the rubber molecule is very large, as it seems to be, then the relative change would be very small,—probably smaller than the error of the method employed.

A 10 per cent solution of unbroken-down rubber forms a solid gel, but after thorough milling of the rubber, a 10 per cent solution is of about the same viscosity as that of the solvent itself. Ultra-violet light also causes a great lowering in the viscosity of a rubber solution, and here again there is no apparent change in the chemical unsaturation (52). Heat and certain acids (e.g. trichloroaceict acid) and other substances also cause a considerable lowering in the viscosity, but in these cases the change is generally in part at least a chemical one, because there is a change in the unsaturation on account of isomerization or polycyclization (53) (see p. 115). Broken-down rubber, if left undisturbed for some time, will slowly regain part of its "nerve." It should be remarked that the more rubber is broken down in the manufacturing process, the less is the strength and other important properties of the vulcanized product made therefrom.

The rubber hydrocarbon can be obtained in a fairly pure condition by extracting the resins of the raw rubber with acetone, dissolving the extracted rubber in benzene, decanting from the insoluble material, precipitating by pouring the solution in alcohol, and repeating these last operations several times. This is Harries's well-known method (54). However, even when this process is carried out in an atmosphere of carbon dioxide, as shown by Pummerer and Burkhard (55), the hydrocarbon still contains small amounts of proteins and sugars. Fractional precipitation of a petroleum ether solution in acetone (56) gives a better product, but it also is not always free from nitrogen. Purification with methyl alcoholic potash (57) gets rid of all the nitrogen, but the last traces of the alkali are very difficult to remove. When acetone-extracted, unbroken-down crude rubber is allowed to stand in a solvent like petroleum ether, the rubber hydrocarbon slowly diffuses through the network of insoluble substances and there is thus obtained a very pure product, free from nitrogen, and analyzing $(C_5H_8)_x$. However, this method, originally due to Caspari (58), and recently used to good advantage by Feuchter (59) and by Pummerer and Miedel (60), accounts for only about

70 per cent of the hydrocarbon present, a difficultly soluble portion remaining behind.

The best and most complete method for purifying the rubber hydrocarbon is that of Pummerer and Pahl (20) by the direct use of latex. This method, which is carried out in an atmosphere of nitrogen in order to avoid any oxidation, is as follows: Preserved latex is treated with a solution of sodium hydroxide (2 per cent of the total solution) for two days at 50°C., to hydrolyze the protein, and is constantly stirred. On standing at the end of this time, creaming takes place. The lower alkaline layer is siphoned off and the treatment repeated four times. Even before the last treatment, the biuret and the ninhydrin reactions for proteins no longer show the presence of any protein. The remaining alkali present in the cream is separated by washing and finally by dialysis. The rubber hydrocarbon is then coagulated by the addition of acetone or acetic acid, extracted with acetone to remove any remaining resins, and dried in a high vacuum. The acetone extract contains practically no resins and serves chiefly as a preliminary removal of water. The product, even in thick pieces, is transparent, pale yellow in color, elastic, and not tacky. The ash content is as low as 0.077 per cent. The analytical figures agree very closely with $(C_5H_8)_x$. The earlier publications stated that the preparations were free from nitrogen. Later, however, Pummerer, Andriessen and Gündel (61) found that, although no protein was present, the samples still contained some nitrogen, 0.04–0.1 per cent, which is probably due to the presence of amines. Pummerer (62) then found that samples with less than 0.04 per cent of nitrogen can be obtained from revertex-S (see p. 60).

Cummings and Sebrell (50), using the method of Pummerer and Pahl, but changing the alkali several more times, have been able to prepare a purified rubber hydrocarbon with a nitrogen content of only 0.004–0.0096 per cent. It is protein-free, and when extracted with acetone the amount of nitrogen falls so low that it cannot be measured with accuracy by the exact method used by them,—namely, colorimetric determination with Nessler's solution.

The highly purified rubber hydrocarbon contains all the original hydrocarbon, including the insoluble or difficultly soluble portion that is left behind in the diffusion method mentioned above. These two portions can now be separated, if desired, by means of absolute ether, the ether-soluble portion being called "sol-rubber" or alpha-rubber and the insoluble portion "gel-rubber," or beta-rubber. This, however, is not an exact separation, because even after ten days of continuous extraction a constant condition is attained where only a very small but weighable constant amount goes into the ether per day. With ether extraction the amount of gel-rubber is about 35 per cent, but with other solvents, it is lower. Both portions give similar analytical results. Sol-rubber is colorless and very elastic; gel-rubber is brownish and very tough, and contains a trace of ash. The analytical figures for these two varieties are as given in table 4. When the gel-rubber is broken down on the mill in an atmosphere of carbon dioxide it becomes completely soluble in ether, and when ether solutions of sol-rubber are evaporated, after standing, traces of gel-rubber insoluble in ether are found. These are interesting points because of their bearing on the theory of a two-phase system in rubber. The breaking down may be due to disaggregation, according to Whitby (63) and Harries (64), but even this term does not fully explain what happens. Furthermore, whether sol-rubber is simply disaggregated gel-rubber, and whether gel-rubber is aggregated sol-rubber still remains to be seen.

TABLE 4

Analysis of sol-rubber and gel-rubber

	CARBON	HYDROGEN
	per cent	*per cent*
Calculated for $(C_5H_8)_x$	88.15	11.85
Ether-sol-rubber: Found	88.00 87.98	11.94 11.90
Ether-gel-rubber: Found	87.72 87.96	11.98 11.93

The rubber hydrocarbon is decomposed by certain surface molds (68). Losses in weight up to 30 per cent have been recorded, but even when 20 per cent of the rubber hydrocarbon was decomposed, the remaining rubber showed very little change in any important properties.

It is of interest to note that rubber was first analyzed by Faraday (65), who gave it the same formula used to-day. Other important contributions to the establishment of this formula, besides those just discussed, have been made by Weber (66), Gladstone and Hilbert (67), and Harries (54).

2. Crystalline rubber

Unstretched frozen rubber exists in a crystalline form as shown by x-ray studies (see p. 67) (69). Also, the rubber hydrocarbon has been obtained in crystalline form at room temperature. Pummerer and Koch (56) isolated the crystals while working with solutions containing the purified hydrocarbon prepared by fractional precipitation. Analysis showed them to have the formula $(C_5H_8)_x$. They are very sensitive to oxidation, probably on account of the relatively larger surface exposed to air as compared with that of the ordinary non-crystalline variety. They become transparent and plastic at about 60°C. and begin to melt at about 92°C. They are colorless, and show relatively little elasticity and "nerve." The crystals shown in the photomicrographs given in the original article are fully described crystallographically, showing that there are three crystalline varieties in six different crystalline formations. Since these did not appear to be modifications of the same substances, the authors concluded that "there are several chemically different substances in the sample."

3. Molecular weight and other physical properties

The molecular weight of rubber is high, as indicated by its colloidal properties. Hinrichsen and Kindscher (70) calculated it to be 3173 by the cryoscopic method in benzene solution. This is probably a good average figure according to the recorded work of the older investigators. Staudinger (71) considers the "macromolecules" of rubber to consist of 100 to 1000 C_5H_8 groups, corresponding to molecular weights of 6800 to 68,000. Very recently, Pummerer, Nielsen and Gündel (72), using camphor as the solvent as suggested by Rast, at concentrations of 1:4 and 1:10 found molecular weights of 1100 to 1600. In menthol at a concentration of 1:50, molecular weights of 1200 to 1600 were obtained; on dilution to 1:100 the values obtained were only 520 to 620, indicating extensive dissociation. Further dilution caused no decrease. These lower figures were obtained with samples of highly purified rubber hydrocarbon prepared by different methods and with samples of both sol- and gel-rubber. The results indicate eight C_5H_8 units or a molecular weight of 544, although the experiments do not warrant the acceptance of this as an established fact as yet. The authors point out that samples of great difference in solubility show the same average molecular weight in camphor and in menthol, and that, therefore, their essential difference must lie in their different powers of aggregation. Staudinger, Asano, Bondy and Signer (73), however, criticize the results obtained with camphor and menthol, stating that these solvents, even with substances of more finite molecular weights, give figures which vary considerably with the time of heating, the amount of supercooling, etc. Purified rubber hydrocarbon from latex gave in menthol values from 363 to 1160, and in camphor, 2200, the concentration being low in each case as in Pummerer's experiments. The authors believe that only a hydrocarbon should be used as the solvent for determining the molecular weight of another hydrocarbon. Pummerer (74) has produced further evidence to support his earlier observations, but the question of the molecular size of the rubber hydrocarbon is not yet settled.

X-ray studies (69) (75) (76) (77) have shown that unstretched raw rubber produces a diagram typical of an amorphous material —that is, a single, broad, diffuse ring. As raw rubber is stretched beyond 75 per cent elongation, the x-ray diagram shows a marked change. In addition to the amorphous ring, which is always evident but decreases in intensity with increase in elongation, there appear instantaneously definite interference spots, which become sharper and more distinct the greater the stretching but retain the same positions. The entire phenomenon is reversible if the sample is not too strongly stretched, the amorphous diagram being obtained again when the tension is released. If, however, the rubber is stretched slowly, no interference spots appear at all (78). When the rubber is stretched, cooled, and then released, the interferences remain unchanged. When the stretched rubber is heated, the interferences become less intense and disappear at 60°C. They also disappear when the stretched rubber is placed in an atmosphere of the vapor of a solvent, such as benzene. The intensity of the diffraction interferences increases in direct proportion to the percentage elongation of the stretched rubber, and this increase in intensity is explained by the continual appearance of new diffracting crystal-like individuals. The evidence seems to support the contention that the crystals do not exist as such prior to the stretching, although rubber which has stood for some time at low temperatures and has become opaque and hard, gives a pattern of sharp, concentric rings, indicative of small crystal grains in random orientation (79). The same results with x-rays have been obtained with both sol- and gel-rubber and with eighteen different samples of crude rubber from various parts of the world. It is evident, therefore, that the structure of raw rubber as revealed by this method is independent of the origin or the type of rubber and is directly related to the structure of the rubber hydrocarbon (80). Also, the stretching of rubber is a molecular, not a macroscopic, phenomenon.

X-ray studies indicate that the rubber hydrocarbon consists of long chains of isoprene groups and that these long chains probably exist as spirals which form definitely aligned fibers when the rubber is stretched. Further work in this field will be awaited with considerable interest.

If a strip of raw rubber is stretched while warm and cooled quickly, under tension, it remains as a thin strip and is then known as "racked rubber." If the tension is released and the racked rubber warmed, it will contract, but not to its original condition. Some of the strains are evidently "frozen in." Repeated racking may stretch the rubber to 9,000 to 10,000 per cent elongation (81). Such racked rubber shows a very intense x-ray diagram. If stretched or racked rubber is frozen with liquid air and then struck with a hammer, it splits into fibres. Unstretched rubber under these conditions shows a conchoidal fracture. Hock (82), who did this work, was also able to show the same effect with "diffusion" rubber, and, working at lower temperatures, with vulcanized rubber. He reasoned, therefore, that the fibrous structure is a property of the molecules or molecular aggregates common to all modifications.

Rubber, upon being stretched, gives off heat and becomes cold again when it is immediately allowed to return to its original position. This heating during the stretching is known as the Joule effect. Recent data show that it is directly proportional to the degree of elongation (83), just as the intensity of the x-ray diagram is also directly proportional to the degree of elongation.

van Geel and Eymers (84) have derived a relation between the double refraction and the elastic tension of rubber. The formula given by them defines double refraction as a function of the tension up to a certain limiting value of the tension, at which point a strict proportionality between double refraction and tension begins. The elongation at this limiting tension is 70 per cent, —the same elongation at which x-ray photographs begin to show fibre diagrams. It appears, therefore, that 70 per cent elongation "is a characteristic constant of pure rubber."

The specific gravity of raw rubber is 0.91–0.93; that of the pure hydrocarbon is 0.920 at 17°/4° (85). Racking causes a decrease in the specific gravity; freezing causes an increase. At 36–8°C., frozen rubber shows a sudden decrease in density and hardness, and an increase in transparency (86). These changes are probably the result of the fusion of a crystalline component. Other physical constants of rubber are given on p. 119.

Rubber forms colloidal solutions in benzene, gasoline, chloroform, carbon tetrachloride, carbon bisulfide, absolute ether, and similar solvents. It is precipitated from solution by alcohol, acetone, etc. Raw rubber is insoluble in water, but, on being allowed to remain in it, will absorb water up to about 25 per cent of its weight (87). Unwashed rubber, of course, absorbs more water than washed rubber on account of the presence of water-soluble components. Solutions of raw rubber in organic solvents are more or less turbid, depending in part on the amount and kind of the non-rubber constituents and in part on the solubility of the gel-rubber portion. Gel-rubber is more soluble in the aromatic hydrocarbons (cumene is the best), and therefore the aromatic hydrocarbon solutions of purified rubber are clear, whereas the petroleum ether and absolute ether solutions are clear only when the gel-rubber has been removed or rendered soluble. All these solutions show the familiar Tyndall effect. They are optically inactive (88).

The viscosity of a rubber solution depends not only on the concentration but to a very great extent on how much the sample has been "worked." As mentioned above (p. 63), a 10 per cent solution of unbroken-down pale crêpe forms a gel, whereas a similar solution of rubber which has been heavily milled, even in an atmosphere of carbon dioxide to prevent oxidation, has about the same viscosity as the solvent itself. In addition to this change and those caused by heat, light, etc., as discussed on p. 63, it should be mentioned that when a solution of rubber is heated to boiling on the steam bath and protected from evaporation as well as from oxidation by carbon dioxide, the viscosity, which becomes less with the rise in temperature, returns to its original value upon cooling, whether the solution is cooled slowly or suddenly (55). Harries (54) had previously reported that the change was not reversible, but he did not guard against oxidation, which causes a considerable lowering. van Rossem (89) showed that oxygen causes a rapid lowering of the viscosity of a solution of rubber during heating, although no oxygen is absorbed for several hours. The oxygen apparently acts as a catalyst, since inert gases do not have this effect. Staudinger and Bondy (90) found that heat alone lowers the viscosity of a solution of rubber, but Pummerer (91) maintains that even traces of oxygen cause a considerable lowering of the viscosity. He also found that oxygen-free solutions which have been heated for a long time (twelve days) on the steam bath show a decrease in viscosity.

Whitby and Jane (93) studied the effects of small amounts of certain substances on the viscosity of solutions of cold-extracted pale crêpe and found that (1) precipitants like alcohol cause practically no change in viscosity, (2) organic acids, especially the chlorinated acetic acids, cause a rapid lowering, (3) organic bases, such as aliphatic amines, piperidine, etc., cause a similar lowering, (4) reactants like bromine and iodine show an immediate lowering which increases with time, while tetranitromethane shows an unusually great lowering, and (5) small quantities of potassium hydroxide cause an increase but larger quantities a decrease. Spence and Kratz (94) had earlier found that trichloroacetic acid caused a considerable lowering. This substance should now, however, be classed with reactants because it also causes a change in the unsaturation (see p. 63).

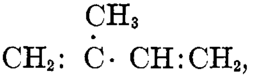
When a solution of rubber in petroleum ether is allowed to form on mercury a film insufficient to cover the entire area, its thickness as given by Sheppard, Nietz and Keenan (92) is only 1.5 Å. This is very small as contrasted, for example, with a molecular film of stearic acid on water which is 21 Å. thick. It appears, therefore, that the rubber particle is of the "macromolecular" type and lies very flat under such conditions.

4. Action of heat

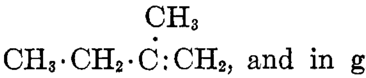
The pure rubber hydrocarbon softens at 130–45°C., sol-rubber at 115–30°C., and gel-rubber at 145–60°C. (20). Crystallized rubber becomes transparent and plastic at 60–2°C. and molten at about 90°C. (56). It will be recalled that the x-ray interference diagram becomes less intense and disappears at 60°C.,—the temperature at which Pummerer's crystals become plastic and isotropic.

At ordinary vulcanization temperatures, around 140°C., rubber softens and becomes plastic but there is apparently no chemical change (52). However, as the temperature rises, and especially as it approaches 270°C., not only does the rubber become semi-liquid, but it also slowly undergoes a chemical change as is noted by the definite lowering of the unsaturation (2.5 per cent in five and one-half hours at 245–65°C.) (52) (95). Heating an ethereal solution of rubber at 250°C. for many hours causes a lowering of about 20 per cent; above this temperature the change is comparatively rapid. For example, heating for 2 hours at 285°C. followed by 5 hours at 345–63°C. caused a drop of 51 per cent.

This change is only in the unsaturation, because the hydrocarbon remains as $(C_5H_8)_x$. It belongs, therefore, to a general type of isomerization and is no doubt due to internal cyclic formation,—polycyclization. This will be discussed again later (p. 117).

Heat decomposition, that is, dry distillation, of rubber has been carried out by several investigators. C. Greville Williams (96) in 1860 isolated a C_5H_8 hydrocarbon boiling at 35°C., and named it isoprene. Tyndall (97) proposed the structure of isoprene as  $CH_2:\overset{CH_3}{\overset{\cdot}{C}}\cdot CH:CH_2$, and Euler (98) proved it by synthesis. Himly (99) had previously isolated a low-boiling product and a high-boiling one, 168–71°C., naming them respectively, "faradayin" and "kautschin." The latter was also called "caoutchene," and was found to be impure dipentene. Bouchardat (100) later obtained isoprene, dipentene and "heveene," $(C_{15}H_{24})$. Ipatief (101) showed that the isoprene fraction contained some trimethylethylene (b.p. 38°C.). This hydrocarbon is probably not a primary decomposition product, but is possibly formed by the partial reduction of isoprene during the heating. Harries (102), working under Emil Fischer in 1902, reinvestigated the subject by more refined methods in a vacuum of 0.25 mm. pressure. He found that the amounts of isoprene (seldom over 1 per cent) and of dipentene were small and that the chief fraction was an oil boiling at 220–60°C. More recent and more complete work in this field is that of Staudinger and Fritschi (103), who heated carefully purified rubber in a vacuum of 0.1–0.3 mm. pressure. The final temperature of the metal bath employed was 350°C. The residue, a resinous mass, amounting to 36.5 per cent, was found to be only about one-half as unsaturated as the original rubber, and was therefore a polycyclo-rubber. Fractionation of the distillate in a high vacuum, and determination of the boiling point, molecular weight, refractive index and bromine absorption of the chief constituents, showed the presence of isoprene, 3.1 per cent; dipentene, 8.8 per cent; a $C_{15}H_{24}$ hydrocarbon with two double bonds and two rings, possibly a hydronaphthalene derivative, 4.4 per cent; a $C_{15}H_{24}$ hydrocarbon containing three double bonds and two rings, 3.8 per cent; a $C_{25}H_{40}$ hydrocarbon containing four double bonds and two rings; and higher boiling terpenes which decomposed on redistillation. No open-chain terpenes were found. The polycyclo-rubber that is formed during the course of the heating can also be decomposed if the temperature is raised to 350–400°C., but no isoprene and no dipentene are obtained (see p. 120).

Staudinger and Geiger (95) later showed that by rapid distillation at ordinary pressure and in an atmosphere of carbon dioxide almost all of the rubber can be converted into volatile products. For example, the distillate from a 500 gram sample of acetone-extracted rubber consisted of 92.8 per cent, and of this, 0.4 per cent was liquid at $-80°C.$, 2.6 per cent boiled at 25–32°, 4.3 per cent was the isoprene fraction boiling at 32–5°, 5.8 per cent boiled at 45–150°, 23.8 per cent, the dipentene fraction, boiled at 50–70° at 12 mm., and 25.9 per cent boiled above 180° at 12 mm. The slower the distillation the greater the polycyclization, and therefore the greater the residue. One hundred grams of plantation rubber distilled slowly *in vacuo* at 300°C. in an atmosphere of carbon dioxide gave 53 grams of residue which consisted almost entirely of polycyclo-rubber.

Since it is known that a rubber-like product can be obtained by polymerizing isoprene, the question naturally arises why a greater amount of isoprene is not obtained in the dry distillation of rubber, and also whether the dipentene and the polyterpenes are primary or secondary decomposition products. Under the conditions necessary to decompose rubber, isoprene readily polymerizes to dipentene and other higher terpenes and not to a rubber-like polymer. Furthermore, the heat decomposition of hydro-rubber (see p. 103) gives no isoprene but does give methylethylethylene,  $CH_3\cdot CH_2\cdot \overset{CH_3}{\dot{C}}:CH_2$, and in greater quantity than it gives its dimer, $C_{10}H_{20}$. Also it has been shown that isoprene at 700–50°C. is converted in part into benzene, toluene, and other aromatic substances (104). Therefore, it is likely, though not completely proven, that isoprene or its straight chain homologues are obtained first and that these then polymerize or rearrange into the terpene products that are isolated.

Further light on this question is given in the most recent work in this field, that of Midgley and Henne (105). They worked with very large amounts and isolated products which ordinarily would escape notice. Pale crêpe was destructively distilled in 16-pound batches in an iron vessel at atmospheric pressure, 200 pounds in all being used. The temperature was always raised as quickly as possible to about 700°C., but no attention was paid to its control. The conditions used gave unusually large yields of isoprene—10 per cent—and this was the chief object of the work. The addition of magnesium, 850 grams to 16 pounds of rubber, did not increase the yield of isoprene or dipentene, but did increase the yield of the other products, especially the aromatic products. Zinc, iron and aluminum have a similar effect but to a smaller extent, copper is without effect, and brass behaves like iron. The products obtained are olefinic, dienic, aromatic and hydroaromatic compounds. No fully saturated compound was detected. In addition to the components separated by fractional distillation, a substantial portion of the original material polymerized, remaining as a jelly in the distilling flask. The materials lost in this way probably consisted largely of dienes.

Because of the preponderance of isoprene, dipentene and $C_{15}H_{24}$ in the products of destructive distillation, the authors hold that the single bond furthest removed from the double bonds is the most easily broken by pyrolysis. They point out that this same conclusion is also arrived at by Hurd (106) from purely theoretical considerations. Accordingly, they postulate that the rubber hydrocarbon breaks at single valences to give sections, each of which contains a given number of carbon atoms, that these points of breakage are represented by partial valences, and that the double bonds are resolved into partial valence forms. Then (*a*) adjacent partial valences may join to form double bonds (Thiele); (*b*) single partial valences six carbons apart may join to form rings; (*c*) any pair of partial valences may accept hydrogen, preferably those not adjacent to others; (*d*) partially hydrogenated aromatic compounds liberate hydrogen to yield the corresponding aromatic compounds; and (*e*) partial valences not joining or not accepting hydrogen may migrate. Thus practically all of the compounds isolated can be predicted.

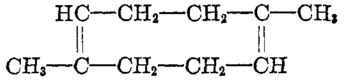
No myrcene, or a terpene boiling at 168–9°C., or dimethylbutadiene was found in the products of destructive distillation. With the exception of benzene, the compounds of the aromatic series obtained were probably all derived by dehydrogenation of the corresponding hydroaromatic compounds, since only those aromatic compounds were formed whose hydro-derivatives were also present. The origin of the benzene is obscure; it may have been formed by pyrolysis in locally overheated spots. The percentage yields in the distillate, except in the cases of isoprene (10 per cent) and dipentene (20 per cent) were all low, being about 0.01–0.10 per cent for the straight distillation, and 0.10–1.0 per cent with magnesium. The compounds positively identified were: 3-methyl-1-butene, 2-methyl-1-butene, isoprene, 2-methyl-2-butene, 2-methyl-2-pentene, benzene, Δ^1-tetrahydrotoluene, toluene, *m*-xylene, *p*-tetrahydroethyltoluene, *p*-ethyltoluene and dipentene. Incomplete evidence was obtained for the presence of 2-methylpentene, 3-methyl-2,4-pentadiene, 3-methylhexene, Δ^3-tetrahydrotoluene, Δ^2-tetrahydrotoluene, 2-methylheptene, thujene, $C_{10}H_{18}$ with 1 double bond and dimethyloctadiene. In the straight distillation the total amount of these substances in the distillate was 0.860 per cent, and with magnesium, 9.05 per cent.

5. *Structure of the hydrocarbon*

There is now no question but that, as pointed out above, the empirical formula of the rubber hydrocarbon is C_5H_8. How many of these groups make up the actual molecule, and in fact, whether the natural hydrocarbon consists of a single molecule, is not yet known. The chief chemical reaction of the rubber hydrocarbon is addition. The substance is therefore unsaturated, and a study of the addition products leads to the conclusion that the fundamental grouping is C_5H_8 (not $C_{10}H_{16}$ as formerly supposed) and that there is one double bond for each C_5H_8 group. This has recently been substantiated by measurement of the refractive index of a film of purified rubber by Macallum and Whitby (107), and of the adsorption spectra by Scheibe and Pummerer (108). Many years ago, Gladstone and Hibbert (67), from measurements of the refractive index of purified rubber in solution, calculated that there were one and one-half double bonds to each C_5H_8 grouping, and concluded "that the main constituent of caoutchouc is a compound which for $C_{10}H_{16}$ has 3 pair of carbon atoms doubly linked." Weber also used the $C_{10}H_{16}$ nucleus, largely because of its relation to the terpenes, and Harries used the same because of his early study of rubber "diozonide."

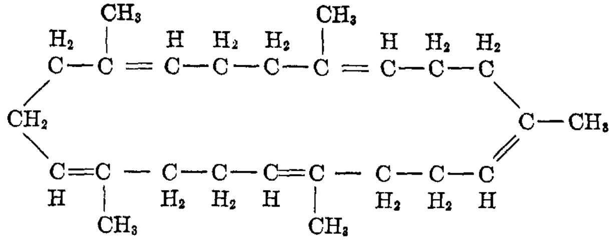
The lowest products of the dry distillation of rubber are gases and isoprene. Since isoprene has the same empirical formula as the rubber hydrocarbon, and since it can be polymerized to rubber-like products, it is reasonable to suppose that rubber itself is a polymer of isoprene. In the course of the polymerization, one of the double bonds in each molecule of isoprene disappears, thus leaving one double bond for each C_5H_8 group. What is known as to the nature of the union of these isoprene molecules and the relative positions of the remaining double bonds was found out chiefly by Harries in his classical work on the ozonides (109). He was led to this work by observing that rubber tubing in contact with ozone rapidly perishes. Ozone adds to the double bond of an olefin forming an ozonide, and on hydrolysis such an ozonide is decomposed into aldehydes or ketones depending on the structure of the original olefin. By identification of the aldehydes or ketones, the position of the double bond can be accurately determined because the oxygen of the carbonyl groups in the decomposition products is attached to those carbon atoms which were originally united by the double bond. The ozonide formed from rubber is a glassy solid, melts at about 50°C., is very explosive, and is saturated toward bromine. The yield is a little better than 80 per cent, and analysis showed that the ozonide had the empirical formula $C_5H_8O_3$,—that is, one mol of ozone to each C_5H_8 group. Molecular weight determinations in glacial acetic acid and in methyl acetate indicated its molecular formula to be $C_{10}H_{16}O_6$. It was on the basis of this work that Harries concluded that the fundamental grouping in rubber must be $C_{10}H_{16}$.

On hydrolysis the ozonide gave levulinic aldehyde, $CH_3COCH_2CH_2CHO$, levulinic acid, $CH_3COCH_2CH_2COOH$, a small amount of levulinic aldehyde peroxide, and of course, the usual by-product, hydrogen peroxide. No other aldehydic or ketonic compounds were found, although the experiments were repeated many times. He therefore reasoned that the structure of the $C_{10}H_{16}$ unit must correspond to 1,5-dimethyl-1,5-cycloöctadiene,

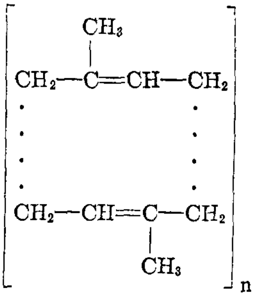


$$\begin{array}{l} \qquad HC-CH_2-CH_2-C-CH_3 \\ \qquad\;\; \| \qquad\qquad\qquad\quad \| \\ CH_3-C-CH_2-CH_2-CH \end{array}$$

Harries assumed that this unit was polymerized by means of residual valences into the rubber hydrocarbon itself. Later, however, he found that the ozonide when dissolved in benzene gave a molecular weight 2.5 times that found in glacial acetic acid, and that its formula should therefore be written $(C_5H_8O_3)_5$ or $C_{25}H_{40}O_{15}$ (110). He also found that when alpha-isorubber, prepared by the removal of hydrogen chloride with pyridine from rubber hydrochloride, was ozonized and the ozonide hydrolyzed, not only was there obtained the customary levulinic aldehyde and acid, but also diacetylpropane, $CH_3COCH_2CH_2CH_2COCH_3$, and other polyketones and ketonic acids. Among these were isolated a triketone with eleven carbon atoms, undecatrione, and a tetraketone with fifteen carbon atoms, pentadecatetrone. It was not difficult to account for the diacetylpropane, because in some cases the chlorine in the rubber hydrochloride was no doubt removed along with an adjacent hydrogen other than the one with which it was originally added, thus forming double bonds in different positions from and adjacent to those in the original hydrocarbon, but it was impossible to account for the presence of an eleven- and a fifteen-carbon chain compound in an eight-carbon cycle or, with the methyl groups, its corresponding ten-carbon unit. Harries, therefore, in 1914, abandoned his cycloöctadiene formula, and adopted the hypothesis, already put forth by Pickles (111) in 1910 that the C_5H_8 groups were united in a large ring, believing from his new data that the ring must contain at least 16 and probably 20 carbon atoms:

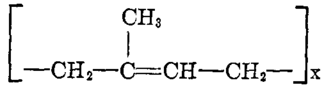


or better yet, as he also expressed it, without definitely stating how large the number represented by n was:



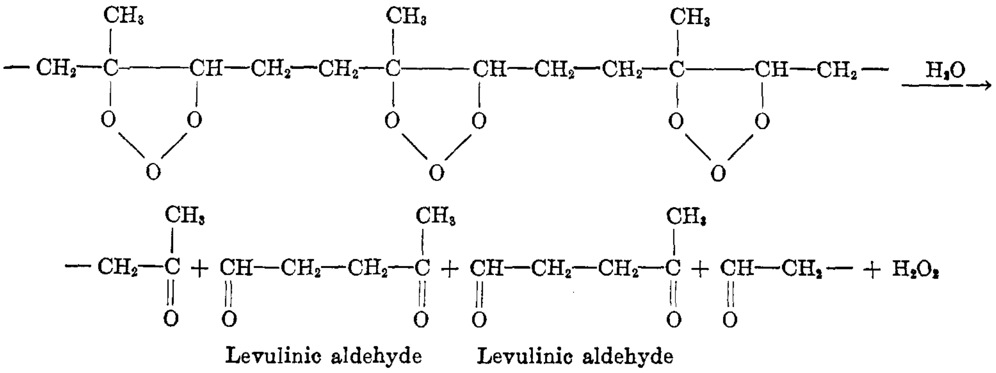
$$\left[\begin{array}{c} CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2 \\ \vdots \qquad\qquad \vdots \\ CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CH_2 \end{array}\right]_n$$

Since it is not known whether the C_5H_8 groups are united in a large ring or as a long straight chain, it is simpler to express what is known as the structure of the hydrocarbon as follows:



$$\left[-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-\right]_x$$

On this basis, it is now possible to indicate the action of ozone and the formation of levulinic aldehyde by hydrolysis, using only a section of the structure and inserting heavier dashes to show the bonds between the original isoprene groups:



The levulinic acid always isolated along with the aldehyde is probably formed by the direct breaking up of the ozonide or by the oxidation of the aldehyde with the hydrogen peroxide.

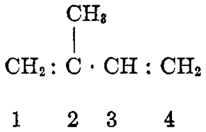
More recent work with ozone, potassium permanganate and hydrogen peroxide has substantiated Harries's work, and, in general, his ideas. Geiger in Staudinger's laboratory (112) has found that ozone gives a mixture of acids containing one that appears to be a dicarboxylic acid with at least 30 carbon atoms in the molecule, as shown by titration. Permanganate oxidation gives acetic acid, succinic acid, levulinic acid, an acid with the formula $C_{13}H_{18}O_7$ and acids of higher molecular weight. The work of Robertson and Mair, discussed in detail on p. 99, also shows the complexity of the rubber molecule and indicates that the size of the simplest rubber molecule or aggregate is not less than $(C_5H_8)_8$.

The chemical structure of the unit group of rubber is fairly well established, but the size of the molecule, whether there are one or many molecules, whether the unit groups are united in a long chain with free valences at the ends or whether they are united in a large ring, are questions unanswered as yet. Staudinger (113) holds to the long chain hypothesis and Pummerer to the large ring hypothesis. The most recent publication up to this writing is that of Pummerer (114), in which he gives chemical evidence, based on iodine and oxygen absorption against the long open chain with free end valences.

The acceptance of the theory that the rubber hydrocarbon consists of a large ring was difficult even a few years ago, because rings of more than nine carbon atoms were unknown. However, Ruzicka and his students (115) have prepared much larger rings, one of them consisting of thirty carbons, $C_{30}H_{60}$. This is very close in size to the ring for rubber postulated by Ostromislenski (116) from his study of polyvinyl chloride and bromide ("cauprene chloride" and "cauprene bromide"),—namely, one of thirty-two carbons. Much of the recent work as already set forth has also indicated a structure corresponding to eight isoprene groups. For the sake of comparison, it might be mentioned that the compound having the largest known ring structure found in nature is civetone, an unsaturated cyclic ketone with seventeen carbons in the ring (117). Other interesting hydrocarbons of high molecular weight are the yellow hydrocarbon carotin, $C_{40}H_{56}$ (M. W. 536); the compound, $C_{43}H_{88}$ (M.W. 604) found in petrolatum wax (118), and the synthetic dimyricyl or hexacontane, $C_{60}H_{122}$ (M.W. 843).

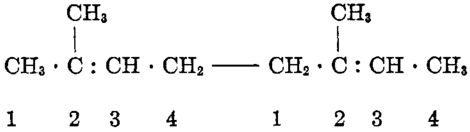
It has been known for some time that isoprene can be polymerized to a rubber-like product in the presence of metallic sodium (119), but there has been no experimental evidence for the mechanism of the reaction. Such evidence is now provided in the excellent work of Midgley and Henne (120), who placed chips of metallic potassium in contact with isoprene and then slowly added ethyl alcohol. A good yield of a light yellow oil resulted, which upon analysis proved to be a mixture of 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes. These isomers are the three possible dihydro dimers of isoprene resulting from a junction at the 1,4-, the 4,4- and the 1,1-carbon atoms, respectively, and the addition of hydrogen to the 1,8-positions of each dimer. No trace of a compound of cyclic nature was detected.

These results help to prove that the synthetic rubber produced by contact of isoprene with the alkali metals is a long chain or large ring formed of isoprene units linked together by means of their 1 and 4 carbon atoms. The methyl groups would not necessarily be in regular order as they probably are in natural rubber. The structural formulas of isoprene and of the three dimethyloctadienes are given below, and also a possible skeleton structure of a section of a synthetic rubber chain (121). The numbers are the same in all cases, and the junction of the isoprene units is indicated by a longer bond. If such a synthetic rubber were ozonized, it can be seen that the decomposition products would be levulinic aldehyde, succinic aldehyde (or acid), and acetonylacetone. As a matter of fact, these are the products actually obtained, although the proportions vary considerably, levulinic aldehyde being the greatest in amount (122).



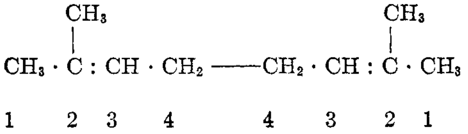
$$\underset{1}{CH_2}:\underset{2}{\overset{\overset{CH_3}{|}}{C}}\cdot\underset{3}{CH}:\underset{4}{CH_2}$$

Isoprene



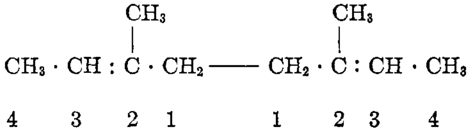
$$\underset{1}{CH_3}\cdot\underset{2}{\overset{\overset{CH_3}{|}}{C}}:\underset{3}{CH}\cdot\underset{4}{CH_2}\text{——}\underset{1}{CH_2}\cdot\underset{2}{\overset{\overset{CH_3}{|}}{C}}:\underset{3}{CH}\cdot\underset{4}{CH_3}$$

2,6-Dimethyl-2,6-octadiene



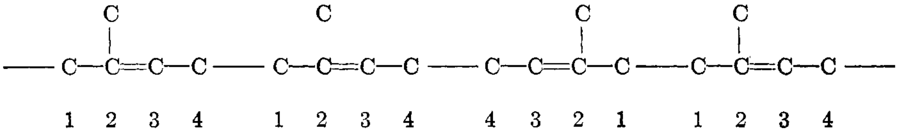
$$\underset{1}{CH_3}\cdot\underset{2}{\overset{\overset{CH_3}{|}}{C}}:\underset{3}{CH}\cdot\underset{4}{CH_2}\text{——}\underset{4}{CH_2}\cdot\underset{3}{CH}:\underset{2}{\overset{\overset{CH_3}{|}}{C}}\cdot\underset{1}{CH_3}$$

2,7-Dimethyl-2,6-octadiene



$$\underset{4}{CH_3}\cdot\underset{3}{CH}:\underset{2}{\overset{\overset{CH_3}{|}}{C}}\cdot\underset{1}{CH_2}\text{——}\underset{1}{CH_2}\cdot\underset{2}{\overset{\overset{CH_3}{|}}{C}}:\underset{3}{CH}\cdot\underset{4}{CH_3}$$

3,6-Dimethyl-2,6-octadiene



$$\text{——}\underset{1}{C}\text{—}\underset{2}{\overset{\overset{C}{|}}{C}}\text{=}\underset{3}{C}\text{—}\underset{4}{C}\text{——}\underset{1}{C}\text{—}\underset{2}{\overset{\overset{C}{|}}{C}}\text{=}\underset{3}{C}\text{—}\underset{4}{C}\text{——}\underset{4}{C}\text{—}\underset{3}{C}\text{=}\underset{2}{\overset{\overset{C}{|}}{C}}\text{—}\underset{1}{C}\text{——}\underset{1}{C}\text{—}\underset{2}{\overset{\overset{C}{|}}{C}}\text{=}\underset{3}{C}\text{—}\underset{4}{C}\text{——}$$

Section of possible chain in synthetic rubber

III. CHEMICAL REACTIONS AND DERIVATIVES

1. Introduction

As already mentioned, the chief chemical reaction of the rubber hydrocarbon is addition, and a study of the addition products leads to the conclusion that there is one double bond for each C_5H_8 group. Practically all of the addition reactions take place at room temperature or below, sulfur alone adding completely only at comparatively high temperatures. Accordingly, it seems most likely that there is no change in the position of the double bond during the reactions. Generally, as would be expected, the best results are obtained in solution because the reaction can then be regulated more readily. Solution may, however, have an even more important effect. Some of the addition reactions only go on or at least only go to completion when the amount of rubber hydrocarbon present corresponds to a 1 per cent solution or less. This is significant because the reactions at this dilution may possibly be linked up with the change in the molecular or "particle" size of the rubber hydrocarbon found in the determination of the molecular weight as discussed above (p. 66), but these facts are all too new and incomplete for the drawing of any general conclusions. Whether the difference in reactivity is due to dissociation, disaggregation, or depolymerization, or something else, the fact remains that a definite change takes place, and some reactions can be carried to completion only under such conditions and apparently not otherwise. Mastication and higher temperatures sometimes bring about the same or similar conditions of reactivity (52).

The addition products are amorphous substances of high, undetermined molecular weight. Some are soluble in the same solvents as rubber, some in acetone, alcohol and glacial acetic acid, and some in water or aqueous alkalies; some are insoluble in all solvents tried. When they do dissolve they form colloidal solutions. Some are unstable and some are remarkably stable. Some are white or colorless, some are yellow or brown. All these general properties belong not only to the immediate addition products but to the derivatives prepared from them as well. Since they do not crystallize and cannot be distilled without decomposition, they are difficult to purify, but when purified as much as possible, they show a definite chemical composition. On this account it is assumed that the rubber hydrocarbon from which they are prepared is a chemical individual, or consists of complexes made up of this chemical individual, such complexes acting like a chemical individual.

In discussing the derivatives themselves, greater emphasis will be laid upon the more recent work and upon the more significant properties of the older and better known derivatives which are already rather fully described in the general text-books on rubber. The C_5H_8 group will be used as the basis of nomenclature instead of $C_{10}H_{16}$. This will create scarcely any confusion because so few names based on the old system were well-known. Under this newer system, the older name, rubber tetrabromide, becomes rubber dibromide or simply rubber bromide; rubber dihydrochloride and dihydrobromide become rubber hydrochloride and hydrobromide, respectively. The number of derivatives of rubber is comparatively small, and it is believed that all the known ones that have been substantiated by their properties and analyses are included herein. The order of presentation is by classes and somewhat in historical sequence.

2. The halogen products and their derivatives

The halogens all react with the rubber hydrocarbon. Chlorine ordinarily gives a white, fibrous product in which substitution as well as addition has taken place. Substitution is the chief reaction in the early stages, as shown by McGavack (123) in a study of the effluent gases by an ingenious use of flow-meters. The product is soluble in benzene, chloroform and acetone, and these solutions upon evaporation leave a rather tough, transparent film. Chlorinated rubber is a mixture containing about 65 per cent of chlorine with the approximate formula $(C_{10}H_{13}Cl_7)_x$, and has, therefore, been spoken of as the "heptachloride." It is remarkably resistant to the action of concentrated sulfuric, nitric and chromic acids even at 100°C. It slowly decomposes, especially in sunlight, giving off hydrogen chloride.

Ostromislenski (116) states that when a 9 per cent solution of chlorine in carbon tetrachloride, containing the theoretical amount of chlorine, is added to an 18 per cent solution of extracted Para rubber in the same solvent at 0°C., there is formed rubber dichloride. It was purified by precipitation from acetone solution and analyzed for chlorine. The result was very close to the theory. He assumed it had a molecular weight corresponding to that of cauprene chloride (see p. 116), and, therefore, formulated it as a compound having eight isoprene residues, $C_{32}H_{40}(CH_3)_8Cl_{16}$.

Bromine acts like chlorine, substituting as well as adding, but in cold, very dilute solutions it gives the addition product $(C_5H_8Br_2)_x$. The formula was formerly written $C_{10}H_{16}Br_4$, and the compound was known as "rubber tetrabromide" (124). When properly prepared, it is a white, amorphous solid, which swells in some solvents but dissolves in only a very few, such as the simple halogenated hydrocarbons. If it is allowed to stand for some time as a dry powder, it then becomes practically insoluble in all solvents. This phenomenon is characteristic of a number of rubber derivatives. Rubber bromide contains 70.13 per cent of bromine and is stable for many months under ordinary laboratory conditions, but on being heated it slowly evolves hydrogen bromide. It is not appreciably attacked at ordinary temperatures by hydrochloric, nitric, sulfuric and chromic acids. Its formation has been employed for some time for estimating the rubber hydrocarbon, either directly by isolation of the solid product (125) or more recently indirectly by determining the amount of bromine used (126) (127).

Weber (124) states that the action of boiling alcoholic sodium hydroxide upon rubber bromide is "surprisingly slight," but sodium ethylate has "a more pronounced effect." At 120°C., during 10 hours, a solution of sodium ethylate removed all but 13.38 per cent of the bromine. The resulting product weighed more than calculated from the loss of bromine, and he therefore concluded that some of the bromine atoms must have been replaced with ethoxyl groups. Hinrichsen, Quensell and Kindscher (128) stated that they could not remove all the bromine, and Kirchhof (129) found that he could not go lower than 4.5 per cent of bromine, even when he heated the rubber bromide successively with metallic calcium and alcohol, and with aniline, up to 190°C. under pressure. He also found that after such drastic treatment as heating with a mixture of metallic sodium and sodium ethylate in xylene for four hours at 150–60°C., there still remained about 9 per cent of bromine.

Iodine gives various unstable products of no definite composition, sometimes containing oxygen in addition to iodine (130). Iodine chloride has recently been used by Kemp (131) in a modified Wijs solution for estimating the rubber hydrocarbon. The method is not very difficult to carry out and the results are accurate within 0.5 per cent. A. E. Gray, in collaboration with the writer, isolated the products formed under two different conditions and found that the iodine chloride probably adds as such (see table 5). The products had apparently decomposed partially during the purification.

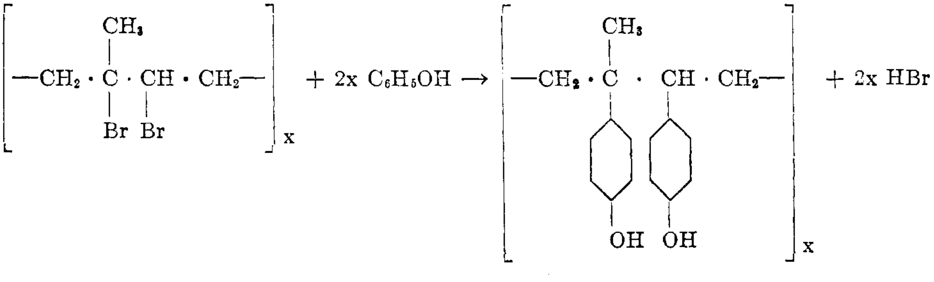
In 1900, C. O. Weber (132) showed that rubber "tetrabromide" and melted phenol react with the evolution of hydrogen bromide and the formation of a brownish compound, $C_{34}H_{36}O_4$, for which he obtained excellent analyses. He considered it to be an ether and named it "tetroxyphenyl-polyprene," $C_{10}H_{16}(O \cdot C_6H_4)_4$. Other phenols reacted similarly; thiophenol gave a different reaction although hydrogen bromide was evolved, and phenol ethers such as anisole did not react at all. The phenol product was found to form dark brown solutions in alcohol, acetone, ether, ethyl acetate and aqueous alkalies, and to be insoluble in benzene, chloroform, carbon bisulfide, turpentine and petroleum ether. Since there was no reaction of the rubber tetrabromide with anisole, even though it dissolved in alkalies, he decided that "this is almost conclusive evidence that it is the hydroxyl hydrogen of the phenol which forms the point of attack in the reaction in question, and this fact is at the same time the reason why, in the above formula, the oxygen appears as ether oxygen and not as hydroxyl oxygen." Recently, Fisher, H. Gray and McColm (133) repeated Weber's work and verified it, but found that the phenol product could easily be methylated with dimethyl sulfate in the presence of alkali at the ordinary temperature. The methylated product is soluble in benzene and insoluble in aqueous alkalies. These facts show that the phenol groups contain free hydroxyl groups, and that the linkage between the rubber carbon and the phenol is at the ring, presumably in the para position. The reaction, using C_5H_8 as the fundamental group, could be represented as follows:

TABLE 5

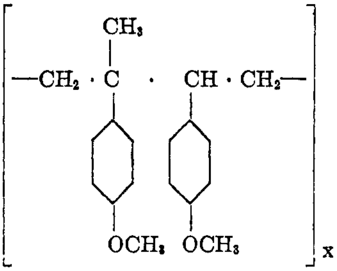
Analysis of the product formed by the action of iodine chloride on the rubber hydrocarbon

	IODINE	CHLORINE
	per cent	*per cent*
Found: Preparation No. 1	54.92	11.43
" " No. 2	57.05	7.14
Calculated for C_5H_8ICl	55.02	15.39

These results have not been published previously

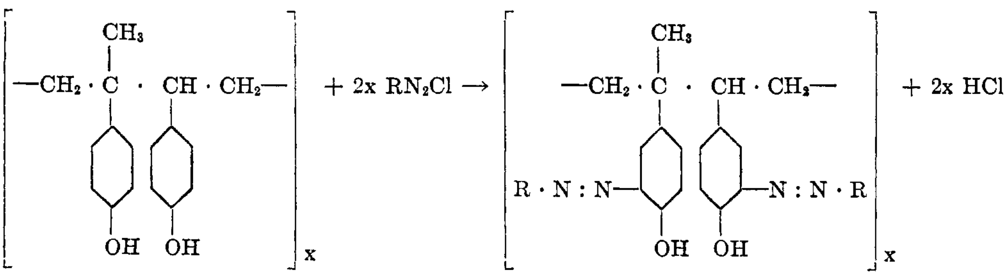


The product is therefore rubber di(hydroxyphenyl) or di(hydroxyphenyl)-hydrorubber and the methylated product, given below, is rubber di(methoxyphenyl) or di(methoxyphenyl)-hydrorubber.



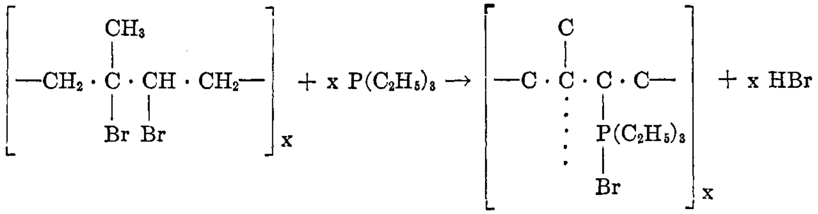
Weber's yields of the phenol product were all approximately 50 per cent. The author's yields were 65–77 per cent, even when aluminum chloride or zinc chloride was added, but became practically quantitative when anhydrous ferric chloride was used. The reaction may be like the Friedel-Crafts reaction. The yields of the methylated product are almost quantitative. The latter gave no depression of the freezing point in benzene. This is of special interest, because here we have a substance still showing colloidal properties even though it is the result of three successive reactions from rubber. The original rubber grouping therefore is probably a large colloidal molecule, a "eucolloid" as termed by Staudinger (71).

More recently Geiger (134), a former student of Staudinger, has published two excellent papers extending and elaborating this work considerably. He gives detailed results with phenol, *o*-cresol, resorcinol and pyrogallol, using ferric chloride as the catalyst. He also found that in the presence of ferric chloride the phenol ethers reacted like phenol itself. Anisole, for example, gave in one step the same methylated product described above. Fisher, Gray and McColm reported its melting point as 151–6°C. (corr.) and Geiger, 150–60°C. Such a verification of a physical property of a substance of this type prepared in two different ways is of considerable interest. Phenetole and methyl α-naphthyl ether reacted similarly. Furthermore, by means of benzoyl chloride and alkali he formed the benzoates of the phenol product, $[C_5H_8(C_6H_4 \cdot O \cdot CO \cdot C_6H_5)_2]_x$ and of the *o*-cresol and the resorcinol products. Such of these compounds as were tested showed no depression of the freezing point in benzene solution. The phenol product and its benzoate were examined with x-rays, but only an "amorphous" ring was obtained in each case. In the second paper Geiger reported the coupling of some of these phenol products with diazotized aromatic amines (see also (135)). The reaction in each case went smoothly and rapidly at temperatures around 0°C., indicating that the coupling was similar to the usual azo dye formation. The products are colored brown to greenish-black, and are generally soluble in toluene and insoluble in petroleum ether, this difference in solubilities offering a means of purification by precipitation. They have very high molecular weights, probably over 4000, and x-ray examination gives "amorphous" rings. The phenol and resorcinol products were used chiefly, and they were coupled with such amines as aniline, *p*-nitroaniline, and benzidine; also with sulfanilic acid and naphthionic acid. The coupled products made from the two acids are readily soluble in aqueous alkalies, and from their red-brown alkaline solutions they can be precipitated with acids or salted out as the alkali salt. In dilute solutions they behave as indicators for acids and bases. The other products are difficulty soluble or are insoluble in alkali. All the products were not completely analyzed, but those that were have one diazo-grouping for each phenyl group. Since hydrorubber, the parent hydrocarbon, is so very unreactive, it is assumed that the coupling takes place on the phenyl groups and probably adjacent to the hydroxyl groups, as follows:



The reaction mixture of rubber bromide and phenol is always of a characteristic purplish color. The bromides of gutta-percha and of various isomerized rubbers give somewhat different colors, and Kirchhof (136) has used these color reactions as laboratory tests to distinguish these substances.

One other type of derivative has been prepared from rubber dibromide,—that is, phosphonium salts. Staudinger, Geiger and Reuss (137) have found that triphenylphosphine and triethylphosphine react with the dibromide as they do with ordinary alkyl halides. The reaction is not complete, however, since some of the bromine goes off as hydrogen bromide and analyses show that there is even less than one phosphorus group for each C_5H_8 group. The product behaves like a saturated compound, and therefore the loss of hydrogen bromide must result in internal ring formation. The position of the ring closure is not known, and for this reason the product is best represented in skeleton formation, a dotted line being used to indicate the probable position of the lost atom of bromine, and nothing being given to show where the hydrogen atom is lost:

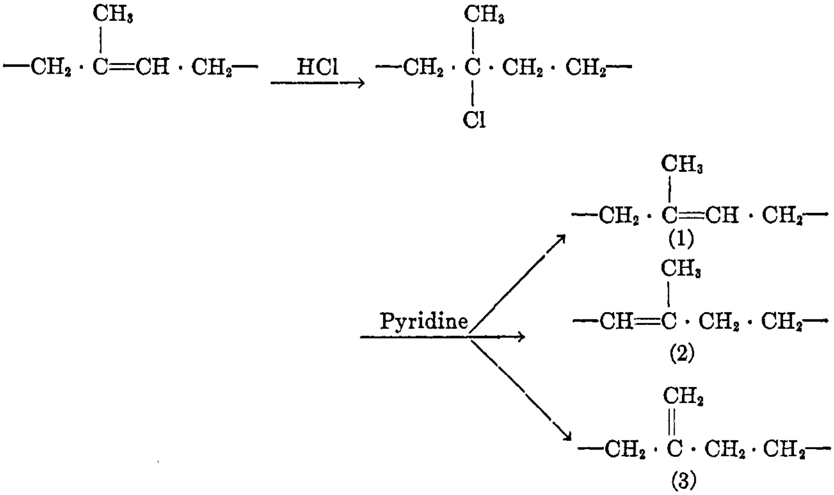


$$\left[-CH_2\cdot\overset{CH_3}{\underset{Br}{C}}\cdot\underset{Br}{CH}\cdot CH_2-\right]_x + x\,P(C_2H_5)_3 \rightarrow \left[-C\cdot\overset{C}{\underset{\vdots}{C}}\cdot\underset{\underset{Br}{P(C_2H_5)_3}}{C}\cdot C-\right]_x + x\,HBr$$

The products are insoluble in benzene, chloroform, etc., but the triphenylphosphonium compound is soluble in alcohol and ether and slightly soluble in water, and the triethylphosphonium compound is fairly soluble in water. The water solution of the latter is neutral in reaction, indicating that no hydrolysis takes place. The substance is strongly dissociated in water but is not dialyzable. In higher concentrations, the solutions are very viscous! The solid form is elastic, like rubber. With bromine they give difficulty soluble perbromides. In methylene chloride solution, the triphenyl compound gave no rise in the boiling point, and therefore it must have a high molecular weight. These are very interesting substances, and their properties show very clearly the complex nature of the rubber molecule. Staudinger believes these reactions substantiate the theory that the rubber hydrocarbon reacts with normal valences.

3. The hydrohalides and their derivatives

Hydrogen chloride, hydrogen bromide and hydrogen iodide add to rubber to form definite addition products: $(C_5H_9Cl)_x$ (138), $(C_5H_9Br)_x$ (139) and $(C_5H_9I)_x$ (139). The reactions are usually carried out in chloroform solution, and the products precipitated with absolute alcohol. The yields of the first two are practically quantitative. In order to obtain a complete reaction, however, it is necessary to let the solution saturated with the dry hydrogen halide stand for at least twelve hours. The rubber hydrocarbon in solution also takes up hydrogen chloride slowly from concentrated hydrochloric acid. After forty-eight hours on the steam bath, a sample was found to contain 2.6 per cent of chlorine (140). The rubber hydrochloride apparently cannot be purified from unreacted rubber. The hydrohalides are white when first precipitated, but the hydrobromide and hydroiodide turn brown or black on standing because of decomposition. The hydrochloride is at first somewhat elastic, but soon becomes hard and somewhat crumbly. Its solutions, like those of chlorinated rubber, upon evaporation leave tough, transparent films, not as harsh as those of chlorinated rubber. Harries and his students have done considerable work on the hydrochloride, in the study not only of its preparation, but also of its properties. On continued purification by dissolving and reprecipitating it, hydrogen chloride splits off, and on heating it also loses hydrogen chloride. In five days at 100°C. in a vacuum it loses one-third of its chlorine as hydrogen chloride, and in twenty days, two-thirds. Heating with pyridine under pressure for 20 hours at 130°C. removes all of the chlorine as hydrogen chloride and forms "alpha-isorubber." This isorubber is softer and less elastic than natural rubber. Analysis shows $(C_5H_8)_x$, and analysis of the hydrochloride, hydroiodide and ozonide formed from it show, as in the original rubber, that there is one double bond for each C_5H_8 group. The hydrochloride, when heated with pyridine under pressure, gave "beta-isorubber," which was more difficult to purify because it did not precipitate readily with alcohol. According to the analysis, it was probably somewhat oxidized, and the chlorine of its hydrochloride was low. Harries did a great deal of fine work on the ozonide of the alpha-isorubber and its hydrolytic products in an effort to elucidate further the structure of the original rubber hydrocarbon. In order to understand his work, the following theoretical possibilities are sketched as structural formulas using a five-carbon section. The original position of the chlorine has not been proved but it is placed on the tertiary carbon atom according to analogous cases (Markonikof's rule).



$$-CH_2\cdot\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH\cdot CH_2- \xrightarrow{HCl} -CH_2\cdot\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\cdot CH_2\cdot CH_2-$$

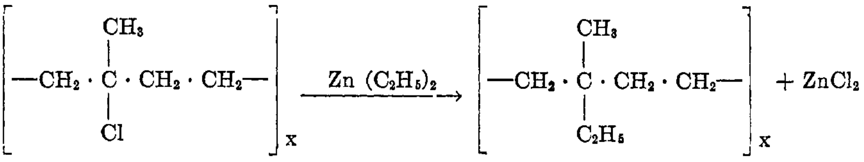
$$\xrightarrow{\text{Pyridine}} \begin{cases} -CH_2\cdot\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH\cdot CH_2- & (1)\\ -CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\cdot CH_2\cdot CH_2- & (2)\\ -CH_2\cdot\overset{\overset{\displaystyle CH_2}{\|}}{C}\cdot CH_2\cdot CH_2- & (3)\end{cases}$$

Comparison with the scheme of decomposition of natural rubber on p. 78 shows that if all the reaction went like (1), ozonization and hydrolysis would yield only levulinic aldehyde and levulinic acid as with natural rubber; if according to (2) or combinations of (1) and (2), polyketones containing the CH_3CO group would result, such as diacetyl propane, $CH_3COCH_2CH_2CH_2COCH_3$, which was actually isolated in fairly large quantities; if according to (3), then long straight chain polyketones would be formed in addition to formaldehyde or formic acid. Undecatrione and pentadecatetrone were isolated as already mentioned (p. 77), and a great deal of formic acid was obtained. Large amounts of levulinic aldehyde and levulinic acid were also obtained, and in addition to these and the other substances given above, there were isolated succinic acid and a keto dibasic acid,—namely, hydrochelidonic acid, $HOOC\cdot CH_2CH_2COCH_2CH_2\cdot COOH$. The formation of all these substances is therefore readily explained and involves nothing "irregular."

The rubber hydrochloride and the rubber hydrobromide have provisional structural formulas which make them an inviting field for the synthetic organic chemist. On paper many reactions for the preparation of a great variety of derivatives can be very easily outlined. But their low solubility, the very limited number of solvents available and the type of these solvents, together with their instability and their colloidal properties, all tend to make laboratory barriers which offer very considerable difficulties.

Harries, evidently in an effort to reduce the rubber hydrochloride and thus prepare hydrorubber, tried the action of zinc dust on it in ethylene chloride solution saturated with hydrogen chloride. He succeeded in removing the chlorine, but the product was somewhat unsaturated. The analytical figures for carbon and hydrogen were not very concordant but averaged pretty well for $C_{10}H_{18}$. On the C_{10}-basis this appeared to be a "dihydride," and he named it "alpha-hydrorubber" (141). But Staudinger and Widmer (85), in repeating this work, found that the chlorine-free product analyzed very well for $(C_5H_8)_x$. It is a white, hard, brittle, thermoplastic substance which is a little less than half as unsaturated as the original rubber hydrocarbon. The same or a similar substance can also be obtained from rubber hydrobromide. The disappearance of the other double bonds is most satisfactorily explained at present by polycyclic formation. These substances are representative of a series of products formed by polycyclization which will be discussed in a later section (p. 115).

Alkyl derivatives of hydrorubber have also been prepared from the hydrohalides, by Staudinger and Widmer (142). The method comprises the double decomposition between the rubber hydrohalide and zinc methyl or zinc ethyl at low temperature. The reaction may be formulated (without balancing) as follows:



$$\left[-CH_2\cdot\underset{Cl}{\overset{CH_3}{C}}\cdot CH_2\cdot CH_2-\right]_x \xrightarrow{Zn\ (C_2H_5)_2} \left[-CH_2\cdot\underset{C_2H_5}{\overset{CH_3}{C}}\cdot CH_2\cdot CH_2-\right]_x + ZnCl_2$$

Benzene or toluene solutions were used. The hydrobromide reacted more vigorously than the hydrochloride and even at low temperatures (−20°C.) not only was some hydrogen bromide given off but methane or ethane was also evolved. At room temperature and higher, considerable amounts of methane or ethane were obtained. The ethyl compound was best prepared from rubber hydrochloride at 0°C. during 3–4 days. On account of the loss of a small amount of ethane the analytical figures are slightly low. The product however does not have unsaturated properties because it is stable toward bromine, cold and warm nitric acid, and potassium permanganate. The authors believe that the small amount of unsaturation as indicated by the analyses consists of internal ring formation. The products may be considered as chemical derivatives of hydrorubber. Like hydrorubber, ethyl hydrorubber forms colloidal solutions in benzene and chloroform, and in ether, and is insoluble in alcohol and acetone. It gives no depression of the freezing point in benzene. Dry distillation of small samples gave olefins which could not be properly purified. The methyl hydrorubber was prepared similarly, but the methane formed was somewhat larger in amount than the ethane formed in the preparation of the ethyl compound. It was therefore not as pure, although the analyses were very comparable. Otherwise its properties are practically the same. Zinc ethyl does not react with rubber itself.

4. Sulfur, sulfur chloride, selenium, and selenium oxychloride

The chemical addition of sulfur is connected with the one great process of the rubber industry—vulcanization. Ordinary soft vulcanized rubbers, such as automobile inner tubes and rubber bands, contain from 1.5 to 5 per cent of chemically combined sulfur, and ordinary hard rubber contains 25–30 per cent of combined sulfur. Practically no products are manufactured containing any intermediate amounts. Completely sulfurized rubber—that is, rubber that has had all the double bonds saturated with sulfur as in $(C_5H_8S)_x$—can be prepared by heating rubber with an excess of the theoretical amount of sulfur for many hours to 140–60°C.(143). It contains 32.00 per cent of sulfur, which is in accord with the theory. It can be obtained pure as a brown, insoluble powder by heating a cumene solution of purified rubber and a large excess of sulfur for several hours at 170°C.(144). Sulfur does not add at all, or certainly not to any perceptible extent, at room temperature. Under the influence of certain so-called "ultra-accelerators," after standing for several months, rubber may contain 0.5–0.7 per cent of chemically combined sulfur and be vulcanized (145). Practically all vulcanizations are carried on at 110–60°C., chiefly at 130–45°C.; higher temperatures are sometimes used for hard rubber. Sulfur is soluble in crude rubber and in vulcanized rubber (146). The "free" or uncombined sulfur can be removed from vulcanized rubber by extraction with acetone. When the extracted vulcanized rubber is treated with bromine (147) or iodine chloride (148), the amount that adds in each case is equivalent to the amount of sulfur that would be taken up to form the saturated compound $(C_5H_8S)_x$. No one as yet has ever isolated any rubber sulfide from ordinary vulcanized rubber; nor does incorporating purified rubber sulfide in crude rubber and then heating the mixture give a product resembling vulcanized rubber in any way. Perhaps the right method of doing this has not yet been found. So far, a true explanation of what constitutes vulcanization is still lacking (149).

The temperature rise during ordinary vulcanization of soft rubber goods is small (150). Furthermore, on account of the comparative thinness of the average articles manufactured, the heat from the reaction is rapidly conducted away and scarcely need be considered. In the manufacture of hard rubber, the case is different. Sometimes in vulcanizing thick articles such as bowling balls, the temperature rise in the center is very great, and the heat does not disseminate quickly because rubber is a poor conductor. Violent explosions have occurred when the external heating, especially the initial rise or "stepping up," has not been regulated properly. The internal temperatures under such conditions may reach 250°C. or higher, and much H_2S is formed. If mixtures of rubber containing the seldom-used amounts of sulfur, 8–16 per cent, be heated in bulk, they too show a similar rise after the reaction sets in, and the products instead of being soft, resilient and elastic, are rather hard and thermoplastic, somewhat like a low-softening gutta-percha or a highly resinous gum such as pontianac. Kemp (151), who prepared these products, showed how they differed from ordinary vulcanized rubber, not only in these properties but also in their solubility in benzene and, according to a personal remark to the writer, in their being about half as unsaturated as the original rubber.

Sulfur monochloride in small proportions at ordinary temperatures also vulcanizes rubber. It is used in the so-called "acid" or "vapor cure" process for manufacturing rubber gloves, toy balloons, dental dam, etc. The method can be used only with thin sheets, because with thick sheets the outside becomes over-vulcanized and hard before the reagent can penetrate into the interior. When an excess of the theoretical amount for saturating each double bond is used, there is obtained, according to Weber (152), $(C_5H_8SCl)_x$, or as expressed by him, $C_{10}H_{16}S_2Cl_2$. According to Hinrichsen and Kindscher (144), only half of this amount of sulfur monochloride is added; in other words, the product is $(C_{10}H_{16})_2S_2Cl_2$ or $(C_{10}H_{16}SCl)_x$; and Bernstein (153) claims to have verified this. Weber gives a complete elemental analysis which agrees very well with the theoretical calculations for his formula. The theory for sulfur in this compound is 23.62 per cent. Hinrichsen and Kindscher isolated several products which ranged from 15.58 to 28.37 per cent of sulfur, and they then determined indirectly how much sulfur chloride had been used up, by analyzing the supernatant liquid after the precipitate had formed. Three out of eight experiments checked the formation of the product mentioned above,—namely, $(C_{10}H_{16})_2S_2Cl_2$ or $(C_{10}H_{16}SCl)_x$. Bernstein's products contained 21.35, 28.00 and 34.68 per cent of sulfur. He also analyzed for chlorine, the respective results being 28.00, 26.30 and 23.28 per cent, while this theory calls for 26.19 per cent. He finally used only a slight excess of the reagent in dilute solutions, isolated the products, and showed that the per cent of chlorine and sulfur was close to the values required by the formula arrived at indirectly by Hinrichsen and Kindscher. Later, Kirchhof (154) passed the vapors of sulfur chloride into solutions of rubber and analyzed the effluent gases. From these results, the compounds formed were found to be midway between the two types. The sulfur content of the isolated products, however, varied considerably, the lowest figure being above that for the "half" addition and the highest rather close to that of Weber's compound. He stated that Weber's compound was probably formed first and then partially decomposed.

TABLE 6

Analysis of the product formed by the action of sulfur chloride on rubber

	CALCULATED FOR $C_{10}H_{16}SCl_2$	FOUND	CALCULATED FOR $C_{10}H_{16}S_2Cl_2$	WEBER'S RESULTS
	per cent	*per cent*	*per cent*	*per cent*
Carbon	50.42	47.96	44.28	43.61, 43.51
Hydrogen	6.72	5.76	5.90	6.21, 6.14
Sulfur	13.42	14.83	23.62	23.88, 23.81
Chlorine	29.50	29.53	26.19	25.97, 26.11

After the lapse of many years, Meyer and Mark (155) took up the study of this reaction and compared it with the now familiar action of sulfur chloride on ethylene,—the "mustard gas" reaction. In this case an atom of sulfur separates as indicated in the following equation:

$$2\ CH_2 : CH_2 + S_2Cl_2 \rightarrow (CH_2Cl \cdot CH_2)_2S + S$$

With rubber, the product would then have the empirical formula $C_{10}H_{16}SCl_2$. The results obtained by Meyer and Mark are shown in table 6. If Weber had had this compound, he would not have obtained the compound $C_{10}H_{14}S_2$ (32.3 per cent S) by the treatment of $(C_{10}H_{16}SCl)_x$ with alcoholic sodium hydroxide, as mentioned below, because the sulfur content of $C_{10}H_{14}S$ is only 19.3 per cent. All the work so far done on this problem has, therefore, not yet settled it.

The sulfur chloride compound is a white, insoluble powder which slowly decomposes giving off hydrogen chloride. As in the case of sulfur vulcanization, no one has been able to isolate any of the sulfur chloride addition product from rubber vulcanized with sulfur chloride or from rubber gels prepared with the same reagent. Only small amounts of the reagent are taken up during the ordinary vulcanization, probably not over 1–2 per cent. Articles so vulcanized are sometimes treated with ammonia to remove any hydrochloric acid that is formed at the same time (in part from moisture and the reaction with the non-rubber constituents).

When the rubber sulfur chloride product, $(C_5H_8SCl)_x$, is heated with an alcoholic solution of sodium hydroxide, all of the chlorine is removed along with the equivalent amount of hydrogen, and Weber found that a brown powder remains with the formula $(C_5H_7S)_x$, confirmed by complete elemental analysis. Hinrichsen and Kindscher repeated this experiment with one of their products, apparently selecting only the one that approximated the "half" addition product, $(C_{10}H_{16}SCl)_x$. Their product contained 20.87 and 20.75 per cent of sulfur, and the calculated value for $(C_{10}H_{15}S)_x$ is 19.2 per cent. The products are insoluble, inert and generally similar to hard rubber dust.

Weber (156) also treated rubber in solution with pure sulfur monobromide and obtained a product which lost hydrogen bromide readily, even during the purification. Its sulfur content was higher and the bromine content lower than the values calculated for $(C_5H_8SBr)_x$. However, upon being heated with aniline, it gave what was apparently the same compound as that obtained from sulfur chloride,—namely, $(C_5H_7S)_x$—and this was also confirmed by elemental analysis. He concluded, therefore, that sulfur bromide adds like sulfur chloride. The use of sulfur bromide as a vulcanizer is umpromising because of the loss of hydrogen bromide. Gels can be formed with the reagent. Sulfur monoiodide acts very slowly and the product is low in iodine. Removal of the iodine as hydrogen iodide with aniline gave a substance with only about one-fifth the required amount of sulfur, indicating that the reaction was very incomplete.

Selenium also vulcanizes rubber, as shown by Boggs (157). It is generally necessary to use an accelerator, and the amount of selenium chemically combined is probably very small. Selenium melts at 217°C., and its solubility in rubber has been shown by Williams (158) to be less than 0.05 per cent at 80°C. Fused mixtures of sulfur and selenium have certain advantages, especially in extending the life of the rubber product (159).

According to Frick (160), selenium oxychloride, $SeOCl_2$, reacts with rubber forming insoluble, amorphous substances which contain approximately 25 per cent of selenium and also of chlorine. The ratios are close to those of selenium and chlorine in the reagent. They also contain about the same amount of oxygen, indicating that considerable oxidation has taken place, and yet the content of hydrogen is proportionately very high. The products were prepared from several different kinds of rubber and from sodium-isoprene-rubber, and no formulas have been assigned to them.

5. Oxygen, ozone and oxidizing agents

Oxygen when pure or as in the air attacks rubber, especially in the presence of light, and slowly changes it to resin-like substances. Purified rubber is attacked very readily, whereas a good quality of crude rubber withstands the action of oxygen for a long time because of the presence of the naturally-occurring "antioxidant" discussed in the section on latex (p. 59). The action of oxygen has been studied on rubber films and on rubber in solution, and in both cases a number of products have been isolated and analyzed, and formulas such as $C_{25}H_{40}O_2$, $C_{10}H_{16}O_3$, and $C_{10}H_{16}O$ assigned to them (161) (162) (163). However, since the analytical results reported are not so close to those required by the theory as is desirable and since in the investigations only single experiments seem to have been carried out in many cases, these formulas have not yet been completely substantiated. They indicate that oxygen adds progressively just as sulfur does. It has been demonstrated that peroxides are formed during the reaction and that therefore the reaction is probably one of autoxidation (164). In "tacky" rubber formed by exposure to air and light, Whitby (165) found levulinic aldehyde which was identified by the preparation of its pyridazine derivative. It is interesting to note that when air is passed into a benzene solution of rubber, the viscosity of the solution drops considerably. Similar changes have probably often been misinterpreted, especially when solutions have been heated in the presence of air, because the changes have been ascribed to depolymerization of the rubber complex, whereas they seem to be almost, if not entirely, due to oxidation. If air is kept out, the change in viscosity by heating is reversible (p. 70). Air oxidation to produce tacky rubber is accelerated in the presence of compounds of copper (166), manganese (167), iron (25), etc. Therefore these substances are rigidly excluded in the preparation of crude rubber and of rubber goods.

Excellent results have been obtained in this field by Pummerer and Burkhard (55), who found that the amount of oxygen gas absorbed by the pure rubber hydrocarbon in very dilute solutions at room temperature agrees very well with the formula $(C_5H_8O)_x$. The result was the same with or without platinum black, and the absorption was complete in 40 to 50 hours. The products were not isolated. The same authors also found that perbenzoic acid, $C_6H_5CO \cdot OOH$, reacted normally toward the rubber hydrocarbon, one mol being used for each C_5H_8 nucleus. The course of this reaction was followed by titration of the reagent and was verified by the isolation of the rubber oxide formed. It is a white, tough substance, much less elastic than rubber, and insoluble in all the ordinary solvents. The analysis is in excellent agreement with the formula $(C_5H_8O)_x$. Since previous work had indicated that the lowest compound with oxygen had the formula $(C_{10}H_{16}O)_x$, this newer work helps much to substantiate the C_5H_8 group as the fundamental group in rubber.

The action of ozone on rubber has already been discussed (p. 76). Mention should also be made of the fact that, according to Harries (168), when a solution of purified rubber is treated with oxygen containing a high percentage of ozone which has not been passed through aqueous sodium hydroxide and concentrated sulfuric acid, there is formed an "oxozonide," $(C_5H_8O_4)_x$. This oxozonide resembles the normal ozonide in its properties although, strangely enough, in spite of its greater proportion of oxygen, it is not so explosive. On hydrolysis it gives the same decomposition products as the normal ozonide but in different quantities.

The rubber hydrocarbon is fairly stable toward potassium permanganate, and the use of this reagent in Baeyer's simple test for the double bond is not practicable. Harries (169), in his early work on rubber, tried to break it down with this reagent (2.5 per cent), but his results showed that a considerable amount of "depolymerization" took place and otherwise only a small portion was attacked, there being obtained "a small amount of fatty acids." Rubber that had been heavily milled or masticated was found to be more easily attacked than the unmasticated rubber, and yet no definite products were isolated. Boswell (163) has shown that a 7.5 per cent solution of permanganate acting on a 4 per cent carbon tetrachloride solution of rubber for five days, gives upon precipitation with methyl alcohol a white plastic mass which has the approximate empirical formula $C_{25}H_{40}O$. More recently, the action of permanganate has been studied in considerable detail by Robertson and Mair (170). These investigators used neutral and alkaline permanganate solutions of several different concentrations and isolated various acidic and neutral products. The acids consisted of formic, acetic, oxalic, levulinic and some complex colloidal resin acids. The neutral products contained increasing amounts of oxygen, more or less in proportion to the strength of the reagent used, and gave analytical results corresponding to such formulas as $C_{35}H_{56}O_4$, $C_{26}H_{42}O_6$, $C_{24}H_{38}O_6$, $C_{36}H_{56}O_5$, $C_{30}H_{48}O_{10}$, etc., which indicate approximate ratios of oxygen to C_5H_8 of from 1:9 to 5:3. They are insoluble in ethyl alcohol and acetone, and vary from pale yellow, slightly elastic substances to white, brittle substances. Nothing really very definite can be gleaned from this work beyond the fact that oxidation products containing varying amounts of oxygen can be obtained and that they are of high molecular weight, but it is recorded here in order to emphasize the difficulties involved in the study of such a complex material as rubber.

These same authors also oxidized rubber with hydrogen peroxide and isolated as a primary oxidation product a mixture of a white pasty material of neutral reaction, with alcoholic properties and of the average composition $C_{59}H_{102}O_{16}$. This, along with the work just referred to, indicates that the size of the simplest rubber particle is not less than $C_{40}H_{64}$ or $(C_5H_8)_8$. Boswell, Hambleton, Parker and McLaughlin (163) give $C_{30}H_{48}O$ as the primary product of oxidation with hydrogen peroxide.

6. Hydrogen

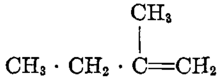
Although the chemical reactions of the rubber hydrocarbon all indicated the presence of double bonds in its structure, until recently one of the chief reactions of such an unsaturated compound, hydrogenation, had not been realized. Harries (171) and Hinrichsen (172) had tried to hydrogenate it in the presence of platinum black, but without success. Doubt was, in fact, cast upon there being an unsaturated linking, and one author (163) a short time ago, after having failed in a similar attempt, placed himself on record against this hypothesis. He stated: "It is conceivable that the rubber molecule itself contains no double bonds whatever, and that these are only produced by the breaking up of the complex rubber molecule by the action of bromine or hydrochloric acid." The printing of his article was scarcely begun before a report of successful catalytic hydrogenation was being read at Leipzig by Pummerer and Burkhard (55) and an account of a similar and independent successful attempt was being published by Staudinger and Fritschi (103).

Pummerer and Burkhard found it necessary to use a solution with a concentration of less than 1 per cent and a rubber that was highly purified. In fact, in a later paper Pummerer and Koch (56) say that "a good criterion of the purity of the rubber is its behavior toward cold hydrogenation, since this reaction is very sensitive to impurities." A record of fifteen experiments is given in their first article demonstrating that at the ordinary temperature in the presence of a catalyst the rubber hydrocarbon adds two atoms of hydrogen for each C_5H_8 nucleus. The purified rubber was dissolved in either hexane or hexahydrotoluene, and a concentration of 0.2 to 0.6 per cent was found to be the best to obtain a complete reaction. The catalyst was platinum black activated by oxygen according to the method of Willstätter and Waldschmidt-Leitz (173). The total time necessary for the complete absorption of the gas varied from 3 to 170 hours, the shorter time usually at temperatures of 70–80°C. By very careful work the hydrorubber was isolated and analyzed, and the results were found to check completely the theory for $(C_5H_{10})_x$. The hydrorubber, as isolated in the earlier experiments, was elastic, but later preparations were not. This property probably depends on the treatment given the original rubber. The hydrorubber of Pummerer and Burkhard is almost colorless and is soluble in ether, giving a colloidal solution. The earlier preparations were very susceptible to air oxidation, especially in solution, but this property was later shown to be due to the presence of traces of the platinum black. Pummerer and Koch repeated the earlier work, using purified rubber that gave a clear solution in ether and excluding air throughout the entire process. The platinum black was not activated by oxygen, and on this account it was necessary to use a much larger amount, approximately ten times the weight of the sample. A pressure of 0.5 atmosphere of hydrogen was used and the amount absorbed by the mixtures was much more than the theoretical, possibly on account of the larger amount of colloidal platinum. These preparations of hydrorubber were stable toward air oxidation, and also stable toward bromine and potassium permanganate. When dissolved in camphor the hydrorubber gave no depression of the melting-point, although when it was previously heated for twelve hours at 200°C. and then for twenty minutes at 300°C. under a pressure of 12 mm. of carbon dioxide, during which time no trace of decomposition was observed, it showed a molecular weight of 1700.

On distillation of the hydrorubber under 1 mm. pressure of hydrogen, no change occurred under 350°C., and the chief product (60 per cent of the original) appeared to be a saturated compound, $C_{50}H_{100}$ or $C_{50}H_{102}$; molecular weight (in camphor), calculated, 700 or 702; found, 714. Its ether solution showed a distinct Tyndall effect. The difference between the molecular weight of the distilled product, 714, and that of the portion remaining in the distilling flask, 1500, together with that of the heated sample mentioned above, 1700, is discussed by the authors, and they consider that even saturated hydrocarbons may have residual valences and can be "aggregated" into higher "structures" ("Gebilden"), as is indicated by Gomberg's (174) addition products of hexaphenylethane and paraffins.

Staudinger and Fritschi's (103) method of hydrogenating rubber consists in the use of a catalyst but no solvent, and of very high temperatures and pressures. They employed ordinary platinum black which was incorporated into purified rubber by mixing it in a benzene solution, then precipitating it with alcohol and drying *in vacuo*. This platinized rubber without any solvent was placed in a glass container in a rotating autoclave filled with hydrogen at 93 atmospheres and heated for 10 hours at 270°C., or at 102 atmospheres and 280°C. Lower temperatures gave only partial hydrogenation. At ordinary pressure, but with the same high temperature, only partial hydrogenation was effected after 7 days with hydrogen passing through all the time. Nickel works much like platinum, but not so rapidly and completely. Their hydrorubber is a colorless, transparent, tough mass, without the elastic properties of rubber. The loss in color is said to be very characteristic of the reaction. The analyses check very closely the empirical formula, $(C_5H_{10})_x$, and the authors state that according to the properties of the hydrorubber it can be considered as a saturated hydrocarbon with so great a molecular weight that, so far as can be shown by analysis, no distinction can be made between $C_{5x}H_{10x}$ and $C_{5x}H_{10x+2}$. The product is soluble in benzene, chloroform and ether, and insoluble in alcohol and acetone. Its solutions are colloidal, and in benzene it shows no depression of the freezing-point. Its solutions do not decolorize bromine solution, but on standing in the sunlight a substitution product is formed with the evolution of hydrogen bromide. By complete bromination, followed by removal of the bromine as hydrogen bromide, a regenerated rubber is obtained. The hydrorubber is unattacked by sulfur monochloride in solution, being recovered unchanged, whereas rubber itself is vulcanized by this reagent.

Harries (175) criticized the work of Staudinger and Fritschi, saying that their hydrorubber might be hydrogenated pyrogenetic decomposition products of rubber. But Staudinger (176), in reply, pointed out (1) that such products would not be colloidal because they are of finite molecular weights; (2) that the hydrorubber has the properties of a paraffin hydrocarbon, and is, in fact, the first known colloidal paraffin; and (3) that the lowest-boiling heat-decomposition product of their hydrorubber was proved to be methylethylethylene,



$$CH_3\cdot CH_2\cdot \overset{\overset{CH_3}{|}}{C}{=}CH_2$$

Therefore, the hydrogenation of the rubber must have taken place before any decomposition of the rubber had set in. He also repeated Pummerer and Burkhard's work, but used a temperature of 100°C. and 60 atmospheres pressure. The product was apparently the same as that obtained without the use of a solvent, and was much tougher than the high temperature product.

Dry distillation of the high-temperature hydrorubber (103) at 350–400°C., under 1 mm. pressure, gave a series of olefins and only a small residue (0.6 per cent). As already mentioned, the lowest member was found to be methylethylethylene, C_5H_{10}. The amount was about 5 per cent. From the remainder of the distillate there was isolated $C_{10}H_{20}$, $C_{15}H_{30}$, a mixture of $C_{40}H_{80}$ and $C_{45}H_{90}$, and $C_{50}H_{100}$ which boiled at 268–75°C. at 0.014 mm. and was equivalent to 24 per cent of the crude distillate. The isolation of these olefins shows that there is no doubt that the hydrogen is combined with the double bonds of the rubber-hydrocarbon just as it can be combined with any ordinary olefins.

Harries (177), after his work on shellac in which he was able to change the alcohol-insoluble, "aggregated," unreactive form into the alcohol-soluble, "disaggregated," reactive form, believed that rubber had not been hydrogenated because it was in the aggregated, unreactive form. He, therefore, tried to hydrogenate rubber which had been thoroughly plasticized or masticated on the mill, and was successful. He used platinum black as his catalyst, and applied for a patent in April, 1921 (178), seventeen months before the first publications discussed above. He, evidently recalling his bitter experience in his fight for priority in the synthesis of rubber, remarks "but I expressly state that I do not wish to use this fact as the basis for any claim of scientific priority over Pummerer." He published no analytical results on his hydrogenated rubber.

It should be added that Pummerer and Koch (56), in the course of their study of hydrogenation, also found that when no excess of pressure was used and the time was therefore much longer than usual, they sometimes obtained products which were stable toward bromine, that is, chemically saturated, and yet were low (about 1.5 per cent) in hydrogen according to the analyses. They therefore concluded that since the substance shows the presence of no double bonds when treated with bromine, the double bonds must have entered into reaction with one another, presumably by internal ring formation.

As already mentioned, high temperatures cause more or less internal ring formation (polycyclization) and Staudinger (71) and his co-workers found that at the high temperatures used by them for the hydrogenation of rubber, considerable polycyclo-rubber was formed along with the hydrorubber unless a rapid reaction with an active catalyst was obtained. The polycyclo-rubber absorbs much less hydrogen under similar conditions. The hydro-polycyclo-rubber does not add bromine and is not attacked by hot nitric acid and cold potassium permanganate, whereas the polycyclo-rubber itself reacts with all these reagents.

Staudinger (179) has made the interesting observation that the hydrogenated hydrocarbons of rubber, gutta-percha and balata are, according to the analyses and refractive indices, identical.

	n_D^{15}
Hydrorubber	1.4768
Hydrogutta-percha	1.4740
Hydrobalata	1.4762

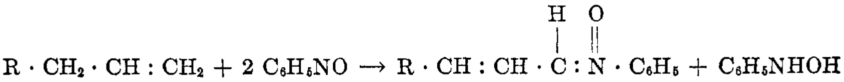
7. *The "nitrosites"*

Terpenes add nitrogen trioxide, N_2O_3, forming nitrosites. For example, α-terpinene forms the nitrosite, $C_{10}H_{16}N_2O_3$. It was known for many years that gases containing certain oxides of nitrogen harden rubber tubing and rubber stoppers, and these facts led Harries to study the action of nitrogen trioxide on purified rubber. The compounds formed (180) are yellowish powders which are usually soluble in acetone, ethyl acetate and aqueous alkalies, and insoluble in benzene and ether. They slowly decompose with loss of nitrogen or its oxides. At 80°C. this decomposition is more noticeable, and at higher temperatures it is quite rapid. On this account it is very difficult to analyze the compounds. Furthermore, the purity of the gaseous reagent, the oxidation due to prolonged action, and the slow decomposition even during purification, together with the difficulties of analysis, have all tended to cause considerable difficulty and some controversy in the interpretation of the results. The work on these substances is well summed up in Harries's book referred to above, and in Rosenbaum's translation of Gottlob's "Technology of Rubber." The chief product appears to be Harries's "nitrosite C," for which he obtained excellent analytical results and a molecular weight determination by the Landsberger-Rüber method in acetone corresponding to $(C_{10}H_{15}N_3O_7)_2$. A true nitrosite of similar molecular weight would have the formula $(C_{10}H_{16}N_2O_3)_2$. "Nitrosite C" decomposes at 158–62°C. Oxidation with potassium permanganate gives a mixture of aliphatic acids consisting chiefly of succinic and oxalic acids. The formation of "nitrosite C" was adapted by Harries (181) to the quantitative determination of the rubber hydrocarbon in crude and in vulcanized rubbers. After the nitrosite is formed it is isolated and weighed as such, or its carbon may be determined by combustion (182).

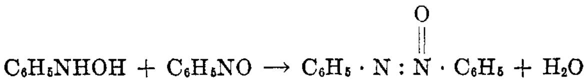
Weber (183) studied the action of nitrogen tetroxide, N_2O_4, on rubber in solution and claimed to have isolated a substance with the formula $(C_{10}H_{16}N_2O_4)_x$. Several other investigators have tried but have been unable to obtain this "nitrosate." Weber reported but a single analysis which agreed very well with the theory, but all others have found much more oxygen than is accounted for in his formula. Harries (184) states that the product closely resembles his "nitrosite C." Very recently Emden (185) has carefully reinvestigated the whole question. He used purified rubber and worked at temperatures around 0°C., where the N_2O_4 is practically not at all dissociated into NO_2. The N_2O_4 and rubber were separately dissolved in carbon tetrachloride and the solutions mixed, with the N_2O_4 always kept in excess. The time interval was short and never over 2 hours. The product in each case is pure white, sinters at 90–5°C. with incipient decomposition, reduces hot Fehling's solution, and does not dissolve in dilute ammonium hydroxide even after several days, but does dissolve gradually in aqueous sodium hydroxide. It dissolves only slowly in acetone, finally giving a clear red-brown solution from which it can be reprecipitated with water. This precipitate is slightly yellow and is now easily soluble in acetone. The original compound dissolves readily in hot acetone and no gases are evolved during the heating. The products from plantation rubber and guayule are apparently the same. The yields and the analyses agree with the composition $C_{10}H_{16}N_2O_6$. No molecular weights are recorded. The author thinks that the compound $C_{10}H_{16}N_2O_4$ is probably not capable of existence, that the addition of N_2O_4 is accompanied by oxidation and that the nitrosate $C_{10}H_{16}N_2O_6$ may be regarded as the primary product of the reaction. When rubber and an excess of N_2O_4 are allowed to stand for 24 hours at room temperature, the product becomes easily soluble in acetone, dilute ammonium hydroxide and sodium hydroxide, and when refluxed in acetone now evolves 0.1 mol of carbon dioxide. No analyses are given for these products. The author believes that the formation of this nitrosate can be satisfactorily used in a method of analysis.

8. *Nitrones*

In 1915 Allesandri (186) found that nitrosobenzene formed an addition product with the rubber hydrocarbon and gave it the following approximate composition, $C_{58}H_{61}O_9N_5$. Bruni and Geiger (187) studied this reaction in greater detail and prepared some very interesting derivatives. Angeli, with whom Allesandri had worked, discovered and explained the action of nitrosobenzene on olefinic compounds in 1910. He showed that two mols of nitrosobenzene react with the double bond, one adding and the other oxidizing, the latter being reduced to phenyl hydroxylamine which in turn reacts with a third mol of nitrosobenzene forming azoxybenzene:

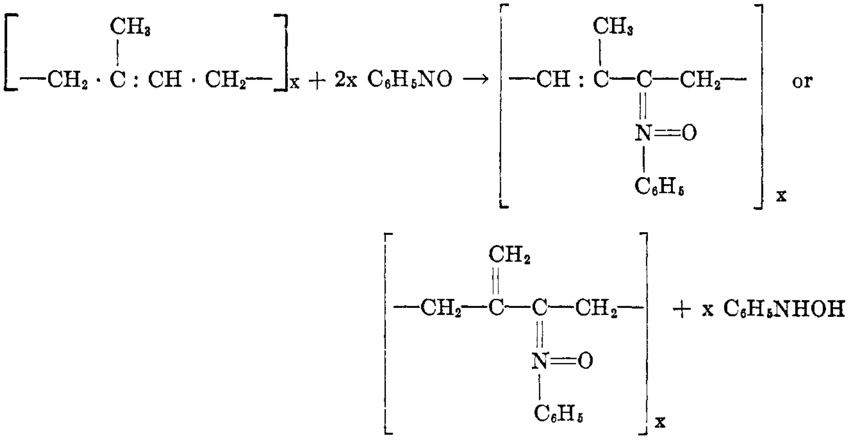


$$R\cdot CH_2\cdot CH:CH_2 + 2\,C_6H_5NO \rightarrow R\cdot CH:CH\cdot \overset{\overset{H}{|}}{C}:\overset{\overset{O}{\|}}{N}\cdot C_6H_5 + C_6H_5NHOH$$



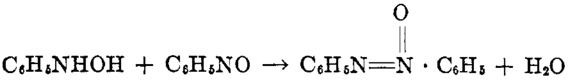
$$C_6H_5NHOH + C_6H_5NO \rightarrow C_6H_5\cdot N:\overset{\overset{O}{\|}}{N}\cdot C_6H_5 + H_2O$$

It should be noted that the position of the double bond has shifted. The reaction between nitrosobenzene and rubber takes place readily when they are mixed in benzene solution in the proportion of 3 mols to each C_5H_8 group, and warmed for a few minutes on the steam bath. The product is precipitated by means of petroleum ether. It is a powder, has the empirical formula $C_{11}H_{11}ON$, and decomposes at 135–40°C. From the mother liquor, azoxybenzene can be obtained. The product contains a double bond as shown by the addition of bromine, giving $C_{11}H_{11}ONBr_2$. These facts all prove that the reaction is similar to that outlined above. It can be formulated as follows:



$$\left[-CH_2\cdot \overset{\overset{CH_3}{|}}{C}:CH\cdot CH_2-\right]_x + 2x\,C_6H_5NO \rightarrow \left[-CH:\overset{\overset{CH_3}{|}}{C}-\underset{\begin{array}{c}\|\\ N=O\\ |\\ C_6H_5\end{array}}{C}-CH_2-\right]_x \text{ or }$$

$$\left[-CH_2-\overset{\overset{CH_2}{\|}}{C}-\underset{\begin{array}{c}\|\\ N=O\\ |\\ C_6H_5\end{array}}{C}-CH_2-\right]_x + x\,C_6H_5NHOH$$

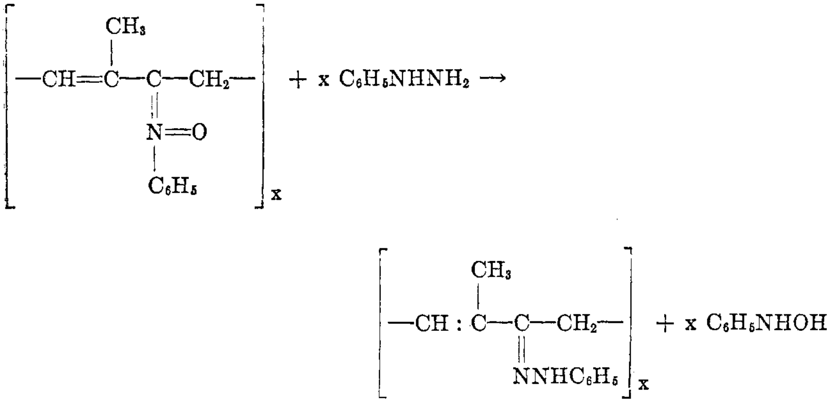


$$C_6H_5NHOH + C_6H_5NO \rightarrow C_6H_5N=\overset{\overset{O}{\|}}{N}\cdot C_6H_5 + H_2O$$

The position of the double bond in the new derivative has not yet been established, but it is probably in the first of the two places indicated. Since the position of the double bond is different from that in the natural rubber hydrocarbon, the new product is a derivative of an isorubber, and has been termed a nitrone of isorubber. The same reaction occurs when latex of *Hevea brasiliensis* is diluted with pyridine and mixed with nitrosobenzene in pyridine.

Solutions of the nitrone show colloidal properties, and when examined by x-rays, the photographs give no indication of even minute crystals. The reaction is rapid and complete, and the authors expect to be able to adapt it to a quantitative method of determining the rubber hydrocarbon.

Phenyl hydrazine reacts with the nitrone and a phenyl hydrazone of isorubber is thus formed:

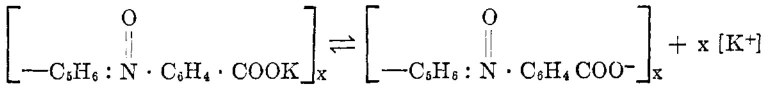


$$\left[-CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle C_6H_5}{\underset{|}{N{=}O}}}{\underset{\|}{C}}-CH_2-\right]_x + x\,C_6H_5NHNH_2 \rightarrow$$

$$\left[-CH:\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle NNHC_6H_5}{\|}}{C}-CH_2-\right]_x + x\,C_6H_5NHOH$$

It is expected that this hydrazone can be hydrolyzed and a ketone of isorubber prepared.

True nitroso compounds react with rubber like nitrosobenzene itself. *o*-, *m*-, and *p*-Nitrosotoluene and the methyl ether of *o*-nitrosophenol, *o*-nitrosoanisole, form the corresponding nitrones. Ethyl *o*-nitrosobenzoate reacts similarly. On hydrolysis it gives the free acid which is insoluble in water, but the potassium salt is readily soluble. The solution has the character of a true salt solution and the authors point out that here is a typical case of a colloidal electrolyte with a colloidal anion and molecularly dispersed cations.



$$\left[-C_5H_6:\overset{\overset{O}{\|}}{N}\cdot C_6H_4\cdot COOK\right]_x \rightleftharpoons \left[-C_5H_6:\overset{\overset{O}{\|}}{N}\cdot C_6H_4COO^-\right]_x + x\,[K^+]$$

The hydrocarbon of gutta-percha gives a nitrone similar to that of rubber.

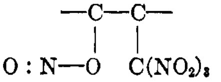
Further work is promised and should yield important results. It should be mentioned that the work of Bruni and Geiger is only a report and contains no analytical data.

Pummerer, Andriessen and Gündel (188) have substantiated the above work and have found it necessary to prepare the isorubber nitrone in the absence of oxygen. The molecular weight in benzene and in nitrobenzene is 1200–1400, corresponding to eight isoprene groups. The calculated value for $(C_{11}H_{11}ON)_8$ is 1384.

9. Tetranitromethane

Tetranitromethane unites with olefin hydrocarbons to give yellow unstable addition products (189), and Pummerer and Koch (56) found the reaction useful in proving the completeness of the hydrogenation of rubber. Pummerer and Pahl (20) have now shown that in hexahydrotoluene solution the reaction mixture at first turns yellow, and after 5 to 6 days (at 0°C.) it becomes almost colorless or only faintly yellow or pink, and a stable addition product separates. It does not lose tetranitromethane even when dried in a high vacuum for 6 hours at 60°C. The reagent is therefore probably bound by primary valences to the rubber. Upon analysis it is found that not all the double bonds react, since under the conditions used one mol of tetranitromethane corresponds to 4.5–6 C_5H_8 groups. There is no oxidation, because the ratio of nitrogen to oxygen remained as in the reagent, namely 1:2. With pale crêpe or smoked sheet, pure rubber or gel-rubber in suspension or completely broken down on the mill, the ratio of rubber to the reagent is 1:5, but with sol-rubber or with the completely broken down purified rubber obtained by the alkaline treatment of latex, it is 1:6. In higher concentrations of pure rubber the ratio is sometimes 1:4. The differences may be due chiefly to colloidal factors not fully understood.

The rubber tetranitromethanate suspended in inert solvents still decolorizes bromine. No data, however, are given to show whether an addition product is formed or whether the bromine simply replaces the tetranitromethane. From the present accepted structure of tetranitromethane the partial structure of the product may be indicated as follows:



$$\begin{array}{rl} & -\mathrm{C}-\mathrm{C}- \\ & \quad\;\, | \quad\; | \\ \mathrm{O:N{-}O} & \quad\;\mathrm{C(NO_2)_3} \end{array}$$

10. Nitric acid

Concentrated nitric acid reacts slowly with crude rubber in the cold, but on warming or adding fuming nitric acid the reaction may become very violent. In any case a solution is finally obtained which when poured into water gives a voluminous, yellow, flocculent precipitate. The yield of the dry yellow powder is surprisingly constant, about 22 per cent. This nitric acid product is soluble in ethyl acetate, acetone, benzaldehyde, nitrobenzene, aniline, acetic anhydride and aqueous alkalies with a deep maroon color. Although the reaction is one that was known for a long time, Ditmar (190) seems to have been the first one to study the product and analyze it. He found that it could be methylated and acetylated and that it could be reduced with sodium methoxide. Since the substance was somewhat explosive, its combustion analysis was difficult. The results varied as much as 2 per cent in the carbon, but the averages and the molecular weight determination approximated the formula $C_{10}H_{12}N_2O_6$. On the basis of this formula and of results obtained by titration with alkali and on the assumption that rubber was related to dipentene, he suggested that the compound was "5,6-dinitro-2,5-dihydrocumic acid." This formula, given twenty-eight years ago, has never been verified. From our present knowledge nothing definite structurally is known of this product. Harries (191) repeated Ditmar's work and stated that in general he substantiated Ditmar's results, although he gave no analytical figures. He found that on concentration of the aqueous filtrate considerable oxalic acid crystallized out and the residual liquor contained a very soluble, syrupy, nitrogenous acid whose silver salt had the approximate composition $C_6H_8NO_5Ag$. The writer might add that recalculation of Harries's results shows that the acid might be a nitrolevulinic acid, $C_5H_7O_5N$. This structure would be logical but it has not yet been substantiated. The same or a similar nitric acid product of rubber can be obtained by the prolonged action of dilute nitric acid on thin strips of rubber (192).

A different product has been obtained by Fisher (193) from nitric acid and rubber. He uses a carbon tetrachloride solution of rubber. The yield from a 5 per cent solution and an excess of concentrated nitric acid is approximately quantitative for a substance having the formula $(C_5H_7NO_2)_x$. Like Ditmar's nitric acid product it is unstable toward heat and is difficult to analyze. The highest nitrogen determination checked the theoretical value for the formula given, but a good duplicate determination has not yet been obtained. The substance is a bright yellow, slightly hygroscopic powder which is soluble in the same solvents as those mentioned above, but insoluble in sodium carbonate solution, whereas Ditmar's product is soluble in sodium carbonate solution. The new product decomposes slowly at room temperature and explodes when heated. It can be alkylated and acylated, forming compounds which are much more stable toward heat. Its unsaturation as determined by the iodine chloride method in a 1 per cent nitrobenzene solution was found to be 24.8 per cent of the unsaturation calculated for a nitro-rubber. It is very probable that the nitric acid has caused the change in unsaturation just as other acids do, and the product is therefore probably a nitro-polycyclo-rubber.

11. Chromyl chloride

The terpenes react readily with chromyl chloride forming addition products, $C_{10}H_{16} \cdot 2CrO_2Cl_2$, which are decomposed by water into aldehydes or ketones, chromic acid, etc. Spence and

Galletly (194), in 1911, found that chromyl chloride also reacts with rubber forming a similar addition product, to which they gave the same formula $C_{10}H_{16} \cdot 2CrO_2Cl_2$. Since very complex substances are obtained from it, and the molecular weight has not been determined, the formula should probably be written $(C_5H_8 \cdot CrO_2Cl_2)_x$. Robertson and Mair (170) have recently confirmed the formation and composition of this product. The substance is a brownish powder, insoluble in nearly all organic solvents. It is soluble in alcohol and acetone with decomposition, and in water by which it is immediately decomposed into resinous products. The decomposition products can be separated by alcohol and acetone into a soluble portion which has the properties of an aldehyde, and an insoluble portion which is of indefinite composition and contains chromium and chlorine. The aldehydic substance was converted into a phenylhydrazone by the first investigators and into a semicarbazone by the second. Oxidation transforms it into a resin acid and a complex insoluble product. Spence and Galletly found that what appeared by analysis to be the same chromyl chloride addition product was obtained from rubber of very different sources. They tried to use the reaction in a quantitative way but could not very well because of the rapid decomposition of the product by moisture.

12. Stannic chloride, ferric chloride, etc.

Stannic chloride reacts with the rubber hydrocarbon in benzene solution to form colored addition products, as recently shown by Bruson, Sebrell, and Calvert (195). The two products formed remain in solution and are isolated by evaporation of the liquid *in vacuo* at 70°C. The residue forms a reddish-brown, brittle vitreous solid, which redissolves with difficulty in benzene. In moist air it slowly decomposes, evolving fumes of stannic chloride. It slowly decomposes when heated, and at 170°C. swells and evolves copious fumes of stannic chloride. All the operations must be carried out in a dry inert atmosphere because the products are very hygroscopic and readily oxidize in the air.

Complete elemental analyses agree very well with the empirical composition $(C_5H_8)_{10} \cdot SnCl_4$. The substance dissolves in alcohol, but at the same time the stannic chloride is split off, remaining in solution, and the hydrocarbon is simultaneously precipitated as a white amorphous powder. This powder has the same composition as the original rubber hydrocarbon, $(C_5H_8)_x$, but is less unsaturated. Therefore, it no doubt belongs to the polycyclic rubbers already mentioned and discussed below. The authors call it a "polymeride." Maybe it is. Definitions in rubber chemistry are at present in a state of flux. The amorphous powder consists of two substances of the same composition, and of the approximate ratio 3:1, as shown by their solubility in benzene, the greater proportion being the soluble variety. It is from this difference that it is inferred that there are two addition products formed, as stated at the beginning. The authors show satisfactorily that the soluble and insoluble "polymerides" come from the corresponding varieties of rubber—the sol- and gel-rubbers—and offer these facts as additional evidence for the "two-phase" system of rubber.

The authors assume the validity of Staudinger's chain theory of the structure of rubber with free end valences (196), and conclude that the addition of the stannic chloride occurs at these end valences. "Since $SnCl_4$ possesses two reactive secondary valences, it is probable that two molecules of rubber hydrocarbon add to the $SnCl_4$ in such a manner that upon subsequent treatment with alcohol some of the double bonds of the hydrocarbon bridge across to form rings in the more reactive positions of the double molecule, leaving other unsaturated bonds intact." This is a graphic explanation but is supported by no experimental demonstration. The authors have, however, shown very nicely that 1 $SnCl_4$ reacts with 10 C_5H_8 groups, thus giving added evidence as to the size of the reactive portions of the rubber molecule.

Titanium tetrachloride behaves like stannic chloride, giving both the soluble and insoluble "polymers" of rubber. Ferric chloride and antimony pentachloride react to give insoluble jellies, which with alcohol form white insoluble "polymerides" of rubber even when sol-rubber is used. These three reagents must be used in chloroform or carbon tetrachloride solutions because they react with benzene.

13. Sulfuric acid

Everyone working in a laboratory is familiar with the fact that concentrated sulfuric acid reacts with rubber tubing and stoppers. It also reacts slowly with crude rubber, as has been known for many years. It finally dissolves the rubber, slowly oxidizing it at the same time. Kirchhof (197) has isolated from such a solution an aldehydic acid to which he has given the formula $C_{20}H_{30}O_3$.

Harries (198), in an effort to polymerize rubber into a higher modification and perhaps convert it into gutta-percha, tried the action of concentrated sulfuric acid on a benzene solution of rubber. It was rapidly transformed into an insoluble variety which separated as flocks. This amorphous precipitate was washed with aqueous sodium carbonate but could not be freed from ash. Harries believed, however, that the powdery product had the same composition as the rubber hydrocarbon, but that it was of a higher molecular weight.

Marquis and Heim (199) used this same reaction in chloroform solution as a quantitative method for estimating the rubber hydrocarbon. When the amount of acid was not too great and the time of shaking not too long, they obtained a white, amorphous powder which was soluble in chloroform and benzene, and contained no sulfur. The analysis of the product did not check up exactly for C_5H_8, and they thought that the acid had caused the addition of the elements of water. The discrepancy can probably be accounted for by oxidation. Increase in the amount of acid or in the time of the reaction gave an insoluble product.

During the last few years Kirchhof (197) has continued this work, has substantiated the foregoing, and has shown from the bromine content of the reaction product with bromine that the "sulfuric acid-rubbers" are probably not more than about one-quarter as unsaturated as rubber. Since bromine substitutes as well as adds in these cases, the unsaturation may even be a little less because the analytical value represents the maximum. Samples which are heated with sulfur contain not over 10 per cent of combined sulfur, which is equivalent to approximately 25 per cent of the unsaturation of rubber. Ozonization work gives no levulinic aldehyde, because no products are formed that give the pyrrole reaction. Concentrated sulfuric acid also produces similar products directly from latex. It is almost impossible to obtain these products pure, and they generally contain a small amount of ash and sulfur. Kirchhof stated that the decrease in unsaturation was probably due to the mutual saturation of some of the double bonds in the rubber molecule, forming tetramethylene rings, but later added that it might be due to some other form of cyclization. The softer varieties of wild rubbers give products which soften under moderate heat and can be molded. When melted they are converted into hard shellac-like substances which are soluble in benzene.

Fisher (200) found that concentrated sulfuric acid can be mixed directly into rubber on a rubber mill, and when batches containing 5 per cent of the acid are heated under various conditions they are converted into moldable thermoplastic masses. The products are somewhat oxidized, are only partially soluble in benzene and chloroform, and are much less unsaturated than rubber itself.

If one part of rubber dissolved in petroleum ether is treated with ten times its weight of concentrated sulfuric acid, and then with three times its weight of formalin, two parts of an insoluble powder is obtained. Kirchhof (201) has named this "rubber formolite." Heating does not melt but simply chars it. Bromine reacts with it, probably adding and substituting, the resulting product containing only 12.6 per cent of bromine.

14. Polycyclo-rubbers

In the last section an account was given of Harries's (198) attempt in 1910 to polymerize rubber into gutta-percha by treating it in solution with sulfuric acid. Although he was unable to free the resulting powdery, non-elastic product from inorganic salts, he considered that it had the same empirical formula as rubber but that it was in a higher state of polymerization.

Ostromislenski (202), by comparing the properties of polyvinyl bromide and erythrene-rubber dibromide, found that when the latter was heated with zinc dust the bromine was removed and a hydrocarbon formed, to which he assigned the formula

$C_{32}H_{48}$ and for which he coined the name "cauprene" (from kautschuk and polyprene). Cauprene adds much less bromine and hydrogen chloride than would be expected, forming compounds with the formulas $C_{32}H_{48}Br_4$ and $C_{32}H_{48} \cdot 2HCl$, respectively. These are saturated compounds and he therefore concluded: "the formation of cauprene from cauprene bromide, its composition, the composition and chemical character of the bromide and hydrochloride of cauprene, characterize it as a representative of a new, peculiar class of 32-membered polycyclic hydrocarbons."

Kirchhof (197), as also described in the previous section, studied further the action of sulfuric acid on rubber in solution and found that the products were about 25 per cent as unsaturated as the rubber hydrocarbon itself. He concluded that sulfuric acid does not polymerize the rubber hydrocarbon but changes it into a new hydrocarbon, physically and chemically distinct, and probably containing tetramethylene rings.

At about this same time Harries and Evers (141), by the action of zinc dust on a solution of rubber hydrochloride containing an excess of free hydrogen chloride, obtained a hydrocarbon which was thermoplastic, and from a series of varying analyses concluded that they had prepared a partially hydrogenated rubber of the formula $(C_{10}H_{18})_4$, to which they gave the name "alpha-hydrorubber." Later, Staudinger and Widmer (85) in repeating the work of Harries and Evers, and using the hydrobromide as well as the hydrochloride, found that the product is not a hydrorubber, because it has the same empirical formula as the rubber hydrocarbon, and, from the absorption of bromine, that it is less than half as unsaturated as the rubber hydrocarbon. Harries and Evers had prepared the hydrochloride and the ozone derivative, and a study of the analytical figures for these substances also shows approximately the same change in the unsaturation. The product is therefore a cyclic rubber.

In the course of their work on the destructive distillation of rubber, Staudinger and Fritschi (203) reported that the resinous residue, according to its bromine absorption, was approximately one-half as unsaturated as the rubber hydrocarbon. Staudinger continued the study of the action of heat on rubber and with

Geiger (95) gave a complete account of this work (see p. 72). The change in unsaturation begins to take place around 200°C. and is rapid above 270°C. An almost quantitative yield of the product with the lesser unsaturation is obtained when rubber in the presence of ether is heated in an autoclave for two days at 250° C. The product can be isolated by precipitation with alcohol. Fisher and A. E. Gray (52) obtained similar products from rubber which had been heated in sealed tubes.

Fisher (200), working independently, discovered that by mixing comparatively small amounts, approximately 10 parts to 100 of rubber, of an organic sulfonyl chloride or an organic sulfonic acid into rubber on the mill, and then heating the mix in sheet form at 125–35°C., the rubber is converted into tough, thermoplastic products resembling gutta-percha and hard balata. If heated simlarly in bulk there is a pronounced exothermic reaction and the products formed are hard and thermoplastic, like shellac. A study of the chief constituents of these various products, wherever it was possible to isolate them, shows that they consist of hydrocarbons of high molecular weight with the same composition as that of rubber, $(C_5H_8)_x$ (204). In order to differentiate these products which are isomeric with rubber, they have been given the general name "thermoprene," signifying a thermoplastic unsaturated hydrocarbon derived from polyprene, Weber's name for the rubber hydrocarbon. In order to distinguish between the varieties, certain letters are added to signify the type, such as GP for gutta-percha, HB for hard balata, and SL for shellac-like, —for example, thermoprene-GP.

The addition products formed with rubber in solution by the action of stannic chloride, ferric chloride, etc. (p. 112), when treated with alcohol also give products of these same general characteristics. The action of aluminum chloride (205) is probably also fundamentally the same. Staudinger (85) concluded that the action of zinc dust and hydrogen chloride on the rubber hydrochloride in solution really consists of the action of zinc chloride on the rubber (or isorubber) regenerated from the hydrochloride by the loss of hydrogen chloride, because he found that zinc chloride converts rubber in solution into a less unsaturated hydrocarbon. The product, however, is soft and sticky.

When rubber is mixed on the mill with ferric chloride, ferric bromide, or other amphoteric metal halides, and the mixture heated at about 175°C., it is converted into similar products which probably are of the same type of less unsaturated rubber hydrocarbons (206).

Other methods of isomerizing rubber have also been developed by Fisher (207). These consist of heating rubber with such agents as trichloroacetic acid, concentrated hydrochloric acid, diphenylamine hydrochloride, pinene hydrochloride, etc., chiefly in the presence of phenols, sometimes in solution and sometimes not. Pummerer, Nielsen and Gündel (72) have cyclicized sol-rubber by heating it for several hours at 90°C. and 60 atmospheres of hydrogen in the presence of platinum black. When nitrogen was used there was no cyclization. A very interesting method of isomerizing rubber has been discovered by Fromandi (208). It consists of the action of a high tension alternating current on a solution of rubber in decalin in an atmosphere of hydrogen.

Although these substances vary considerably in their physical characteristics, from rubbery types through the gutta-percha and hard balata types to hard shellac-like types, all, when pure, consist of a hydrocarbon or a mixture of hydrocarbons with the formula $(C_5H_8)_x$ and have less unsaturation than that of the rubber hydrocarbon itself. The unsaturation varies from about 57 per cent of that of rubber to about 20 per cent. Since there is no change in the composition, and since the molecular weights are not definitely known, the only explanation at present is that the change in unsaturation must be due to internal cyclic formation.

Staudinger spoke of these products as monocyclo-rubbers and polycyclo-rubbers, depending upon whether the unsaturation was half or less than half that of rubber. They have also been spoken of as polymers of rubber. Polymerization of unsaturated hydrocarbons involves the loss of double bonds, and since the new products are less unsaturated than the starting material it would seem at first as if this were a proper designation. Polymerization would also involve an increase in the molecular weight. Now the soluble products form solutions which show typical colloidal properties, and molecular weight determinations give values from 8500 to 1570, depending partly on the solvent employed (73). These figures compare favorably with those for rubber itself and indicate that there is no increase in the size of the molecular particle. The molecular weights of the insoluble products are not known. These may be very high.

If the products had the same molecular weight as that of the rubber from which they are prepared, then they would be called isomers and, more particularly, metamers. It is not certain whether they do have the same molecular weight, although this is indicated in some of the known results. Since there is no change in composition, the reaction is an isomerization and the products are therefore rubber isomers, if we use this term in its generic sense. It would seem best to use the term "rubber isomer" and not "isorubber," because this latter term should be kept for those derivatives which are more strictly isomeric, for example, position isomers, such as Harries's isorubbers obtained from the hydrochloride, and for the parent substance of Bruni's nitrones.

Other physical constants also substantiate the conclusions discussed above,—namely, that the products have an internal cyclic formation. Most of the examples given below are from the work of Staudinger and his collaborators.

The density is greater than that of rubber: for the rubber hydrocarbon $d_4^{17} = 0.920$; for polycyclo-rubber $d_4^{17} = 0.992$. The terpene hydrocarbons show similar increases in going from an open chain $C_{10}H_{16}$ compound to a monocyclic and to a bicyclic compound:

Myrcene = 0.803 Limonene = 0.845 Pinene = 0.862
(open chain) (monocyclic) (bicyclic)

The molecular refraction indicates the loss of double bonds and shows good agreement with the calculated values:

Rubber hydrocarbon $n_D^{16} = 1.5222$ Polycyclo-rubber $n_D^{17} = 1.5387$
$M_{D(100)}$ $(C_5H_8)_4 + 4$ ╒ Calculated* 32.28. Found for rubber, 32.19.
$(C_5H_8)_4 + 1$ ╒ " 31.36. " " polycyclo-rubber, 31.56.

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* These calculations are based on an unsaturation of 25 per cent of that of the rubber hydrocarbon, that is, the loss of 3 out of every 4 double bonds. The symbol ╒ stands for "double bond," and the molecular formula is given just for unit comparison.

The heat of combustion of polycyclo-rubber is less than that of rubber:

Polycyclo-rubber	10,500 calories per gram
Rubber hydrocarbon	10,970 calories per gram

Kirchhof's figure for sulfuric acid-cyclicized rubber is 10,075 calories, recalculated to ash-, sulfur- and oxygen-free sample, because his product could not be purified properly (209). Weber (210) gives 10,669 calories for the rubber hydrocarbon. The figure given in the comparison above was obtained by Messenger (211) and is the most accurate yet published. It follows therefore that the cyclization, as would be expected, is an exothermic reaction. This is in accord with the facts.

The products formed by cyclization are, when pure, white in powdered form, and amber-colored in the melted condition. The x-ray spectrograms show them to be amorphous substances. When soluble, they dissolve in benzene, chloroform, carbon tetrachloride, carbon bisulfide, gasoline, turpentine, tetralin, sometimes in ether, and do not dissolve in alcohol and acetone. These solutions vary in color from colorless to yellowish or yellow-green. They are much less viscous than solutions with corresponding amounts of ordinary masticated rubber. Concentrations of 25 per cent are easily obtained. The softening and melting points depend on the method of preparation, varying from room temperature to 280°C. They are much more stable toward heat than is rubber, as already mentioned. Extensive decomposition does not begin until about 350°C. The distillate contains neither isoprene nor dipentene but consists of other terpenes and polyterpenes. If any isoprene is formed it is completely polymerized by the heat.

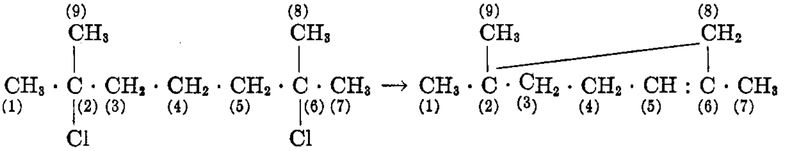
The amount of unsaturation is determined by titration with bromine or iodine chloride solutions. Bromine substitutes rather vigorously sometimes. The results obtained have been checked in a few cases by other means,—for example, by analyzing the addition products formed with hydrogen and with sulfur. Sulfur under vulcanizing conditions adds chemically, converting the polycyclo-rubbers (thermoprenes) eventually into hard, insoluble non-thermoplastics. This change resembles the formation of hard rubber. If the thermoprenes are saturated with sulfur in solution they remain soluble and thermoplastic. The highest amounts of sulfur found by heating direct mixtures and solutions are 21.11–21.78 per cent, corresponding to 57.5–59.0 per cent unsaturation (204). Sulfur chloride in a solution slowly forms a gel, and the isolated products show irregular amounts of sulfur and chlorine (204). Hydrogen chloride and hydrogen bromide add in various amounts, apparently because they cause a further change in the unsaturation during the reaction. Sulfur chloride probably does the same thing.

The polycyclo-rubbers slowly absorb oxygen from the air. Ozone forms an insoluble product which is quite different from rubber ozonide in that it is not explosive. Furthermore, when boiled with water it yields no levulinic aldehyde or acid. Analysis, in fact, shows that it is not an ozonide but a simple oxide $(C_5H_8O)_x$. This composition is the same as that of the rubber oxide obtained with perbenzoic acid from rubber. A similar product of the same composition has also been obtained from thermoprene-GP by the action of perbenzoic acid. Potassium permanganate on polycyclic rubber produces another oxide of the same composition but different solubility. These products are very interesting theoretically, because although the polycyclic rubber contains a smaller proportion of double bonds than does rubber, strong oxidizing materials open up not only the double bonds but also the newly formed cycles. Sulfur apparently does not do this but adds only to the double bonds.

The polycyclo-rubbers can be hydrogenated like rubber itself in the presence of a catalyst at high temperatures and pressures (85) (95). The hydro-polycyclo-rubbers are colorless, do not add bromine, and are stable toward hot nitric acid and potassium permanganate. The amount of hydrogen added, as determined by elementary analysis, corresponds to the unsaturation shown by other means.

Concentrated nitric acid reacts with polycyclo-rubber less energetically than with rubber but converts it into the same or a similar product. Long boiling with dilute nitric acid slowly decomposes it, forming a water-soluble, nitrogen-containing acid, large amounts of hydrocyanic and oxalic acids, and unidentified products. In solution nitric acid forms what is probably a nitropolycyclo-rubber, $(C_5H_7NO_2)_x$, as judged by its properties and the yield. It is more stable toward heat than is the corresponding derivative of rubber (see p. 111).

Structure. None of the derivatives or decomposition products have given any inkling as to the structure of the polycyclo-rubbers. Staudinger, working by analogy, has presented some results, however, which make it possible to build up a tentative scheme of the course of the reaction. He studied the action of zinc dust in the presence of hydrogen chloride on mono- and dichloroparaffin hydrocarbons and terpenes, in which the chlorine was attached to a carbon atom to which a methyl group was also attached—a structure corresponding to the probable structure of rubber hydrochloride—and found that the chlorine was always split off as hydrogen chloride. 3-Ethyl-3-chlorononane, $C_{11}H_{23}Cl$, was converted into the corresponding undecene, $C_{11}H_{22}$, which has one double bond the position of which was not determined. 2,6-Dimethyl-2,6-dichloroheptane gave very interesting results; two equivalents of hydrogen chloride were removed and the compound was converted into alpha-cyclogeraniolene, the constitution of which is well known (212). The yield was 31.5 per cent.



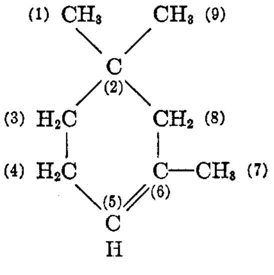
$$\underset{(1)}{CH_3} \cdot \underset{Cl}{\overset{\overset{(9)}{CH_3}}{\underset{(2)}{C}}} \cdot \underset{(3)}{CH_2} \cdot \underset{(4)}{CH_2} \cdot \underset{(5)}{CH_2} \cdot \underset{Cl}{\overset{\overset{(8)}{CH_3}}{\underset{(6)}{C}}} \cdot \underset{(7)}{CH_3} \rightarrow \underset{(1)}{CH_3} \cdot \overset{\overset{(9)}{CH_3}}{\underset{(2)}{C}} \cdot \underset{(3)}{CH_2} \cdot \underset{(4)}{CH_2} \cdot \underset{(5)}{CH} : \overset{\overset{(8)}{CH_2}}{\underset{(6)}{C}} \cdot \underset{(7)}{CH_3}$$

2,6-Dimethyl-2,6-dichloroheptane

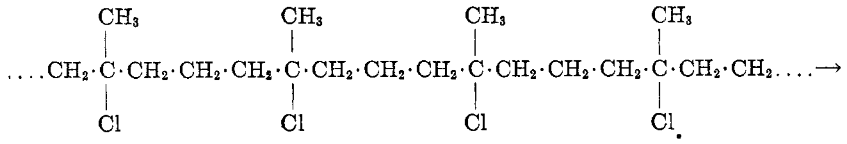
α-Cyclogeraniolene

(For the sake of comparison, the numbering of the carbon atoms is the same as in the straight chain compound.)

or

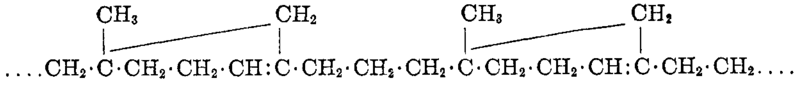


If the reaction is the same in the conversion of rubber hydrochloride into polycyclo-rubber, then by analogy it can be represented as follows:



$$\ldots\ldots CH_2\cdot\overset{CH_3}{\underset{Cl}{C}}\cdot CH_2\cdot CH_2\cdot CH_2\cdot\overset{CH_3}{\underset{Cl}{C}}\cdot CH_2\cdot CH_2\cdot CH_2\cdot\overset{CH_3}{\underset{Cl}{C}}\cdot CH_2\cdot CH_2\cdot CH_2\cdot\overset{CH_3}{\underset{Cl}{C}}\cdot CH_2\cdot CH_2\ldots\ldots\rightarrow$$

Rubber hydrochloride



$$\ldots\ldots CH_2\cdot\overset{CH_3}{C}\cdot CH_2\cdot CH_2\cdot CH{:}\overset{CH_2}{C}\cdot CH_2\cdot CH_2\cdot CH_2\cdot\overset{CH_3}{C}\cdot CH_2\cdot CH_2\cdot CH{:}\overset{CH_2}{C}\cdot CH_2\cdot CH_2\ldots\ldots$$

Polycyclo-rubber

It is obvious that there are other possibilities in writing this structure, with the double bonds and the cycles in different positions, but this one gives a good analogous picture.

15. Vulcanization, acceleration and aging

Vulcanization, acceleration and aging are of the utmost importance in rubber technology, and yet at the present time complete chemical and physical explanations of them are not available. The practice generally precedes the theory, and, in this case, with the practice well developed, science apparently has a long way to go before it will provide complete explanations. The writer has no intention of going into a lengthy review of all the theories already set forth to explain these subjects, nor of propounding any new theories. He believes, however, that a résumé of the important contributions to these subjects would be worth while.

Vulcanization. When a mixture of rubber and sulfur is heated under proper conditions at "vulcanizing" temperatures, around 140°C., there takes place a gradual change from a plastic, tacky mixture to a very elastic, very strong, non-tacky product, which is familiar to all in the form of rubber bands, inner tubes, etc. In the industry this condition is designated as a good "cure." The early stages are known as "under cures," and the later stages, when the product on longer heating becomes weaker, as "over cures." The most important difference between raw and vulcanized rubber is the increased resistance to plastic flow, or its permanent set. Properly vulcanized rubber, when stretched and allowed to return, goes back practically to its original shape, whereas raw rubber does not. Furthermore, this stretching and returning can be done many times without causing any particular change in the original shape. Too long heating produces a "reversion," and the product becomes softer and sometimes tacky, and on standing slowly "perishes." The time of heating for a good rubber-sulfur cure is about three hours, and such a vulcanizate will contain at least 2.5 per cent of combined sulfur. Weber (213), in order to make a proper comparison between combined sulfur and the rubber hydrocarbon in compounded stocks, suggested the use of a coefficient of vulcanization. This coefficient is an arbitrary number, being the percentage ratio of sulfur and the original rubber present. Vulcanizates, even of rubber and sulfur alone, do not necessarily have the same physical properties when the coefficients are the same. The rate of combination is the same, but the properties vary with the previous treatment of the rubber (214). Sulfur is soluble in both raw and vulcanized rubber (146), and the portion uncombined with the hydrocarbon, the "free" sulfur, slowly crystallizes out on the surface as a grayish powder, commonly known as "bloom."

The evidence for the chemical combination with sulfur is chiefly as follows: (1) that when extracted with a liquid which dissolves sulfur but not rubber—for example, acetone—the sulfur is not removed beyond a certain definite amount, this amount depending on the conditions under which the rubber was vulcanized (215) (216); (2) that when so extracted with acetone to remove the free sulfur, and then extracted with hot benzene, each fraction, dissolved and undissolved, contains the same proportion of combined sulfur as any other fraction and as the original (215) (217); (3) that there is no measurable transfer of sulfur when vulcanized rubber is heated with some raw rubber in solution (217); (4) that when raw rubber is heated in solution with as much as 1000 per cent excess of sulfur, the product contains no more combined sulfur than the amount required for saturation of the rubber hydrocarbon as determined by other means, both chemical and physical (144); (5) that the amount of unsaturation of vulcanized rubber, as determined by the addition of bromine (147) and iodine chloride (148) corresponds to the difference between that which can be accounted for by the combined sulfur, using one atomic equivalent of sulfur for each C_5H_8 group, and the unsaturation of the original rubber; and (6) that the rate of chemical combination is regular, and the velocity coefficient of the reaction has been found to be 2.65 for 10 degrees increase in temperature, a value agreeing with that generally obtained in the case of a chemical reaction (214). The combined sulfur has never been removed from vulcanized rubber and the original rubber regenerated. In other words, rubber has never been completely devulcanized. Furthermore, completely saturated rubber, hydrorubber, is not affected by treatment with sulfur chloride (see p. 103). These facts leave no doubt that sulfur combines chemically with the rubber hydrocarbon, and they help to show that the theory of adsorption put forth by Wo. Ostwald (218) is untenable. Nevertheless, they do not explain all that constitutes vulcanization. A brief statement, therefore, of some of the other theories of vulcanization may not be amiss.

Brande (219), as far back as 1852, expressed the opinion that "the rubber acquires its new and distinct properties . . . . by the assumption of a new molecular condition; that, like phosphorus, it has assumed an allotropic state." Axelrod (220) postulated a depolymerization by the heat and a repolymerization by the sulfur, with simultaneous formation of a sulfur addition product. Kirchhof (221) regarded vulcanization as the transformation of rubber from a relatively unstable to a stable form, the chemical combination of sulfur being a subsidiary process. Ostromislenski (222) stated that "the process of vulcanization consists of two fundamental stages, (1) a chemical reaction in which only a small part of the rubber participates, and (2) an adsorption or swelling of the unchanged part of the rubber in the product of the chemical reaction." Harries's (223) theory resembled Kirchhof's. He thought of the raw rubber as a metastable form which passes into a stable form in the presence of sulfur, and that the combination of sulfur is a secondary reaction or a post-vulcanization. Stevens (224) suggested that vulcanized rubber may consist of two phases, one the soft, unchanged, raw rubber, and the other the hard, tough, completely sulfurized compound, C_5H_8S, and that the latter is dispersed in the former. Twiss (225) likened these dispersed rubber sulfide particles to particles having reënforcing properties such as carbon black, etc., and this idea has been elaborated with further experimental evidence by Stevens (226); this viewpoint is contested by Boiry (227) who showed that mixtures of rubber and carbon black could be separated into fractions containing different proportions of carbon black. Stevens's most recent work (228) includes an account of experiments in which hard rubber is made at low temperatures, 100°C., by the use of ultra-accelerators, and vulcanized products are obtained containing coefficients of vulcanization much beyond 47, the coefficient for C_5H_8S.

Twiss (229) has investigated the vulcanizing action of the different modifications of sulfur, such as S_λ (ordinary crystalline sulfur), S_μ, and S_π, and has shown that the differences, if any, are small. Peachey (230) vulcanizes rubber at ordinary temperatures by forming the sulfur directly in the rubber through the action of hydrogen sulfide and sulfur dioxide, to which gases the rubber is exposed alternately. Some of the sulfur combines chemically. Such a vulcanization can also be carried out in solution, and Bedford and Sebrell (231) attribute the reactivity of the sulfur under these conditions to the formation of thiozone, following the earlier suggestion of Erdman (232) for regular sulfur vulcanization. Romani (233), working in Bruni's laboratory, discovered that rubber can be vulcanized with tetramethylthiuram disulfide, especially when zinc oxide is present. He believes that a form of active sulfur is split off from the disulfide. Helbronner and Bernstein (234) vulcanized rubber in solution in the presence of ultra-violet light. The dried films contained upwards of 0.78 per cent of combined sulfur. All the above methods use sulfur in some form or other (234a).

Ostromislenski (222), working on the theory that the vulcanizing agent is one which both adds to the double bond and oxidizes it, discovered two new classes of agents, neither of which contains sulfur: the polynitrobenzenes, especially *m*-dinitrobenzene and 1,3,5-trinitrobenzene, and benzoyl peroxide. The polynitrobenzenes work with and without the presence of certain oxides, such as litharge, and the vulcanizates are comparable to those made with sulfur. The amounts used are only 0.5–2 parts with 100 parts of rubber. The benzoyl peroxide must usually be present up to about 10 parts, but no other ingredient is necessary. Ostromislenski states that the action is probably chiefly an oxidation. Fisher and A. E. Gray (235) found that the unsaturation of these vulcanizates was not changed from that of the original rubber, within the accuracy of the method employed. Therefore, if there is any oxidation it is very small in amount. It is possible, of course, that oxidation would not involve the double bonds, but this seems improbable. Oxygen and sulfur have many properties in common, and oxygen may act like sulfur in this case. If it does, then the amount necessary to cause the change is very small. If the above is correct, then by analogy ordinary vulcanization is a change in the hydrocarbon brought about by the sulfur, perhaps acting catalytically, and the chemical union of sulfur is a secondary reaction producing a further change which gives properties that are very important in the manufacture of rubber goods, but which is a change of degree only, not of kind. When the sulfur adds, it is not known whether an atom adds to a double bond forming an ethylene sulfide type, or whether two atoms unite with two double bonds forming a bridge either in the same molecule or between different molecules or aggregates.

It is not unreasonable to assume that the change is a type of polymerization. The relative decrease in unsaturation caused by the polymerization of such large units would be very small indeed,—probably too small to be measured by our present methods. Now, rubber itself is regarded as a polymerization product of isoprene, and isoprene can be polymerized into rubber-like products. In this polymerization the liquid isoprene is transformed into an elastic solid which is soluble in the rubber solvents but no longer soluble in many of the other solvents capable of dissolving isoprene itself. Moreover, some forms of synthetic rubber are apparently so highly polymerized that they are practically insoluble in all organic solvents. It seems possible, therefore, that raw rubber may be further polymerized into a product that is more resistant to solvents than raw rubber itself, and it seems possible that such a change may be the same as that occurring during the first stage of vulcanization. An objection which may be raised to this idea is that the reverse of the process, depolymerization, has never been carried out, or, in other words, as stated above, rubber has never really been devulcanized (236) (217).

The question is quite open, and further work must be done to find out whether vulcanization is chiefly a polymerization, whether the method of combination of the sulfur causes the change, or whether the change is due to reaggregation, the dispersion of sulfur addition products, etc. Time will surely tell.

Reclaimed rubber, which is frequently spoken of commercially as "devulcanized" rubber, is manufactured not by removing the combined sulfur but by replasticizing old vulcanized rubber goods. The process in most general use is the Marks alkali process (237), which consists in heating the rubber under pressure with an aqueous solution of about 5 per cent of its weight of sodium hydroxide. It is then thoroughly washed, strained, and "refined" by milling. About 250,000 tons of reclaimed rubber were manufactured in the United States in 1929. Only about 60 per cent of this represents the original raw rubber, the other 40 per cent consisting of the compounding ingredients used in making the articles. Reclaimed rubber in rubber goods has a tendency to cause poor aging, but now with the use of antioxidants reclaimed rubber can be used to a far greater extent than formerly, and thus its use makes for a better economic condition.

Acceleration. Accelerators (237a) of vulcanization not only shorten the time of vulcanization, but also make it possible to use lower temperatures and to obtain products with enhanced physical properties and frequently with better aging qualities. Accelerators are used in small amounts, approximately 0.01 to 1.0 part with 100 parts of rubber. Zinc oxide is often necessary for proper activation of the accelerator. Inorganic accelerators such as litharge and magnesia have been known for a long time, but organic accelerators, used commercially in 1906 by Oenslager, were first given to the world in the published patents of Bayer and Co. (238) in 1912. Oenslager used aniline and thiocarbanilide, and the Bayer patents disclosed the use of piperidine and its CS_2-addition product. The latter is typical of an "ultra-accelerator." In its presence rubber can be vulcanized in 2–3 minutes at 140°C., and also on standing for several weeks at ordinary temperatures. It will also gel a rubber cement containing sulfur and zinc oxide. Most organic accelerators contain nitrogen, some nitrogen and sulfur, and some, such as the xanthates, sulfur but no nitrogen. They apparently act by causing the formation of an active form of sulfur.

Aging. A rubber band around papers set aside in a drawer becomes hard and brittle, the side wall of an automobile tire becomes cracked and crumbly, the rubber covering of a raincoat allowed to remain in the sun on the beach changes to a sticky mass; these familiar changes are typical of the aging of vulcanized rubber. All rubber goods, however, do not deteriorate like these. The old red hot-water bottles and red rubber bands showed excellent keeping qualities, and on this account even today many people still think of rubber as being red. These articles were vulcanized with crimson antimony sulfide (a polysulfide), and for some little understood reason such articles age very well. Nowadays very little "crimson antimony" is used, but since people have been so used to the good aging qualities of the goods manufactured by its use, articles are made with a red dye added to imitate the color and an organic "age-resister" to assure proper keeping qualities. The short life of ordinary rubber goods has kept rubber from being used in many places where it would be of great assistance, especially in building operations, machines, etc., and now that its life can be prolonged considerably, whole new fields have been opened up.

Aging is the result of the action of air and light, separately or together. Only comparatively recently have chemists studied this question intensively, and they have found that certain chemicals can be added to rubber to prolong its life. These chemicals are termed "anti-agers," "age-resisters" or "antioxidants."

They are usually organic compounds, and the most useful have been the condensation products of aliphatic aldehydes and aromatic amines (acetaldehyde and aniline, and acetaldol and α-naphthylamine), and the phenyl naphthylamines. It is easy enough to test a chemical for its action as an accelerator of vulcanization because the time factor is small, but ordinary aging requires a long time. In order to provide an accelerated aging test, Geer (241) used an oven in which strips of rubber were hung and through which warm air, previously heated to 70°C., was passed. The strips of rubber were removed every other day during two weeks and tested for reduction of tensile strength and elongation. This method gives good predictions except for articles containing traces of copper or for those exposed to sunlight (242). Another method, and one very widely used today, is that devised by Bierer and Davis (243). The test pieces are kept in a bomb under 300 pounds pressure of oxygen and at about 70°C. This test is much shorter, does not predict sun cracking, and conclusions may also be drawn from the tensile strength and elongation.

A very fine review and bibliography of the subject is given by Kohman (244), together with much experimental work on the absorption of pure oxygen under constant, atmospheric pressure and constant temperature, 80°C. In the course of the absorption, the rubber first becomes tacky, then less tacky and dry, then weak and finally hard and brittle. The absorption of oxygen is autocatalytic in nature and appears to be both an addition and a decomposition reaction. Vulcanized rubber absorbs oxygen at a greater rate than raw rubber, and the rate of absorption increases with the degree of the cure. The deterioration is apparently proportional to the amount of oxygen absorbed, 0.5 per cent of oxygen decreasing the tensile strenth by nearly 50 per cent. The action of anti-agers is probably one of negative catalysis rather than of preferential absorption. The rate of oxygen absorption may be greatly retarded by their presence, and their effectiveness varies with their concentration and chemical constitution. Stretched rubber deteriorates much more rapidly than when at its original length (245). In ozone and sunlight it deteriorates most rapidly when stretched to 105–10 per cent. During the initial stage of oxidation, the per cent of oxidation products increases much more rapidly than is indicated by the acetone extract, and on further oxidation, the products become insoluble in ether (246). Heating compounds in inert gases results at first in an increase in tensile strength because of a curing action, and then in a slow decrease which is insignificant as compared with the effect produced by oxygen.

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