

POLYTERPENES

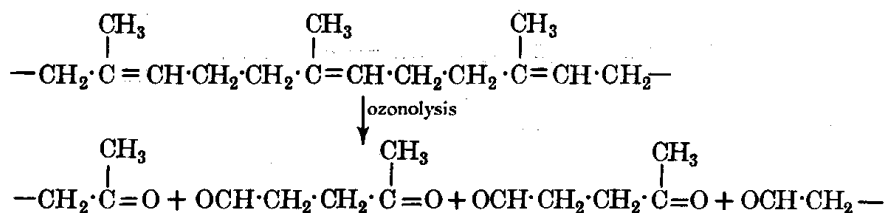
§33. Rubber. *Rubber (caoutchouc)* is obtained from latex, which is an emulsion of rubber particles in water that is obtained from the inner bark of many types of trees which grow in the tropics and sub-tropics. When the bark of the rubber tree is cut, latex slowly exudes from the cut. Addition of acetic acid coagulates the rubber, which is then separated from the liquor and either pressed into blocks or rolled into sheets, and finally dried in a current of warm air, or smoked.

Crude latex rubber contains, in addition to the actual rubber hydrocarbons (90–95 per cent.), proteins, sugars, fatty acids and resins, the amounts of these substances depending on the source. Crude rubber is soft and sticky, becoming more so as the temperature rises. It has a low tensile strength and its elasticity is exhibited only over a narrow range of temperature. When treated with solvents such as benzene, ether, light petrol, a large part of the crude rubber dissolves; the rest swells but does not dissolve. This insoluble fraction apparently contains almost all of the protein impurity. On the other hand, rubber is insoluble in acetone, methanol, etc. When unstretched, rubber is amorphous; stretching or prolonged cooling causes rubber to crystallise.

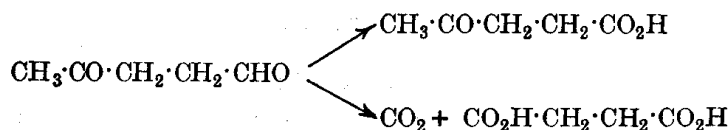
Structure of rubber. The destructive distillation of rubber gives isoprene as one of the main products; this led to the suggestion that rubber is a polymer of isoprene, and therefore to the molecular formula $(\text{C}_5\text{H}_8)_n$. This molecular formula has been confirmed by the analysis of pure rubber. Crude rubber may be purified by fractional precipitation from benzene solution by the addition of acetone. This fractional precipitation, however, produces molecules of different sizes, as shown by the determination of the molecular weights of the various fractions by osmotic pressure, viscosity and ultracentrifuge measurements; molecular weights of the order of 300,000 have been obtained.

The halogens and the halogen acids readily add on to rubber, *e.g.*, bromine gives an addition product of formula $(\text{C}_5\text{H}_8\text{Br}_2)_n$, and hydrogen chloride the addition product $(\text{C}_5\text{H}_9\text{Cl})_n$. Pure rubber has been hydrogenated to the fully saturated hydrocarbon $(\text{C}_5\text{H}_{10})_n$ —this is known as *hydrorubber*—by heating with hydrogen in the presence of platinum as catalyst (Pummerer *et al.*, 1922). Rubber also forms an ozonide of formula $(\text{C}_5\text{H}_8\text{O}_3)_n$. All these addition reactions clearly indicate that rubber is an unsaturated compound, and the formulæ of the addition products show that there is one double bond for each isoprene unit present.

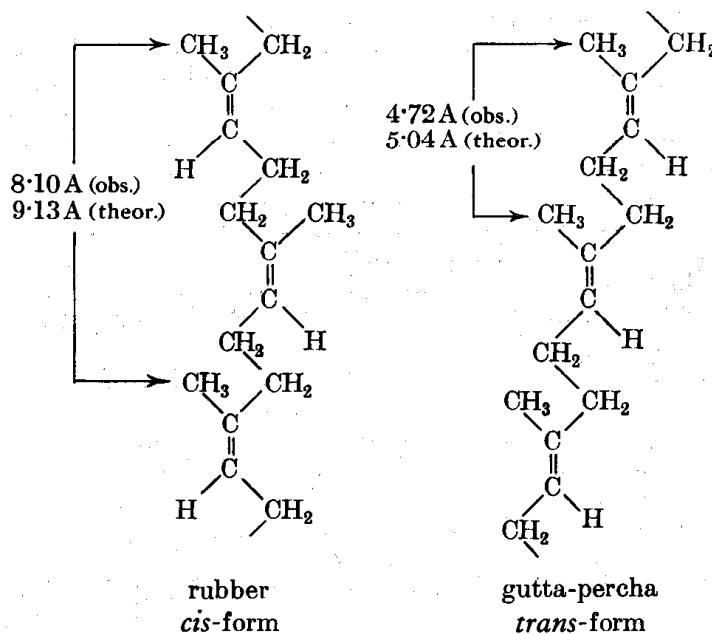
Ozonolysis of rubber produces lævulaldehyde and its peroxide, lævulic acid and small amounts of carbon dioxide, formic acid and succinic acid (Harries, 1905–1912). Pummerer (1931) showed that the lævulic derivatives comprised about 90 per cent. of the products formed by the ozonolysis. This observation led to the suggestion that rubber is composed of isoprene units joined head to tail. Thus, if rubber has the following structure, the formation of the products of ozonolysis can be explained:



Some of the lævulaldehyde is further oxidised to lævulic and succinic acids.



Gutta-percha (which is also obtained from the bark of various trees) is isomeric with rubber; their structures are the same, as shown by the methods of analysis that were used for rubber. X-ray diffraction studies (Bunn,



1942) have shown that rubber is composed of long chains built up of isoprene units arranged in the *cis*-form, whereas gutta-percha is the *trans*-form. Gutta-percha is hard and has a very low elasticity.

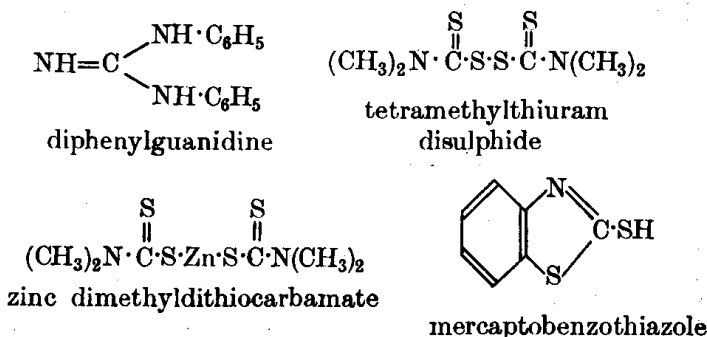
In rubber, the chain repeat unit is 8.10 Å, whereas in gutta-percha it is 4.72 Å. Both of these values are shorter than the theoretical values of the repeat distances (9.13 Å and 5.04 Å respectively) calculated from models. The reasons for these discrepancies are not clear, but for gutta-percha it has been explained by assuming that the isoprene units are not coplanar. The infra-red absorption spectrum of rubber has bands which are in keeping with the structure that has been proposed. Also, the *linear* shape of the molecule is indicated by viscosity measurements of rubber solutions. Schulz *et al.* have examined *cyclohexane* solutions of rubber by light-scattering methods, and obtained a value of 1,300,000 for the molecular weight. Their other work also supports the linear nature of the chain.

§33a. Vulcanisation of rubber. When crude rubber is heated with a few per cent. of sulphur, the rubber becomes *vulcanised*. Vulcanised rubber

is less sticky than crude rubber, and is not so soluble and does not swell so much in organic solvents. Furthermore, vulcanised rubber has greater tensile strength and elasticity than crude rubber.

The mechanism of vulcanisation is still not clear. Vulcanised rubber is not so unsaturated as rubber itself, the loss of one double bond corresponding approximately to each sulphur atom introduced. It therefore appears that *some* sulphur atoms enter the chain, vulcanisation thus occurring through intramolecular and intermolecular cross-links; it is the latter type of reaction that is desirable in vulcanisation. It should be noted that not all the sulphur is in a combined state; some is *free*, and this can be readily extracted.

Vulcanisation may be accelerated and carried out at lower temperatures in the presence of certain organic compounds. These compounds are consequently known as *accelerators*, and all of them contain nitrogen or sulphur, or both, *e.g.*,



Mercaptobenzothiazole is the most widely used accelerator. Many inorganic compounds can also act as accelerators, *e.g.*, zinc oxide. Organic accelerators are promoted by these inorganic compounds, and current practice is to vulcanise rubber with, *e.g.*, mercaptobenzothiazole in the presence of zinc oxide.

The actual properties of vulcanised rubber depend on the amount of sulphur used, the best physical properties apparently being achieved by using about 3 per cent. sulphur, 5 per cent. zinc oxide and about 1 per cent. of the accelerator. When 30–50 per cent. sulphur is used, the product is *ebonite*.

The elasticity of rubber is believed to be due to the existence of rubber as long-chain molecules which are highly “kinked” in the normal state. When subjected to a stretching force, these chains “unkink”, and return to their normal condition when the force is removed.

§33b. Synthetic rubbers. There are many synthetic rubbers in use, each type possessing certain desirable properties. A great deal of work has been done on the synthesis of *natural* rubber, but the difficulty has been to obtain the isoprene units in the all-*cis* configuration. Wilson *et al.* (1956) have achieved this by using stereospecific catalysts.

Buna rubbers. Under the influence of sodium, butadiene polymerises to a substance which has been used as a rubber substitute under the name of *Buna* (see Vol. I). *Buna N* is a synthetic rubber which is produced by the copolymerisation of butadiene and vinyl cyanide. *Buna S* or *Perbunan* is a copolymer of butadiene and styrene.

Butyl rubber. Copolymerisation of *isobutylene* with a small amount of isoprene produces a polyisobutylene known as *Butyl rubber*.

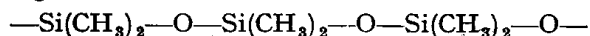
Neoprene. When passed into a solution of cuprous chloride in ammonium chloride, acetylene dimerises to vinylacetylene. This dimer can

add on one molecule of hydrogen chloride to form *Chloroprene* (2-chlorobuta-1:3-diene), the addition taking place in accordance with Markownikoff's rule (see also Vol. I).



Chloroprene readily polymerises to a rubber-like substance known as *Neoprene*. Actually, the nature of the polychloroprene depends on the conditions of the polymerisation.

Silicone rubbers. These are chemically similar to the silicone resins. The chief silicone rubber is prepared by treating the hydrolysis product of dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$, with various compounds capable of increasing the molecular weight without the formation of cross-links, *i.e.*, they produce long-chain molecules.



Silicone rubbers have very high electrical insulating properties, and do not deteriorate on exposure to light and air, and are resistant to the action of acids and alkalis.

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