

UNITED STATES PATENT OFFICE.

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CAOUTCHOUC SUBSTANCES AND PROCESS OF MAKING SAME.

1,058,056.

Specification of Letters Patent.

Patented Apr. 8, 1913.

No Drawing.

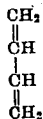
Application filed November 4, 1911. Serial No. 658,536.

To all whom it may concern:

Be it known that I, CARL HARRIES, professor of chemistry, doctor of philosophy, citizen of the German Empire, residing at Kiel, Germany, have invented new and useful Improvements in Caoutchouc Substances and Processes of Making Same, of which the following is a specification.

I have made the surprising discovery that the alkali-forming metals, namely, the alkali and alkaline earth metals, both in an isolated state and in the form of their mixtures, alloys and amalgams, are capable of converting hydrocarbons of the butadiene series, such as butadiene, its homologues and substitution products, (alkyl substituted butadienes, etc.,) which hydrocarbons are generically characterized by containing in their molecule the nucleus graphically represented, —C=C—C=C— , into new caoutchouc substances.

In order to illustrate the new process more fully the following example is given, the parts being by weight:—5 parts of sodium wire prepared in the usual way are pressed into 1000 parts of butadiene (condensed by strong cooling) having the formula:



The vessel is closed and allowed to stand for a week or two. The sodium is then destroyed by alcohol or water and the caoutchouc substance which has been formed is rolled into sheets. It is an elastic whitish substance soluble in benzene. It forms a nitrosite which is a yellowish powder which becomes brown and is decomposed on being heated to 140° C. Its brom addition product is a whitish powder. Its ozonid obtained with ozone (6-7 per cent.) is a colorless oil which detonates when heated. In the vulcanized state it is whitish and non-adhesive.

If in the example the quantity of sodium is replaced by 100 parts of sodium amalgam containing 10 per cent. of sodium, the product obtained from the mixture after several days standing is identical with the caoutchouc described in the example.

100 parts of isoprene are mixed with 35 parts of sodium and the mixture is heated in

an autoclave to 36° C. for 6 weeks. The mass is then further treated as above described.

Instead of sodium, calcium, potassium, lithium or mixtures of these metals such as calcium-sodium and instead of sodium amalgam other amalgams such as ammonium amalgam, etc., may be used. These metals, whether used in an isolated condition alone or in the form of mixtures or alloys or amalgams, are all embraced within the generic term,—alkali-forming metals. Other hydrocarbons of the butadiene series can be employed *e. g.* alpha-methyl-, alpha-alpha-dimethyl-, beta-gamma-dimethyl-, gamma-methyl-, beta-isobutyl-, beta-normalpropyl-butadiene, etc.

The new caoutchouc substances are whitish substances soluble in benzene. They are free from protein substances which are always contained in the natural caoutchouc and play an important part in it with regard to the elasticity of the natural caoutchouc. They form ozonids, nitrosites and brom addition products which are in the vulcanized form grayish, non-adhesive substances.

The new compounds thus obtained are different from the caoutchouc hitherto obtained from butadiene or its homologues, etc., and yield different derivatives.

The insoluble nitrosite for instance of the known isoprene caoutchouc (probably formula $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_3$) decomposes at about 120° C. the soluble one (formula of soluble product $\text{C}_{10}\text{H}_{16}\text{N}_3\text{O}_7$) decomposes at about 162° C. while the corresponding derivatives obtained from the products of the present application (probably formula of soluble product $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_5$) are not even decomposed at 220° C. The ozonids show characteristic differences. The decomposition products obtained by the action of water or of glacial acetic acid on the ozonids prepared from products of the present application do not show at all or only very weakly the pyrrol test while the ozonids of the known caoutchoucs show this test under the same treatment in a very marked manner.

The process of polymerization can also be effected by bringing the polymerizing agent (alkali-forming metal) in contact with the vapor of the hydrocarbon instead of with the hydrocarbon in liquid form.

I claim:—

1. The process of producing caoutchouc

substances which comprises subjecting hydrocarbons of the butadiene series to the action of an alkali-forming metal.

2. The process of producing caoutchouc substances which comprises subjecting hydrocarbons of the butadiene series to the action of an alkali metal.

3. The process of producing caoutchouc substances which comprises subjecting hydrocarbons of the butadiene series to the action of sodium.

4. The process of producing caoutchouc substances which comprises subjecting butadiene to the action of an alkali-forming metal.

5. The process of producing caoutchouc substances which comprises subjecting butadiene to the action of an alkali metal.

6. The process of producing caoutchouc substances which comprises subjecting butadiene to the action of sodium.

7. New caoutchouc substances obtained by polymerization of unsaturated hydrocarbons with two double bonds which are characterized by being whitish substances soluble in benzene, being free from protein substances and forming nitrosites, ozonids and brom addition products and in the vulcanized

form are whitish to grayish substances which are not adhesive and the ozonids of which on decomposition with water do not show the pyrrol test or show it only very weakly, substantially as described.

8. A new caoutchouc substance comprising butadiene caoutchouc obtained by treatment of butadiene with an alkali forming metal which is a whitish substance soluble in benzene, forming a nitrosite which is a yellowish powder which becomes brown and is decomposed on being heated to 140° C.; forming a brom addition product which is a whitish powder, forming an ozonid which is a colorless oil detonating when heated and which on decomposition with water does not show the pyrrol test or shows it only very weakly; and in the vulcanized form is a whitish not adhesive powder, substantially as described.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

CARL HARRIES.

Witnesses:

JULIUS ROPKE,
FRIEDRICH BUROW.