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## EMULSION POLYMERIZATION OF BUTADIENES

Helmut Meis, Leverkusen-Wiesdorf, and Richard Ludwig, Leverkusen-I. G. Werk, Germany, assignors, by mesne assignments, to Jasco, Incorporated, a corporation of Louisiana

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5 Claims. (Cl. 260—23)

The present invention relates to improvements in the emulsion polymerization of butadienes-1.3 in an aqueous alkaline medium.

The polymerization of butadienes-1.3 to form synthetic rubber-like materials is usually effected in an aqueous emulsion. In case of working in an alkaline medium there are employed as emulsifying agents either alkali metal salts of higher fatty acids such as oleic acid or of sulfonic acids exerting an emulsifying action such as alkylated naphthalene sulfonic acids. After polymerization, the resulting latex-like emulsions are usually worked up by salting out and/or by acidification. Both types of emulsifying agents suffer from certain disadvantages. Thus, higher fatty acids exert a sufficient emulsifying effect only if employed in relatively high proportions of f. i. 15–20% (calculated on the compounds to be polymerized); moreover, they are liable to form pasty or jelly-like solutions thus preventing the working in high concentrations; finally, on acidification, they are precipitated together with the synthetic rubber and must be removed therefrom by an after-treatment by means of alkali metal hydroxides. On the other hand, alkylated naphthalene sulfonic acids though being free from these disadvantages yield polymerizates which are inferior as to plasticity to those prepared in the presence of higher fatty acids, thus impairing the workability of the products on the roller, the incorporation of filling materials and the like.

It is the object of the present invention to develop emulsifying agents for the purpose in question which combine the valuable properties of both types defined above without being accompanied by the disadvantages inherent thereto. Other objects will be apparent from the following description and claims.

We have found that satisfactory results are obtained by working in the presence of a mixture of

(*a*) Water soluble surface active emulsifying agents and

(*b*) Water soluble salts of unsaturated carboxylic acids the esters of which represent drying oils, particularly alkali metal salts.

The term "water soluble surface active emulsifying agents" comprises all such emulsifying agents as are soluble in an acid medium as well as in an alkaline medium. These products usually contain sulfonic acid groups, examples of such compounds being alkylated naphthalene sulfonic acids, fatty alcohol sulfonates, products of the following constitution:

$$R.CO.X.R'.SO_3H$$

R standing for a chain of at least 8 carbon atoms,
X standing for —O— or —NH— or



and
R′ standing for a lower alkyl group such as $C_2H_4$

and finally higher fatty acids containing in addition to the carboxylic acid group a true sulfonic acid group. Moreover, there can be employed the products of the condensation of fatty alcohols (i e. those containing more than 8 carbon atoms) such as oleyl alcohol and several mols of ethylene oxide or glycide. Products of type *b* are f. i. the alkali metal salts of linoleic acid, wood oil acid, and the isomers thereof and, finally, the acids obtained by saponification of drying train oils.

The present invention is based on the discovery that when working as described above there are obtained products of excellent plasticity and of excellent mechanical properties in the vulcanized state. In accordance with a preferred form of our invention the capillary active substances of type *a* are employed in excess over the products of type *b* so that the emulsifying action necessary to keep the polymerizable substances as well as the polymerics in suspension is chiefly exerted by the former. The products of type *b* are employed in a relatively small proportion of f. i. up to about 5% of the compounds to be polymerized, preferably not more than 2%. It follows therefrom that the present invention is free from the inconveniences inherent to the prior known processes in that the products of type *a* are not precipitated in the course of the working up operations, whereas the products of type *b*, though being precipitated together with the synthetic rubber are present in such a small amount that they may remain within the rubber without exerting any detrimental effect. On the contrary, they have a certain catalytic effect on the course of the plastifying process which is described in application Serial No. 196,903 filed March 19, 1938 by Albert Koch and Erich Gartner and in the continuation-in-part of that application which bears Serial No. 384,210, filed January 28, 1941. According to this application, synthetic rubber like materials such as emulsion polymerizates of butadiene hydrocarbons and emulsion copolymerizates of butadiene hydrocarbons with copolymerizable materials such as styrene, acrylic acid nitrile and the like are plasticized by subjecting the polymerizates to an oxidizing treatment at elevated temperatures of about 80° C. or above

and in the presence of up to about 4% based upon the polymerizate of an antioxidant. The excellent emulsifying effect of the compounds of type *a* allows one to work in high concentrated emulsions, f. i. of the proportion of 1:1.

The present invention may be employed in connection with every butadiene-1.3 hydrocarbons such as butadiene-1.3 itself, isoprene or dimethylbutadiene and also in case of the conjoint polymerization of such butadienes with other polymerizable compounds such as styrene or acrylic acid nitrile.

The following examples illustrate the present invention without, however, restricting it thereto the parts being by weight:

*Example 1*

In 60 parts of water there are dissolved 0.6 part of sodium isobutylnaphthalene sulfonate, 0.3 part of linoleic acid and 0.08 part of sodium hydroxide. 21 parts of dimethyl butadiene are emulsified therein and after the addition of 2 parts of a 10% hydrogen peroxide solution the whole is heated while stirring to 30° for several days. The polymerization being finished the resulting emulsion is acidified and the precipitation is completed by the addition of methyl alcohol or a sodium chloride solution. The precipitated synthetic rubber is washed with water and dried. It shows a better plasticity than the product obtained without the addition of linoleic acid.

*Example 2*

In 46 parts of water there are dissolved 1.8 part of sodium isobutylnaphthalene sulfonate, 0.45 part of linoleic acid and 0.1 part of sodium hydroxide. A mixture of 24 parts of butadiene-1.3 and 8.46 parts of styrene is emulsified therein. After the addition of 3 parts of 10% hydrogen peroxide solution the whole is heated for 150 hours to 30–35° in an autoclave. The resulting polymerization product is worked up as described in Example 1. It shows a relatively good plasticity.

*Example 3*

In 24.5 parts of water there are dissolved 0.48 part of sodium isobutylnaphthalene sulfonate, 0.04 part of sodium hydroxide and 0.09 part of an unsaturated higher aliphatic acid obtained by saponification of a drying train oil (iodine number being 169). The solution is stirred in an autoclave with 6.5 parts of butadiene-1.3 and 2.16 parts of acrylic acid nitrile and 0.8 part of a 10% hydrogen peroxide solution for several days at 30° C. After working up as described in Example 1 a product of good plasticity and workability is obtained.

*Example 4*

25 parts of styrene and 75 parts of butadiene-1.3 are emulsified in 180 parts of a 2% aqueous solution of a condensation product of oleyl alcohol and 8 molecules of ethylene oxide. After the addition of 1.8 part of sodium linoleate and 0.5 part of ammonium persulfate the emulsion is stirred for 5–6 days at 30° C. There are obtained about 75 parts of a polymeric product of excellent properties.

*Example 5*

75 parts of butadiene-1.3 and 25 parts of styrene are emulsified in 200 parts of a 2% aqueous solution of the sodium salt of α-sulfostearic acid. After the addition of 2 parts of sodium linoleate, 0.3 part of sodium pyrophosphate and 0.45 part of ammonium persulfate the emulsion is stirred for 6–7 days at 30° C. The polymerizate which is obtained in a yield of about 65–75% is distinguished by a good plasticity and workability.

Similar results are obtained by replacing the sulfostearic acid by oleyltaurine.

We claim:

1. The process of producing a butadiene-styrene interpolymer which upon subjecting to a plasticizing treatment by oxidizing the interpolymer at elevated temperatures in the presence of antioxidants yields a product of especially good plasticity, which comprises polymerizing an aqueous emulsion of butadiene-1.3 and styrene in an aqueous alkaline medium in the presence of an emulsifying agent which is soluble in an acid medium as well as in an alkaline medium and in the further presence of a water soluble salt of a drying oil fatty acid.

2. The process of producing a butadiene-styreneinterpolymer which upon subjecting to a plasticizing treatment by oxidizing the interpolymer at elevated temperatures in the presence of antioxidants yields a product of especially good plasticity, which comprises polymerizing an aqueous emulsion of butadiene-1.3 and styrene in an aqueous alkaline medium in the presence of an alkylated naphthalene sulfonic acid emulsifying agent and in the further presence of a water soluble salt of a drying oil fatty acid.

3. The process of producing a butadiene-styrene interpolymer which upon subjecting to a plasticizing treatment by oxidizing the interpolymer at elevated temperatures in the presence of antioxidants yields a product of especially good plasticity, which comprises polymerizing an aqueous emulsion of butadiene-1.3 and styrene in an aqueous alkaline medium in the presence of an alkylated naphthalene sulfonic acid emulsifying agent and in the further presence of a water soluble salt of linoleic acid.

4. The process as defined in claim 2 wherein the alkylated naphthalene sulfonic acid is used in excess over the salt of the drying oil fatty acid and the latter is used in amounts of up to 5% of the compounds to be polymerized.

5. The process as defined in claim 3 wherein the alkylated naphthalene sulfonic acid is used in excess over the salt of linoleic acid and the latter is used in amounts up to 5% of the compounds to be polymerized.

HELMUT MEIS.
RICHARD LUDWIG.