

ALIEN PROPERTY CUSTODIAN

PROCESSES FOR THE AMELIORATION OF RUBBER

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The present invention relates to processes for the amelioration of natural rubber. They essentially consist in causing a copolymerization of rubber and unsaturated bodies, more particularly polymerizable vinylic monomers, the vinyl remainder of which is attached to at least one atom, or group of atoms, having electro-negative features.

It is known that copolymerization consists in effecting polymerization on a mixture of monomers, the properties of said copolymers being often very different from that of the polymers of each of the monomers. Many examples of copolymerization are known and many products thus obtained have acquired industrial importance. For instance, can be cited the copolymers of vinyl chloride and vinyl acetate, acrylic acid and vinylic esters, acrylic acid and butadiene, and, in the particular field of synthetic rubber, the copolymers of butadiene and styrolene, of butadiene and acrylic nitrile, etc. It is moreover remarkable to find that in the copolymerization can be caused to intervene products which are not, in themselves, polymerizable: such is the case for instance, for maleic anhydride which forms copolymers with styrolene, vinyl chloride

It must be noted from now that, as regards rubber, the terms "polymerization" and "depolymerization" are most often used without keeping sufficiently to their strict chemical sense. Rubber being already a polymerized substance, mention can scarcely be made but of an increase of its degree of polymerization in the case of the union of its fillform molecules. On the other hand, depolymerization must designate, substantially, the return to the monomer, isoprene in this case, and not only a breaking up of the molecular chain into more or less long links; however, it can logically be said that depolymerization occurs when said breaking up takes place with formation of double bonds at the ends of the links.

As regards the term "copolymerization," it is used herein in the exact sense attributed to this word, that is to say that it is admitted that the rubber molecules are united together, either by chain, or by bridge, or by both these means, through the medium of molecules of the other monomer utilized. It will be easily understood that said polymerization can apply either to rubber hydrocarbon, or to unions of the molecules of said hydrocarbon, or finally to sections of said molecules.

It has already been proposed to introduce into

the latex, emulsions of polymerized vinylic derivatives, in order to obtain in the midst of the rubber, a perfect dispersion of said polymers and to eventually improve the properties of the mixture; but, in these prior methods, there is no chemical connection between the rubber and said polymers, and the improvement produced is relative and due to charge effect. The tests subsequently effected in order to obtain, in the very midst of the latex, the polymerization of the monomers have given no practical result, according to literature.

On the contrary, according to the present invention, copolymerization involves a profound modification of the properties of the product obtained, modification which is due to variations of the chemical structure and which, most often, results in nearly complete insolubility in the usual rubber solvents, of the coagulation product of the aqueous dispersions treated.

The principle of said invention is to cause rubber, from any botanical source, to react in an aqueous dispersion, in presence of a protecting colloid and of a suitable catalyser, with unsaturated derivatives such as those above mentioned.

As aqueous dispersions can be used natural latex, or any product of its coagulation, or of its evaporation, put again in suspension. In both cases, the rubber may have been previously subjected to a treatment for degrading it (malaxation, heating, oxidation, etc.), to peptization, or to a treatment for increasing its degree of polymerization.

As protecting colloid, use can be made of agents generally recommended for emulsifying and stabilizing latex in particular, for instance, oleates, stearates, various sulphonates, albuminoids.

The catalyser can be, for instance, a peroxide or a mixture of peroxides. Good results have been obtained with hydrogen peroxide, or organic peroxides usually used for polymerizations.

As example of copolymerizable monomers can be cited styrolene, acrylic acid, acrylic esters, acrylic nitrile, acrolein, separately or in mixtures.

The reaction also takes place, as in the general case of copolymerization, with products which are not polymerizable in themselves.

The monomer and the catalyser are added to the duly stabilized rubber dispersion; the whole is then stirred; the temperature and the time of contact depend on the degree of polymerization it is desired to obtain. After reaction, the dispersion is coagulated in the usual manner; it can also be evaporated.

The coagulation products differentiate, most

often, from ordinary latex coagulum, by a practically complete insolubility in rubber solvents (benzene, gasoline . . .) and a relatively limited swelling. They can however be malaxated and can be vulcanized according to the usual methods; according to the starting monomer and the conditions of polymerization, the vulcanized products obtained by means of the rubber thus modified can swell considerably less in the solvents than those obtained by the same rubber non-modified.

The examples previously cited and the experimental details hereinafter are given in order that the invention may be clearly understood, but must not be considered as limiting the same in any way whatever.

Example 1

Latex free from ammonia is brought to a 20% content in dry rubber. Thereto are added one or more emulsifying stabilizers, such as sulpho-nated fatty alcohol, soap, etc. (1 to 2 grs. for 100 cubic centimeters of diluted latex), and a protecting colloid (gelatin: 1%). Acrylic nitrile is added (50 parts for 100 parts of dry rubber) and then hydrogen peroxide so as to obtain 2 to 10 cubic centimeters of active oxygen per gram of dry rubber.

The mixture is carefully emulsified, then maintained at a temperature of 50 to 60° for 24 hours.

The reaction product, constituted by a homogeneous jelly, is treated with diluted acetic acid, then filtered and dried. An opaque and somewhat fibrous mass is obtained which gives, after passage through a mixer, a translucent crepe quite similar to ordinary crepe. It differentiates therefrom by certain of its properties, in particular its insolubility in ordinary rubber solvents.

This crepe can be mixed, charged and vulcanized in the usual manner.

The vulcanized product possesses a clearly improved resistance to swelling agents.

Example 2

The same operations are effected as in the preceding example with the only difference that hydrogen peroxide is replaced by ethyl hydroperoxide.

Example 3

The same operations are effected as in the preceding example, by replacing acrylic nitrile by styrolene.

Example 4

To the latex stabilized as previously stated are added ethyl hydroperoxide, styrolene (30 parts for 100 parts of dry rubber) and acrylic nitrile (30 parts).

Example 5

The same operations as in example 2 are effected, but by replacing acrylic nitrile by butyl methacrylate.

Example 6

The rubber contained in the latex is degraded by heating said latex with or without hydrogen peroxide, then treated as previously.

Example 7

The same operations are effected as in any one of the preceding examples by progressively adding the monomer or monomers and the catalyser, and stirring.

Example 8

Examples 1 and 2 are applied to an artificial latex prepared in the following manner:

Rubber is malaxated for $\frac{3}{4}$ of an hour in the cold state, then heated for an hour and a half at 250° in an inert gas; in these conditions, a viscous liquid mass is obtained having a non saturation only slightly lower than that of raw rubber.

This liquid rubber is placed in solution at 50% in benzene; the solution is emulsified in water containing a soap (oleate of Na: 1%), a dispersing agent (darvan: 1%), a protecting colloid (casein: 1%); after elimination of the benzene, the emulsion very rapidly gives a cream which contains about 50% of liquid rubber.

The copolymerization product obtained from said cream is a solid and plastic mass which can be worked and vulcanized as ordinary rubber.

In the preceding description, only reactions are mentioned concerning natural rubber or such rubber which has been subjected to treatments affecting the rubber-hydrocarbon, but, of course, the reaction can also be used for a natural rubber, which has been subjected to treatments affecting the components having not the character of rubber, for instance deproteination.

The description mentions as a catalyser for facilitating the reaction of the organic peroxydes, but this reaction can also be facilitated by means of all other physical or chemical agent promoter of polymerisation.

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