PATENT SPECIFICATION

658,520

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COMPLETE SPECIFICATION

Process for the Preparation of Aqueous Dispersions of Cyclized Natural or Synthetic Rubber and of Articles therefrom

We, RUBBER ~~STICHTING~~ STICHTING, a Foundation incorporated under the laws of the Netherlands, of Julianalaan 134, Delft, Holland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

According to the present invention an aqueous dispersion of cyclized rubber is obtained in a simple and cheap manner by reacting a cyclizing agent with an aqueous dispersion of ~~material~~ natural or synthetic rubber which is acid resistant in a large *p*H-range. From the dispersion obtained a solid cyclized rubber can be recovered by evaporation, precipitation or other methods and it can then be redispersed in water or can be worked up into articles.

By cyclized rubber is understood a substance having the same ratio of carbon and hydrogen as rubber but in which the unsaturation compared with rubber has decreased.

In contradistinction to the known method for the cyclization of rubber in latex the rubber is not broken down beforehand, which may be advantageous. At the same time the possibility exists of obtaining the cyclized rubber in dispersed state which may be advantageous for further working up or in applications.

It is known to cause the conversion of rubber into cyclized rubber to take place by mixing the rubber in the form of sheet, crepe or reclaimed rubber on the mill with sulphuric acid or sulphonic acids (*p*-toluene sulphonic acid) and thereupon to heat same some time (e.g. 8 hours at 120° C.). The same conversion can also be obtained with the aid of HBF_4, $AlCl_3$, $SnCl_4$, $FeCl_3$, $ZnCl_2$, acids and phenols, PCl_5 and acid crystalhydrates (alum e.g.) or benzene-diazoboron tetrafluoride. This conversion on the mill yields generally darkly coloured products which are difficulty soluble. It is also known to prepare cyclized rubber by dissolving the rubber in organic solvents, such as benzene, toluene, xylene or white spirit, to heat this solution and to add substances such as H_2SO_4, sulphonic acids, HF, $SnCl_4$, BF_3, $AlCl_3$, $ZnCl_2$, $HClO_4$, acid anhydrides or acid chlorides; further also HCl (in the presence of a phenol), H_3PO_4, H_3BO_3 trichloro acetic acid P_2O_5 and phenols are suitable. Cyclized rubber prepared in this way usually is a light coloured powder soluble in most rubber solvents. The use of solvents renders this process expensive. Since a solution of cyclized rubber gives a glossy film after evaporation of the solvent, which film becomes hard by exposure to the air, cyclized rubber can be used in the paint- and lacquer-industry. Commercial products such as "Pliolite" (registered Trade Mark) and Marbon B are rather pure cyclized rubber products which are used for the said purposes.

Cyclized rubber may also be used for adhering rubber to metal. The rubber is superficially treated with a cyclizing agent and thus covered with a layer of cyclo rubber. The metal is then applied and the whole vulcanised. Alternatively, a solution of cyclo rubber may be rubbed on metal, rubber applied thereto and the whole vulcanised. In both cases the cyclo rubber serves as an adhesive. The product can also be used as insulating material.

Further cyclized rubber is important for the rubber industry because the addition of cyclized rubber to rubber can improve various properties of the vulcanisates.

Cyclized rubber can further be used as a substitute for gutta percha, e.g. in the manufacture of golf balls. Finally, cyclized rubber can be used for the manufacture of waterproof paper, since this substance is very impermeable to water.

According to United States Specification No. 1,853,334 rubber is reacted with

[Price 2/-]

Revised Price 2s. 8d.

a compound of boron and fluorine under the influence of heat. The said compound is prepared by the reaction of hydrofluoric acid and boric acid or its salts of boric oxide either before or after incorporation into the rubber. It is stated that the reaction is not only applicable to ordinary raw rubber but also to reclaimed rubber and latex. There is no suggestion that the latex should be rendered acid-resistant prior to the treatment.

It has now been found possible to prepare cyclized rubber without the use of expensive solvents and without mixing on the mill being necessary, but by reacting cyclizing agents directly on an aqueous rubber dispersion. The initial aqueous rubber dispersion may be a naturally-occurring or artificially-produced dispersion of natural rubber or synthetic rubber (e.g. polyisoprene and its copolymers, polydimethyl butadiene and its copolymers or polymethyl pentadiene and its copolymers) or a flocculate (i.e. a dispersion in which some of the rubber particles are agglomerated). The following description is given with reference to natural rubber latex, which is the preferred initial dispersion, but it will be understood that any of the other aqueous dispersions mentioned may equally well be used.

According to the invention the cyclization in the latex becomes possible since the latex has first been pretreated in such a manner that it is acid resistant in a larger *p*H range.

Latex, which is stabilized with ammonia only is not sufficiently stable to be used as a starting material for the cyclization reaction. By the addition of casein, saponin, hæmoglobin and the like products latex can be rendered considerably more stable but also this latex is not suitable as a starting material for the cyclization reaction. A better method for rendering acid resistant, which is suitable for the process according to the invention, is the addition to the latex of cationic soaps, such as cetylpyridinium bromide, dialkylaminoethyloleylmethosulphate diethyl-aminoethyloleysulphate, and

$$C_{17}H_{33}CONCH_3$$
$$|$$
$$C_2H_4SO_3Na$$

In this manner a latex of higher concentration which is acid resistant in a large *p*H range can be obtained. Still more satisfactory is the addition of a non ionogenic emulsifyng agent such as dodecylphenylpolyglycolether and polyglycolether. According to the invention cyclized rubber is prepared by first rendering latex acid resistant, thereupon adding the cyclizing agent, and if desired, heating. Finally the solid product can be recovered from the thus obtained dispersion of cyclized rubber.

The cyclizing agent first gives a certain acid concentration in the aqueous phase. This point is reached at a moment which is dependent on the velocity of the introduction and/or the kind and concentration of the cyclizing agent; thereupon the cyclizing agent reacts with the rubber globule. The rate of the reaction depends on the pressure and temperature. In this manner one is able to control the beginning as well as the rate of the reaction within wide limits. Also in this manner the obtaining of a certain degree of cyclization can be controlled. During the reaction the above factors can be altered.

After termination of the reaction mostly a dispersion is obtained in which the cyclized rubber parts are dispersed in the same manner as is the case with rubber particles in latex. The cyclized rubber dispersion cannot be microscopically distinguished from the starting latex. Because of the fact that the cyclized rubber is obtained in emulsion all kinds of purification methods, such as are known for latex, can be easily applied.

The form in which the cyclized rubber is present in the dispersion is determined by the greater or less agglomeration of the cyclized rubber particles. If substantial agglomeration occurs the agglomerates formed can be easily redispersed.

Solid cyclized rubber can be recovered from the dispersion of cyclized rubber by precipitation, flocculation, sedimentation; combined, if desired, with centrifuging or by means of other methods. The separation of solid cyclized rubber can e.g. be effected by the addition of alcohol, toluene, and the like. This solid cyclized rubber which can be recovered from the dispersions has, in contradistinction to the known cyclized rubber, a finely divided powder form. This cyclized rubber is insoluble but can be made soluble by milling.

A particular manner of recovering solid cyclized rubber from the dispersion is by long prosecuted cyclization reaction in which the cyclized rubber separates automatically in a finely divided state.

Very suitable cyclizing agents are HF and ~~H_2SO_4~~. When H_2SO_4 is used as a cyclizing agent this acid is preferably added in concentrated form. Increase of temperature and pressure promotes the reaction. Especially when using HF as a cyclizing agent the application of

pressure is to be recommended.

Some of the known cyclizing agents are inactive in aqueous or acid medium and these agents therefore are unsuitable for this process. If the cyclizing agent is capable of giving rise either to the formation of rubber addition products or to the cyclization of the rubber depending on the reaction conditions, the latter should be chosen so that the cyclization occurs and not the addition reaction.

In order to modify the properties of the cyclized rubber latex and the cyclized rubber to be recovered therefrom softeners (e.g. dibutyl phthalate), plasticizers, stabilizers, active and inactive fillers, vulcanization ingredients, pigments and the like can be added to the starting latex, the cyclized rubber dispersion or to the solid cyclized rubber.

It is known that vulcanization of

Time in min.	2	5	10	13	16	19	30
Temperature	98°	98°	111°	122°	120°	113°	94°
Unsaturation (rubber=100)	86	82	47	36	24	20	20

From this table the heat evolved during the reaction clearly appears. After completion of the reaction the latex is coagulated with alcohol and thereupon soda lye is added to neutralize the sulphuric acid. Thereupon filtering off, washing and drying take place.

Example 2.

HF is passed through 60% latex which is stabilized with Emulphor O (see Example 1).

The latex is in a vessel lined with paraffin. After the serum has been saturated HF is passed through for another three hours. Thereupon the latex is coagulated with methanol and the product is filtered and dried.

Example 3.

To 20 ccs of 60% latex, to which 250 mg. of Emulphor O were added 15 ccs of liquid HF were carefully added. After standing for two hours the product was precipitated by means of alcohol and isolated. Determination of the unsaturation showed that 60% of the double bonds had disappeared.

Example 4.

Into a double walled vessel of acid resistant material are brought 100 litres of 60% latex stabilized with 2,5 kg. of Emulphor O. 129 kg. of concentrated sulphuric acid are slowly added hereto. During the addition stirring takes place and the heat is carried off in such a manner that the temperature does not rise over 80° C.

After termination of the addition of sulphuric acid the reaction mixture is cyclized rubber can e.g. take place with S, sulphides, S_2Cl_2, $ClSO_3K$, SO_2Cl_2.

The cyclized rubber latex can also be vulcanized by these substances provided that the aqueous medium and the acidity do not cause difficulties.

It is advantageous to start from concentrated latex because then less acid is needed.

The following examples will further illustrate the invention.

Example 1.

To 100 ccs of 60% latex 8 ccs of a 36% Emulphor O (a polyglycolether) solution in water are added. To 100 ccs of this mixture 75 ccs of sulphuric acid are slowly added while cooling. Thereupon heating takes place to 94° C. and the temperature is measured at certain intervals.

Time in min.	2	5	10	13	16	19	30
Temperature	98°	98°	111°	122°	120°	113°	94°
Unsaturation (rubber=100)	86	82	47	36	24	20	20

kept at 90° C. during approximately 2 hours with the aid of steam, during which cyclization takes place.

The heat developed during the cyclization reaction (see Example 1) can make the temperature of the reaction mixture rise to far ~~beyond~~ 100° C. By efficient cooling care should be taken that the temperature does not rise over 140° C., since otherwise carbonization of the material occurs. During the reaction stirring takes place. After 5 to 10 hours, depending on the maximum temperature of the reaction mixture during the reaction the reaction product separates and can be filtered off after dilution with water. The material is thoroughly washed in order to remove the last traces of sulphuric acid. The still moist material separated by filtration can, if necessary, be redispersed in water, in which case an aqueous dispersion of cyclized rubber is obtained.

Specification No. 634,879 (which was not published until after the present application was ~~filed~~) claims, *inter alia*, a method of cyclizing rubber which comprises adding an aqueous acid to a rubber latex containing a non-ionic stabiliser to being the *p*H value to less than 5, adding concentrated sulphuric acid or oleum to the acidified latex to form a dispersion of rubber in a hydrated sulphuric acid medium containing at least 60% sulphuric acid and maintaining the dispersion at a suitable temperature until the desired degree of cyclication has been effected. According to the present invention the latex is not initially brought to *p*H less than 5 prior to the addition of the cyclizing agent, but on the contrary the

latter is added directly to the acid-resistant latex.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the preparation of aqueous dispersions of cyclized rubber or of cyclized synthetic rubber characterised in that a cyclizing agent is reacted on an acid resistant aqueous rubber or synthetic rubber dispersion (including a flocculate), particularly on acid resistant natural rubber latex.

2. Process for the preparation of solid cyclized rubber or synthetic rubber and of articles therefrom characterized in that the solid cyclized rubber or synthetic rubber is separated in powder form from the aqueous dispersion thereof prepared according to claim 1, and if desired, worked up into articles.

3. Process according to claim 1 or 2 characterised in that the operation takes place at increased temperature and/or pressure.

4. Process for the preparation of cyclized rubber substantially as described in any of the foregoing examples.

5. Products obtained according to the process claimed in any of claims 1 to 4.

Dated this 4th day of June, 1948.

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1. Process for the preparation of aqueous dispersions of cyclized rubber or of cyclized synthetic rubber characterised in that a cyclizing agent is reacted on an acid resistant aqueous rubber or synthetic rubber dispersion (including a flocculate), particularly on acid resistant natural rubber latex.

2. Process for the preparation of solid cyclized rubber or synthetic rubber and of articles therefrom characterized in that the solid cyclized rubber or synthetic rubber is separated in powder form from the aqueous dispersion thereof prepared according to claim 1, and if desired, worked up into articles.

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