PATENT SPECIFICATION

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713,482

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Index at acceptance:—Class 70, E18.

COMPLETE SPECIFICATION

Improvements in the preparation of Rubber Dispersions and the manufacture of Cyclised Rubbers

We, RUBBER TECHNICAL DEVELOPMENTS LIMITED, a Body Corporate duly organised under the Laws of Great Britain, Market Buildings, Mark Lane, London E.C.3, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of rubber dispersions and the manufacture of cyclised rubber.

The preparation of cyclised rubber by treatment of solid rubber, or rubber dissolved in organic solvents by suitable reagents has been practised for many years. The use of rubber in the form of latex or other aqueous dispersion offers many advantages, in particular the avoidance of the heavy machinery required to break down the rubber for reaction with the chemical or for subsequent solution in solvent, and, by the second process, the avoidance of large volumes of inflammable and expensive solvents is achieved.

In one method for the preparation of cyclised rubber, employing aqueous dispersions, the reagent, sulphuric acid, is reacted with the rubber in the presence of a non-ionic stabiliser, such as a polyethylene glycol ether, heat being applied.

According to the present invention, the rubber dispersions are stabilised with tertiary amines, prepared from long chain fatty amines by condensation with ethylene oxide, which behave as cationic agents in an acid medium, in amount less than 2.5% on the dry rubber content of the dispersion. Such stabilisation by these compounds enables the acidification of the dispersion to be carried out, and subsequent reaction of the reagent with the rubber at elevated temperatures to take place.

Since for the cyclisation reaction to occur a high concentration of acid is required in the aqueous phase of the dispersion, it is economic to start with as high a concentration of rubber in the dispersion as possible. The treatment of the dispersion with the cationic soap of the kind defined can be carried out after concentration by one of the usual techniques, for example centrifuging.

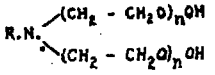
When using economically low proportions of certain types of cationic soap other than that defined herein their addition is liable to cause premature coagulation of the latex unless the latex or other rubber dispersion is added to the solution of the cationic soap and the mixture immediately and rapidly treated with sulphuric acid which has the effect of redispersing the micro-flocks which are formed.

With latex stabilised according to the invention by the addition of a tertiary amine prepared from a long chain fatty amine by condensing with ethylene oxide neither immediate nor rapid addition of the acid is necessary thus giving better control over the acidification step.

Conveniently, the sulphuric acid employed is 98% concentration, and the quantity added is sufficient to make up a concentration by weight of between 60 and 85% in the serum of the dispersion, whereafter, the temperature of the mixture is raised to bring about the reaction; the temperature and time of heating being chosen appropriate to the concentration of the acid present. Preferably, also as described in co-pending application No. 2871/52 (Serial No. 713,481), a coagulum consisting of a mixture of rubber and cyclised rubber is formed by admixture under the conditions therein defined of a proportion of a dispersion of uncyclised rubber. The rubber obtained may thereafter be sheeted, washed

and dried by any of the known procedures, and preferably by the technique mentioned in the aforementioned co-pending application and be used as a master batch. The invention, however, is not limited to the production of such a coagulum and sheetable product which would be used as a master batch, but also relates to the production of a fully or partially cyclised rubber by suitable precipitation technique.

The cationic soap compounds consist essentially of a long chain aliphatic residue attached to a radical capable of ionising in solution in such a way that a positive charge is assumed by the polar end of the long chain molecule. The aliphatic chain may be composed of twelve or more carbon atoms, and the ionisable radical may be represented by a tertiary amine or quaternary ammonium group. Tertiary amines prepared from long chain fatty amines by condensation with ethylene oxide behave as cationic agents in an acid medium. These latter substances are of the general formula:—



where the radical R is the long alkyl chain of 12 or more carbon atoms and the value of n can vary from 5 upwards.

The following example illustrates the practice of the invention.

500 g. of concentrated latex of total solids content 69.5%, is stirred into a warm solution of 5g. of stearylamineethylene oxide, condensate known as ~~Ethomeen~~ 18/60 in 5 ml. of water. Into this is stirred 250 mls. of 98% sulphuric acid with sufficient cooling to prevent temperature rise above 100° C.

The temperature of the mixture is raised to and maintained at 100—105° C. for 2½ hours with stirring, to bring about and complete the cyclisation of the rubber. Since the cyclisation reaction is exothermic some cooling may be necessary in the earlier stages of reaction.

The resultant flocculated cyclised rubber is separated by suitable filtration methods, washed, neutralised and dried.

In Specification No. 658,520 a process for the preparation of aqueous dispersions of cyclised rubber or of cyclised synthetic rubber is described characterised in that a cyclising agent is reacted on an acid resistant aqueous rubber of synthetic rubber dispersion (including a flocculate), particularly on acid resistant natural rubber latex.

What we claim is:—

1. In the preparation of a rubber dispersion in a hydrated sulphuric acid medium and the manufacture of cyclised rubber, the stabilisation of the rubber dispersion with tertiary amines, prepared from long chain fatty amines by condensation with ethylene oxide, which behave as cationic agents in an acid medium, the compound being present in an amount less than 2.5% on the dry rubber content of the dispersion.

2. In the preparation of a rubber dispersion in a hydrated sulphuric acid medium and the manufacture of cyclised rubber according to the preceding claim, the step of concentrating the rubber dispersion by centrifuging or creaming prior to the acid addition.

3. Processes for the preparation of rubber dispersions or for the manufacture of cyclised rubber substantially as described.

4. Stabilised dispersions of rubber in hydrated sulphuric acid media when prepared by the processes substantially as described.

5. Cyclised rubber when prepared by processes substantially as herein described.

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PROVISIONAL SPECIFICATION

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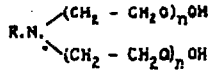
This invention relates to the preparation of rubber dispersions and the manufacture of cyclised rubber.

In one method for the preparation of cyclised rubbers and aqueous dispersions of cyclised rubber, reagents, usually sulphuric acid, are reacted with rubber in latex in the presence of a non-ionic stabiliser such as polyethylene glycol ether, heat being applied.

According to the present invention the rubber dispersions are stabilised with cationic soap compounds, the compound being present

and dried by any of the known procedures, and preferably by the technique mentioned in the aforementioned co-pending application and be used as a master batch. The invention, however, is not limited to the production of such a coagulum and sheetable product which would be used as a master batch, but also relates to the production of a fully or partially cyclised rubber by suitable precipitation technique.

The cationic soap compounds consist essentially of a long chain aliphatic residue attached to a radical capable of ionising in solution in such a way that a positive charge is assumed by the polar end of the long chain molecule. The aliphatic chain may be composed of twelve or more carbon atoms, and the ionisable radical may be represented by a tertiary amine or quaternary ammonium group. Tertiary amines prepared from long chain fatty amines by condensation with ethylene oxide behave as cationic agents in an acid medium. These latter substances are of the general formula:—



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The resultant flocculated cyclised rubber is separated by suitable filtration methods, washed, neutralised and dried.

In Specification No. 658,520 a process for the preparation of aqueous dispersions of cyclised rubber or of cyclised synthetic rubber is described characterised in that a cyclising agent is reacted on an acid resistant aqueous rubber of synthetic rubber dispersion (including a flocculate), particularly on acid resistant natural rubber latex.

What we claim is:—

1. In the preparation of a rubber dispersion in a hydrated sulphuric acid medium and the manufacture of cyclised rubber, the stabilisation of the rubber dispersion with tertiary amines, prepared from long chain fatty amines by condensation with ethylene oxide, which behave as cationic agents in an acid medium, the compound being present in an amount less than 2.5% on the dry rubber content of the dispersion.

2. In the preparation of a rubber dispersion in a hydrated sulphuric acid medium and the manufacture of cyclised rubber according to the preceding claim, the step of concentrating the rubber dispersion by centrifuging or creaming prior to the acid addition.

3. Processes for the preparation of rubber dispersions or for the manufacture of cyclised rubber substantially as described.

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According to the present invention the rubber dispersions are stabilised with cationic soap compounds, the compound being present

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in less than 2.5% by weight on the dry rubber content of the rubber dispersion and the acid or at least a portion thereof is added immediately the rubber dispersion is stabilised.

When using such economically low proportions of cationic stabiliser in order to avoid premature coagulation it is necessary for the latex or other rubber dispersion to be added to a solution of the cationic soap and for the acid, usually sulphuric acid, to be added immediately afterwards under controlled temperature conditions with rapid stirring in order to obtain a stable dispersion of rubber in the hydrated acid medium.

Conveniently the sulphuric acid employed is 98% concentration and only a portion of that necessary fully to cyclise the rubber is initially added to form the stable dispersion, the balance to make up a concentration by weight of between 60 and 85% in the serum of the dispersion being added subsequently whereafter the temperature of the mixture is raised to bring about the reaction; the temperature and time of heating being chosen appropriate to the concentration of acid present.

Preferably also as described in co-pending Application No. 2871/52 (Serial No. 713,481) a coagulum consisting of a mixture of rubber and cyclised rubber is formed by adding a proportion of such acid aqueous dispersion of cyclised rubber to an anionically stabilised uncyclised rubber dispersion.

The rubber obtained may thereafter be sheeted, washed and dried by any of the known procedures and preferably by the technique described in the aforementioned co-pending Application, and be used as a master batch.

The cationic soap compounds consist essentially of a long chain aliphatic residue attached to a radical capable of ionising in solution in such a way that a positive charge is assumed by the polar end of the long-chain molecule. The aliphatic chain may be composed of 12 or more carbon atoms and the ionisable radical may be represented by a quaternary ammonium group in combination with a suitable anion such as halogen ion or sulphate ion. Typical examples are cetyl pyridinium bromide, cetyl tri-methyl ammonium chloride and lauryl pyridinium chloride. The technique for preparing acid cationic soap stabilised latex or rubber dispersions involves the addition of concentrated latex to a 10 or 20% solution of the cationic soap with rapid agitation. The mixture tends to thicken and, if stirring is continued too long, coagulation will occur. On the other hand, if an immediate addition is made of concentrated sulphuric acid, the dispersion again becomes fluid and a few minutes stirring is sufficient to disperse any aggregates.

In the practice of the invention according to one mode of carrying out the process, to 600 ccs. of a solution of cationic soap containing 10% of active ingredient is added 4500 ccs. of 60% centrifuged latex. Immediately afterwards is added, with rapid stirring, 900 ccs. of 98% sulphuric acid. A further 1800 ccs. of sulphuric acid is subsequently added, so that the concentration by weight in the serum of the dispersion is 75%. The temperature of the mixture is raised to and maintained at 102.5° C. ± 5° C. for two hours. 310 g. of a commercial anionic soap product containing 30% of cetyl sodium sulphate is dissolved in water and added to 4500 ccs. of 60% latex, water is added to reduce the concentration of the rubber to approximately 15% and the temperature raised to 40° C. Into this anionic soap stabilised latex is poured the cationic stabilised cyclised latex dispersion with rapid stirring. Flocculation and subsequently coagulation take place. The mixture is warmed to 80° C. and maintained at this temperature for approximately 30 minutes, after which time the coagulum is easily removed and sheeted on washing mills, with free flow of warm water, neutralised, re-washed and dried, as described in copending Application.

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