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PROVISIONAL SPECIFICATION

Rubber Dispersions and the Use Thereof.

We, DUNLOP RUBBER COMPANY LIMITED, a British Company of 1, Albany Street, London, N.W.1, and MANFRED GORDON, a British Subject of the aforesaid Company's Works at Fort Dunlop, Erdington, Birmingham, 24, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in the production of rubber dispersions, and to the use thereof particularly in the production of cyclised rubber.

Rubber latices as obtained from rubber-bearing trees or other natural sources consist of particles of rubber dispersed in an alkaline aqueous medium or serum containing, among other constituents a stabiliser which is effective to keep the rubber dispersed so long as the medium remains alkaline, but which is no longer effective when the medium becomes acid as the result of putrefaction or by the deliberate addition of acid. Artificially prepared dispersions of vulcanised or unvulcanised natural rubber and dispersions of synthetic rubber are also normally prepared using an alkaline stabiliser which becomes ineffective under acid conditions.

The inability of rubber dispersions to remain stable under acid conditions is disadvantageous, since many processes are known where it is desired to treat rubber with acid-reacting reagents, e.g., halogenation processes and cyclising processes, and in such processes it has been necessary to forego the advantages which would accrue from the use of an aqueous dispersion and to treat the rubber in the solid condition or dissolved in an organic solvent. Thus methods hitherto employed for the production of cyclised rubber involve heating an intimate mixture of solid rubber with sulphuric acid or other cyclising agent, or heating a solution of the rubber in an organic solvent with such a cyclising agent. In the first of these methods the working of the mass necessary for uniform treatment involves considerable expenditure of power, while the other method involves the use of considerable amounts of organic solvent which have to be recovered. Neither method yields directly a product in a finely divided condition, though such a product would be valuable for many purposes. Moreover it is difficult to remove the cyclising agent from the product.

It is an object of the invention to provide a method of making acid aqueous rubber dispersions. It is a further object of the invention to provide a method of producing rubber derivatives in a finely divided condition which can readily freed from acid reactants.

It is a still further object of the invention to provide a method of producing cyclised rubber which avoids both heavy power consumption and the use of organic solvents.

According to the present invention acid aqueous rubber dispersions are made from an alkaline rubber dispersion by incorporating therewith a non-ionic stabiliser and subsequently rendering the dispersion acid by adding a water-soluble acidic substance thereto. Suitably the stabiliser is a polyethylene glycol etherified by means of a long chain aliphatic alcohol.

By a non-ionic stabiliser is meant a compound which is known to confer stability on aqueous dispersions, and which does not undergo electrolytic dissociation in aqueous solution. We have found that the incorporation of such a stabiliser in an alkaline rubber dispersion, in particular in a natural rubber latex, enables the rubber to remain dispersed even though the serum becomes acid. It is thus possible, for example, to react such dispersions with acid reagents, for example in halogenating or oxidation processes, and to recover the rubber conversion product in a finely divided condition substantially free from the acid reagent.

In particular we have found that the rubber will remain dispersed even if suffi-

cient of an acid cyclising agent such as concentrated sulphuric acid is added to the acid dispersion as to render the medium capable of bringing about cyclisation of the rubber on heating.

Thus according to a further feature of the invention rubber is cyclised by heating a dispersion of the rubber in an aqueous acid cyclising medium. Suitably the rubber is dispersed in an aqueous acid medium containing at least 60% by weight of sulphuric acid.

The invention will be further described with reference to the production of acid dispersions suitable for use in producing cyclised rubber and to the production of cyclised rubber therefrom.

Thus in preparing an acid dispersion of rubber in strong aqueous sulphuric acid, there is first added to a concentrated natural rubber latex a polyethylene glycol etherified with an aliphatic alcohol containing 8 to 24 carbon atoms, for example oleyl alcohol. One product of this type is that known under the trade name Emulphor—O. A suitable amount to add is an amount of the order of 2 to 5 parts by weight per 100 parts by weight of the rubber in the latex. Suitably the stabilising agent is first dissolved in a relatively small amount of water, and the solution so obtained is added to the latex. Aqueous sulphuric acid is then added to the latex containing the stabiliser until the aqueous phase is strongly acid, preferably with a pH not greater than 5, and then oleum or concentrated sulphuric acid is added until the aqueous phase contains at least 60% acid, say between 70% and 80% by weight of acid. The acid added initially should not be so concentrated that it has dehydrating power, or flocculation of the rubber may occur. Aqueous sulphuric acid containing not more than 80% H_2SO_4 is suitable for the initial addition. Thus aqueous acid containing 70% to 80% by weight of H_2SO_4 may be added initially in amount of order of 15 to 20 volumes for every 100 volumes of latex.

Instead of adding aqueous sulphuric acid to the latex containing a non-ionic stabilizer, other acids or acidic substances may be used, for example, aqueous hydrochloric acid or aqueous phosphoric acid. Substances which hydrate with the evolution of heat, e.g., oleum, or phosphorus pentoxide, should, however, not be added until the dispersion is strongly acid, especially with concentrated dispersions. It appears that in the range of pH values corresponding to weakly acid conditions the rubber dispersions are sensitive to heat or dehydrating influences which would be created by the introduction of such agents and flocculation may occur. Once this range of pH values has been passed concentrated sulphuric acid, or oleum can be added without inducing flocculation and the concentration of sulphuric acid brought up to values over 60% H_2SO_4 referred to above, suitable for carrying out the cyclisation step, with the least increase in bulk.

To cyclise the rubber in the resultant dispersion containing over 60% by weight of sulphuric acid, the resultant acidified material is heated to a temperature at which cyclisation of the rubber proceeds. As is well known, the cyclisation of rubber occurs with the evolution of heat, and it is in general necessary to cool the reaction mixture once the reaction temperature is reached so as to maintain it within a temperature range at which cyclisation occurs at a convenient rate. Suitably the temperature is maintained between 80°C. and 120°C. A convenient method of maintaining the appropriate temperature is to cause the dispersion to flow through a coil immersed in a fluid medium maintained at reaction temperature. When no further evolution of heat occurs, and reaction may thus be judged complete, the treated rubber can be recovered by pouring the dispersion into a large volume of water, preferably hot water, and recovering the powdered product which is thereby precipitated. The product may then be washed out with water and dried, or it may be redispersed in water containing a suitable dispersing agent.

Instead of using a natural rubber latex in the above cyclisation process an aqueous dispersion of an unsaturated synthetic rubber may also be treated according to the invention, and also aqueous dispersions of reclaim rubber. Other strongly acid aqueous reaction media may also be employed instead of sulphuric acid in the cyclisation step for example, strong aqueous solution of benzene sulphonic acid, acetyl sulphuric acid, or a phenolsulphonic acid, the media being obtained by adding the corresponding acid to the acidified latex. In order for the cyclising reaction to proceed at a technically feasible rate it is necessary to pay due regard to the concentration of the cyclising agent in the cyclising medium.

Instead of carrying the cyclisation process to completion it may be stopped at an intermediate stage, whereby a product may be obtained intermediate in properties between natural rubber and fully cyclised rubber. The method of the present invention is a particularly suitable one to use in the production of such intermediate products since it lends itself to a careful control of the time and temperature during the reaction stage, and permits a very

uniform treatment of the rubber to be given.

The following example illustrates but does not limit the invention all parts being by weight.

EXAMPLE.

95 parts of a concentrated natural rubber latex containing 60 parts of rubber were stabilised by the addition of 2.4 parts of Emulphor O. 27 parts of 75% aqueous sulphuric acid were then added gradually and then 155 parts of 98% sulphuric acid were added. The resultant dispersion of the rubber in strong aqueous sulphuric acid was then heated to 85°C. and maintained at that temperature for 3 hours. The cyclised rubber thus produced was flocculated by pouring the product into 2,000—4,000 parts of hot water, filtered off, washed with water, and dried.

The dried product was a resinous powder softening to a rubbery mass on heating to 120°C., and had an unsaturation of approximately half that of natural rubber. It was substantially free of sulphur.

Dated this 21st day of August, 1947.

R. F. McKAY,
Acting for the Applicants.

COMPLETE SPECIFICATION.

Rubber Dispersions and the Use Thereof.

We, DUNLOP RUBBER COMPANY LIMITED, a British Company of 1, Albany Street, London, N.W.1, and MANFRED GORDON, a British Subject of the aforesaid Company's Works at Fort Dunlop, Erdington, Birmingham, 24, 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:—

This invention relates to the production of rubber dispersions and to the use thereof, particularly in the production of cyclised rubber.

Rubber latices as obtained from rubber-bearing trees or other natural sources consist of particles of rubber dispersed in an alkaline aqueous medium or serum containing, among other constituents a stabiliser which is effective to keep the rubber dispersed so long as the medium remains alkaline, but which is no longer effective when the medium becomes acid as the result of putrefaction or by the deliberate addition of acid. Artificially prepared dispersions of vulcanised or unvulcanised natural rubber and dispersions of synthetic rubber are also normally prepared using an alkaline stabiliser which becomes ineffective under acid conditions.

It is known to prepare acid rubber latices by incorporating with an alkaline natural or artificial rubber latex a suitable dispersing agent e.g., saponin, or glycyrrhyzin salts or certain sulphonated products, e.g., sulphonated castor oil, and then making the latex acid by addition of a mineral acid. Stable latices can thus be obtained which have an acidity as great in some cases as 3N, but the latices become unstable if the acidity is made much greater than this. Thus it has not been possible to add so much sulphuric acid to a latex containing such a stabiliser that the rubber remains dispersed in what is essentially hydrated sulphuric acid, i.e., a medium containing at least as much sulphuric acid as corresponds to the formula $H_2SO_4 4H_2O$, which is approximately 60% H_2SO_4.

Because of this inability to prepare rubber dispersions containing such a high proportion of sulphuric acid it has been usual to carry out processes involving the treatment of rubber with, or in the presence of, sulphuric acid of such concentrations with the rubber in the solid state or in solution in an organic solvent. Thus cyclised rubber has been made by heating an intimate mixture of solid rubber with concentrated sulphuric acid, with or without a phenol, or by heating a solution of the rubber in an organic solvent with concentrated sulphuric acid with or without a phenol. The advantages of working with rubber in a dispersed condition have therefore been forfeited, for in the first of the methods the working of the mass necessary for uniform treatment involves considerable expenditure of power, while the other method involves the use of considerable amounts of organic solvent which have to be recovered. Neither method yields directly a product in a finely divided condition, though such a product would be valuable for many purposes. Moreover it is difficult to remove the cyclising agent from the product.

It is an object of the invention to provide a dispersion of rubber in a hydrated sulphuric acid medium. It is also an object of the invention to provide a method of making such a dispersion. It is a still further object of the invention to provide a method of producing rubber derivatives in a finely divided condition which can be readily freed from acid reactants. It is a still further object of the invention to provide a method of producing cyclised rubber which avoids both heavy power consumption and the use of organic solvents.

According to the present invention a rubber dispersion comprises a dispersion of rubber in a hydrated sulphuric acid medium containing a non-ionic stabiliser, the concentration of sulphuric acid in the medium being between 60% and 90% H_2SO_4.

According to a further feature of the invention a method of making a dispersion of rubber in a hydrated sulphuric acid medium comprises acidifying a rubber latex containing a non-ionic stabilizer by adding an aqueous acid thereto to bring the pH value to less than 5, and subsequently adding concentrated sulphuric acid or oleum to the acidified latex to bring the sulphuric acid content of the medium to between 60% and 90%.

According to a still further feature of the invention a method of cyclising rubber comprises adding an aqueous acid to a rubber latex containing a non-ionic stabiliser to bring the pH value thereof to less than 5, subsequently adding concentrated sulphuric acid or oleum to the acidified latex to bring the sulphuric acid content of the medium to above 60% and maintaining the said dispersion at a suitable temperature until the desired degree of cyclisation has been effected. If desired a phenol may be added to the dispersion before effecting cyclisation.

The incorporation of a non-ionic stabiliser in the rubber latex, in particular in a natural rubber latex, enables the rubber to remain dispersed even though so much concentrated sulphuric acid or oleum is added to the acidified latex that the serum becomes essentially hydrated sulphuric acid. It is thus possible, for example, to subject the rubber in such a dispersion to cyclisation, oxidation or nitrosation whereby a dispersion of the corresponding rubber conversion product is obtained from which the rubber conversion product can be isolated in a finely divided condition substantially free from the conversion reagent.

Cyclisation of the rubber takes place rapidly at atmospheric temperature if the concentration of the hydrated sulphuric acid medium is greater than about 90%, while at concentrations below about 85% it is necessary for the reaction mixture to be at superatmospheric temperature, the temperature range which is most suitable being dependent upon the acid concentration. If a dispersion of uncyclised rubber in hydrated sulphuric acid is desired as the final product it is therefore preferable to cool the dispersion during the step of adding concentrated sulphuric acid or oleum, or otherwise the heat of dilution of the added acid may cause such a rise in temperature that partial cyclisation occurs. It is also preferable to avoid adding so much acid as to increase the acid concentration above 85%. If it is desired to produce cyclised rubber, the dispersion can, if desired, be allowed to become hot during the addition of concentrated sulphuric acid or oleum and the concentration of acid may be increased above 85%. The heating subsequently necessary to cyclise the rubber will depend on the conditions observed during the addition of acid or oleum, and also on whether or not it is desired to carry the cyclisation as far as possible. In carrying out the present invention, therefore, the conditions must be chosen according to whether it is desired to produce a dispersion of rubber or of cyclised rubber.

By a non-ionic stabiliser is meant a surface active agent which does not undergo electrolytic dissociation in aqueous solution. Suitable compounds are hydrophilic organic compounds of high molecular weight having an aromatic or long chain aliphatic group linked to a radical containing an ether or ester group and a hydroxyl group. Preferred stabilisers are polyethylene glycol ethers of the formula $RO(C_2H_4O)_nH$ where R is a straight chain alkyl radical having from 8 to 20 carbon atoms and n is at least 4. Such products can be obtained by reacting ethylene oxide with the corresponding long chain aliphatic alcohol whereby compounds result conforming to the above formula in which n is between 20 and 25. Commercially available compounds of this type which may be used in the present invention are Emulphor-O, Lubrol-W and Vulcastab LW, each of which is believed to be a compound according to the above formula in which RO- is an oleyl alcohol residue. ("Lubrol" and "Vulcastab" are Registered Trade Marks). Other non-ionic stabilisers which may be used include polyethylene glycol esters, e.g., Emulphor A which is a condensation product of oleic acid and 6 mols of ethylene oxide; polyethylene glycol aryl ethers, e.g., a polyethylene glycol phenyl monether and alkylated phenyl monoethers of polyethylene glycol; and partial esters of polyhydric alcohols, e.g., that known as "Tweens 60" which is believed to be a polyalkylene ether of a partial sorbitol ester of stearic acid. These compounds may be added to the latex in amounts of 2 to 5 parts by weight for every 100 parts by weight of rubber in the latex.

The latex containing a non-ionic stabiliser is preferably acidified by means of aqueous sulphuric acid. Such acid should not be so concentrated that it has dehydrating power, or flocculation of the rubber may occur, on the other hand if very dilute acid is used, correspondingly

greater amounts of concentrated sulphuric acid, i.e., approximately 98% acid, or of oleum will be needed subsequently to raise the sulphuric acid concentration to above 60%. Instead of adding aqueous sulphuric acid to the latex containing a non-ionic stabiliser, other aqueous acids may be used, for example, aqueous hydrochloric acid or aqueous phosphoric acid. Substances which hydrate with the evolution of heat, e.g., oleum, concentrated sulphuric acid or concentrated phosphoric acid should, however, not be added to acidify the latex, for it appears that in the range of pH values corresponding to weakly acid conditions the rubber dispersions are sensitive to heat or dehydrating influences which would be created by the introduction of such agents, and flocculation may occur. Preferably the pH is brought to a value of less than 5 before adding concentrated sulphuric acid or oleum.

Once the pH value has been brought to below 5 concentrated sulphuric acid or oleum can be added without inducing flocculation to bring the concentration of sulphuric acid over 60% H_2SO_4.

In one method of preparing a dispersion of natural rubber in a hydrated sulphuric acid medium there is first added to a concentrated natural rubber latex 2 to 5 parts by weight per 100 parts by weight of the rubber of Emulphor-O. Suitably the stabilising agent is first dissolved in a relatively small amount of water, and the solution so obtained is added to the latex. Aqueous sulphuric acid is then added to the latex containing the stabiliser until the pH of the aqueous phase is less than 5, and then oleum or concentrated sulphuric acid is added until the aqueous phase contains at least 60% H_2SO_4, e.g., between 70% and 85% by weight of acid. Aqueous sulphuric acid containing not more than 80% H_2SO_4 is suitable for the initial addition. Thus aqueous acid containing 70% to 80% by weight of H_2SO_4 may be added initially in amount of the order of 15 to 20 volumes for every 100 volumes of latex.

Cyclisation of the rubber in the resultant dispersion can be effected by maintaining the resultant dispersion under temperature conditions appropriate to the sulphuric acid concentration. With an acid medium in which the sulphuric acid concentration is over 90%, cyclisation is complete in the time taken to add all the necessary concentrated acid or oleum at a convenient rate, though such a large amount of acid has to be added to attain this concentration that this procedure is generally not feasible. With acid concentration of about 85% to 90% cyclisation proceeds at ordinary temperature and is complete in less than a day, or the process may be speeded up by warming. If the concentration of acid is between 60% and 85% the dispersion should be kept hot in order that cyclisation may be completed in a reasonable time. As is well known, the cyclisation of rubber occurs with the evolution of heat, and though it is necessary to heat the dispersion initially to bring it to a suitable temperature, it is in general necessary to cool the reaction mixture once the reaction temperature is reached, so as to maintain it within a temperature range at which cyclisation occurs at a convenient rate. This temperature is lower the greater the H_2SO_4 concentration; with a sulphuric acid concentration of 70-75% for example, cyclisation can be effected conveniently by maintaining the temperature between 80°C. and 120°C. A convenient method of maintaining the appropriate temperature is to cause the dispersion to flow through a coil immersed in a fluid medium maintained at reaction temperature. When the cyclisation has proceeded as far as desired the product can be recovered by pouring the dispersion into a large volume of water, preferably hot water, whereby the product is precipitated and can be separated as a powder. The powdery product may then be washed with water and dried, or it may be redispersed in water containing a suitable dispersing agent.

Cyclisation is characterised by a diminution in the degree of unsaturation, although a completely saturated product is never obtained. The progress of cyclisation is evidenced by the evolution of heat and an increase in density of the rubber material; either of these phenomena may be used to follow the course of the cyclisation. Treatment may be continued until no further diminution in unsaturation occurs, the product being then what is termed a fully cyclised rubber, or cyclisation may be stopped at an intermediate stage, whereby a product is obtained which is intermediate in properties between natural rubber and fully cyclised rubber. The method of the present invention is particularly suitable for the production of such intermediate products since it lends itself to a careful control of the time and temperature during the reaction, and permits a very uniform treatment of the rubber to be given.

Instead of using a natural rubber latex in the above cyclisation process an aqueous dispersion of an unsaturated synthetic rubber which is a polymer of a conjugated diene, or a copolymer rubber of such a diene with a minor amount of a second unsaturated compound, may also be treated according to the invention, and also

aqueous dispersions of reclaim rubber. The term rubber latex is used in the present specification and claims to include such aqueous dispersions.

The dispersion of rubber in the hydrated sulphuric acid medium may also be used in the manufacture of oxidised rubber by adding hydrogen peroxide to the dispersion. Oxidation then proceeds at room temperature, and the oxidised rubber can be recovered subsequently by pouring the reaction product into water as described for cyclised rubber. Instead of treating the dispersion with hydrogen peroxide another per-compound soluble in the medium may be added, as for example a persulphate or persulphuric acid, and the dispersion may be warmed if necessary to induce reaction. Nitrosated rubber can also be obtained by heating the dispersion in hydrated sulphuric acid with nitric acid or nitrate.

The following examples illustrate but do not limit the invention, all parts being by weight.

EXAMPLE I

95 parts of concentrated natural rubber latex containing 60 parts of rubber were stabilised by the addition of 2.4 parts of Emulphor-O. 27 parts of 75% aqueous sulphuric acid were added rapidly with cooling. The strength of the sulphuric acid medium was then increased to 79% by the addition of 155 parts of 98% sulphuric acid.

EXAMPLE II

The dispersion of rubber in 79% sulphuric acid obtained according to Example I was heated to 85°C. and maintained at that temperature for 3 hours. The cyclised rubber thus produced was flocculated by pouring the product into 4,000 parts of hot water, filtered off, washed with water and dried.

The dried product was a resinous powder softening to a rubbery mass on heating to 120°C., and had an unsaturation of approximately half that of natural rubber. It was substantially free of sulphur. The particle size of the powder was approximately that of the original rubber particles in the latex (of the order of 1μ) though a proportion of loose aggregates was also present.

EXAMPLE III

To 18.5 parts of a natural rubber latex containing 60.7% solids were added 0.11 parts of molten Lubrol W with constant stirring while keeping the vessel warm. 5.96 parts of 35% aqueous hydrochloric acid were then added quickly while cooling and stirring. 30 parts of concentrated sulphuric acid were added, very gradually because of excessive frothing, thus producing a dispersion of rubber particles in a medium containing approximately 70% H_2SO_4.

EXAMPLE IV

100 parts of a concentrated natural rubber latex containing 60% rubber were mixed with Emulphor-O, aqueous sulphuric acid, and concentrated sulphuric acid, as in Example I to give a dispersion of rubber in a hydrated sulphuric acid medium containing 79% H_2SO_4 46 parts of 85-90% hydrogen peroxide were then added at intervals in 30 equal portions; the temperature rose gradually by about 10-15°C. after each addition, and the reaction mixture was allowed to cool before adding the next.

After the last addition the latex was flocculated by pouring into 10 times its volume of cold water, and the product was freed from acid by several times re-dispersing it in water by shaking and then allowing it to settle; it was then dried at 50°C.

The product was a brown powder which fused to a weak flexible film at 100°C. capable of being distorted at temperatures above 31°C. The powder could be converted to a sheet by milling; it was substantially insoluble in benzene, acetone and carbon tetrachloride; it had a relative density of 1.022 at 27°C., and its analysis for carbon and hydrogen corresponded to the empirical formlua C_5H_8O.

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. A dispersion of rubber in a hydrated sulphuric acid medium containing a non-ionic stabiliser, the sulphuric acid content of the medium being between 60% and 85%.

2. A dispersion according to Claim 1 in which the non-ionic stabiliser is a polyethylene glycol ether.

3. A dispersion according to Claim 2 in which the stabiliser is a polyethylene glycol ether of oleyl alcohol.

4 A method of making a dispersion of rubber in a hydrated sulphuric acid medium which comprises adding an aqueous acid to a rubber latex containing a non-ionic stabiliser to bring the pH value to less than 5, and adding concentrated sulphuric acid or oleum to the acidified latex to bring the sulphuric acid content of the medium to between 60% and 90%.

5. A method of cyclising rubber which comprises adding an aqueous acid to a rubber latex containing a non-ionic stabiliser to bring the pH 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

aqueous dispersions of reclaim rubber. The term rubber latex is used in the present specification and claims to include such aqueous dispersions.

The dispersion of rubber in the hydrated sulphuric acid medium may also be used in the manufacture of oxidised rubber by adding hydrogen peroxide to the dispersion. Oxidation then proceeds at room temperature, and the oxidised rubber can be recovered subsequently by pouring the reaction product into water as described for cyclised rubber. Instead of treating the dispersion with hydrogen peroxide another per-compound soluble in the medium may be added, as for example a persulphate or persulphuric acid, and the dispersion may be warmed if necessary to induce reaction. Nitrosated rubber can also be obtained by heating the dispersion in hydrated sulphuric acid with nitric acid or nitrate.

The following examples illustrate but do not limit the invention, all parts being by weight.

EXAMPLE I

95 parts of concentrated natural rubber latex containing 60 parts of rubber were stabilised by the addition of 2.4 parts of Emulphor-O. 27 parts of 75% aqueous sulphuric acid were added rapidly with cooling. The strength of the sulphuric acid medium was then increased to 79% by the addition of 155 parts of 98% sulphuric acid.

EXAMPLE II

The dispersion of rubber in 79% sulphuric acid obtained according to Example I was heated to 85°C. and maintained at that temperature for 3 hours. The cyclised rubber thus produced was flocculated by pouring the product into 4,000 parts of hot water, filtered off, washed with water and dried.

The dried product was a resinous powder softening to a rubbery mass on heating to 120°C., and had an unsaturation of approximately half that of natural rubber. It was substantially free of sulphur. The particle size of the powder was approximately that of the original rubber particles in the latex (of the order of 1μ) though a proportion of loose aggregates was also present.

EXAMPLE III

To 18.5 parts of a natural rubber latex containing 60.7% solids were added 0.11 parts of molten Lubrol W with constant stirring while keeping the vessel warm. 5.96 parts of 35% aqueous hydrochloric acid were then added quickly while cooling and stirring. 30 parts of concentrated sulphuric acid were added, very gradually because of excessive frothing, thus producing a dispersion of rubber particles in a medium containing approximately 70% H_2SO_4.

EXAMPLE IV

100 parts of a concentrated natural rubber latex containing 60% rubber were mixed with Emulphor-O, aqueous sulphuric acid, and concentrated sulphuric acid, as in Example I to give a dispersion of rubber in a hydrated sulphuric acid medium containing 79% H_2SO_4 46 parts of 85-90% hydrogen peroxide were then added at intervals in 30 equal portions; the temperature rose gradually by about 10-15°C. after each addition, and the reaction mixture was allowed to cool before adding the next.

After the last addition the latex was flocculated by pouring into 10 times its volume of cold water, and the product was freed from acid by several times re-dispersing it in water by shaking and then allowing it to settle; it was then dried at 50°C.

The product was a brown powder which fused to a weak flexible film at 100°C. capable of being distorted at temperatures above 31°C. The powder could be converted to a sheet by milling; it was substantially insoluble in benzene, acetone and carbon tetrachloride; it had a relative density of 1.022 at 27°C., and its analysis for carbon and hydrogen corresponded to the empirical formlua C_5H_8O.

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. A dispersion of rubber in a hydrated sulphuric acid medium containing a non-ionic stabiliser, the sulphuric acid content of the medium being between 60% and 85%.

2. A dispersion according to Claim 1 in which the non-ionic stabiliser is a polyethylene glycol ether.

3. A dispersion according to Claim 2 in which the stabiliser is a polyethylene glycol ether of oleyl alcohol.

4. A method of making a dispersion of rubber in a hydrated sulphuric acid medium which comprises adding an aqueous acid to a rubber latex containing a non-ionic stabiliser to bring the pH value to less than 5, and adding concentrated sulphuric acid or oleum to the acidified latex to bring the sulphuric acid content of the medium to between 60% and 90%.

5. A method of cyclising rubber which comprises adding an aqueous acid to a rubber latex containing a non-ionic stabiliser to bring the pH 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

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acid medium containing at least 60% sulphuric acid and maintaining the dispersion at a suitable temperature until the desired degree of cyclisation has been effected.

6. A method according to Claim 5 in which the hydrated sulphuric acid medium contains between 70% and 75% sulphuric acid and the dispersion is maintained at a temperature between 80°C. and 120°C. until the desired degree of cyclisation has been effected.

7. A method according to Claim 5 or Claim 6 in which a phenol is added to the acid dispersion before cyclisation is effected.

8. A method of oxidising rubber which comprises adding an aqueous acid to a rubber latex containing a non-ionic stabiliser to bring the pH 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 between 60% and 90% sulphuric acid, dissolving a per-compound in the dispersion and permitting the oxidation reaction to proceed at atmospheric temperatures.

9. A method according to Claim 8 in which the per-compound is hydrogen peroxide, persulphuric acid or a persulphate.

10. A method according to any of Claims 4 to 9 in which the non-ionic stabiliser is a polyethylene glycol ether.

11. A method according to Claim 10 in which the stabiliser is a polyethylene glycol ether of oleyl alcohol.

12. A method according to any of Claims 4 to 11 in which the rubber latex contains the non-ionic stabiliser in an amount of from 2 to 5 parts by weight per 100 parts of rubber.

13. A method according to any of Claims 4 to 12 in which the aqueous acid added to the rubber latex is aqueous sulphuric acid containing less than 80% sulphuric acid.

14. A method according to any of Claims 4 to 13 in which the rubber latex is an unvulcanised natural rubber latex.

15. A method of making a dispersion of rubber in a hydrated sulphuric acid medium substantially as hereinbefore described with reference to example 1 or 3.

16. A method of oxidising rubber substantially as hereinbefore described with reference to example 4.

17. A method of cyclising rubber substantially as hereinbefore described with reference to example 2.

Dated this 11th day of August, 1948.

R. F. McKAY,
Acting for the Applicants.

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