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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Treatment of Natural Rubber Latex.

We, THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, a British Body Corporate, of 19 Buckingham Street, Adelphi, London, W.C.2, 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 is for improvements in or relating to the treatment of natural rubber latex and has for an object to provide a process whereby natural rubber latex concentrates may be treated so as to improve their freeze-thaw stability.

It is well-known that concentrated natural rubber latices are liable to gel if subjected to temperatures varying above and below freezing and such gelation is an indication of a low freeze-thaw stability. This is an important matter in connection with the storage and transportation of latex concentrates. Although a variety of other aqueous emulsions have been the subject of much investigation and emulsion paints, bitumen emulsions and synthetic rubber latices have been treated with a variety of additives in order to improve their freeze-thaw stability, the only known reference to this problem in relation to natural rubber latices is a suggestion that high molecular weight colloidal substances, such as casein and styrene/maleic anhydride copolymers have been found to provide some improvement.

There are broadly three ways in which natural rubber latex concentrates are prepared, namely by centrifuging, by creaming or by evaporation with the aid of heat. These concentrates are ordinarily prepared on or near the rubber plantations by the treatment of the field latex. The most com-

mon method is the centrifuging treatment which gives concentrates having a dry rubber content of approximately 60% by weight, but appreciable amounts of concentrate are also prepared by the addition of a creaming agent, such as ammonium alginate, this treatment usually producing products having a dry rubber content of approximately 66%. The third general method produces concentrates, sold under the Registered Trade Mark "Revertex", having either a dry rubber content of about 60%, in which case ammonia is the preserving alkali, or a dry rubber content of about 67% when potassium hydroxide is the preserving agent.

It is, of course, well known to add a variety of substances such as preservatives (to prevent the development of the bacterial population), stabilising agents, such as ammonium laurate, and the purpose of these additives is to preserve the latex against deterioration by bacterial action and to preserve the mechanical stability of the latices, i.e. stabilise them against the coagulating effect of rapid stirring.

We have now found that the freeze-thaw stability of ammonia-preserved natural rubber latex concentrates can be improved by the addition of special combinations of additives, which combinations are hereinafter described.

According to the present invention, therefore, there is provided a stabilised natural rubber latex concentrate which may be produced by centrifuging, creaming or evaporation, which concentrate contains from 0.2 to 0.8% by weight of ammonia, from 0.02 to 0.2% by weight of a fatty acid soap and from 0.1 to 2.0% by weight of an inorganic sodium or potassium salt and/or from 0.02 to 0.3% by weight of a mono-or poly-

[Price 4s. 6d.]

chloro-phenol or of a nuclear alkyl substitution derivative thereof. The said chloro-phenols may be used as such or in the form of the sodium, potassium or ammonium salts thereof.

The preferred inorganic sodium or potassium salts are derived from mono-basic acids, preferably hydrochloric acid or nitric acid, whilst the fatty acid soaps are preferably those based on fatty acids containing from 8 to 18 carbon atoms in the molecule. Amongst the soaps which are preferred in the practice of the present invention, we wish to mention ammonium laurate, ammonium oleate, potassium or sodium oleates and potassium ricinoleate.

With regard to the amount of salt employed, we do not use more than the stated maximum amount of 2% because we have found that, above this amount, the viscosity of the latex concentrate tends to increase even when the latex is held at room temperature.

With regard to the chloro-phenol compounds, some of which have already been proposed for use in rubber latices as preservatives, we may use any of the simple chlorinated phenols containing from 1 to 5 chlorine atoms as well as the chlorine derivatives of the alkyl phenols, such as cresol and xlenol.

The invention, of course, includes a process for the production of natural rubber latex concentrates having an improved freeze-thaw stability which comprises adding to an ammonia-stabilized latex concentrate the above-stated amount of fatty acid soap and the sodium or potassium salt and/or chloro-phenol as described above.

As a test giving an indication of the freeze-thaw stability of a latex concentrate, we find that the ratio of its viscosity after freezing to its viscosity prior to freezing provides a measure of the freeze-thaw stability of the latex, provided that it has not actually gelled. Under fixed conditions, therefore, of freezing and thawing, we find that the higher the viscosity ratio is found to be, then the lower is the freeze-thaw stability of the latex.

The following examples are given to illustrate the manner in which the invention may be carried into effect:

Example 1. 0.5 lb. of a 30% w/w solution of ammonia in water was added to 50 lb. of freshly tapped latex and the mixture allowed to stand for 24 hours. The bulk of the latex was then removed from the sludge which had sedimented and was centrifuged to give a concentrate of 62% dry rubber content. The ammonia content of the concentrate was then raised to 0.7% by absorption of gaseous ammonia. To 10 lb. of this concentrate was added 0.05 lb. of a 10% w/w solution of ammonium

laurate in water and 0.02 lb. of ortho-chloro-phenol dissolved in 0.08 lb. of 1% w/w sodium hydroxide solution. To a second 10 lb. of the concentrate was added 0.05 lb. of a 10% w/w solution of ammonium laurate in water and 0.02 lb. of 6-chloro-orthocresol dissolved in 0.08 lb. of a 1% w/w sodium hydroxide solution. To a third 10 lb. of the concentrate was added 0.13 lb. of water, as control. After storing $\frac{1}{2}$ lb. portions of the above three samples of concentrate at -26°C . for 30 hours, and then thawing at room temperature (25°C), the control sample had set irreversibly to form a latex gel but the samples containing ammonium laurate and ortho-chlorophenol or 6-chloro-orthocresol were still fluid.

Example 2. A concentrate of natural latex containing 61.5% rubber and 0.7% w/w of ammonia was prepared by centrifuging, as in Example 1. To 10 lb. of the concentrate was added 0.05 lb. of a 10% w/w solution of potassium oleate in water, followed by 0.05 lb. of sodium chloride dissolved in 0.15 lb. of water. To a second 10 lb. sample of the concentrate was added 0.2 lb. of water, as control. After storing $\frac{1}{2}$ lb. portions of these samples at -26°C . for 36 hours and then thawing at room temperature (25°C), it was found that the control sample had gelled irreversibly whereas the sample containing potassium oleate and sodium chloride was still fluid.

Example 3. A concentrate of natural latex having 62% dry rubber content was prepared by centrifuging as described in Example 1, but the ammonia content of the concentrate was then adjusted to 0.2% w/w, instead of 0.7% w/w, by absorption of gaseous ammonia. To 10 lb. of this concentrate was added 0.16 lb. of a 12.5% w/w solution of sodium pentachlorophenate in water and 0.03 lb. of a 16% w/w solution of ammonium laurate in water followed by the addition of 0.05 lb. of sodium nitrate dissolved in 0.06 lb. of water. To another 10 lb. sample of the concentrate was added 0.16 lb. of a 12.5% w/w solution of sodium pentachlorophenate in water and 0.09 lb. of water, as a control. After storing $\frac{1}{2}$ lb. portions of these samples at -26°C . for 100 hours and then thawing at room temperature (25°C), the control sample was found to be gelled irreversibly whereas the sample containing ammonium laurate and sodium nitrate in addition to sodium pentachlorophenate was still fluid.

Example 4. A concentrate of natural latex containing 62% rubber was prepared by centrifuging as in Example 1 but the ammonia content of the concentrate was then adjusted to 0.24% w/w by absorption of gaseous ammonia. To 10 lb. of this concentrate was added 0.1 lb. of a 20% w/w solution of boric acid in aqueous ammonia

(5% w/w), 0.08 lb. of a 10% w/w solution of ammonium laurate in water and 0.02 lb. of orthochlorophenol dissolved in 0.08 lb. of a 1% w/w sodium hydroxide solution. To another 10 lb. sample of the concentrate was added the same amounts of the boric acid solution and of the ammonium laurate solution as in the first sample, but in place of the ortho-chlorophenol solution 0.08 lb. of a 1% w/w sodium hydroxide solution was added. This second sample served as a control. After storing $\frac{1}{2}$ lb. portions of the samples at -26°C . for 65 hours and then thawing at room temperature (25°C .), the control sample had gelled irreversibly but no gelation had occurred in the sample containing ortho-chlorophenol.

Example 5. A concentrate of natural latex containing 62% rubber and 0.2% w/w ammonia was prepared by centrifuging, as in Example 3. To 10 lb. of this concentrate was added 0.025 lb. of a 40% w/w dispersion of zinc diethyldithiocarbamate in water, 0.08 lb. of a 10% w/w solution of ammonium laurate in water, and 0.02 lb. of 6-chloro-orthocresol dissolved in 0.08 lb. of a 1% w/w sodium hydroxide solution. To another 10 lb. sample of the concentrate was added the same amounts of the zinc diethyldithiocarbamate dispersion and of the ammonium laurate solution as in the first sample, but in place of the 6-chloro-orthocresol solution 0.08 lb. of 1% w/w sodium hydroxide solution was added. This sample served as control. After storing $\frac{1}{2}$ lb. portions of these samples at -26°C . for 36 hours and then thawing at room temperature (25°C .), the control sample had gelled irreversibly but the sample containing 6-chloro-orthocresol was still fluid.

Example 6. To 10 lb. of a commercial concentrate of natural latex which had been produced by creaming with ammonium alginate to give a concentrate of 66% dry rubber content was added 0.05 lb. of a 10% w/w solution of ammonium laurate in water and 0.05 lb. of sodium chloride dissolved in 0.15 lb. of water. To a second 10 lb. sample of the concentrate was added 0.2 lb. of water, as control. After storing $\frac{1}{2}$ lb. portions of the samples at -26°C . for 30 hours and then thawing at room temperature (25°C .), it was found that the control sample had gelled irreversibly whereas in the sample containing ammonium laurate and sodium chloride no gelation had occurred.

It will be understood that the details given in the foregoing Examples are not to be construed as limiting the present invention to the details thereof and that the invention is to be construed as covering ammonia-stabilised latex concentrates containing the specified soaps, salts and/or chlorophenols as hereinbefore described. It is pos-

sible to add the inorganic sodium or potassium salts to the latex before concentration thereof, the quantities added being such that the above-defined desired amounts remain in the concentrated latex; the fact that some of the added salt is lost in the skim is not of great significance since the cost of the salts is low and the loss may be compensated for by the fact that there may be a lesser risk of flocculation on addition of the salt to a latex containing about 30% of dry rubber as compared with the risk of flocculation of concentrated latices containing 60% or more of dry rubber.

WHAT WE CLAIM IS:—

1. A stabilised natural rubber latex concentrate containing from 0.2 to 0.8% by weight of ammonia, from 0.02 to 0.2% by weight of a fatty acid soap and from 0.1 to 2.0% by weight of an inorganic sodium or potassium salt and/or from 0.02 to 0.3% by weight of a mono—or poly-chlorophenol or of a nuclear alkyl substitution derivative thereof.
2. A latex concentrate according to claim 1 wherein the said chloro-phenol is present in the form of a sodium, potassium or ammonium salt thereof.
3. A latex concentrate according to claim 1 or claim 2 wherein the inorganic sodium or potassium salt is derived from a mono-basic inorganic acid.
4. A latex concentrate according to any preceding claim wherein the said soap is derived from a fatty acid containing from 8 to 18 carbon atoms in its molecule.
5. A latex concentrate according to any preceding claim wherein the soap is a sodium, potassium or ammonium soap.
6. A process for the production of a stabilised natural rubber latex concentrate which comprises adding to an ammonia-stabilised latex concentrate containing 0.2 to 0.8% by weight of ammonia, an amount of a fatty acid soap of from 0.02 to 0.2% by weight thereof and of from 0.1 to 2.0% by weight of an inorganic sodium or potassium salt and/or from 0.02 to 0.3% by weight of a mono—or poly-chloro-phenol or of a nuclear alkyl substitution derivative thereof.
7. A process of the production of a stabilised natural rubber latex concentrate which comprises adding an inorganic sodium or potassium salt to an ammoniated latex, and concentrating said latex to a dry rubber content of about 60 to 66% by weight by centrifuging, creaming or evaporating it, the amounts of ammonia and inorganic salt used being such that the final latex concentrate contains 0.2 to 0.8% by weight of ammonia, and 0.1 to 2.0% by weight of said salt, a fatty acid soap being added to the latex before or after concentration in an

(5% w/w), 0.08 lb. of a 10% w/w solution of ammonium laurate in water and 0.02 lb. of orthochlorophenol dissolved in 0.08 lb. of a 1% w/w sodium hydroxide solution. To another 10 lb. sample of the concentrate was added the same amounts of the boric acid solution and of the ammonium laurate solution as in the first sample, but in place of the ortho-chlorophenol solution 0.08 lb. of a 1% w/w sodium hydroxide solution was added. This second sample served as a control. After storing $\frac{1}{2}$ lb. portions of the samples at -26°C . for 65 hours and then thawing at room temperature (25°C .), the control sample had gelled irreversibly but no gelation had occurred in the sample containing ortho-chlorophenol.

Example 5. A concentrate of natural latex containing 62% rubber and 0.2% w/w ammonia was prepared by centrifuging, as in Example 3. To 10 lb. of this concentrate was added 0.025 lb. of a 40% w/w dispersion of zinc diethyldithiocarbamate in water, 0.08 lb. of a 10% w/w solution of ammonium laurate in water, and 0.02 lb. of 6-chloro-orthocresol dissolved in 0.08 lb. of a 1% w/w sodium hydroxide solution. To another 10 lb. sample of the concentrate was added the same amounts of the zinc diethyldithiocarbamate dispersion and of the ammonium laurate solution as in the first sample, but in place of the 6-chloro-orthocresol solution 0.08 lb. of 1% w/w sodium hydroxide solution was added. This sample served as control. After storing $\frac{1}{2}$ lb. portions of these samples at -26°C . for 36 hours and then thawing at room temperature (25°C .) the control sample had gelled irreversibly but the sample containing 6-chloro-orthocresol was still fluid.

Example 6. To 10 lb. of a commercial concentrate of natural latex which had been produced by creaming with ammonium alginate to give a concentrate of 66% dry rubber content was added 0.05 lb. of a 10% w/w solution of ammonium laurate in water and 0.05 lb. of sodium chloride dissolved in 0.15 lb. of water. To a second 10 lb. sample of the concentrate was added 0.2 lb. of water, as control. After storing $\frac{1}{2}$ lb. portions of the samples at -26°C . for 30 hours and then thawing at room temperature (25°C .) it was found that the control sample had gelled irreversibly whereas in the sample containing ammonium laurate and sodium chloride no gelation had occurred.

It will be understood that the details given in the foregoing Examples are not to be construed as limiting the present invention to the details thereof and that the invention is to be construed as covering ammonia-stabilised latex concentrates containing the specified soaps, salts and/or chlorophenols as hereinbefore described. It is pos-

sible to add the inorganic sodium or potassium salts to the latex before concentration thereof, the quantities added being such that the above-defined desired amounts remain in the concentrated latex; the fact that some of the added salt is lost in the skim is not of great significance since the cost of the salts is low and the loss may be compensated for by the fact that there may be a lesser risk of flocculation on addition of the salt to a latex containing about 30% of dry rubber as compared with the risk of flocculation of concentrated latices containing 60% or more of dry rubber.

WHAT WE CLAIM IS:—

1. A stabilised natural rubber latex concentrate containing from 0.2 to 0.8% by weight of ammonia, from 0.02 to 0.2% by weight of a fatty acid soap and from 0.1 to 2.0% by weight of an inorganic sodium or potassium salt and/or from 0.02 to 0.3% by weight of a mono- or poly-chlorophenol or of a nuclear alkyl substitution derivative thereof.

2. A latex concentrate according to claim 1 wherein the said chloro-phenol is present in the form of a sodium, potassium or ammonium salt thereof.

3. A latex concentrate according to claim 1 or claim 2 wherein the inorganic sodium or potassium salt is derived from a mono-basic inorganic acid.

4. A latex concentrate according to any preceding claim wherein the said soap is derived from a fatty acid containing from 8 to 18 carbon atoms in its molecule.

5. A latex concentrate according to any preceding claim wherein the soap is a sodium, potassium or ammonium soap.

6. A process for the production of a stabilised natural rubber latex concentrate which comprises adding to an ammonia-stabilised latex concentrate containing 0.2 to 0.8% by weight of ammonia, an amount of a fatty acid soap of from 0.02 to 0.2% by weight thereof and of from 0.1 to 2.0% by weight of an inorganic sodium or potassium salt and/or from 0.02 to 0.3% by weight of a mono- or poly-chloro-phenol or of a nuclear alkyl substitution derivative thereof.

7. A process of the production of a stabilised natural rubber latex concentrate which comprises adding an inorganic sodium or potassium salt to an ammoniated latex, and concentrating said latex to a dry rubber content of about 60 to 66% by weight by centrifuging, creaming or evaporating it, the amounts of ammonia and inorganic salt used being such that the final latex concentrate contains 0.2 to 0.8% by weight of ammonia, and 0.1 to 2.0% by weight of said salt, a fatty acid soap being added to the latex before or after concentration in an



amount such that the concentrate contains 0.02 to 0.2% by weight thereof.

5 8. A process according to claim 7 wherein a mono— or poly-chloro-phenol or a nuclear alkyl substitution derivative thereof is added before or after concentration in an amount such that the concentrate contains 0.02 to 0.3% by weight thereof.

10 9. A process according to any of claims 6 to 8 wherein the soap is derived from a fatty acid containing from 8 to 18 carbon atoms in its molecule.

15 10. A process according to any of claims 6 to 9 wherein the inorganic salt is derived from a mono-basic acid.

11. A process according to any of claims 6 and 8 to 10 wherein the said chlorophenol is used in the form of the sodium, potassium or ammonium salt thereof.

12. The process for the production of a 20 stabilised ammoniated natural rubber latex concentrate containing a soap, an inorganic salt and/or a chloro-phenol substantially as described in any of Examples 1 to 6.

13. Stabilised latex concentrates when 25 prepared by the process claimed in any of claims 6 to 12.

14. Stabilised ammoniated natural rubber latex concentrates containing a soap, an inorganic salt and/or a chlorophenol substantially as described in any of Examples 1 to 6. 30

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