

PATENT SPECIFICATION

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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Improvements in or relating to the Treatment of 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 or synthetic rubber latex and has for an object to provide a process whereby natural rubber latex concentrates and synthetic rubber latices 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 the rubber plantations by the treatment of the

field latex. The most common 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 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 natural rubber latex and of the synthetic rubber latices can be improved by the use of salts of salicylic acid which may be used in combination with other additives which will provide for a satisfactory mechanical stability of the latex.

According to the present invention, therefore, there is provided a natural rubber latex (which may be a concentrate produced by centrifuging, creaming or evaporation) containing from 0.2 to 0.8% by weight of ammonia, or a stabilised latex of a synthetic cis-polyisoprene, which contains as a freeze-

[Price 4s. 6d.]

thaw stabiliser a small amount of a salt of salicylic acid, preferably in an amount of from 0.05 to 0.5% by weight. The natural latex may optionally contain small amounts of a surface-active agent and, if desired, of additional preservatives for the latex. The amounts of surface-active agents which can be employed would ordinarily be less than 0.2% by weight.

Amongst the preservatives for the natural latex which may be employed in addition to ammonia are the sodium or ammonium pentachlorophenates, boric acid and zinc diethyldithiocarbamate.

Referring to the surface-active agents, these are preferably fatty acid soaps based on fatty acids containing from 8 to 18 carbon atoms in the molecule. Amongst these 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.

The invention is to be understood as including a process for producing the stabilised latices having an improved freeze-thaw stability as mentioned above which comprises adding to an ammonia-preserved natural latex or a concentrate thereof or to a synthetic ~~air~~-polyisoprene rubber latex, a salicylate with or without the above indicated amount of fatty acid soaps and with or without additional preservatives.

At 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

To 50 lb. of freshly tapped latex was added 0.5 lb. of a 30% w/w solution of ammonia in water. Having allowed the mixture to stand for 24 hours, the bulk of the latex was removed from the sedimented sludge 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. 0.05 lb. of a 10% w/w aqueous solution of ammonium laurate was then added to 10 lb. of this concentrate followed by 0.05 lb. of a 40% w/w aqueous solution of sodium salicylate, prepared either by dissolving sodium salicylate in water or by adding 1 part by weight of free salicylic acid to 2 parts of a 15% w/w sodium hydroxide

solution. To a further 10 lb. of concentrate was added 0.08 lb. of water as control.

After storing $\frac{1}{2}$ lb. portions of the above samples at -15°C . for 10 days and then thawing at room temperature (25°C .), the control sample had set irreversibly to form a gel but the other sample, containing ammonium laurate and sodium salicylate, was still fluid. Similarly, after 4 days storage at -26°C . a control sample was found, after thawing at 25°C . to have set to a gel, whereas a sample of the treated latex was still fluid.

EXAMPLE 2

A natural latex concentrate with 62% dry rubber content was prepared as described in Example 1, except that the ammonia level was adjusted to only 0.2% w/w. 0.4 lb. of a 10% solution of sodium pentachlorophenate (a secondary preservative) was then added to 20 lb. of the concentrate. To 10 lb. of this concentrate containing sodium pentachlorophenate was added 0.02 lb. of salicylic acid dissolved in 0.05 lb. of 16% w/w potassium hydroxide solution. A further 10 lb. sample was treated with 0.05 lb. of water as control.

$\frac{1}{2}$ lb. portions of the above samples were stored at -26°C . for 3 days and then thawed at 25°C . It was found that the control sample had set irreversibly to a gel, while the sample containing potassium salicylate was still fluid.

EXAMPLE 3

Freshly tapped latex was treated to give a concentrate of 62% dry rubber content as described in Example 1, but the ammonia level 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 aqueous solution of ammonium laurate and 0.015 lb. of salicylic acid, dissolved in 0.04 lb. of 5% w/w aqueous ammonia. To another 10 lb. of the concentrate was added 0.1 lb. of a 20% w/w solution of boric acid in aqueous ammonia (5% w/w), 0.05 lb. of a 10% w/w ammonium laurate solution and 0.07 lb. of water. This latex served as control.

Freezing of $\frac{1}{2}$ lb. portions of the control sample for 1 week at -15°C . or 4 days at -26°C . followed by thawing at 25°C . led to complete gelation of the latex, whereas $\frac{1}{2}$ lb. portions of the sample containing ammonium salicylate were still fluid after the same freezing and thawing treatment.

EXAMPLE 4

To 10 lb. of a commercial natural latex concentrate, which had been produced by creaming with ammonium alginate to give a concentrate of 66% dry rubber content, was



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added 0.05 lb. of a 10% w/w solution of ammonium laurate and 0.05 lb. of a 40% w/w aqueous solution of sodium salicylate. A further 10 lb. of the concentrate was treated with 0.08 lb. of water to give a control sample.

When $\frac{1}{2}$ lb. portions of the concentrate were frozen for either 4 days at -15°C . or 2 days at -26°C . and then allowed to thaw at 25°C ., it was found that the control samples had gelled irreversibly but the samples with ammonium laurate and sodium salicylate were still fluid.

EXAMPLE 5

To 10 lb. of a synthetic cis-polyisoprene latex (sold under the Registered Trade Mark "Cariflex" IR 700) was added 0.1 lb. of a 10% w/w aqueous potassium laurate solution and 0.03 lb. of salicylic acid dissolved in 0.08 lb. of a 16% w/w aqueous solution of potassium hydroxide. To a second 10 lb. sample of the synthetic latex was added 0.15 lb. of water; this sample served as a control.

After storing $\frac{1}{2}$ lb. portions at -26°C . for 12 hours and then thawing at 25°C . the sample with potassium laurate and potassium salicylate was still fluid, whereas the control sample had set irreversibly to form a very firm gel.

The salts of salicylic acid can be made *in situ* by the addition of the salicylic acid to a suitable alkaline solution or they can be made previously and added as such in solution in water. It is preferred to employ those salts of salicylic acid whose solubility in water is greater than 5% by weight at room temperature as thereby the addition of undesirable amounts of water to a latex concentrate can be avoided.

Amongst the specific salicylates which we use we would mention the sodium, potassium and ammonium salts as examples of inorganic salicylates and triethanolamine salicylate as an example of a suitable organic salt of salicylic acid.

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. It is possible to add the various additives to the latex before concentration thereof, the quantities being such that the above-defined desired amounts remain in the concentrated latex; the fact that some of the additive is lost in the skim is not of great significance since their cost is low and the loss may be compensated for by the fact that there may be a reduction in the risk of flocculation on addition 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.

It is also to be understood that the procedures of the Examples may be applied to normal unconcentrated ammonia-preserved natural rubber latices without any significant departure from the details thereof.

WHAT WE CLAIM IS:—

1. A latex which comprises a natural rubber latex containing from 0.2 to 0.8% by weight of ammonia or which is a stabilised latex of a synthetic cis-polyisoprene and which contains a small amount of a salt of salicylic acid acting as a freeze-thaw stabiliser.
2. A latex according to claim 1 wherein the salt of salicylic acid is present in an amount between 0.05% to 0.5% by weight of the latex.
3. A natural rubber latex according to claim 1 or claim 2 containing a surface-active agent.
4. A natural rubber latex according to claim 3 wherein the amount of the surface-active agent is less than 0.2% by weight thereof.
5. A natural rubber latex according to claim 3 or claim 4 wherein the surface-active agent is a sodium, potassium or ammonium salt of a long chain fatty acid.
6. A natural rubber latex according to claim 5 wherein the long chain fatty acid radical in the surface-active agent contains from 8 to 18 carbon atoms.
7. A natural rubber latex according to any of claims 3 to 6 wherein an additional preservative comprising sodium or ammonium penta-chlorophenate, boric acid or zinc diethyldithiocarbamate is incorporated therein.
8. A latex according to any of the preceding claims wherein the salicylate salt has a water-solubility greater than 5% by weight at room temperature.
9. A latex according to any of the preceding claims wherein a sodium, potassium or ammonium salt of salicylic acid is employed.
10. A latex according to any of claims 1 to 8 wherein triethanolamine salicylate is employed as the salt of salicylic acid.
11. A latex according to any of the preceding claims wherein the natural rubber latex is a concentrate.
12. A process for the production of a latex having an improved freeze-thaw stability which comprises adding a salt of salicylic acid to a natural rubber latex containing 0.2% to 0.8% by weight of ammonia or a stabilised latex of a synthetic cis-polyisoprene.
13. A process according to claim 12 wherein said salt is added in an amount of from 0.05% to 0.5% by weight of a



dissolved



chlorophenate

added 0.05 lb. of a 10% w/w solution of ammonium laurate and 0.05 lb. of a 40% w/w aqueous solution of sodium salicylate. A further 10 lb. of the concentrate was treated with 0.08 lb. of water to give a control sample.

When $\frac{1}{2}$ lb. portions of the concentrate were frozen for either 4 days at -15°C . or 2 days at -26°C . and then allowed to thaw at 25°C ., it was found that the control samples had gelled irreversibly but the samples with ammonium laurate and sodium salicylate were still fluid.

EXAMPLE 5

To 10 lb. of a synthetic cis-polyisoprene latex (sold under the Registered Trade Mark "Cariflex" IR 700) was added 0.1 lb. of a 10% w/w aqueous potassium laurate solution and 0.03 lb. of salicylic acid dissolved in 0.08 lb. of a 16% w/w aqueous solution of potassium hydroxide. To a second 10 lb. sample of the synthetic latex was added 0.15 lb. of water; this sample served as a control.

After storing $\frac{1}{2}$ lb. portions at -26°C . for 12 hours and then thawing at 25°C . the sample with potassium laurate and potassium salicylate was still fluid, whereas the control sample had set irreversibly to form a very firm gel.

The salts of salicylic acid can be made *in situ* by the addition of the salicylic acid to a suitable alkaline solution or they can be made previously and added as such in solution in water. It is preferred to employ those salts of salicylic acid whose solubility in water is greater than 5% by weight at room temperature as thereby the addition of undesirable amounts of water to a latex concentrate can be avoided.

Amongst the specific salicylates which we use we would mention the sodium, potassium and ammonium salts as examples of inorganic salicylates and triethanolamine salicylate as an example of a suitable organic salt of salicylic acid.

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. It is possible to add the various additives to the latex before concentration thereof, the quantities being such that the above-defined desired amounts remain in the concentrated latex; the fact that some of the additive is lost in the skim is not of great significance since their cost is low and the loss may be compensated for by the fact that there may be a reduction in the risk of flocculation on addition 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.

It is also to be understood that the procedures of the Examples may be applied to normal unconcentrated ammonia-preserved natural rubber latices without any significant departure from the details thereof.

WHAT WE CLAIM IS:—

1. A latex which comprises a natural rubber latex containing from 0.2 to 0.8% by weight of ammonia or which is a stabilised latex of a synthetic cis-polyisoprene and which contains a small amount of a salt of salicylic acid acting as a freeze-thaw stabiliser.

2. A latex according to claim 1 wherein the salt of salicylic acid is present in an amount between 0.05% to 0.5% by weight of the latex.

3. A natural rubber latex according to claim 1 or claim 2 containing a surface-active agent.

4. A natural rubber latex according to claim 3 wherein the amount of the surface-active agent is less than 0.2% by weight thereof.

5. A natural rubber latex according to claim 3 or claim 4 wherein the surface-active agent is a sodium, potassium or ammonium salt of a long chain fatty acid.

6. A natural rubber latex according to claim 5 wherein the long chain fatty acid radical in the surface-active agent contains from 8 to 18 carbon atoms.

7. A natural rubber latex according to any of claims 3 to 6 wherein an additional preservative comprising sodium or ammonium penta-chlorophenate, boric acid or zinc diethyldithiocarbamate is incorporated therein.

8. A latex according to any of the preceding claims wherein the salicylate salt has a water-solubility greater than 5% by weight at room temperature.

9. A latex according to any of the preceding claims wherein a sodium, potassium or ammonium salt of salicylic acid is employed.

10. A latex according to any of claims 1 to 8 wherein triethanolamine salicylate is employed as the salt of salicylic acid.

11. A latex according to any of the preceding claims wherein the natural rubber latex is a concentrate.

12. A process for the production of a latex having an improved freeze-thaw stability which comprises adding a salt of salicylic acid to a natural rubber latex containing 0.2% to 0.8% by weight of ammonia or a stabilised latex of a synthetic cis-polyisoprene.

13. A process according to claim 12 wherein said salt is added in an amount of from 0.05% to 0.5% by weight of a



natural rubber latex prior to concentration thereof.

stability substantially as described in any of the Examples.

14. The process for the production of a latex having improved freeze-thaw stability substantially as described in any of the Examples.

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15. Latices having improved freeze-thaw

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