PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Stabilising Natural Rubber Latex

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 1, Albany Street, London, N.W.1, 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 methods of stabilising natural rubber latex and to stabilised aqueous dispersions so obtained

It is known that natural rubber letex, whether or not it has been concentrated, contains small amounts of protein and that on storage of untreated latex the protein tends to decompose through bacterial or fungal action and renders the latex unstable, i.e. causes coagulation of the rubber. It is known to improve the stability of the latex by adding to it ammonia, or ammonia and a bactericidal agent, for example pentachlorophenol or its sodium salt. However, these compounds are soluble in the serum of the latex so that if they are added to a latex which is subsequently concentrated by creaming or by centrifugal action, they become separated from the rubber, and the concentrate has to be treated with further quantities of ammonia and bactericidal agent. When these bactericidal agents are present less ammonia is needed than if ammonia alone is used, but is has not been found possible to avoid the use of ammonia altogether, presumably because enzymatic decomposition of the protein occurs which the bactericidal agents are not effective in preventing. For some purposes, however, it is desirable to avoid the use of ammonia as a preservative for latex, since it affects the non-rubber constituents of the latex.

It is an object of the invention to improve the stability of natural rubber latex against decomposition and coagulation without the use of ammonia.

According to the present invention a method of stabilising natural rubber latex comprises incorporating with it a salt of a dicarboxylic acid in which one carboxylic acid radical is neutralised by a basic radical of a microbicidal quaternary ammonium compound having a phenol coefficient (as determined by the Rideal-Walker test) greater than 100 and the other is unneutralised or is neutralised by a metal or by a substituted or unsubstituted ammonium radical.

Salts of the above type which are suitable for use in the process of the present invention are further described and claimed in copending Application No. 7858/49 (Serial No. 685,614). Examples of such salts are the divalent and trivalent metal salts having the formula

$$(QOOC.C_6H_4.COO)_nM$$

where the groups QOOC and COO are in the ortho position in the benzene ring, M is the metal of valence n, n being 2 or 3, and Q is the radical of a microbicidal quaternary ammonium compound having a phenol coefficient greater than 100. Suitable quaternary ammonium radicals are of the type

$$R_1R_2R_3R_4N\text{-}$$

where R_1 is an alkyl radical containing 10 to 20 carbon atoms,

R_2 is an aryl or an alkyl radical, and

R_3 and R_4 are alkyl radicals

or where R_1 is a radical containing a terminal alkyl-substituted aryl radical and at least two alkylene radicals linked by ether linkages,

R_2 is an alkyl radical, and

R_3 and R_4 are alkyl radicals

or the radicals may be pyridinium radicals containing a N-alkyl group having at least 10 carbon atoms. Specific examples of these radicals are the *p*-tertiary-octylphenoxyethoxyethyl dimethyl benzyl ammonium radical the bromide of which has a phenol coefficient of 223, the diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium radical, the dodecyl trimethyl ammonium radical, the hexa-

decyl trimethyl ammonium radical or the hexadecyl pyridinium radical, the chloride of which has a phenol coefficient of 350. The alkyl dimethyl benzyl ammonium chloride have phenol coefficients of from 150 to 362. Particularly suitable as stabilisers are the aluminium, mercuric, iron and cadmium salts of the above structural formula, Q being one of the radicals specifically mentioned above. Salts which are specially useful for stabilising a latex which is to be concentrated subsequently by creaming or centrifuging, are salts which will not separate from the rubber in the concentration process owing to their low solubility in water, i.e. a solubility in water at 25° C. of less than 0.5 parts by weight for every 100 parts by weight of water. Examples of the salts with low solubility are the aluminium, mercuric, iron and aluminium salts specified above.

The latex may be stabilised by adding thereto a small proportion of the stabilising agent, for example, an amount of from 0.01% to 1% by weight of the latex. The stabilising agents confer upon the latex resistance to decomposition by bacterial, fungal and enzymatic action and thus enable the latex to be preserved for long periods of time without causing decomposition or coagulation of the latex. The compounds which have only very small solubility in water, for example the above-mentioned mercury, aluminium, iron and cadmium salts may be added to the latex as a dispersion in water containing a small amount of a suitable dispersing agent, e.g. casein.

In the examples given below emulsions of the stabilising agent were made up as follows:—

One part of the stabilising agent used was fused with one part by weight of benzyl benzoate, one part by weight of oleic acid was added, and while the mixture was kept at 95° C. a solution of one part by weight of casein and two parts by weight of ammonia (s.g. 0.880) in 17 parts by weight of water was stirred into this mixture. The resultant white emulsion was passed through an emulsifier and was then diluted with water until the emulsion contained one per cent of the mercuric compound.

In the examples below also, prior to addition of the stabiliser, concentrated ammonia-free natural rubber latex containing 60% by weight of rubber solids was treated by sterilizing the latex through heating for 30 minutes at 60° C. on 3 successive days. 0.02% by weight of catalase was added to the latex and then the latex was divided into three equal portions. This procedure was carried out for the purpose of obtaining reproduceable conditions for comparing the rate of decomposition of the portions so obtained.

The following examples illustrate the invention, all parts and percentages being by weight.

EXAMPLE 1

6.7 parts of hexadecyl trimethyl ammonium bromide was dissolved in 67 parts of water and a solution of 2.88 parts of disodium phthalate in 12.4 parts of water was added to the solution. After warming for one hour on a water bath a solution in water of 1.86 parts of mercuric chloride was added. The resultant mercuric salt of acid hexadecyl trimethyl ammonium phthalate was precipitated, filtered, washed and dried.

An emulsion prepared as above was made of the mercuric hexadecyl trimethyl ammonium phthalate and it was then added to one portion of the latex as treated above until the latex contained 0.1% of the mercuric compound. The latex stabilised in this way was kept in a closed container and no decomposition had taken place after 8 weeks.

EXAMPLE 2

An emulsion of the mercuric salt of acid *p*-tertiary-octylphenoxyethoxyethyl dimethyl benzyl ammonium phthalate was made up as above and added to the second portion of the latex treated as above until the latex contained 0.1% of the mercuric salt. The third portion of latex treated as above without the addition of a stabiliser and the latex containing the mercuric salt of acid *p*-tertiary-octylphenoxyethoxyethyl dimethyl benzyl ammonium phthalate were kept in closed containers and stored for several weeks at ordinary temperature. The portion containing no stabilising agent had decomposed with coagulation of the rubber in two weeks but the portion containing the stabilising agent was still stable and undecomposed after 8 weeks.

What we claim is:—

1. A method of stabilising natural rubber latex which comprises incorporating with it a salt of a dicarboxylic acid in which one carboxylic acid radical is neutralised by a basic radical of a microbicidal quaternary ammonium compound having a phenol coefficient (as determined by the Rideal-Walker test) greater than 100 and the other carboxylic acid radical is unneutralised or is neutralised by a metal or by a substituted or unsubstituted ammonium radical.

2. A method according to claim 1 in which the quaternary ammonium radical is a radical of the type

$$R_1R_2R_3R_4N.$$

decyl trimethyl ammonium radical or the hexadecyl pyridinium radical, the chloride of which has a phenol coefficient of 350. The alkyl dimethyl benzyl ammonium chloride have phenol coefficients of from 150 to 362. Particularly suitable as stabilisers are the aluminium, mercuric, iron and cadmium salts of the above structural formula, Q being one of the radicals specifically mentioned above. Salts which are specially useful for stabilising a latex which is to be concentrated subsequently by creaming or centrifuging, are salts which will not separate from the rubber in the concentration process owing to their low solubility in water, i.e. a solubility in water at 25° C. of less than 0.5 parts by weight for every 100 parts by weight of water. Examples of the salts with low solubility are the aluminium, mercuric, iron and aluminium salts specified above.

The latex may be stabilised by adding thereto a small proportion of the stabilising agent, for example, an amount of from 0.01% to 1% by weight of the latex. The stabilising agents confer upon the latex resistance to decomposition by bacterial, fungal and enzymatic action and thus enable the latex to be preserved for long periods of time without causing decomposition or coagulation of the latex. The compounds which have only very small solubility in water, for example the above-mentioned mercury, aluminium, iron and cadmium salts may be added to the latex as a dispersion in water containing a small amount of a suitable dispersing agent, e.g. casein.

In the examples given below emulsions of the stabilising agent were made up as follows:—

One part of the stabilising agent used was fused with one part by weight of benzyl benzoate, one part by weight of oleic acid was added, and while the mixture was kept at 95° C. a solution of one part by weight of casein and two parts by weight of ammonia (s.g. 0.880) in 17 parts by weight of water was stirred into this mixture. The resultant white emulsion was passed through an emulsifier and was then diluted with water until the emulsion contained one per cent of the mercuric compound.

In the examples below also, prior to addition of the stabiliser, concentrated ammonia-free natural rubber latex containing 60% by weight of rubber solids was treated by sterilizing the latex through heating for 30 minutes at 60° C. on 3 successive days. 0.02% by weight of catalase was added to the latex and then the latex was divided into three equal portions. This procedure was carried out for the purpose of obtaining reproduceable conditions for comparing the rate of decomposition of the portions so obtained.

The following examples illustrate the invention, all parts and percentages being by weight.

EXAMPLE 1

6.7 parts of hexadecyl trimethyl ammonium bromide was dissolved in 67 parts of water and a solution of 2.88 parts of disodium phthalate in 12.4 parts of water was added to the solution. After warming for one hour on a water bath a solution in water of 1.86 parts of mercuric chloride was added. The resultant mercuric salt of acid hexadecyl trimethyl ammonium phthalate was precipitated, filtered, washed and dried.

An emulsion prepared as above was made of the mercuric hexadecyl trimethyl ammonium phthalate and it was then added to one portion of the latex as treated above until the latex contained 0.1% of the mercuric compound. The latex stabilised in this way was kept in a closed container and no decomposition had taken place after 8 weeks.

EXAMPLE 2

An emulsion of the mercuric salt of acid *p*-tertiary-octylphenoxyethoxyethyl dimethyl benzyl ammonium phthalate was made up as above and added to the second portion of the latex treated as above until the latex contained 0.1% of the mercuric salt. The third portion of latex treated as above without the addition of a stabiliser and the latex containing the mercuric salt of acid *p*-tertiary-octylphenoxyethoxyethyl dimethyl benzyl ammonium phthalate were kept in closed containers and stored for several weeks at ordinary temperature. The portion containing no stabilising agent had decomposed with coagulation of the rubber in two weeks but the portion containing the stabilising agent was still stable and undecomposed after 8 weeks.

What we claim is:—

1. A method of stabilising natural rubber latex which comprises incorporating with it a salt of a dicarboxylic acid in which one carboxylic acid radical is neutralised by a basic radical of a microbicidal quaternary ammonium compound having a phenol coefficient (as determined by the Rideal-Walker test) greater than 100 and the other carboxylic acid radical is unneutralised or is neutralised by a metal or by a substituted or unsubstituted ammonium radical.

2. A method according to claim 1 in which the quaternary ammonium radical is a radical of the type

$$R_1R_2R_3R_4N.$$

* C L M S *

where R_1 is an alkyl radical containing from 10 to 20 carbon atoms,

R_2 is an aryl radical or an alkyl radical, and

R_3 and R_4 ar alkyl radicals.

3. A method according to claim 2 in which R_2, R_3 and R_4 are methyl radicals.

4. A method according to claim 2 or 3 in which R_1 is the hexadecyl radical.

5. A method according to claims 2 or 3 in which R_1 is the dodecyl radical.

6. A method according to claim 1 in which the quaternary ammonium radical is a radical of the type

$$R_1R_2R_3R_4N\text{-}$$

where R_1 is a radical containing a terminal alkyl-substituted aryl group and at least two alkylene radicals linked by ether linkage,

R_2 is an aralkyl radical, and

R_3 and R_4 are alkyl radicals.

7. A method according to claim 6 in which R_1 is the *p*-tertiary octylphenoxyethoxyethyl or the diisobutylphenoxyethoxyethyl radical, R_2 is the benzyl radical and R_3 and R_4 are methyl radicals.

8. A method according to claim 1 in which the ammonium radical is a pyridinium radical containing a N-alkyl group having at least 10 carbon atoms.

9. A method according to claim 8 in which the N-alkyl group is the hexadecyl radical.

10. A method according to any of the preceding claims in which the carboxylic acid is phthalic acid.

11. A method according to any of the preceding claims in which the salt of the dicarboxylic acid is present in an amount of from 0.01 to 1 part by weight for every 100 parts by weight of the rubber latex

12. A method according to any of the preceding claims in which the salt of the phthalic acid is the mercuric, cadmium, aluminium or iron salt

13. A method according to any of the preceding claims in which the salt of the dicarboxylic acid has a solubility in water at 25° C. of less than 0.5 parts by weight for every 100 parts by weight of water.

14. A method of stabilising natural rubber latex which comprises incorporating with it a salt of a dicarboxylic acid substantially as herein described and as illustrated by Example 1 or 2.

15. Stabilised natural rubber latex containing a salt of a dicarboxylic acid in which one carboxylic acid radical is neutralised by a basic radical of a microbicidal quaternary ammonium compound having a phenol coefficient (as determined by the Rideal-Walker test) greater than 100 and the other carboxylic acid radical is unneutralised or is neutralised by a metal or by a substituted or unsubstituted ammonium radical.

G. W. I. SHEAVYN,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Improvements in or relating to Stabilising Natural Rubber Latex

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 1, Albany Street, London, N.W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to a method of stabilising natural rubber latex.

It is known that natural rubber latex, whether or not it has been concentrated, contains small amounts of protein and that on storage of untreated latex the protein tends to decompose through bacterial or fungal action and renders the latex unstable, i.e. causes coagulation of the rubber. It is known to improve the stability of the latex by adding thereto ammonia, or ammonia and a bactericidal agent for example pentachlorophenol or its sodium salt. However, these compounds are soluble in the serum of the latex so that if they are added to a latex which is subsequently concentrated by creaming or by centrifugal action they become separated from the rubber, and the concentrate has to be treated with further quantities of ammonia and bactericidal agent. When these bactericidal agents are present less ammonia is needed than if ammonia alone is used, but it has not been found possible to avoid the use of ammonia altogether, presumably because enzymatic decomposition of the protein occurs which the bactericidal agents are not effective in preventing. For some purposes, however, it is desirable to avoid the use of ammonia as a preservative for latex, since it affects the non-rubber constituents of the latex.

We have now found that the stability of uncompounded natural rubber latex against decomposition and coagulation can be improved by incorporating with the latex a small proportion of a salt of a dicarboxylic acid in which one carboxylic acid radical is neutralised by a basic radical of a microbicidal quaternary ammonium compound and the other is unneutralised or is neutralised by a metal or by a substituted or unsubstituted ammonium radical. Preferably the salt is one which has a low solubility in water, particularly if the latex is to be concentrated subsequently by creaming or centrifugal action for the salts will not separ-

* C L M S *

ate from the rubber in the concentration process.

Salts of the above type which are suitable for use in the process of the present invention are further described and claimed in copending Application No. 7858/49. Examples of such salts are the divalent and trivalent metal salts having the formula

$$(QOOC.C_6H_4.COO)_nM$$

where the groups QOOC and COO are in the ortho position in the benzene ring, M is the metal of valence n, n being 2 or 3, and Q is a quaternary ammonium radical, which may be, for example a cetyl pyridinium radical, the di-isobutylphenoxyethyl dimethyl benzyl ammonium radical, or the dodecyltrimethyl ammonium radical. Preferred salts are the aluminium, mercuric, iron and cadmium salts, which have a solubility in water at 25° C. less than 0.5 gms per 100 gms of solution.

The latex may be stabilised by adding thereto a small proportian of the stabilising agent, for example, an amount between 0.01% and 1% by weight of the latex. The stabilising agents confer upon the latex resistance to decomposition by bacterial, fungal and enzymatic action and thus enable the latex to be preserved for long periods of time without causing any decomposition or coagulation of the latex. The compounds which have only very small solubility in water, for example the above-mentioned mercury, aluminium, iron and cadmium salts may be added to the latex as a dispersion in water containing a small amount of a suitable dispersing agent, e.g. casein.

The following example illustrates the invention.

EXAMPLE

A concentrated ammonia-free natural rubber latex containing 60% by weight of rubber was sterilised by heating for 30 minutes at 60° C. on three successive days. 0.02% of catalase was added to the letex and then the latex was divided into two equal portions, to one of which was added 0.1% by weight of the mercuric salt of acid di-isobutoxyphenoxyethoxyethyl dimethyl benzyl ammonium phthalate. The portion containing the stabilising agent and the remaining portion to which no stabilising agent had been added were kept in closed containers and stored for several weeks at ordinary temperature; the portion containing no added stabilising agent had decomposed with coagulation of the rubber in two weeks but the portion containing the stabilising agent was still stable and undecomposed after 8 weeks.

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