PATENT SPECIFICATION 692,150

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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 natural rubber latex so obtained.

It is known that natural rubber latex, whether or not it has been concentrated, contains small amounts of protein and that on storage of the 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. When the 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 batericidal agents are not effective is 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 during storage.

It has now been found that the stability of natural rubber latex against decomposition and coagulation can be improved by incorporating with the latex a small proportion of a diphenyl methane derivative as defined hereinafter.

According to the present invention a method of stabilising natural rubber latex comprises incorporating therewith an halogeno derivative of an hydroxydiphenyl methane or a metal salt of it.

Suitable halogeno derivatives of hydroxydiphenyl methanes are, for example, 2,2^1-dihydroxy - 5,5^1 - dichlorodiphenyl methane, 2,2^1 - dihydroxy - 3,5,3^1,5^1 - tetrachlorodiphenyl methane, 2,2^1-dihydroxy-5,5^1-dibromodiphenyl methane, or 2,2^1-dihydroxy-3,6,3^1,6^1 - tetrachloro - 5,5^1 - dibromodiphenyl methane. Salts of these compounds which may be used are the salts of di- and trivalent metals, e.g. zinc, magnesium, aluminium, barium, calcium or divalent mercury, or the salts of univalent metals, e.g. sodium or potassium.

Those halogeno derivatives of hydroxydiphenyl methane or metal salts of them having a small solubility in water, i.e. having a solubility in water at 25° C. of less than 0.20 parts by weight for every 100 parts by weight of water, are suitable for preserving latices which are to be concentrated subsequently, for these compounds will not separate from rubber in the concentration process. Examples of such compounds are 2,2^1 - dihydroxy - 5,5^1 - dichlorodiphenyl methane and its metal salts, for example the zinc, magnesium, aluminium, calcium, barium or mercuric salts. The production of such salts is described in Patent Specification No. 675,200. However, for preserving latices which are not to be concentrated or creamed subsequently other similar salts having a much greater solubility in water may be used, e.g. the sodium or potassium salt of an halogeno derivative of hydroxydiphenyl methane.

Natural rubber latex may be stabilised by adding to it a small proportion of the stabilising agent, preferably an amount of from 0.01% to 1% by weight of the latex. The stabilising agent confers upon the latex resistance to decomposition by bacterial, fungal and enzymatic action and thus enables the latex to be preserved for long periods of time without causing substantial decomposition or coagulation of the latex. The compounds which have only very small

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solubility in water, for example, 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane and the above-mentioned salts thereof, may be added to the latex as a dispersion in water containing a small amount of suitable dispersing agent, e.g. casein.

In the example given below emulsions of the diphenyl methane derivatives used were prepared as follows, all parts and percentages being by weight.

One part of 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane was fused with 1 part of benzyl benzoate and 0.1 part of oleic acid was added. The mixture was kept at 95° C. and 2 parts of a solution containing 1 part of casein, 2 parts of ammonia (s.g. 0.880) and 17 parts of water were stirred in. The resultant emulsion was passed through an emulsifier and then diluted with water until an emulsion containing 1% of the 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane resulted. A 1% emulsion of the mercuric salt of the last compound and a 1% emulsion of the aluminium salts of it were prepared in a similar way.

The following example illustrates the invention, all percentages and parts being by weight.

EXAMPLE.

A concentrated ammonia-free natural rubber latex containing 60% of rubber was sterilised by heating for 30 minutes at 60° C. on three successive days. 0.02% of catalase was added to the latex and then the latex was divided into four equal portions, to one of which was added 0.1% of 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane, to another 0.1% of the mercuric salt of this compound, and to another one 0.1% of the aluminium salt of this compound, using for the last three operations the emulsions as prepared above. The three portions containing stabilising agents 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 portions containing the stabilising agent were still stable and undecomposed after 8 weeks.

In the above example the latex was sterilised before addition of catalase and the catalase was added to establish reproducible conditions for comparing the rate of decomposition of the portions containing the different salts. It will be appreciated that preliminary sterilisation and/or addition of catalase do not form a part of the method of stabilising latex by the addition of the diphenyl methane compounds.

What we claim is:—

1. A method of stabilising natural rubber latex comprising incorporating therewith an halogeno derivative of an hydroxydiphenyl methane or a metal salt of said derivative.

2. A method of stabilising natural rubber latex comprising incorporating therewith an hydroxychlorodiphenyl methane or a metal salt thereof.

3. A method according to Claim 1 or 2, in which the diphenyl methane derivative is added in an amount of from 0.01% to 1.0% by weight of the rubber latex.

4. A method according to any of Claims 1 to 3, in which the metal salt of the diphenyl methane derivative is the zinc, magnesium, mercuric, aluminium, calcium or barium salt.

5. A method according to any of Claims 1 to 4, in which the metal salt of the diphenyl methane derivative has a solubility in water at 25° C. of less than 0.20 parts by weight for every 100 parts by weight of water.

6. A method according to any of Claims 1 to 3, in which the metal salt of the diphenyl methane derivative is the sodium or potassium salt.

7. A method according to any of the preceding claims, in which the diphenyl methane derivative is 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane.

8. A method of stabilising natural rubber latex comprising adding to it a small proportion of a diphenyl methane derivative as herein described and as illustrated by the example.

9. Stabilised natural rubber latex containing an halogeno derivative of an hydroxydiphenyl methane or a metal salt of said derivative.

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

PROVISIONAL SPECIFICATION.

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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

solubility in water, for example, 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane and the above-mentioned salts thereof, may be added to the latex as a dispersion in water containing a small amount of suitable dispersing agent, e.g. casein.

In the example given below emulsions of the diphenyl methane derivatives used were prepared as follows, all parts and percentages being by weight.

One part of 2,2¹-dihydroxy-5.5¹-dichlorodiphenyl methane was fused with 1 part of benzyl benzoate and 0.1 part of oleic acid was added. The mixture was kept at 95° C. and 2 parts of a solution containing 1 part of casein, 2 parts of ammonia (s.g. 0.880) and 17 parts of water were stirred in. The resultant emulsion was passed through an emulsifier and then diluted with water until an emulsion containing 1% of the 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane resulted. A 1% emulsion of the mercuric salt of the last compound and a 1% emulsion of the aluminium salts of it were prepared in a similar way.

The following example illustrates the invention, all percentages and parts being by weight.

EXAMPLE.

A concentrated ammonia-free natural rubber latex containing 60% of rubber was sterilised by heating for 30 minutes at 60° C. on three successive days. 0.02% of catalase was added to the latex and then the latex was divided into four equal portions, to one of which was added 0.1% of 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane, to another 0.1% of the mercuric salt of this compound, and to another one 0.1% of the aluminium salt of this compound, using for the last three operations the emulsions as prepared above. The three portions containing stabilising agents 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 portions containing the stabilising agent were still stable and undecomposed after 8 weeks.

In the above example the latex was sterilised before addition of catalase and the catalase was added to establish reproducible conditions for comparing the rate of decomposition of the portions containing the different salts. It will be appreciated that preliminary sterilisation and/or addition of catalase do not form a part of the method of stabilising latex by the addition of the diphenyl methane compounds.

What we claim is:—

1. A method of stabilising natural rubber latex comprising incorporating therewith an halogeno derivative of an hydroxydiphenyl methane or a metal salt of said derivative.

2. A method of stabilising natural rubber latex comprising incorporating therewith an hydroxychlorodiphenyl methane or a metal salt thereof.

3. A method according to Claim 1 or 2, in which the diphenyl methane derivative is added in an amount of from 0.01% to 1.0% by weight of the rubber latex.

4. A method according to any of Claims 1 to 3, in which the metal salt of the diphenyl methane derivative is the zinc, magnesium, mercuric, aluminium, calcium or barium salt.

5. A method according to any of Claims 1 to 4, in which the metal salt of the diphenyl methane derivative has a solubility in water at 25° C. of less than 0.20 parts by weight for every 100 parts by weight of water.

6. A method according to any of Claims 1 to 3, in which the metal salt of the diphenyl methane derivative is the sodium or potassium salt.

7. A method according to any of the preceding claims, in which the diphenyl methane derivative is 2,2¹-dihydroxy-5,5¹-dichlorodiphenyl methane.

8. A method of stabilising natural rubber latex comprising adding to it a small proportion of a diphenyl methane derivative as herein described and as illustrated by the example.

9. Stabilised natural rubber latex containing an halogeno derivative of an hydroxydiphenyl methane or a metal salt of said derivative.

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on storage of the 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 the 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 during storage.

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 hydroxydiphenylmethane or a chloro derivative thereof, or a metal salt of such a compound. Compounds having a small solubility in water are preferred for preserving latices which are to be concentrated subsequently, for these compounds will not separate from the rubber in the concentration process. Particularly suitable are 2,2^1-dihydroxy-5,5^1-dichlorodiphenyl methane and the metal salts thereof having a solubility in water at 25° C. less than 0.20 parts by weight of solution, for example, the zinc, magnesium, mercuric and aluminium salts. The production of these salts is described in co-pending Application No. 7516/49 (Serial No. 675,200).

The latex may be stabilised by adding thereto a small proportion 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 2,2^1-dihydroxy-5,5^1-dichlorodiphenyl methane and the above-mentioned salts thereof, 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 latex and then the latex was divided into four equal portions, to one of which was added 0.1% by weight of 2,2^1-dihydroxy-5,5^1-dichlorodiphenyl methane, to another 0.1% by weight of the mercuric salt of this compound, and to another one 0.1% by weight of the aluminium salt of this compound. The three portions containing stabilising agents and the remaining portion to which no stabilising agent had been added were kept in closed containers and stored for several weeks at ordinary temperatures; the portion containing no added stabilising agent had decomposed with coagulation of the rubber in two weeks, but the portions containing the stabilising agent were still stable and undecomposed after 8 weeks.

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