PATENT SPECIFICATION 738,279

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COMPLETE SPECIFICATION

Treatment of natural rubber latices

We, REVERTEX LIMITED, formerly of King William Street House, Arthur Street, London, E.C.4, now of 51 to 55, Strand, London, W.C.2, a British Company, 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 a process of vulcanising natural rubber latex or concentrates of natural rubber latex.

Hitherto, sulphur-containing compounds have usually been employed for effecting the vulcanisation of rubber or rubber latex.

It has however already been proposed to cause organic peroxides to react with dry rubber at elevated temperatures in order to bring about cross-linking between rubber molecules. In this process it is generally found that in order to achieve a satisfactory degree of cross-linking in the dry rubber, substantial quantities of relatively expensive organic peroxides are required so that this method of vulcanisation is uneconomic.

In general it would appear that peroxides, of the type usually employed for vulcanising dry rubber, dissociate to form active species in sufficient quantity to facilitate the desired degree of reaction in a reasonable time at temperatures in excess of 140°C.

A method of curing rubber has already been proposed which consists in treating rubber latex dispersions in water with an added active-oxygen curing agent such as organic active-oxygen compounds including peroxides e.g. benzoyl peroxide and nitro compounds, a few of the latter containing aliphatic radicles, such treatment taking place at a temperature of the order of 95°C. while agitating the latex dispersion, for example by blowing dry steam through the mixture.

It has now been found that natural rubber latex and rubber latex concentrates prepared therefrom can be heated under conditions precluding loss of water, i.e. under pressure, in the presence of an organic peroxide to temperatures in excess of 140°C. and even up to 170°C. (or slightly more) without appreciable coagulation and with only slight loss of mechanical stability as measured by standard methods.

Based on the foregoing discovery, the present invention contemplates a process of vulcanising natural rubber latices and rubber latex concentrates which comprises reacting said latices or concentrates with an organic peroxide under superatmospheric pressure and at temperatures in excess of 100°C. and preferably in excess of 140°C. in order to bring about cross-linking between the rubber molecules.

It has been found that the amount of organic peroxide which is required for effecting vulcanisation varies inversely with the reaction temperature employed and with the reaction period. Consequently, since organic peroxides are relatively expensive chemicals, it is more economical to employ comparatively small percentages thereof, e.g. within the limits of 1 to 5% by weight of the total solids content of the latex or concentrate and reaction temperatures lying between 140° and 170°C.

In order to avoid or to minimise any coagulation of the rubber latex, one or more of the usual stabilisers such as soaps, sulphated vegetable oils, sulphated long chain hydrocarbons, proteins and the like may be incorporated therewith prior to the vulcanisation with organic peroxide.

The reaction product can be dried or coagulated and yields a vulcanised rubber film having properties not obtainable in vulcanised rubbers prepared by the conventional methods.

Films prepared from rubber latex vulcanised in accordance with the present

[*Price* 3*s.* 0*d.*]

invention have an excellent resistance to heat ageing. Such films also exhibit a greater degree of transparency and a paler colour than films obtained from sulphur vulcanisates and are moreover substantially tasteless and odourless.

The invention will be illustrated by the following Examples:—

EXAMPLE I

200 ml. of 60% centrifuged rubber latex stabilised with ammonia were mixed by stirring with a mixture of 2% of di-tertiary-butyl peroxide and 0.4% of oleic acid, both calculated on the total solids weight of the latex. The mixture was sealed in a pressure vessel which was then immersed in an oil-bath at 170°C. and maintained at this temperature for a period of 15 minutes, after which the product was extracted and filtered. The rubber in the resultant stable latex was found to be in a vulcanised condition, yielding films which were very pale and transparent.

EXAMPLE II

200 ml. of centrifuged rubber latex stabilised with ammonia were mixed with 2% of di-tertiary butyl peroxide and the mixture treated in the manner set forth in Example I.

The resultant vulcanised latex was of satisfactory stability and exhibited properties similar to that described in Example I.

EXAMPLE III

170 ml. of 60% centrifuged latex were diluted with 30 ml. of water and mixed with 1% of di-tertiary butyl peroxide. The mixture was heated in a sealed vessel to 170°C. for 6 minutes, and rapidly cooled before being extracted and filtered.

Rubber films were cast from the resultant stable pre-vulcanised latex, and the physical properties measured before and after ageing artificially in a Geer oven at 70°C.

The results obtained were:—

	Elongation at Break %	*Load at Break* kg/cm²
Unaged films ...	745	168
Aged 14 days ...	757	200
Aged 29 days ...	756	191

showing that the physical properties of the said films were virtually unaffected by heat ageing.

EXAMPLE IV

170 ml. of 60% centrifuged latex stabilised with ammonia were mixed with 30 ml. water and with 2% of di-tertiary butyl peroxide, reckoned on the total solids weight of the latex. The mixture was placed in a sealed vessel and heated to 140°C. for 30 minutes. It was then rapidly cooled, the product extracted and filtered.

The resultant latex on evaporation yielded a film which showed a breaking elongation of 873% and a load at break of 251 kg/cm².

EXAMPLE V

To 200 ml. of 60% centrifuged latex stabilised with ammonia was added a mixture of 2% di-tertiary butyl peroxide and 0.4% of lauric acid, both based on the total solids weight of the latex.

After placing the mixture in a sealed vessel and heating at 170°C. for 8 minutes, the resultant latex yielded a film which showed a load at break of 211 kg/cm².

EXAMPLE VI

To 170 mls. of 60% centrifuged latex stabilised with ammonia was added 4% di-tertiary butyl peroxide, based on the total solids weight of the latex. The mixture was placed in a sealed vessel and heated to 170°C. for 2 minutes. The vessel was then rapidly cooled and the resultant vulcanised latex extracted and filtered.

A film from this product showed an elongation at break of 812% and a load at break of 150 kg/cm².

What we claim is:—

1. A process of vulcanising natural rubber latex or concentrates of natural rubber latex, which comprises reacting said latex or concentrate with an organic peroxide under conditions precluding loss of water, i.e. under super-atmospheric pressure and at temperatures in excess of 100°C. and preferably in excess of 140°C. in order to bring about cross-linking between the rubber molecules.

2. Process as claimed in Claim 1, in which the organic peroxide employed is di-tertiary butyl peroxide.

3. Process as claimed in Claim 1 or 2, in which the organic peroxide is employed within the limits of 1 to 5% based on the weight of the total solids content of the latex or concentrate treated.

4. Process as claimed in any of Claims 1 to 3, in which the reaction is carried out at a temperature of approximately 170°C.

5. Process as claimed in any of Claims 1 to 4, in which one or more per se known stabilisers are incorporated with the latex or concentrate prior to vulcanisation.

6. Process as claimed in any of Claims 1 to 5, in which the mixture of latex or concentrate and organic peroxide, and if desired stabiliser, is sealed in a pressure vessel which is thereupon heated.

7. Process as claimed in any of Claims 1 to 5, in which the mixture of latex or concentrate and organic peroxide, and if

invention have an excellent resistance to heat ageing. Such films also exhibit a greater degree of transparency and a paler colour than films obtained from sulphur vulcanisates and are moreover substantially tasteless and odourless.

The invention will be illustrated by the following Examples:—

EXAMPLE I

200 ml. of 60% centrifuged rubber latex stabilised with ammonia were mixed by stirring with a mixture of 2% of di-tertiary-butyl peroxide and 0.4% of oleic acid, both calculated on the total solids weight of the latex. The mixture was sealed in a pressure vessel which was then immersed in an oil-bath at 170°C. and maintained at this temperature for a period of 15 minutes, after which the product was extracted and filtered.

The rubber in the resultant stable latex was found to be in a vulcanised condition, yielding films which were very pale and transparent.

EXAMPLE II

200 ml. of centrifuged rubber latex stabilised with ammonia were mixed with 2% of di-tertiary butyl peroxide and the mixture treated in the manner set forth in Example I.

The resultant vulcanised latex was of satisfactory stability and exhibited properties similar to that described in Example I.

EXAMPLE III

170 ml. of 60% centrifuged latex were diluted with 30 ml. of water and mixed with 1% of di-tertiary butyl peroxide. The mixture was heated in a sealed vessel to 170°C. for 6 minutes, and rapidly cooled before being extracted and filtered.

Rubber films were cast from the resultant stable pre-vulcanised latex, and the physical properties measured before and after ageing artificially in a Geer oven at 70°C.

The results obtained were:—

	Elongation at Break %	*Load at Break* kg/cm²
Unaged films ...	745	168
Aged 14 days ...	757	200
Aged 29 days ...	756	191

showing that the physical properties of the said films were virtually unaffected by heat ageing.

EXAMPLE IV

170 ml. of 60% centrifuged latex stabilised with ammonia were mixed with 30 ml. water and with 2% of di-tertiary butyl peroxide, reckoned on the total solids weight of the latex. The mixture was placed in a sealed vessel and heated to 140°C. for 30 minutes. It was then rapidly cooled, the product extracted and filtered.

The resultant latex on evaporation yielded a film which showed a breaking elongation of 873% and a load at break of 251 kg/cm².

EXAMPLE V

To 200 ml. of 60% centrifuged latex stabilised with ammonia was added a mixture of 2% di-tertiary butyl peroxide and 0.4% of lauric acid, both based on the total solids weight of the latex.

After placing the mixture in a sealed vessel and heating at 170°C. for 8 minutes, the resultant latex yielded a film which showed a load at break of 211 kg/cm².

EXAMPLE VI

To 170 mls. of 60% centrifuged latex stabilised with ammonia was added 4% di-tertiary butyl peroxide, based on the total solids weight of the latex. The mixture was placed in a sealed vessel and heated to 170°C. for 2 minutes. The vessel was then rapidly cooled and the resultant vulcanised latex extracted and filtered.

A film from this product showed an elongation at break of 812% and a load at break of 150 kg/cm².

What we claim is:—

1. A process of vulcanising natural rubber latex or concentrates of natural rubber latex, which comprises reacting said latex or concentrate with an organic peroxide under conditions precluding loss of water, i.e. under super-atmospheric pressure and at temperatures in excess of 100°C. and preferably in excess of 140°C. in order to bring about cross-linking between the rubber molecules.

2. Process as claimed in Claim 1, in which the organic peroxide employed is di-tertiary butyl peroxide.

3. Process as claimed in Claim 1 or 2, in which the organic peroxide is employed within the limits of 1 to 5% based on the weight of the total solids content of the latex or concentrate treated.

4. Process as claimed in any of Claims 1 to 3, in which the reaction is carried out at a temperature of approximately 170°C.

5. Process as claimed in any of Claims 1 to 4, in which one or more per se known stabilisers are incorporated with the latex or concentrate prior to vulcanisation.

6. Process as claimed in any of Claims 1 to 5, in which the mixture of latex or concentrate and organic peroxide, and if desired stabiliser, is sealed in a pressure vessel which is thereupon heated.

7. Process as claimed in any of Claims 1 to 5, in which the mixture of latex or concentrate and organic peroxide, and if

* C L M S *

desired stabiliser, is caused to react under pressure in a continuous manner.

8. Process of vulcanising natural rubber latex or concentrates of natural rubber latex, substantially as hereinbefore described with reference to the foregoing Examples.

9. Vulcanised rubber latices whenever produced by the process claimed in any of the preceding Claims.

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PROVISIONAL SPECIFICATION

Treatment of natural rubber latices

We, REVERTEX LIMITED, of King William Street House, Arthur Street, London, E.C.4, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to a process of vulcanising natural rubber latex or concentrates of natural rubber latex.

The vulcanisation of rubber or rubber latex has hitherto usually been effected with the aid of sulphur containing compounds.

It has already been proposed to cause organic peroxides to react with dry rubber at elevated temperatures in order to bring about cross-linking between rubber molecules. In this process it is generally found that in order to achieve a satisfactory degree of cross-linking in the dry rubber, substantial quantities of organic peroxide are required.

In general it would appear that peroxides, of the type usually employed, dissociate to form active species in sufficient quantity to facilitate the desired degree of reaction in a reasonable time at temperatures in excess of 140°C. This fact in itself would seem to preclude the possibility of effecting a reaction similar to that obtained with dry rubber, in natural rubber latex. Nevertheless, contrary to expectation, it has now been found that natural rubber latex and rubber latex concentrates prepared therefrom can be heated under pressure in the presence of an organic peroxide to temperatures in excess of 170°C. without appreciable coagulation and with only slight loss of mechanical stability as measured by standard methods.

Based on the foregoing discovery, the present invention contemplates a process of vulcanising natural rubber latices and rubber latex concentrates which comprises reacting said latices or concentrates with an organic peroxide at temperatures in excess of 100°C. and preferably in excess of 140°C. to bring about cross-linking between the rubber molecules.

In order to avoid or to minimise any coagulation of the rubber latex, one or more of the usual stabilisers may be incorporated therewith prior to the vulcanisation with organic peroxide.

The reaction product can be dried or coagulated and yields a vulcanised rubber film having properties not obtainable in vulcanised rubbers prepared by the conventional methods.

Films prepared from rubber vulcanised in accordance with the present invention have an excellent resistance to heat ageing and an improved resistance to deterioration by light and metallic copper-catalysed oxidation. Such films also exhibit a greater degree of transparency and a paler colour than films obtained from sulphur vulcanisates and is moreover substantially tasteless and odourless.

The invention will be illustrated by the following Examples:

EXAMPLE I

200 ml. of 60% centrifuged rubber latex are mixed by stirring with 2% of tertiary butyl peroxide and 0.4% oleic acid (calculated on the T.S.C.) This mixture is sealed in a suitable pressure vessel which is then immersed in an oil bath at 170°C. and maintained at this temperature for 15 minutes, after which the vessel is rapidly cooled and the product extracted and filtered.

EXAMPLE II

200 ml. of centrifuged rubber latex are mixed with 2% of tertiary butyl peroxide and the mixture treated in the manner set forth in Example I.

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