PATENT SPECIFICATION

Inventors: EVELYN WILLIAM MADGE, HUGH MARTIN COLLIER and JOHN DEREK PEEL.

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COMPLETE SPECIFICATION.

Method of improving the Stability of 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 a method of improving the stability of natural rubber latex.

Rubber latex as obtained from the tree is essentially a dispersion of rubber particles in an aqueous medium containing proteinaceous material which acts as a stabiliser. Before the latex is shipped it is usually concentrated, e.g. by creaming or centrifuging, to increase the rubber content, e.g. to a value of the order of 60%, and ammonia is added to inhibit bacterial or enzymatic decomposition of the proteinaceous material. In some cases alkali metal hydroxide is employed instead of the ammonia or the latex may be preserved with a bactericidal agent e.g. a pentachlorophenate and smaller amounts of ammonia. Latices from different clones, i.e. different strains of rubber trees, differ in their mechanical stability, and the latices from some clones may have so poor a mechanical stability that they are not satisfactory for commerical purposes if they are preserved in the usual way by the addition of ammonia or with ammonia and a bactericidal agent. Latices with a poor mechanical stability also tend to gel under the influence of sodium silicofluoride at a relatively high *p*H value. Ammonia-preserved latex from the clone known as "Glenshiel I" is an example of a latex which has a particularly poor mechanical stability and a high gelling *p*H value with sodium silicofluoride.

In addition to containing rubber and proteinaceous material latex also contains minor amounts of other materials, including compounds of magnesium and phosphorus; and, normal centrifuged rubber latex may contain 0.03% phosphorus and 0.0025% magnesium, both percentages being based on the total weight of the solids in the latex. The percentage of magnesium however may be in some cases very much higher even though the phosphorus content is the same, for example a centrifuged latex containing phosphorus in amount of 0.03% by weight of the total solids may contain as much as 0.05% by weight of magnesium calculated on the same basis. At least the major portion of the magnesium present is in a compound or compounds containing the magnesium in ionisable form, the amount in non-ionisable form being less than that present in a normal latex.

It has now been found that for ammonia-preserved latices there is a correlation between the ratio of ionisable magnesium to phosphorus in the latex and its mechanical stability, latices in which the ratio is abnormally high having a poor mechanical stability and that the mechanical stability of such a latex having a high ionisable magnesium/phosphorus ratio can be improved, by sequestering, or by converting to an insoluble salt, ionisable magnesium present in excess of that corresponding to the normal magnesium: phosphorus ratio.

By an ammonia-preserved latex is meant at latex containing ammonia as the sole added preservative, latex which has been preserved with a bactericidal agent, e.g. sodium pentachlorophenate or formaldehyde, and some ammonium hydroxide, or with a major amount of ammonium hydroxide and a small amount of a preserving agent other than a microbicidal agent, e.g. an amount of

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potassium hydroxide of the order of 5% by weight based on the total amount of preservative.

It is an object of the present invention to increase the mechanical stability of unstable ammonia-preserved rubber latices having an excessively high ratio of magnesium to phosphorus.

According to the present invention a process for increasing the mechanical stability of an unstable ammonia-preserved rubber latex having an abnormally high ratio of magnesium to phosphorus comprises reducing the ionisable magnesium content thereof by adding to the latex either a compound capable of sequestering ionisable magnesium or a compound capable of converting it to an insoluble salt.

By a latex having an abnormally high ratio of magnesium to phosphorus is meant a latex containing a greater quantity of magnesium than 25 parts by weight for every 100 parts by weight of phosphorus measured on a concentrate containing 60% of rubber. Commercially available latices which are unstable due to a high ratio of magnesium to phosphorus usually contain magnesium in amount at least half the weight of the phosphorus..

The mechanical stability of latex having an abnormally high ratio of magnesium to phosphorus (hereinafter referred to as abnormal latices) can be improved satisfactorily by sequestering the excess magnesium, by for example, the addition of the compound tetrasodium ethylenediaminetetracetate. Alternatively the mechanical stability may be improved by adding as a precipitating agent a water-soluble phosphate which converts the magnesium in the latex to a water-insoluble salt. Suitable salts for this purpose are diammonium hydrogen orthophosphate or disodium hydrogen orthophosphate; a soluble pyrophosphate, e.g., sodium pyrophosphate, may also be used.

The amount of precipitating agent or sequestering agent to be added to the abnormal latex will be that chemically equivalent to the amount of ionisable magnesium it is desired to remove, and is preferably such that the amount of magnesium left in the latex is 5 to 20 parts by weight for every 100 parts by weight of phosphorus, measured on a concentrate containing 60% of rubber. The addition of a precipitating agent or sequestering agent in amount substantially in excess of that needed to precipitate or sequester the magnesium is undesirable, since the compounds then have an adverse effect on the stability of the latex; there is thus an optimum amount to add, namely the amount which suffices to sequester or to convert to an insoluble salt all the excess magnesium.

According to a preferred form of the invention there is also added to the latex a small proportion, e.g. up to 0.5%, of water-soluble soap, e.g. ammonium oleate and ammonium laurate; preferably the amount of soap which may be added is an amount corresponding to from 0.05% to 0.2% by weight of the latex. Such an addition further increases the mechanical stability of latex treated as described above.

The precipitating agent or the sequestering agent and the soap, if such is present, may be added to the latex prior to concentrating the latex, e.g. by centrifuging, creaming or electrodecanting, though it may be added to a latex which has already been concentrated. If the treatment is applied to the latex before concentrating it the latex should be left to stand for a time before concentration is effected so that reaction between the magnesium and the precipitating agent or the sequestering agent may occur; any precipitate of insoluble magnesium salt which forms when a precipitating agent is used may then be removed.

In one method of carrying out the invention a concentrated rubber latex from the clone "Glenshiel I" is stirred with a small proportion of water-soluble soap, e.g. an amount corresponding to 0.1% by weight of the latex, and a precipitating agent as hereinbefore defined is added to the mixture. The treated latex is then allowed to stand for a short time, e.g. one hour. The amount of precipitating agent to be added to the latex is best found by making several experiments on a small scale, varying the amount of precipitating agent added each time, and measuring the mechanical stability of the treated latex. A suitable method of testing the mechanical stability of the latex is described by Dawson in Analytical Chemistry, 1949, Volume 21, page 1066. A graph may then be plotted of the mechanical stability against the amount of precipitating agent added; the optimum of precipitating agent to add is then given by the maximum of the curve and this optimum value so found will be employed in treating succeeding batches of the latex. This method of determining the optimum amount of precipitating agent to add has the advantage that it avoids troublesome quantitative estimations of the non-ionisable and ionisable magnesium present.

By reducing the ionisable magnesium content of a latex in accordance with the invention the mechanical stability of the latex is considerably improved. Improving the mechanical stability of a latex according to the invention also has the advantageous result of reducing the *p*H value at which the latex gels with sodium silicofluoride.

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

EXAMPLE 1.

An unconcentrated rubber latex from the clone "Glenshiel I" which had been preserved with ammonia was stirred with 0.1% of ammonium laurate and 0.3% of diammonium orthophosphate and the treated latex was allowed to mature for 16 hours, during which time magnesium ammonium phosphate was precipitated. The latex was then concentrated by centrifuging to give a latex of 61.8% total solids content. The centrifuged latex had a magnesium content of 0.005% and a phosphorus content of 0.03% based on the total solids content of the latex. The mechanical stability of the centrifuged latex was tested as described by Dawson in Analytical Chemistry, 1949, Volume 21, page 1066 by determining the time required at 35° C. for a flat disc rotating at 14000 revs. per minute to cause coagulation of the latex after adjustment of its concentration to 58% rubber content. The time required was 520 seconds.

The gelling *p*H value of the centrifuged latex was 7.9.

EXAMPLE 2.

A litre of centrifuged concentrated rubber latex from the clone "Glenshiel I" of total solids content 62.1% and containing 0.76% ammonia (each based on the latex), 0.055% magnesium and 0.027% phosphorus (each based on the solids content of the latex) was stirred with a solution of 2.0 g. of diammonium hydrogen phosphate in approximately 65 g. of water. The treated latex was left to stand for one hour and the mechanical stability of the centrifuged latex was then tested as described in Example 1, and found to be 403 seconds. The corresponding time for a sample of the same latex to which no diammonium hydrogen phosphate had been added was 109 seconds, and the time for a normal centrifuged latex containing 60% rubber (based on the latex) 0.0024% magnesium and 0.029% phosphorus (based on the solids content of the latex) was 788 seconds.

The gelling *p*H value of the treated latex was 7.9 and the corresponding value for the untreated latex was 9.9.

EXAMPLE 3.

A litre of the concentrated rubber latex from the clone "Glenshiel I" referred to in Example 2 was stirred with 2.0 g. of diammonium hydrogen phosphate and 1.0 g. of ammonium oleate in approximately 65 g. of water. After letting the latex stand for one hour the mechanical stability of the latex was tested as in Example 1 and found to be 793 seconds. The gelling *p*H value of the latex was 8.3.

EXAMPLE 4.

A litre of the concentrated rubber latex from the clone "Glenshiel I" referred to in Example 2, was stirred with 4 g. of crystalline sodium pyrophosphate dissolved in approximately 65 g. of water. After letting the latex stand for one hour the mechanical stability of the latex was then tested as in Example 1 and found to be 406 secs. The gelling *p*H value was 8.0.

EXAMPLE 5.

A litre of the concentrated rubber latex from the clone "Glenshiel I" referred to in Example 2 was stirred with 4 g. of sodium pyrophosphate and 1.0 g. of ammonium oleate in approximately 65 g. of water. After letting the latex stand for one hour the mechanical stability of the treated latex was tested as in Example 1 and found to be 940 seconds. The gelling *p*H value of the treated latex was 8.2.

EXAMPLE 6.

A litre of a concentrated rubber latex from the clone "Glenshiel -I" of total solids content 63.3% and containing 0.7% ammonia (each based on the latex) was stirred with a solution of 8.1 g. of tetrasodium ethylenediaminetetracetate dihydrate (a sequestering agent for divalent magnesium ions) in approximately 20 g. of water. After letting the latex stand for one hour the mechanical stability of the treated latex was tested as in Example 1 and found to be 330 seconds. The gelling *p*H value of the treated latex was 8.0. The mechanical stability of the untreated latex 89 seconds, and its gelling *p*H value was 10.5.

The gelling *p*H value of the latex referred to in the above examples was measuerd as follows:—

To a mechanically stirred sample of latex a well shaken 20% aqueous dispersion of sodium silicofluoride was added in sufficient quantity to cause gelling of the latex within 4 to 7 minutes. At the time gelling occurred the *p*H was

measured by a glass electrode-calomel electrode assembly.

What we claim is:

1. A process for increasing the mechanical stability of ammonia-preserved rubber latex having an abnormally high ratio of magnesium to phosphorus which comprises reducing the ionisable magnesium content thereof by adding to the latex either a compound capable of sequestering ionisable magnesium or a compound capable of converting it to an insoluble salt.

2. A process according to claim 1 in which the ratio of magnesium to phosphorus in the rubber latex is reduced to 5 to 20 parts by weight of magnesium for every 100 parts by weight of phosphorus, measured on a concentrate containing 60% of rubber.

3. A process according to either of the preceding claims in which a water-soluble soap is added to the latex in addition to the said compound.

4. A process according to claim 3 in which the soap is added in amount between 0.05% and 0.2% by weight of the latex.

5. A process according to any of the preceding claims in which the compound added is a water-soluble salt forming a water-insoluble magnesium compound.

6. A process according to claim 5 in which the water-soluble salt is a water-soluble phosphate.

7. A process according to claim 6 in which the phosphate is diammonium hydrogen orthophosphate.

8. A process for increasing the mechanical stability of ammonia-preserved rubber latex substantially as herein described and illustrated by any of the examples 1 to 6.

9. Ammonia-preserved latex whose mechanical stability has been increased by a process according to any of the preceding claims.

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

PROVISIONAL SPECIFICATION.

Method of improving the Stability of 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 improving the stability of natural rubber latex.

Rubber latex as obtained from the tree is essentially a dispersion of rubber particles in an aqueous medium containing proteinaceous material which acts as a stabiliser. Before the latex is shipped it is usually concentrated, as by creaming or centrifuging, to increase the rubber content, e.g. to a value of the order of 60%, and ammonia is added to inhibit bacterial or enzymatic decomposition of the proteinaceous material. In some cases alkali metal hydroxide is employed instead of the ammonia. Latices from different clones, i.e. different strains of rubber trees, differ in their mechanical stability, and the latices from some clones may have so poor a mechanical stability that they are not satisfactory for commercial purposes if they are unpreserved or if they are preserved by the addition of ammonia. Latices with a poor mechanical stability also tend to gel at a relatively high *p*H value. Ammonia-preserved latex from the clone known as "Glenshiel I" is an example of a latex which has a particularly poor mechanical stability and a high gelling *p*H value.

In addition to containing rubber and proteinaceous material latex also contains minor amounts of other materials, including compounds of magnesium and phosphorus; a normal centrifuged rubber latex may contain of the order of 0.03% of phosphorus (based on the total solids contents of the latex) and of the order of 0.0025% of magnesium. The magnesium value however may in some cases be very much higher even though the phosphorus content is the same, for example the magnesium content of a centrifuged latex containing phosphorus in amount of the order of 0.03% by weight of the total solids may contain as much as 0.05% by weight of magnesium calculated on the same basis.

It has now been found that for latices which have not been preserved with alkali metal hydroxide there is a correlation between the ratio of magnesium to phosphorus in a latex and its mechanical stability those latices in which the ratio is abnormally high having a poorer mechanical stability, and it has also been found that the mechanical stability of such latices having an abnormally high ratio of magnesium to phosphorus can be improved by sequestering or converting to an insoluble phosphate, magnesium present in excess of that corresponding to the normal magnesium/phosphorus ratio.

In the case of ammonia-preserved latices it appears that poor mechanical stability results if the magnesium is present in

measured by a glass electrode-calomel electrode assembly.

What we claim is:—

1. A process for increasing the mechanical stability of ammonia-preserved rubber latex having an abnormally high ratio of magnesium to phosphorus which comprises reducing the ionisable magnesium content thereof by adding to the latex either a compound capable of sequestering ionisable magnesium or a compound capable of converting it to an insoluble salt.

2. A process according to claim 1 in which the ratio of magnesium to phosphorus in the rubber latex is reduced to 5 to 20 parts by weight of magnesium for every 100 parts by weight of phosphorus, measured on a concentrate containing 60% of rubber.

3. A process according to either of the preceding claims in which a water-soluble soap is added to the latex in addition to the said compound.

4. A process according to claim 3 in which the soap is added in amount between 0.05% and 0.2% by weight of the latex.

5. A process according to any of the preceding claims in which the compound added is a water-soluble salt forming a water-insoluble magnesium compound.

6. A process according to claim 5 in which the water-soluble salt is a water-soluble phosphate.

7. A process according to claim 6 in which the phosphate is diammonium hydrogen orthophosphate.

8. A process for increasing the mechanical stability of ammonia-preserved rubber latex substantially as herein described and illustrated by any of the examples 1 to 6.

9. Ammonia-preserved latex whose mechanical stability has been increased by a process according to any of the preceding claims.

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In addition to containing rubber and proteinaceous material latex also contains minor amounts of other materials, including compounds of magnesium and phosphorus; a normal centrifuged rubber latex may contain of the order of 0.03% of phosphorus (based on the total solids contents of the latex) and of the order of 0.0025% of magnesium. The magnesium value however may in some cases be very much higher even though the phosphorus content is the same, for example the magnesium content of a centrifuged latex containing phosphorus in amount of the order of 0.03% by weight of the total solids may contain as much as 0.05% by weight of magnesium calculated on the same basis.

It has now been found that for latices which have not been preserved with alkali metal hydroxide there is a correlation between the ratio of magnesium to phosphorus in a latex and its mechanical stability those latices in which the ratio is abnormally high having a poorer mechanical stability, and it has also been found that the mechanical stability of such latices having an abnormally high ratio of magnesium to phosphorus can be improved by sequestering or converting to an insoluble phosphate, magnesium present in excess of that corresponding to the normal magnesium/phosphorus ratio.

In the case of ammonia-preserved latices it appears that poor mechanical stability results if the magnesium is present in

amount in excess of that which suffices to form magnesium ammonium phosphate with the phosphorus present in a form available for reaction therewith and the ammonia.

The mechanical stability of the latex can be improved satisfactorily by sequestering the excess magnesium, i.e. converting it to a soluble salt which does not ionise with formation of magnesium ions; this may be effected, for example by the addition of the compound tetrasodium ethylenediaminetetracetate. Alternatively the mechanical stability may be improved by adding a soluble salt of an acid of phosphorus which converts the magnesium to an insoluble phosphate, e.g. diammonium hydrogen orthophosphate or disodium hydrogen orthophosphate. A soluble pyrophosphate, e.g. sodium pyrophosphate, may also be used. The addition of a salt or sequestering agent in amount substantially in excess of that needed to precipitate or sequester the magnesium is undesirable, since the compounds have an adverse effect on the stability of the latex; there is thus an optimum amount to add namely the amount which suffices to sequester, or convert to an insoluble phosphate, all the excess magnesium. Improving the mechanical stability of a latex according to the invention also has the advantageous result of reducing the *p*H value at which the latex gels.

According to a preferred form of the invention there is also added to the latex a small proportion of ammonium oleate, ammonium laurate or other water-soluble soap, e.g. in an amount corresponding to 0.05% to 0.2% by weight of the latex. Such an addition further increases the mechanical stability of latex treated as described above.

The salt of the phosphorus acid or the sequestering agent and the soap, if such is present, is preferably added to the latex prior to centrifuging, creaming or other concentration process, though it may be added to a latex which has already been concentrated in such a manner. If the treatment is applied to the latex before such concentration process is carried out it is preferred to leave the latex to stand for a time before concentration is effected in order that reaction between the magnesium and the salt of the phosphorus acid may occur, insoluble salt thereby formed being then separated from the concentrated latex in the concentration process; if concentration is effected by centrifuging for example it will be removed in the sludge fraction.

The following examples illustrate the invention.

EXAMPLE 1.

An unconcentrated rubber latex from the clone "Glenshiel I" was stirred with 0.1% of its weight of ammonium laurate and 0.3% of its weight of diammonium hydrogen phosphate and the treated latex was allowed to mature for 16 hours, during which time magnesium ammonium phosphate was precipitated. The latex was then concentrated by centrifuging to give a latex of 61.8% total solids content. The centrifuged latex had a magnesium content of 0.005% of the total solids content. The mechanical stability of the centrifuged latex was tested as described by Dawson in Analytical Chemistry 1945, Vol. 21, page 1066 by determining the time required at 35° C. for a flat disc rotating at 14000 revs. per minute to cause coagulation of the latex after adjustment of its concentration to 58% rubber content. The time required was 520 seconds.

The gelling *p*H value of the centrifuged latex (measured as described by Madge & Pounder, Transactions of the Institution of the Rubber Industry 1947, Vol. 23, page 95) was 7.9.

EXAMPLE 2.

A litre of centrifuged concentrated rubber latex from the clone "Glenshiel I" of total solids content 62.1% and containing 0.76% ammonia (each based on the latex), 0.055% magnesium and 0.027% phosphorus (each based on the solids content of the latex) was stirred with a solution of 2.0 gms. of diammonium hydrogen phosphate in approximately 65 gms. of water. The mechanical stability of the centrifuged latex was then tested as described in Example 1, and found to be 403 seconds. The corresponding time for a sample of the same latex to which no diammonium hydrogen phosphate had been added was 109 seconds, and the time for a normal centrifuged latex containing 60% rubber (based on the latex) 0.0024% magnesium and 0.029% phosphorus (based on the solids content of the latex) was 788 seconds.

The gelling *p*H value of the treated latex was 7.9 and the corresponding value for the untreated latex was 9.9

EXAMPLE 3.

A litre of the concentrated rubber latex from the clone "Glenshiel I" referred to in Example 2 was stirred with 2.0 gm. of diammonium hydrogen phosphate and 1.0 gm. of ammonium oleate in approximately 65 gms. of water. The mechanical stability of the latex was

tested as in Example 1 and found to be 793 seconds. The gelling *p*H value of the latex was 8.3.

EXAMPLE 4.

A litre of the concentrated rubber latex from the clone "Glenshiel I" referred to in Example 2, was stirred with 4 gms of sodium pyrophosphate dissolved in approximately 65 gms of water. The mechanical stability of the latex was then tested as in Example 1 and found to be 406 secs. The gelling *p*H value was 8.0.

EXAMPLE 5.

A litre of the concentrated rubber latex from the clone "Glenshiel I" referred to in Example 2 was stirred with 4 gms of sodium pyrophosphate and 1.0 gms of ammonium oleate in approximately 65 gms of water. The mechanical stability of the treated latex was tested as Example 1 and found to be 940 seconds. The gelling *p*H value of the treated latex was 8.2.

EXAMPLE 6.

A litre of a concentrated rubber latex from the clone "Glenshiel I" of total solids content 63.3% and containing 0.7% ammonia (each based on the latex) was stirred with a solution of 8.1 gms of tetrasodium ethylenediaminetetracetate dihydrate in approximately 20 gms of water. The mechanical stability of the treated latex was tested as in Example 1 and found to be 330 seconds. The gelling *p*H value of the treated latex was 8.0. The mechanical stability of the untreated latex was 89 seconds, and its gelling *p*H value was 10.5.

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

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