AMENDED SPECIFICATION

Reprinted as amended in accordance with the decision of the Assistant Comptroller, acting for the Comptroller-General, dated the fourth day of December, 1936, under Section 11, of the Patents and Designs Acts, 1907 to 1932.

PATENT SPECIFICATION

Application Date: March 6, 1934. No. 7101/34. **434,214**

Complete Specification Left: Feb. 26, 1935.

Accepted: Aug. 28, 1935.

PROVISIONAL SPECIFICATION

Process for Improving the Properties of Rubber Latex

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, and Dr. JOHANNES JAENICKE, a German Citizen, both of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, do hereby declare the nature of this invention to be a follows:—

This invention relates to a process for improving the properties of rubber latex.

Rubber latex and its concentrates often exhibit a dark coloration, which makes itself inconveniently apparent in practice, for example by discolouring the articles manufactured from the coloured rubber latex and therefore rendering them unsightly. Exhaustive observations on the discoloration of the latex have led to the hypothesis that this condition is due to the presence of dark-coloured heavy-metal sulphides in the latex through the action of sulphuretted hydrogen resulting from the decomposition of such substances as protein constituents in the latex by, for example, bacterial agency. Every rubber latex contains traces of iron salts, which are transformed by the sulphuretted hydrogen into strongly pigmentary black sulphide. Contact with vessels containing or consisting of heavy metals, and the like, may also introduce into the latex heavy-metal salts which react with the sulphur compounds formed from the latex protein and thus lead to the formation of highly coloured sulphides.

The present invention contemplates preventing the dark coloration of the rubber latex or causing it to disappear, by adding small quantities of preferably finely divided zinc oxide to the latex, which latter may be stabilised with the usual protective substances, such as protective colloids. The zinc oxide is particularly effective when bases such as ammonia or potassium hydroxide, are also present. In such cases, the addition of even such small quantities as about 0.005 parts of zinc oxide per 100 parts of rubber, has a favourable influence on the colour of the latex. Since the iron content in rubber latices varies to a very considerable extent, even smaller amounts of zinc oxide may occasionally be sufficient. In general, for example, when it is a question of counteracting discolouring influences which have found their way into the rubber latex from outside, it is advisable to add somewhat larger quantities such as 0.02 to about 2, and preferably 0.05 to about 1.5 (for example, about 0.07 to about 0.5) parts of zinc oxide per 100 parts of rubber in the latex.

The effect of the zinc oxide is due to the circumstance that it reacts almost completely with all heavy-metal sulphides which are more soluble than zinc sulphide, to form white zinc sulphide, and heavy-metal compounds which are less strongly coloured than their sulphides, so that the strong coloration due to the heavy-metal sulphides does not appear or else vanishes.

Since this reaction is substantially one of the zinc ion, other zinc compounds may be employed in place of, or addition to zinc oxide. In such case, the quantities taken should be such that the zinc content of the mixture varies approximately within the limits corresponding to those specified for zinc oxide. For example, the zinc oxide may first be wholly or partially transformed into a zincate by dissolved alkali, and then added in that form. Alternatively, zinc oxide or hydroxide may be employed in solution or suspension in ammonia or solutions of ammonium salts. The zinc may also be introduced into the rubber latex in the

form of the readily soluble zinc salts, such as zinc chloride or zinc acetate, or of such sparingly-soluble salts as zinc carbonate. It is however, less advisable to employ readily soluble salts because (and particularly when larger amounts are added) a partial coagulation or aggregation of the particles of latex is liable to occur.

In addition to the direct transformation of the heavy-metal sulphides, the employment of small amounts of zinc compounds has a favourable effect insofar as presumably by retarding bacterial growth, the zinc compounds prevent the decomposition of the latex, that is, of its proteids and therefore counteract the formation of sulphuretted hydrogen or other sulphur-bearing fission products capable of transforming metallic salts into sulphides. Thus, already in this respect, the zinc compounds exert a favourable influence on the colour, inasmuch as they repress the chemical or biochemical reactions leading to the formation of the coloured sulphides, and consequently to the discoloration of the latex.

The great increase in the stability of rubber latex through the small addition of zinc compounds is evidenced, for example by the following observations.

Fresh rubber latex which was treated with 90 milli-equivalents of potassium hydroxide and 1 grm. of zinc oxide (in the form of a paste with water) per litre, remained for 3½ weeks before emitting a smell of protein-degradation products, and did not exhibit coagulation until 5 weeks had elapsed, whereas a second sample, differing from the first only in not being treated with zinc oxide already gave off a putrefactive smell at the end of 10 days, and coagulated in 12 days.

Fresh rubber latex treated with 100 milli-equivalents of ammonia per litre as a preservative, omitted a putrescent smell after 8 days, and exhibited a considerably increased internal friction after 12 days. A latex treated similarly in other respects, but containing in addition 4 grms. of zinc oxide per litre did not give off any disagreeable smell after 4 weeks and it was only after a longer period that any increase in viscosity could be detected.

In order to counteract the darkening of colour from the outset and to utilise the favourable influence of the small additions of zinc to the full, it is advisable to make the addition soon after the rubber latex has been produced and therefore prior to its transport (if any) to the countries where it is to be used.

In applying the present invention to rubber latex concentrates, the zinc compounds may be added either before or after concentration. Owing to the strong tendency of rubber latex to coagulate in the warm and when highly concentrated care should be taken in the event of the addition being made prior to concentration and the latter being effected by evaporation, not to employ large additions of zinc compounds, such as zinc chloride, which are powerful electrolytes and therefore possess a high coagulative capacity.

EXAMPLE I.

Rubber latex containing 37% of dry substance was treated with 0.75% (of its weight) of NH_3 and then with 0.07% of ZnO (in the form of a paste with water). A white latex was obtained which did not show any darkening of colour even after standing.

EXAMPLE II.

2.5 kgs. of ZnO were made into a paste with water and mixed with a solution of 18.2 kgs. of KOH in its own weight of water, a large portion of the zinc being thereby transformed into zincate. The mixture was then added to 5000 litres of rubber latex containing 38% of dry substance, that had previously been treated with 30 kg. of soap made from coconut oil and potash. The rubber latex prepared in this manner was afterwards concentrated to a content of 75% of dry substance, in a vacuum evaporator of the type described in Specifications No. 382,235 and No. 393,732. The resulting concentrate was of a pale colour and failed to exhibit any discolouration even after the addition of small quantities of a ferrous salt and potassium sulphide.

Dated the 6th day of March, 1934.

ALBERT L. MOND,
19, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agent for the Applicants.

COMPLETE SPECIFICATION

Process for Improving the Properties of Rubber Latex

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, and Dr. JOHANNES JAENICKE, a German Citizen, both of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, do hereby declare the nature of this invention and in what manner the same is to

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form of the readily soluble zinc salts, such as zinc chloride or zinc acetate, or of such sparingly-soluble salts as zinc carbonate. It is however, less advisable to employ readily soluble salts because (and particularly when larger amounts are added) a partial coagulation or aggregation of the particles of latex is liable to occur.

In addition to the direct transformation of the heavy-metal sulphides, the employment of small amounts of zinc compounds has a favourable effect insofar as presumably by retarding bacterial growth, the zinc compounds prevent the decomposition of the latex, that is, of its proteids and therefore counteract the formation of sulphuretted hydrogen or other sulphur-bearing fission products capable of transforming metallic salts into sulphides. Thus, already in this respect, the zinc compounds exert a favourable influence on the colour, inasmuch as they repress the chemical or biochemical reactions leading to the formation of the coloured sulphides, and consequently to the discoloration of the latex.

The great increase in the stability of rubber latex through the small addition of zinc compounds is evidenced, for example by the following observations.

Fresh rubber latex which was treated with 90 milli-equivalents of potassium hydroxide and 1 grm. of zinc oxide (in the form of a paste with water) per litre, remained for 3½ weeks before emitting a smell of protein-degradation products, and did not exhibit coagulation until 5 weeks had elapsed, whereas a second sample, differing from the first only in not being treated with zinc oxide already gave off a putrefactive smell at the end of 10 days, and coagulated in 12 days.

Fresh rubber latex treated with 100 milli-equivalents of ammonia per litre as a preservative, omitted a putrescent smell after 8 days, and exhibited a considerably increased internal friction after 12 days. A latex treated similarly in other respects, but containing in addition 4 grms. of zinc oxide per litre did not give off any disagreeable smell after 4 weeks and it was only after a longer period that any increase in viscosity could be detected.

In order to counteract the darkening of colour from the outset and to utilise the favourable influence of the small additions of zinc to the full, it is advisable to make the addition soon after the rubber latex has been produced and therefore prior to its transport (if any) to the countries where it is to be used.

In applying the present invention to rubber latex concentrates, the zinc compounds may be added either before or after concentration. Owing to the strong tendency of rubber latex to coagulate in the warm and when highly concentrated care should be taken in the event of the addition being made prior to concentration and the latter being effected by evaporation, not to employ large additions of zinc compounds, such as zinc chloride, which are powerful electrolytes and therefore possess a high coagulative capacity.

EXAMPLE I.

Rubber latex containing 37% of dry substance was treated with 0.75% (of its weight) of NH_3 and then with 0.07% of ZnO (in the form of a paste with water). A white latex was obtained which did not show any darkening of colour even after standing.

EXAMPLE II.

2.5 kgs. of ZnO were made into a paste with water and mixed with a solution of 18.2 kgs. of KOH in its own weight of water, a large portion of the zinc being thereby transformed into zincate. The mixture was then added to 5000 litres of rubber latex containing 38% of dry substance, that had previously been treated with 30 kg. of soap made from coconut oil and potash. The rubber latex prepared in this manner was afterwards concentrated to a content of 75% of dry substance, in a vacuum evaporator of the type described in Specifications No. 382,235 and No. 393,732. The resulting concentrate was of a pale colour and failed to exhibit any discolouration even after the addition of small quantities of a ferrous salt and potassium sulphide.

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be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for improving the properties of rubber latex and latex concentrates.

Rubber latex and its concentrates often exhibit a dark coloration, which makes itself inconveniently apparent in practice, for example by discolouring the articles manufactured from the coloured rubber latex and therefore rendering them unsightly. Exhaustive observations on the discoloration of the latex have led to the hypothesis that this condition is due to the presence of dark-coloured heavy-metal sulphides in the latex through the action of sulphuretted hydrogen resulting from the decomposition of such substances as protein constituents in the latex by, for example, bacterial agency. Every rubber latex contains traces of iron salts, which are transformed by the sulphuretted hydrogen into strongly pigmentary black sulphide. Contact with vessels containing or consisting of heavy metals, and the like, may also introduce into the latex heavy-metal salts which react with the sulphur compounds formed from the latex protein and thus lead to the formation of highly coloured sulphides.

According to the present invention the dark coloration of the rubber latex can be prevented or suppressed by treating the rubber latex with alkaline stabilisers, such as ammonia or potassium hydroxide, in sufficient amount for stabilising and zinc oxide, in amounts of not more than 0.5 parts, for example from 0.05 to 0.07 parts for every 100 parts of rubber, protective colloids being also added, if desired. Even the addition of such small quantities as about 0.005 parts of zinc oxide per 100 parts of rubber, has a favourable influence on the colour of the latex. Since the iron content in rubber latices varies to a very considerable extent, even smaller amounts of zinc oxide may occasionally be sufficient. In general, for example when it is a question of counteracting discolouring influences which have found their way into the rubber latex from outside, it is advisable to add somewhat larger quantities such as from about 0.05 to about 0.07 parts of zinc oxide per 100 parts of rubber in the latex.

The effect of the zinc oxide is due to the circumstance that it reacts almost completely with all heavy-metal sulphides which are more soluble than zinc sulphide, to form white zinc sulphide, and heavy-metal compounds which are less strongly coloured than their sulphides, so that the strong coloration due to the heavy-metal sulphides does not appear or else vanishes.

Since this reaction is substantially one of the zinc ion, other zinc compounds may be employed in place of, or addition to zinc oxide. In such case, the quantities taken should be such that the zinc content of the mixture varies approximately within the limits corresponding to those specified for zinc oxide. For example, the zinc oxide may first be wholly or partially converted into a zincate by dissolved alkali, and then added in that form. Alternatively, zinc oxide or hydroxide may be employed in solution or suspension in ammonia or solutions of ammonium salts. The zinc may also be introduced into the rubber latex in the form of the readily soluble zinc salts, such as zinc chloride or zinc acetate, or of such sparingly-soluble salts as zinc carbonate. It is however, less advisable to employ readily soluble salts because (and particularly when larger amounts are added) a partial coagulation or aggregation of the particles of latex is liable to occur.

In addition to the direct conversion of the heavy-metal sulphides, the employment of the foregoing small amounts of zinc compounds has a favourable effect insofar as presumably by retarding bacterial growth, the zinc compounds prevent the decomposition of the latex, that is, of its proteids and therefore counteract the formation of sulphuretted hydrogen or other sulphur-bearing fission products capable of converting metallic salts into sulphides. Thus, already in this respect, the zinc compounds exert a favourable influence on the colour, inasmuch as they repress the chemical or biochemical reactions leading to the formation of the coloured sulphides, and consequently to the discoloration of the latex.

The great increase in the stability of rubber latex through the small addition of zinc compounds in accordance with the present invention is evidenced, for example by the following observations.

Fresh rubber latex which was treated with 90 milli-equivalents of potassium hydroxide and 1 grm. of zinc oxide (in the form of a paste with water) per litre, remained for 3½ weeks before emitting a smell of protein-degradation products, and did not exhibit coagulation until 5 weeks had elapsed, whereas a second sample, differing from the first only in not being treated with zinc oxide already gave off a putrefactive smell at the end of 10 days, and coagulated in 12 days.

In order to counteract the darkening of colour from the outset and to utilise the favourable influence of the small addi-

tions of zinc to the full, it is advisable to make the addition soon after the rubber latex has been produced and therefore prior to its transport (if any) to the countries where it is to be used.

In applying the present invention to rubber latex concentrates, the zinc compounds may be added either before or after concentration. Owing to the strong tendency of rubber latex to coagulate in the warm and when highly concentrated care should be taken in the event of the addition being made prior to concentration and the latter being effected by evaporation, not to employ relatively large additions of zinc compounds, such as zinc chloride, which are powerful electrolytes and therefore possess a high coagulative capacity.

EXAMPLE I.

Rubber latex containing 37% of dry substance was treated with 0.75% (of its weight) of ammonia and then with 0.07% of zinc oxide (in the form of a paste with water). A white latex was obtained which did not show any darkening of colour even after standing.

EXAMPLE II.

2.5 kgs. of zinc oxide were made into a paste with water and mixed with a solution of 18.2 kgs. of potassium hydroxide in its own weight of water, a large portion of the zinc being thereby transformed into zincate. The mixture was then added to 5000 litres of rubber latex containing 38% of dry substance, that had previously been treated with 30 kgs. of soap made from coconut oil and potash. The rubber latex prepared in this manner was afterwards concentrated to a content of 75% of dry substance, in a vacuum evaporator of the type described in Specifications No. 382,235 and No. 393,732. The resulting concentrate was of a pale colour and failed to exhibit any discolouration even after the addition of small quantities of a ferrous salt and potassium sulphide.

It is already known to treat latex with vulcanising agents and (for activating same) with small amounts of zinc oxide. It is also known to transform latex into a highly viscous condition by adding, in addition to ammonia, water-glass and salts of zinc with weak acids, such as zinc carbonate. In contradistinction thereto, the present process is carried out with latices that contain no substances enabling the rubber in said latices to be vulcanised, and that have not had their viscosity increased by the addition of waterglass.

In the electrophoretic separation of rubber from rubber latex it has already been proposed to add to the latex a metallic salt such as zinc sulphate or aqueous solution thereof and thereafter to cause the rubber to be deposited upon an anode of the same metal as that of the added salt or salt solution and in said process it has moreover been proposed to add to the latex prior to electrophoreses chemicals or drugs such as for example, zinc oxide or sulphur which do not cause premature coagulation of the latex, in order that such chemicals or drugs will become incorporated with the deposited rubber.

In contradistinction to the foregoing proposal however, the present invention is not concerned with the electrophoretic separation of rubber, but aims at preventing or removing the dark coloration of latices and at the same time increasing the stability thereof.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1). A process for preventing or removing the dark coloration of latices and latex concentrates and for increasing the stability thereof, which comprises treating latices or their concentrates (which are free from substances enabling the rubber contained in the latices to be vulcanised and/or which have not been thickened by the addition of waterglass), with stabilisers having an alkaline reaction, such as ammonia or potassium hydroxide, in sufficient quantity for stabilisation, and zinc oxides in quantities of not more than 0.5 parts for example from 0.05 to 0.07 parts for every 100 parts of rubber, protective colloids being also added, if desired.

2). Process as set forth in Claim 1, in which, instead of or in addition to zinc oxide, other compounds furnishing zinc ions are employed the amount thereof being calculated so that the total content of zinc in the latex is approximately the same as introduced into the latex in accordance with Claim 1.

3). Process as set forth in Claim 1 or 2, in which the latex is subjected to a concentration process after the addition of the zinc compounds.

4). The process for improving the properties of rubber latex or latex concentrates, substantially as described.

5). Latex or latex concentrates, whenever improved in respect of its properties by the process particularly described and ascertained.

Dated this 26th day of February, 1935.

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