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MANUFACTURE OF RUBBER AND THE LIKE

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The present invention is for improvements in and relating to the manufacture of rubber and the like.

The invention concerns an improved process of thickening—that is, increasing the viscosity—and stabilizing aqueous dispersions of rubber and the like, and has particular reference to rubber latex. The term "latex" as used herein is to be understood to include crude and vulcanized latex of any kind, which may be preserved with the usual preservatives, such as ammonia, and may be either of natural strength or concentrated.

A number of disadvantages has been commonly encountered in the methods heretofore proposed for the thickening of rubber latex by the addition thereto of agents capable of effecting this change. The agents usually employed for the purpose are required in such quantity as adversely affects the attributes of the finished goods, or renders the latex unstable and difficult to process or necessitates methods of processing which are difficult or uneconomical. The present invention provides an improved process of thickening and stabilizing, which is simple and inexpensive in operation, and in addition, possesses the signal advantage of yielding solid products containing but a very small proportion of extraneous matters. Thus, in conjunction with simplicity in procedure, the invention permits obtaining a thickened, stable latex of a consistency of any desired degree up to that of a thick paste, and with the inclusion in the final goods of so small a proportion of extraneous matter—for example, about 0.25 to 2.0 per cent relatively to dry rubber, according to the degree of thickening and the condition of the original latex—as is, for all practical purposes, negligible.

According to this invention, the improved process of thickening and stabilizing an aqueous dispersion of rubber and the like is characterized by admixing with the dispersion a small proportion of an organic destabilizing reagent together with a small proportion of a fat-derived acid and a substantially non-volatile dispersive agent therefor which is miscible with the dispersion. Alcohols of the general character enumerated below, and esters thereof, may conveniently be used as de-stabilizing reagents. They have the property when mixed with a fat derived acid of forming a thickening and stabilizing reagent which, when added to the rubber dispersion, together with a non-volatile dispersive agent for the fat derived acid, produce a marked thickening and stabilizing effect. These reactions can be adjusted within fairly wide limits.

Cyclohexanol, the acetic ester thereof and any of the isomers of methylcyclohexanol are examples of satisfactory alcohols, and the last named appear to be the most generally effective members of this class. These compounds and their equivalents, and mixtures of such compounds, will hereinafter be designated by the term "alcohols of the type of cyclohexanol" and any one of them will be referred to (unless otherwise designated) as an "alcohol of the type of cyclohexanol." Aliphatic alcohols of dehydrating properties are not so satisfactory and are of limited application. Mixtures may be used. The preferred reagent is a mixture of the three isomers of methylcyclohexanol, in cyclohexanol.

By a fat-derived acid is meant an acid of a fatty or oleaginous nature such as is derivable from oils and fats. Stearic and oleic acids are examples of suitable acids of this type, and as dispersive or emulgating agents therefor may be employed neutral bodies, such as glycerol and Turkey red oil, or non-volatile bases, of which fixed alkalies and substantially non-volatile organic bases, such as triethanolamine, are examples. Triethanolamine or glycerol forms a particularly effective agent in conjunction with oleic acid and methylcyclohexanol. Turkey red oil is in comparison somewhat weak in action. By the term "fixed alkali" is meant any alkali which is not volatile.

The employment in conjunction of an acid such as oleic acid and a fixed alkali gives rise to an ordinary soap, but as dispersions of soap as such, for instance of castile soap or potassium oleate, are as a rule not easily incorporated by simple admixture with cyclohexanol unless they are so attenuated as unduly to dilute the rubber dispersion in accordance with the invention in producing the thickening and stabilizing reagents, we do not use such soaps themselves, but we mix the acid with the alcohol or ester thereof before the addition of the dispersing agent.

It is to be noted that it is combined action of the organic destabilizer and other agents as aforesaid which effects the thickening of the latex.

Cyclohexanol and any of the isomers of methylcyclohexanol when used by themselves do not produce any definite thickening action properly understood. Employed alone, unless with very careful addition to avoid clotting, they render the latex completely unstable—precisely the opposite effects to those attained by the present invention which yields thickened products of excellent stability. The use of substantially non-volatile dispersive agents for the acid appears to be a material factor in the attainment of this desirable property. Comparative tests in this respect indicated a superiority in conferring stability of the oleate of triethanolamine over potassium oleate, and superiority of the latter over ammonium oleate. The results obtained with glycerol in substitution for fixed alkali were also excellent.

The following examples are given more specifically to illustrate the character of the invention and ways in which it may be carried into effect.

Example I

A thickening and stabilizing agent was prepared in two portions as follows:

	Parts by weight
(1) Oleic acid	8.9
Methylcyclohexanol	6.2
(2) Potassium hydrate	1.0
Water	8.6

The two portions were mixed, this final mixture constituting the thickening and stabilizing agent; and we may here observe that it is convenient both for storage and use to have such agent prepared beforehand in the form of component dispersions or solutions. Further examples of thickening agents which may be so prepared are provided by the mixtures comprising triethanolamine and glycerol hereinafter described.

On the addition to 100 parts by weight of latex, preconcentrated by centrifuging to a content of 60 per cent. rubber, of 1 part by weight of the aforesaid agent—equivalent to approximately 0.65 per cent. of solid matter relatively to dry rubber—the comparative viscosity of the latex was increased from 125 to 200 immediately after the addition; to 320 after 24 hours; to 1020 after 72 hours; and after 336 hours to 1080, that is to say, after a maximum of 72 hours there was no substantial increase in viscosity. The so thickened latex displayed very good stability, and the stability and consistency remained constant over many weeks.

Example II

1 part by weight of the same thickening and stabilizing agent was added to 100 parts by weight of vulcanized latex of a rubber content of 50 per cent. The viscosity of the vulcanized rubber dispersion was increased about 4½ times within 72 hours.

Example III

1 part by weight of the same thickening and stabilizing agent as employed in the preceding examples was added to 100 parts by weight of a dilute ordinary latex. The change produced was very small, and the result was the same with a like dilute vulcanized latex. But on adding 2 to 3 per cent. of the agent—corresponding to 2 to 3 per cent. of potassium oleate on the final rubber—marked thickening took place and with production of a thickened latex of good stability.

This example illustrates that the degree of thickening obtainable is, ceteris paribus, dependent upon the concentration of the latex. Thus, while approximately 1 per cent. of the aforesaid agent was found to have very little effect, and even in some cases a slight thinning action, on latices below 40 per cent. in rubber, with a latex, crude or vulcanized, over this strength, the same small proportion of the agent produced a high degree of thickening. In any particular case, a simple preliminary experiment suffices to determine for the specific purpose in view the best operative conditions, such as the concentration of the initial latex and the minimum quantity of agent necessary for attaining the degree of thickening desired. It is advisable to leave the trial mixing to stand for 2 to 3 days as the thickening during that time is progressive; and in the case of the preparation of thick pastes, a period of 3 to 4 days should be allowed as the maximum thickening effect may not be apparent before then.

As a general guide it may be said that latex or vulcanized latex of over 55 per cent., and preferably of 60 per cent., rubber content, is suitable for the production of thick pastes, and that below a rubber concentration of about 55 per cent. it is not possible to obtain a paste. From 60 per cent. latex or vulcanized latex a thick paste may be obtained by adding 1 per cent. relatively to the latex of the thickening agent, and if a still thicker paste be required addition of more of the agent up to 2 per cent. on the latex may be made. In all cases, whether for the preparation of pastes, or for thickening for dipping or for making compounded mixings, the thickening agent should be added gradually, preferably with gentle stirring for the greater convenience of avoiding, as far as possible, the formation of bubbles.

Vulcanized and unvulcanized latex of any concentration may be thickened by an agent according to this invention so as to yield improved deposits on dipping. As a rule, with 60 per cent. latices, about 0.25 per cent. of the agent relatively to the latex will produce an appreciable result, and at first no more agent should be added. For latices of about 40 per cent. rubber content more agent will be needed, for example, 1 to 2 per cent. on the latex.

In general, compounded mixings require less, in some cases appreciably less, thickening agent than uncompounded mixings.

The succeeding examples are further illustrative of the foregoing principles.

Example IV

A thickening and stabilizing agent was prepared in two portions as follows:

	Parts by weight
(1) Oleic acid	6.00
A mixture of isomers of methylcyclohexanol	6.25
(2) Triethanolamine	4.00
Water	9.25

The agent resulting from the mixture of these two components possessed a thickening power greater than that of the agent of the preceding examples in approximately the proportion of 3:2.

On addition of 2 parts by weight of this agent to 100 parts by weight of 60 per cent. vulcanized latex, a thick paste, of very stable and consistent character, was obtained. The paste was so thick that it would not flow in the popular sense of the

term, and was of substantially the consistency of butter.

The addition of the same quantity of the agent to 60 per cent. unvulcanized latex gave a like, although somewhat less, thickening.

Smaller quantities of this agent, even as little as 0.5 part by weight per 100 parts by weight of latex, caused appreciable thickening. Thus, using 0.5 per cent. of the agent upon latex of 50 to 60 per cent. rubber concentration, sufficient thickening was produced to enable dipped goods to be prepared with a substantial reduction in the number of dippings. The addition of 1 per cent. of the agent to ordinary latex (about 40 per cent. rubber concentration), crude or vulcanized, caused a sufficient degree of thickening to improve materially the "dipping" properties.

Example V

A thickening stabilizing agent was made up as follows:

	Parts by weight
Oleic acid	4.00
A mixure of isomers of methylcyclohexanol	6.25
Glycerol	6.00
Water	9.25

Neither any one nor any two of the constituents of this agent possessed a notable thickening action, but the thickening property of the mixture as a whole surpassed that of either of the agents specified in the examples already given.

Example VI

A thickening stabilizing agent was prepared in two portions as follows:

	Parts by weight
(1) Oleic acid	6.23
A mixture of isomers of methylcyclohexanol	9.00
(2) Triethanolamine	2.80
Water	2.00

The aqueous solution of the base was mixed with the united acid and alcohol, and the mixture added to a latex concentrated by centrifuging to a solid content of 55 per cent. and containing ⅛ per cent. of casein, in the proportion of 0.5 per cent. of the thickening agent relatively to the rubber. The product was a stable, slightly thickened latex suitable for making dipped goods such, for instance, as balloons.

Example VII

To a mixture of:

	Parts by weight
Vulcanized latex (58 per cent)	100
Casein solution (10 per cent)	1

there were added 2 parts by weight of the thickening agent of the preceding Example VI. After standing two days, the mixture had passed into a thick paste which would not flow and could be handled in the same way as rubber dough. This product was particularly suitable for making rubber sheeting and like manufactures involving spreading. In the preparation of rubber-sheet by spreading vulcanized rubber on a smooth surface, the disadvantage has been commonly encountered that the fluid vulcanized material flows into depressions on the base of cloth or the like, or over the sides of the deposit, thus giving rise to an uneven sheet. By the use of the paste obtained as described in ths example, such a disadvantageous flow is avoided.

Example VIII

0.5 part by weight of the thickening and stabilizing agent of Example VI was added to a mixing of the following composition:

	Parts by weight
Vulcanized latex (58 per cent)	100
Casein solution (10 per cent)	2
Aluminum flake	23
Lithopone	6
Organic colouring matter	1
Water	35

whereby a thickened mixing was obtained suitable for making bathing shoes, bathing caps, hot water bottles and other dipped articles. By using this thickened mixing, the thickness of the deposit obtained with two dips was equal to the thickness produced by four dips from the untreated mixing.

According to the invention, the reagents employed to effect thickening, other than the alcohol, are retained in their entirety in the solid rubber. As already mentioned, however, the proportion of such extraneous material is extremely small, for example, 0.25 to 0.75 per cent. water-soluble matter on a rubber derived from a pre-concentrated latex. The amount of liquid added to the original latex may also be retained within low limits, for example, 1 to 2 per cent. relatively to the latex.

The lathering properties of soaps tend to be reduced in the presence of cyclohexanol, and this is an advantage in the treatment of latex since undue frothing or bubble formation, which is apt to occur in the use of soaps in the ordinary way, is minimized or eliminated. Most known stabilizers also tend to produce frothing. The present invention therefore also carries an advantage in this respect. Another advantage is this, that if latex thickened by a process as herein provided be used for dipping, the difficulty occasioned by skin-formation encountered in the application of ordinary concentrated latex is avoided. Rubber films made from latex thickened according to this invention are not appreciably affected as regards tensile properties, colour or ageing.

Having thus described our invention, what we desire to claim as new is:

1. The improved process of thickening an aqueous dispersion of rubber and the like which is characterized by admixing with the dispersion a small proportion of an organic destabilizing reagent in conjunction with a small proportion of a fat-derived acid and a substantially non-volatile dispersive agent therefor which is miscible with the dispersion.

2. A process according to claim 1 wherein the fat-derived acid is oleic acid.

3. A process according to claim 1 wherein the dispersive agent for the acid is a neutral body, such as glycerol.

4. A process according to claim 1 wherein the dispersive agent for the acid is a base.

5. The improved process of thickening and stabilizing an aqueous dispersion of rubber and the like which is characterized by admixing with the dispersion a small proportion of a thickening and stabilizing reagent produced by admixing an alcohol with a fat derived acid, and admixing with the composition so formed a substantially

non-volatile dispersive agent for the fat derived acid which is miscible with the dispersion.

6. The improved process of thickening and stabilizing an aqueous dispersion of rubber and the like which is characterized by admixing with the dispersion a small proportion of a thickening and stabilizing reagent produced by admixing an alcohol of the type of cyclohexanol with a fat derived acid, and admixing with the composition so formed a substantially non-volatile dispersive agent for the fat derived acid which is miscible with the dispersion.

7. A process according to claim 6, wherein the fat-derived acid is oleic acid.

8. A process according to claim 6, wherein the dispersive agent for the acid is a neutral body, such as glycerol.

9. A process according to claim 6, wherein the dispersive agent for the acid is a base.

10. A process according to claim 6, wherein the fat-derived acid is oleic acid and the dispersive agent is a neutral body, such as glycerol.

11. A process according to claim 6, wherein the fat-derived acid is oleic acid, and the dispersive agent for the acid is a base.

12. A process according to claim 6, wherein the dispersive agent is a fixed alkali.

13. A process according to claim 6, wherein the dispersive agent is an organic base, such as triethylonamine.

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