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HIGH VISCOSITY DISPERSIONS OF RUBBERY MATERIALS

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This invention relates to aqueous dispersions of rubbery material and is particularly concerned with viscous dispersions having good viscosity stability.

In the commercial utilization of aqueous dispersions of rubbery material it is frequently necessary to employ a dispersion having a relatively high viscosity. When, for example, it is desired to apply a dispersion as a coating by means of a spreader or similar device, it is frequently necessary to employ a dispersion having a viscosity in the range of 70,000 to 100,000 centipoises in order properly to perform this operation. For other commercial applications, viscosities of the order of 10,000 to 18,000 centipoises are commonly required. Various materials have been proposed for addition to rubbery dispersions to increase viscosity as, for example, alkali metal hydroxide caseinates, formed by dissolving casein in alkali metal hydroxide solutions. While increased viscosity has thus been realized, it has been found that dispersions treated in this manner rapidly decrease in viscosity upon standing, that is to say, they lack viscosity stability. This is of course disadvantageous, since a dispersion which may have satisfactory viscosity when shipped by the producer will have so changed in viscosity during transit that, when it arrives at the consumer's plant, it is unsatisfactory for use without special treatment. Further, it has been found that, in the case of dispersions of relatively high pH, i. e. 10.5 or above, alkali metal hydroxide caseinates and similar thickening agents have very little viscosity-increasing action.

It is an object of this invention to provide dispersions of rubbery material having good viscosity stability.

It is a further object of this invention to provide a process for increasing substantially the viscosity of dispersions of relatively high pH.

Other objects and features of the invention will be apparent from the description which follows.

According to the invention, viscous dispersions of good viscosity stability may be prepared by incorporating in a dispersion of rubbery material a small quantity of a thickening agent comprising casein and an alkaline buffer salt. By the term alkaline buffer salt is meant those salts which give an alkaline reaction in aqueous solution and which inhibit change in pH upon addition of acid or alkali to the solution. Examples of such materials which have been found particularly suitable in accordance with my invention are borax, sodium carbonate, sodium silicate and trisodium phosphate. The combination of casein and an alkaline buffer salt, when incorporated even in small amounts in an aqueous dispersion of rubbery material, effects a sharp increase in the viscosity of the dispersion and imparts to the dispersion good viscosity stability whereby the viscosity is maintained for a relatively long period of time, compared with stability periods attainable with alkali metal hydroxide caseinates and like thickening agents. Further, a stable, high viscosity may thus be imparted to a dispersion of rubbery material even though the dispersion has a relatively high alkalinity, i. e., a pH of 10.5 to 12. In the case of dispersions of lower alkalinity, i. e., below about pH 10, for which alkali metal caseinates are to some extent satisfactory, in so far as increasing viscosity is concerned, I have found that by employing my casein-alkaline buffer salt agent, in accordance with the invention, a substantially greater increase in viscosity is realized for a given quantity of thickening agent.

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My invention is applicable both to dispersions of natural rubber and to dispersions of so-called synthetic rubbers, such as neoprene (polymerized 2-chlorobutadiene-1,3) and butadiene-styrene copolymer, known in one commercial form as GR-S. The rubbery dispersions may be in the form of latices or may be artificial dispersions, such as reclaim dispersions. The advantages of my invention are particularly noticeable in the case of artificial dispersions in which alkali metal soaps, e. g., sodium or potassium soaps of oleic acid or tall oil, are employed as the dispersing agent, although the invention is not limited thereto.

The alkaline buffer salt and casein are preferably incorporated in the dispersions in an aqueous medium. The aqueous casein-alkaline buffer salt agent may be prepared, for example, by swelling the casein in water and then adding the alkaline buffer salt to the casein slurry. The aqueous solution preferably contains sufficient water to provide maximum ease of handling and mixing and to provide, at the same time, a solution having maximum thickening properties. I have found a solution containing about 80–85% water to be particularly suitable.

In the case of artificial dispersions, it is particularly advantageous to incorporate at least a part of the casein and alkaline buffer salt during the preparation of the dispersion. It is also desirable to incorporate some of the casein.

and alkaline buffer salt during the compounding of latices. All of the casein-buffer salt thickening agent may, however, be successfully incorporated in the finished dispersions, whether an artificial dispersion or a natural or synthetic rubber latex. In the case of a dispersion in which the casein-buffer salt agent has been incorporated during the preparation thereof, additional quantities of my thickening agent may be readily added to the completed dispersion to adjust the viscosity to any desired value.

Significant increases in viscosity are obtainable with relatively small quantities of my casein-buffer salt thickening agent. I have found, for example, that as little as 0.5–1.5% casein and 0.1–0.3% buffer salt, based on the dry weight of the rubbery material in the dispersion, when incorporated in a dispersion having a viscosity of say, 2000–3000 centipoises raises the viscosity of the dispersion to about 15,000–18,000 centipoises and imparts to the dispersion good viscosity stability. The quantity of casein-buffer salt thickening agent incorporated in the dispersion will, of course, depend upon the ultimate viscosity desired. Increased quantities result in higher viscosities. I have found that the viscosity stabilizing effect of the casein-buffer salt agent is effective even at exceedingly high viscosities, i. e. of the order of 70,000–100,000 centipoises. Such viscosities which are frequently required for dispersions for use as spreader pastes may be obtained by incorporating in the dispersion relatively small amounts of casein and of alkaline buffer salt. For example, the viscosity of a dispersion of reclaimed rubber may be raised from about 2000–3000 centipoises to about 100,000 centipoises by the total addition of about 3% of casein and about 0.6% of alkaline buffer salt, based on the weight of the reclaimed rubber in the dispersion. When part of the casein-buffer salt agent is added during the dispersing operation, or during the compounding step in the case of latices, it is generally desirable to add only sufficient agent to impart stability to the dispersion and thereby facilitate the dispersing or compounding operations. After dispersing or compounding is completed, the viscosity of the product is readily adjusted to the desired value by the direct addition of further quantities of the casein-alkaline buffer salt agent.

The quantity of agent will vary somewhat depending upon the type of rubbery material as well as the type of compounding ingredients in the dispersion. Latices generally require slightly greater quantities than do artificial dispersions to obtain comparable results. Generally speaking, one part of the alkaline buffer salt is used for each 5 parts of casein although this relationship is subject to variation depending upon the specific buffer salt.

The dispersions of rubbery material which may be employed in accordance with the invention may be prepared in any known manner and the invention is not limited to dispersions prepared in accordance with any particular process. Artificial dispersions are generally prepared by incorporating a dispersing agent, such as an alkali metal soap, into previously plasticized rubbery material, and then masticating the batch with gradual continued addition of water until there is brought about an inversion of phase; i. e., the water becomes the continuous phase and the rubbery material becomes the discontinuous or dispersed phase. Plasticizing agents, fillers and the like are commonly incorporated during the dispersing operation to facilitate dispersion and to impart desirable properties to the compound. It is advantageous to incorporate a portion of the casein-buffer salt agent during the preparation of the dispersion to gain the advantage of the dispersing and stabilizing properties of the casein.

The following examples are illustrative of the invention, all parts being by weight.

Example 1

One hundred parts of reclaimed rubber, in the form of digester tube reclaim, were worked for about three minutes in a Banbury. At the end of this time the temperature of the rubber was in the range of 250 to 300° F. The "Banburyed" rubber was added to an internal mixer of the Werner-Pfleiderer type, together with 25 parts of whiting, 8 parts of tall oil, 20 parts of coumarone-indene resin, 2 parts of zinc oxide, 1 part of Agerite Stalite and 0.2 part of Dowicide A and the mass mixed for fifteen minutes. During the mixing operation 2 parts of sulphur and 8.33 parts of water were added, whereupon 4 parts of an aqueous solution of alkali such as a 45% solution of potassium hydroxide were added. Preferably the alkali solution is added in several increments. After a few minutes of further mixing, with gradual addition of further quantities of water, inversion of phase occurred. Substantially immediately following inversion, 3.2 parts of an aqueous solution of casein and borax were added, said solution being composed of approximately 15% casein, 3% borax, 0.2% Dowicide A, and 81.8% water. The dispersion was then diluted to a solids content of about 70% by the gradual addition of a 0.2% solution of KOH-tall oil soap in water.

The viscosity of the thus-prepared dispersion was determined and a small additional amount of the casein-borax solution was added to raise the viscosity to 15,000–18,000 centipoises. This required less than 6 parts of the casein-borax solution. The viscosity was found to be substantially unchanged when tested after 20 days. Higher viscosities are readily obtainable by incorporating additional quantities of the casein-borax solution. For example, a further addition of 2% casein and 0.4% borax, based on the weight of the reclaimed rubber, raises the viscosity of the thus-prepared dispersion to about 100,000 centipoises.

The various compounding agents are those commonly employed in the preparation of rubbery dispersions. The coumarone-indene resin is employed as a plasticizer for the reclaim. Whiting is a filler, zinc oxide functions as a curing agent, and Agerite Stalite is a proprietary anti-oxidant composed essentially of heptylated diphenylamine. Sulphur is the vulcanizing agent. Dowicide A is a proprietary preservative agent for the casein and is, chemically, sodium orthophenyl phenate. Other well-known preservatives for casein, such as beta-naphthol, for example, may be used.

The viscosity determinations were made with a Brookfield viscosimeter, 20 R. P. M. at 77° F.

Example 2

This example shows the use of my casein-buffer salt agent to increase the viscosity of a latex compound.

Commonly employed compounding ingredients

were added to 334 parts of GR–S latex X359 and the following latex compound obtained.

Ingredients	Composition
	Parts
GR–S latex X359 (60% solids)	334
10% KOH solution	5
57.5% clay slurry	87
50% Agerite Powder paste	4
50% sulphur paste	12
50% zinc oxide paste	20
	462

Total solids	58.2
pH	12.1
Viscosity ——centipoises	800

To 231 parts of the above GR–S latex compound were added 13.3 parts of a casein-borax solution (15% casein, 3% borax, 0.4% Dowicide A and 81.6% water). The quantities employed are equivalent to 2% casein and 0.4% borax, based on the weight of GR–S in the latex compound. Agerite Powder is a proprietary antioxidant composed of phenyl-beta-naphthylamine.

The resulting product had a pH of 10.4 and a viscosity of 42,000 centipoises, as determined with a Brookfield viscosimeter.

Since certain changes may be made in the invention without departing from the scope thereof, as defined in the appended claims, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A viscous rubbery dispersion having a viscosity of at least 10,000 centipoises and comprising a rubbery material from the group consisting of natural rubber, polymerized 2-chlorobutadiene-1,3 and butadiene styrene copolymers dispersed in an aqueous medium, said dispersion consisting predominantly of solids, the rubbery material representing the major proportion of the solids, and containing from .5% to 3% of casein and from .1% to .6% of an alkaline buffer salt based on the weight of the rubbery material and being characterized by good viscosity stability, the viscosity of said dispersion remaining substantially unchanged over a period of several days.

2. A viscous rubbery dispersion having a viscosity of at least 10,000 centipoises and comprising a rubbery material from the group consisting of natural rubber, polymerized 2-chlorobutadiene-1,3 and butadiene styrene copolymers dispersed in an aqueous medium, said dispersion consisting predominantly of solids, the rubbery material representing the major proportion of the solids, and containing from .5% to 3% of casein and from .1% to .6% borax based on the weight of the rubbery material and being characterized by good viscosity stability, the viscosity of said dispersion remaining substantially unchanged over a period of several days.

3. A viscous rubbery dispersion having a viscosity between 10,000 and 100,000 centipoises of a rubbery material from the group consisting of natural rubber, polymerized 2-chlorobutadiene-1,3 and butadiene styrene copolymers dispersed in an aqueous medium, said dispersion consisting predominantly of solids, the rubbery material representing the major proportion of the solids, and containing from .5% to 3% of casein and from .1% to .6% of borax based on the weight of the rubbery material and being characterized by good viscosity stability, the viscosity of said dispersion remaining substantially unchanged over a period of several days.

4. A method of imparting a stable viscosity of 10,000 to 100,000 centipoises to an aqueous dispersion of a rubbery material selected from the group consisting of natural rubber, polymerized 2-chlorobutadiene-1,3 and butadiene styrene copolymers dispersed in an aqueous medium, said dispersion consisting predominantly of solids, the rubbery material representing the major proportion of the solids and the viscosity of said dispersion remaining substantially unchanged over a period of several days, which method comprises incorporating in said dispersion from .5% to 3% of casein and from .1% to .6% of borax based on the weight of the rubbery material.

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