United States Patent Office 2,702,796
Patented Feb. 22, 1955

2,702,796

TEXTILE SIZE COMPRISING A PARTIALLY NEUTRALIZED POLYMETHACRYLIC ACID

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No Drawing. Application May 31, 1950, Serial No. 165,381

8 Claims. (Cl. 260—28.5)

The present invention relates to a composition of matter.

An object of the invention is to prepare a composition which is particularly useful for sizing synthetic textiles such as those spun or drawn from polyamides, vinyl and vinylidene polymers, viscose and cellulose derivatives, protein fibers and the like.

Another object is to provide an improved sizing composition of the type comprising polymethacrylic acid and a plasticizer.

A further object is to provide a corrosion inhibited, lubricating sizing composition of the polymethacrylic acid, plasticizer type.

Another object is to provide in dry readily water dispersible form a sizing composition comprising polymethacrylic acid, a plasticizer, and a lubricating compound.

The above and other objects will become apparent in the course of the following description of the invention.

Polymethacrylic acid is a water-soluble film forming compound which in combination with plasticizers has found extensive use as sizes in connection with synthetic textiles such as those spun or drawn from nylon, vinyl polymers, viscose and cellulose derivatives. The polymethacrylic acid (or PMA as it is frequently called) gives both protection and added strength to the filament or filament bundles to protect them during textile operations such as weaving, knitting, and the various handling steps.

The employment of a PMA size presents two outstanding problems; first, the polymethacrylic acid is corrosive and causes injury to the sizing apparatus and also any metal surfaces which the sized textile touches; secondly, the untreated film has insufficient lubricity for high speed mechanical handling and, furthermore, is incompatible with many of the conventional textile lubricants.

In accordance with the present invention a polymethacrylic textile sizing composition has been prepared which is corrosion-inhibited and is of excellent lubricity.

This composition has been prepared by adding to a PMA solution in water a basic material to accomplish partial neutralization of the PMA to a pH not less than 4.5 and adding a water soluble or readily water dispersible polyoxyethylene surface active agent. Some of these agents are useful as effective and scourable lubricating agents per se. All are useful as emulsifying agents for more difficultly dispersible textile lubricants. Attempts to combine polyoxyethylene compounds with PMA solutions without previous neutralization causes immediate precipitation of a gummy material. Only if the acidic nature of the PMA is decreased to within critical ranges prior to addition of the polyoxyethylene compound is a compatible mixture formed.

It was discovered that the neutralization should not be complete and preferably should not be carried above a pH of about 6. As the pH of the compounded conditioning compositions is carried above 6 an undesirable rise in viscosity occurs. Furthermore, the amount of neutralizing agent employed in raising the pH above 6 is sufficiently great to exert an adverse effect on the film properties of the composition. Also at pH values greater than 7 ester-type polyoxyethylene compounds and ester-type textile lubricants tend to saponify with consequent loss of emulsion stability and other properties.

The polyoxyethylene compounds referred to are members of a well-known class of non-ionic compounds which are characterized by the presence in the molecule of one

or more polyoxyethylene chains, forming the hydrophilic portion, and one or more high molecular weight hydrocarbon radicals, forming the lipophilic portion. Particularly adaptable are those derivatives containing 12 to 18 carbon atoms in the lipophilic portion of the molecule and more than three polyoxyethylene groups forming the hydrophilic portion. The polyoxyethylene portion can be chemically connected to the hydrocarbon portion through a carboxyl group (as where the hydrocarbon radical is in a long chain acyl group), an ether linkage (as where the hydrocarbon radical is in the residue of a long chain aliphatic alcohol, or an alkyl substituted phenol, or where the hydrocarbon radical is attached through a carboxyl or ether linkage to the residue of a polyhydroxylic compound which in turn is linked through oxygen to the polyoxyethylene chain), an amine linkage (as where the hydrocarbon radical is in the residue of a long chain aliphatic amine), an amide linkage (as where the hydrocarbon radical is in the residue of a long chain fatty acid amide), or a thioether linkage (as where the hydrocarbon radical is in the residue of a long chain aliphatic mercaptan). Polyoxyethylene compounds of these types are described for example in Patents Nos. 1,959,930 to Schmidt and Meyer, 1,970,578 to Schoeller and Wittwer.

As described in the patents referred to, the polyoxyethylene compounds are preferably made by the direct reaction of ethylene oxide and the compound containing the hydrocarbon radical and an active hydrogen atom. The number of oxyethylene groups added should be sufficient to render the resulting polyoxyethylene compound water-soluble or at least readily water-dispersible.

The basic materials useful in partially neutralizing the PMA are any of the inorganic alkaline compounds, ammonia, or organic nitrogen bases. Examples of these materials are sodium hydroxide, trisodium phosphate, ammonium hydroxide, triethanolamine, morpholine, 2-amino-2-methyl-1,3-propanediol, and 2-amino-2-methyl-1-propanol. The solid organic nitrogen bases typified by 2-amino-2-methyl-1,3-propanediol have the advantage that they can be used in the preparation of dry mixtures with PMA and the other ingredients of the composition of the invention. Table I exemplifies the effect of various neutralizing agents upon the pH of PMA solutions.

Table I

Wt. of neutralizer per 100 grams 10% PMA	Neutralizing Agent	pH
0.4	Sodium hydroxide	4.9
1.0	Triethanolamine	4.85
2.8	$Na_3PO_4.12H_2O$	5.1
1.2	Morpholine	5.0
1.0	2-amino-2-methyl-1,3 propanediol	5.15
1.0	2-amino-2-methyl-1-propanol	4.95
4.0	Urea	4.5
1.25	Ammonium hydroxide (28%)	5.0

Films produced by PMA are of a brittle character in their unmodified state and it is, therefore, standard practice in the art to use a plasticizer which is generally a water-soluble polyhydroxylic humectant, suitably a polyhydric alcohol such as ethylene glycol, glycerol or sorbitol. Sorbitol is preferred because of its superior humectant properties. A further advantage of sorbitol is that it is available in dry form and so can be used in the preparation of dry mixtures whereas the lower polyhydric alcohols cannot.

Thus far reference has been made to the four components which are essential to the composition of the invention, namely, PMA, neutralizing material, PWA plasticizer, and the polyoxyethylene compound. For the best textile lubricating compositions it is desirable to have, in addition to these four components, a portion of a harder, higher melting wax which is insoluble in water and which is incompatible with the PMA so that the films produced on textile materials contain separated particles of the wax. These separated particles are found largely at the surface of the films and contribute valuable lubricating properties. Examples of suitable insoluble waxes are paraffin waxes, natural waxes such as beeswax and

carnauba wax, high titer long chain fatty acids such as stearic acid, palmitic acid, and the like, high titer esters of long chain fatty acids and polyhydroxylic compounds such as glycerol mono-, di-, and tristearates or palmitates, sorbitan mono-, di-, tri-, and tetrastearates or palmitates, sorbide mono-, and distearates or palmitates, tetra- and pentastearates, or palmitates of polyoxyethylene glucose containing an average of six oxyethylene groups per mol, and the tetra-, penta-, and hexastearates or palmitates of polyoxyethylene sorbitol containing an average of six oxyethylene groups per mol. Many other chemical variations of waxes could be employed such as high titer long chain alcohols, amides, amines and nitriles, but the foregoing list is intended to be illustrative of the fact that the wax is to be selected on the basis of physical properties rather than chemical structure.

The water insoluble waxes require emulsifiers to disperse them in water. The water-soluble to readily water-dispersible polyoxyethylene compounds hereinbefore described are excellent emulsifiers for this purpose. Any of the well-known wax dispersing agents may be employed. However, in compounding complete textile conditioning compounds according to the invention, it has been found preferable to select water-insoluble waxes and polyoxyethylene emulsifiers for them and to employ them in proportions such that the resulting mixtures are just sufficiently dispersible in the partially neutralized and plasticized PMA solution to produce relatively coarse emulsions which maintain stability during the period of application. When a dispersion of this type is applied to a textile material the insoluble wax deposits in relatively large particles giving maximum lubrication.

The properties of the several components of the composition of the invention are subject to wide variation, except in the case of the neutralizing agent which must be controlled with respect to the amount of PMA present to give partial neutralization.

The amount of PMA with respect to the lubricant determines the degree of lubrication obtained. For some purposes it is desirable to have strong, tough films with only a small amount of lubricant while for other purposes the lubrication is the most important object and the PMA film is desired to obtain adhesion to the fiber. While there is a great deal of variation in the effects of different lubricant combinations on the PMA films, it is generally the case that the total lubricant should be not over ½ the quantity of PMA but not less than about ⅕ the quantity of PMA. In the preferred specific compositions of the examples the ratio is about 1/2.7.

Where the lubricant is compounded of water-insoluble waxes and polyoxyethylene emulsifiers the proportions of these ingredients are preferably selected to use the greatest quantity possible of the water-insoluble components and the least possible quantity of the polyoxyethylene emulsifiers.

The PMA plasticizer is also variable in quantity within a wide range, the limits being determined by the degree of softness desired for the film. In the case of sorbitol as a plasticizer the range is suitably from ½ to 1 part by weight of sorbitol to 1 part of PMA with 0.8 part sorbitol to 1 part PMA being preferred in the specific formulations of the examples.

Blends of the various plasticizers, emulsifiers and lubricants may be used to impart desired properties to the finished product.

The following examples illustrate preferred textile lubricating compositions according to the invention.

Example I

A lubricant composition was prepared by melting together 45% white scale wax (124/126 AMP), 30% stearic acid and 25% polyoxyethylene stearic acid containing an average of 20 oxyethylene groups per mol.

A mixture was prepared composed of 8 grams PMA, 6.4 grams crystalline sorbitol, and 0.96 gram of morpholine. Sufficient water was added to dissolve the mixture. The lubricant composition described above was dispersed by constant agitation into this solution in the proportion of 1 part of lubricant per 5 parts of plasticized, partially neutralized PMA. The dispersion was diluted with water to a solids concentration of 20%. This dispersion required occasional stirring to prevent separation.

The lubricant tends to migrate to the surface as the film produced on drying forms giving a tough, well lubricated surface.

Example II

A lubricant composition was prepared by mixing together 60% sorbitan monolaurate, which is an oily viscous liquid, and 40% polyoxyethylene castor oil containing an average of 127 oxyethylene groups per mol. This mixture was a soft waxy composition.

A solution consisting of 10 grams of PMA, 7.5 grams of glycerol and 4.0 grams of sodium hydroxide was prepared. To 5 parts of this partially neutralized solution one part of the lubricant composition described above was added and dispersed by mixing. The dispersion was diluted with water to a solids concentration of 20%. This dispersion did not separate on standing. A slight creaming was observed but it was readily overcome by occasional stirring.

In this composition the lubricant had a higher degree of compatibility with the PMA in consequence of which there was a somewhat lessened lubricity of the film on drying than that produced by the composition of Example I.

Example III

A water dispersion of partially neutralized PMA, sorbitol and lubricant was prepared following the procedure outlined in Example I employing the following lubricant:

45% white scale wax (124/126 AMP)
30% diethylene glycol monostearate
6% sorbitan monopalmitate
6% polyoxyethylene sorbitan monopalmitate containing 20 oxyethylene groups per mol
13% polyoxyethylene castor oil containing an average of 81 oxyethylene groups per mol.

The films produced when this wax is used are tough and waxy with fairly good continuity. The emulsions exhibit a satisfactory order of stability. The lubricant has a tendency to migrate to the surface of the film.

Example IV

A satisfactory sizing composition of the dry mix type has the following composition:

43% polymethacrylic acid
34.4% crystalline sorbitol
16.1% lubricant as prepared in Example III
6.5% 2-amino-2-methyl-1,3-propanediol.

These materials were mixed by charging a No. 3 Lancaster mixer with proportionate quantities of finely powdered polymethacrylic acid, sorbitol and 2-amino-2-methyl-1,3-propanediol. These ingredients were milled together until intimately mixed. The lubricant was then added as a molten mass. Mixing was continued until the mass was of uniform consistency. After cooling the charge was transferred to a Stokes Granulator in which it was granulated through a U. S. S. No. 10 wire screen.

A 29% dispersion of this composition in water at 90° C. has a pH of 5.1 and is stable. The resulting film is tough, adhesive and well lubricated.

It will be apparent that many variations can be made without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. A textile sizing composition comprising, as a film forming agent, polymethacrylic acid partially neutralized to a pH of about 4.5 to 6; a plasticizer therefor; and as an emulsifiable lubricant, a polyoxyethylene condensate of a lipophilic aliphatic organic compound wherein the condensate contains at least 3 oxyethylene groups and the said organic compound is selected from the group consisting of alcohols, carboxylic acids, amides, amines and mercaptans which contain lipophilic hydrocarbon radicals of from 12 to 18 carbon atoms; and wherein the ratio of polymethacrylic acid to emulsifiable lubricant ranges from 2/1 to 5/1.

2. A textile sizing composition comprising as a film forming agent, polymethacrylic acid partially neutralized to a pH of about 4.5 to 6; a plasticizer therefor; a water insoluble wax; and as an emulsifiable lubricant, a polyoxyethylene condensate of a lipophilic aliphatic organic compound wherein the condensate contains at least 3 oxyethylene groups and the said organic compound is selected from the group consisting of alcohols, carboxylic acids, amides, amines and mercaptans which contain lipophilic hydrocarbon radicals of from 12 to 18 carbon atoms; and wherein the ratio of polymethacrylic acid to emulsifiable lubricant ranges from 2/1 to 5/1.

3. An essentially dry textile sizing composition comprising as a film forming agent, polymethacrylic acid; a plasticizer therefor; sufficient solid neutralizer to adjust the pH of the composition to about 4.5 to 6 upon solution in water; a water insoluble wax; and as an emulsifiable lubricant, a polyoxyethylene condensate of a lipophilic aliphatic organic compound wherein the condensate contains at least 3 oxyethylene groups and the said organic compound is selected from the group consisting of alcohols, carboxylic acids, amides, amines and mercaptans which contain lipophilic hydrocarbon radicals of from 12 to 18 carbon atoms; and wherein the ratio of polymethacrylic acid to emulsifiable lubricant ranges from 2/1 to 5/1.

4. A composition as described in claim 1 wherein the organic compound is an amine containing from 12 to 18 carbon atoms.

5. A composition as described in claim 1 wherein the organic compound is an amide containing from 12 to 18 carbon atoms.

6. A composition as described in claim 1 wherein the organic compound is an alcohol containing from 12 to 18 carbon atoms.

7. A composition as described in claim 1 wherein the organic compound is a carboxylic acid containing from 12 to 18 carbon atoms.

8. A composition as described in claim 1 wherein the organic compound is a mercaptan containing from 12 to 18 carbon atoms.

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