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2,793,142

AQUEOUS DISPERSIONS COMPRISING N,N'-OXYDIMETHYLENE-BIS-ACYLAMIDES AND USEFUL AS WATER-REPELLENCY AGENTS FOR TEXTILE FIBERS

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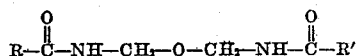
7 Claims. (Cl. 117—135.5)

This invention relates to aqueous dispersions comprising long chain N,N'-oxydimethylene-bis-acylamides, and to a process of applying them to textiles whereby to produce a durable water-repellent finish on the treated fabric.

Heretofore, many different treatments of fabric have been proposed to render them repellent to water. Difficulties are encountered in treating fabrics without impairing their natural feel or "hand" and their resistance to repeated washing, dry-cleaning and normal wear. In addition to water-proofing the fabric, it is often desirable to render it crease-resistant or to impart some other desirable property. In such cases the water-proof treatment should be compatible therewith. In addition to the above considerations, the water-repellent agent should not tender or discolor the fabric nor should it be toxic, inflammable or have any other dangerous or undesirable properties.

It is an object of the present invention to provide an aqueous dispersion comprising a water-repellent agent which combines the above required properties. Another object is the provision of a dispersion of this character which is stable on storage and may be applied to a fabric by known commercial methods of application. A still further object is a simple and economical method of making and dispersing the water-repellent agent. Other objects will be apparent as the description of the invention proceeds.

These and related objects are accomplished by preparing a long chain N,N'-oxydimethylene-bis-acylamide having a formula of the following type:



in which R and R' are straight chain aliphatic hydrocarbon radicals having from 9 to 29 carbon atoms and in which the R's may be the same or different. These agents may be conveniently prepared by heating the corresponding N-hydroxymethyl amides at a temperature of about 40° to 75° C. in an inert vehicle which contains less than about 3% of water based on the methylol amide. The reaction is carried out under mildly acid conditions the proper acidity of which is best determined by an amount and kind of acid which just turns dry Congo red paper blue.

These compounds are then used to prepare compositions for impregnating fabrics, such compositions preferably taking the form of aqueous dispersions of the above defined oxydimethylenediacylamides containing about 2 to 5% by weight of a protective colloid and about 5 to 8% by weight of a heat-labile, transitory dispersing agent, both percentages being based on the weight of the amide. The protective colloid may be any which forms a protective envelope over the colloidal particles of the water-repellent agent. The common protective colloids are polyvinyl alcohol, starch, carboxymethyl cellulose, sodium alginate, and the like. The dispersing agents are of the type which are non-rewetting either because of their

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inherent properties or because their ability to rewet is destroyed when the textile is cured. Examples of these two types, respectively, are the commercial polyoxyalkylene derivatives of sorbitan monostearate and stearamidomethyl pyridinium chloride.

The invention also includes impregnating textile fibers with one of the above dispersions in the presence of at least 0.1% but preferably not more than 50% by weight of a mildly acid or potentially acid catalyst based on the weight of the ether followed by heating to a temperature of about 110° to 150° C.

The starting materials for making the water-repellency agent may be any N-hydroxymethyl fatty acid amide having from 9 to 29 carbon atoms in the hydrocarbon chain although the preferred starting material is one sold commercially under the name of N-hydroxymethylstearamide. Actually however, it consists essentially of a mixture of N-hydroxymethyl amides of stearic and palmitic acids which may vary considerably although the stearamide content is between 50 and 95% of the total. It will be apparent therefore, that the ether prepared using this product as the starting material will not be symmetrical but may contain mixed ethers or varying amounts of N,N'-oxydimethylene-bis-stearamide and N,N'-oxydimethylene-bis-palmitamide.

As in most chemical reactions, several factors influence the rate of reaction and the products obtained. In the present case the reaction proceeds particularly satisfactorily at a temperature between about 40° and 75° C. and for 1 to 2 hours. Higher or lower temperatures may be used with a corresponding increase or decrease in the time. Elevated temperatures in a pressure vessel also may be used if desired but for economy, it is preferable to operate between about 50° C. and the boiling point of the reaction medium.

It has been found that the optimum acidity of the reaction is that which just turns dry Congo red paper blue. Any amount which gives a blue spot on the dry paper immediately is satisfactory. If the paper turns black, the acidity is far too great, and if it fails to turn blue, it is insufficient.

Any relatively strong acid may be used in the invention. The preferred acids are hydrochloric, 85% phosphoric, and p-toluene sulfonic. Various heat-labile acid salts, such as pyridine hydrochloride, are also suitable, but not preferred. The acidity should not be sufficiently strong to produce N,N'-methylenedistearamide. The residual acid catalyst may be neutralized by adding ammonia, a carbonate, such as sodium carbonate, or an amine.

When acids weaker than the above, such as formic and malonic, are employed, more acid is required to obtain rapid conversion. If too much acid is used, ethers as described above will not be obtained, but N,N'-methylenediacylamide is invariably formed as the major reaction product. A test with Congo red paper under such conditions gives a black spot indicating a pH of about 1.5, whereas in the present invention, a pH of 3 to 4 is necessary to turn Congo red paper blue.

The reaction may be carried out in a solvent mixture provided the solvents are inert and do not take part in the reaction. Water should be avoided together with primary and secondary alcohols which are too reactive. The preferred media are 1,4-dioxane, isopropyl acetate and methylethyl ketone. Other operable liquids are diethyl ether, dibutyl ether, methyl acetate, ethyl acetate, benzene, toluene, nitrobenzene, monochlorobenzene, chloroform, carbon tetrachloride, kerosene and other hydrocarbon solvents, tert-butyl alcohol and tetrahydrofuran.

The products of this process can be differentiated readily from the corresponding N,N'-methylenediacyl-

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amides which are formed if the acid is too strong and which should be avoided. The latter compounds are insoluble in methylethyl ketone and many other compounds in which the ethers of this invention are soluble. Another method of distinguishing them is to compare their melting ranges. The ethers melt at about 85°–115° C., whereas the methylenediacylamides melt at about 145°–150° C.

The oxydimethylene-bis-acylamides employed as water-repellency agents in this invention may also be prepared by heating the aforementioned N-hydroxymethyl fatty-acid amides, in the absence of solvents and acid catalysts, at temperatures above their melting points, say at 100° to 140° C. This process is described more fully and claimed in my copending application Serial No. 395,586 of even filing date herewith.

The compositions of this invention are applied to textile fibers by any convenient method such as padding. The pad-bath can be either an aqueous dispersion or a solution in suitable solvent. The former is accomplished by dispersing the agent at the desired concentration in water containing the curing catalyst. Suitable solvents include alcohols, medium to high-boiling hydrocarbons, halogenated hydrocarbons, ketones, esters, etc. Specific examples are isopropyl alcohol, Stoddard solvent, chloroform, carbon tetrachloride, acetone, methylethyl ketone, ethyl or butyl acetate, etc.

The loading of the water repellent agent on the fibers is controlled by the concentration in the dispersion or solution and by the amount of bath picked up by the fibers.

The fibers operable in this invention are any of the common textile fibers including cotton, regenerated cellulose, cellulose acetate, nylon, polyethylene terephthalate, and polyacrylonitrile.

Any mildly acidic or potentially acidic catalyst is operable for the application process. These include compounds such as tartaric acid, ammonium tartrate, ammonia or amine hydrochlorides, ammonium acid phosphates and zinc nitrate. The amount of catalyst used may vary from about 1.0% up to about 50% by weight based on the weight of the ether compound. The agent is fixed on the fibers by heating at 110°–180° C. Above this temperature, curing occurs, but there is a tendency to decompose the finish.

It is believed, but not firmly established, that the ethers of this invention decompose on the fabric under these conditions to give the corresponding methylenediacylamides.

An essential feature of the fabric treatment is the decomposition of the heat-labile N,N'-oxydimethylene-bis-acylamide on the fabric to give a highly water-repellent surface, durable to laundering and dry-cleaning. Simple deposition of pre-formed N,N'-methylenedistearamide, for example, from solution or dispersion, does not give an equivalent result. Such a deposit is readily removed. This was shown by applying acetic acid solutions of N,N'-methylenedistearamide to cotton cloth. A single extraction with chloroform destroyed completely the water-repellent effect.

The water-repellency of the textile fibers is measured by standard AATCC test method 22–41.

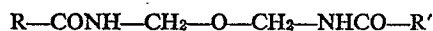
If it is desired to impart other properties, such as crease-resistance, dimensional stability, etc., the agents of this invention can be applied successively or co-applied with various textile resins well known in the trade. Common ones are 1,3-bis(hydroxymethyl)imidazolidone, urea-formaldehyde and melamine-formaldehyde resins. The curing of these resins requires substantially the same conditions described above for the curing of the ethers. In some cases the high durability of the finish is improved slightly.

Example I

30 grams of N-hydroxymethylstearamide (consisting of about equal amounts by weight of N-hydroxymethyl-

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hexadecanoic acid and -octadecanoic acid amides, melting at 110°–111.8° C., and containing 4.98% N) was suspended in 125 g. dry 1,4-dioxane, heated to 60° C., with stirring, and made just barely acid to Congo red paper (light blue coloration) by the addition of 10 drops of 24% isopropyl alcoholic hydrogen chloride solution. After one-half hour the slurry had become almost too thick to stir and 100 g. additional dioxane was added. A sample of the product was removed, dried on a porous plate and the melting point determined. It melted at 106°–107° C., and the melting point of samples taken after two hours and four and one-half hours further reaction at 60° C. was identical. The mixture was allowed to cool and the white solid collected on a funnel and washed with 100 g. methylethyl ketone. The air-dried solid weighed 25.0 g., melted at 108.2°–110.4° C., and contained 4.48% N. Melting range tests and infrared absorption-spectra studies have established that the product is an N,N'-oxydimethylene-bis-acylamide, essentially free of the initial N-hydroxymethyl acylamides. Its formula accordingly is



wherein R and R' represent alkyl radicals of the group $\text{C}_{15}\text{H}_{31}$ and $\text{C}_{17}\text{H}_{35}$ in about equal proportions throughout the product.

Similar results are obtained by substituting isopropyl acetate or methylethyl ketone for 1,4-dioxane.

In a similar manner, by starting with N-hydroxymethyl-behenamide (M. R. 119.5° to 120.5° C.), N-hydroxymethyl-lauramide (M. R. 102° to 104.5° C.), or the N-hydroxymethylamide of capric, myristic or montanic acid, the corresponding N,N'-oxydimethylene-bis-acylamides are obtained. The oxydimethylene derivative of lauramide melts in the range of 97° to 100° C.; that from behenamide, melts at 111.5° to 112.5° C.

Example II

25.0 grams N-hydroxymethylstearamide of Example I was suspended at 60° C. in 100 g. of a medium boiling paraffinic hydrocarbon solvent (B. R. about 100°–130° C.) and made definitely acid to Congo red paper by the addition of 24% hydrogen chloride solution. After two hours reaction a sample melted at 108°–110.5° C. and gave a mixed melting point (with an equal weight of the starting material) of 100°–102.5° C. The mixture was therefore, made slightly alkaline by the addition of a few drops of 10% sodium hydroxide solution to stop further reaction and 50 g. water added. The solvent was removed as a water azeotrope at a reduced pressure such as to maintain an internal temperature of 40° C. At atmospheric pressure 25 g. water and 25 g. of 10% polyvinyl alcohol solution were added to suspend the solid which had separated. One-half gram of stearamidomethylpyridinium chloride was added with very rapid stirring and a smooth thin dispersion formed.

Example III

Commercial N-hydroxymethylstearamide flakes (30.6 lbs.) are mixed with 89.2 lbs. of isopropyl acetate and 1.4 lbs. of 85% phosphoric acid. The vessel is closed and the pressure reduced to 300±20 mm. Hg. The charge is heated to 55±3° C., and 18 lbs. of distillate is collected at 52–55° C./300 mm. Hg. The pressure is restored to 1 atmosphere and the charge is held at 60±1° C. for 2–4 hours.

After completion of the reaction, agitation is continued and 1.0 lb. of a commercial polyoxyalkylene derivative of sorbitan monostearate in 10 lbs. of hot water is added over about 5 minutes. Then 10 lbs. of a 10% aqueous solution of partially-saponified polyvinyl acetate is added over 30–45 minutes.

The remaining isopropyl acetate (about 90–95 lbs.) is distilled at about 52° C./300±20 mm. Hg 41 lbs.

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of water being added at a slow rate during the distillation.

A freshly prepared dispersion of 2.0 lbs. of stearamidomethyl pyridinium chloride in 10.2 lbs. of 35°-45° C. water is added to the charge, which is agitated 10-15 min. more with cooling to about 35° C. The resulting 100 lbs. of paste is then passed through a colloid mill and is ready for use.

The latter addition may be 2.0 lbs. commercial polyoxyalkylene derivative of sorbitan monostearate in place of stearamidomethyl pyridinium chloride. The resulting product has improved dilute pad-bath stability.

Example IV

Commercial stearamide (78.8 lbs.) is broken into small pieces and charged into a steam-jacketed kettle, where it is melted at 105° C. Then 8.8 lbs. of paraformaldehyde is added. The charge is stirred at 105°-110° C. for 3 hours and converted to flakes in a conventional flaker.

A mixture of 76.5 lbs. of the resulting flakes, 223 lbs. of isopropyl acetate and 3.5 lbs. of 85% phosphoric acid is agitated for 4 hours in a closed kettle at 60±1° C. To this is added 25 lbs. of a 10% aqueous solution of polyvinyl acetate which has been 86-89% hydrolyzed and has a viscosity of 35-45 centipoises in a 4% water solution at 20° C., followed by 127.5 lbs. of water and 7.5 lbs. of a commercial polyoxyethylene sorbitan monostearate.

The isopropyl acetate is distilled from the charge at 54°-55° C. (pot temperature) and 300±20 mm. Hg. The vapor temperature is about 65° C., and 190-200 lbs. of distillate is obtained. The paste is passed through a colloid mill, giving 250 lbs. of a white, thixotropic paste suitable for preparation of textile-treating pad-baths.

Example V

2.0 grams of N,N'-oxydimethylenedistearamide of Example I was pasted with 2.5 cc. of 95% ethyl alcohol and

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5.0 g. of 10% polyvinyl alcohol solution worked in. The smooth paste was diluted to 100 g. with water. After standing three days a milky white dispersion remained with a small amount of sediment. It was applied to cotton poplin at an 80% pick-up, and the fabric cured at 160° C. for 5 minutes. The fabric was tested according to AATCC standard test method 22-41. The rating was judged to be 50 to 70.

When 0.1 g. tartaric acid was added to 50 g. of the 2% dispersion and the solution of pH about 3, padded on cotton poplin, cured and tested as before, a water-repellency rating of 100 was observed. When diammonium phosphate was added instead of tartaric acid in the same amount, the rating obtained was 90 to 90+.

Example VI

Dispersions were made by mixing the following:

20.0 g. N,N'-oxydimethylenedistearamide
20.0 g. 10% polyvinyl alcohol solution in water
1.0 g. stearamidomethylpyridinium chloride
1.0 g. pyridine
58.0 g. water

The water was added slowly after first stirring the other ingredients until a smooth paste was obtained. Various resins and catalysts were added to the above dispersion, which was further diluted with water to such a concentration that 2% of the water-repellent agent was deposited on the indicated fabrics in each case by the ordinary textile padding operation. The fabrics were cured without drying (350° C., 2 minutes), neutralized (0.05% sodium dodecyl sulfate, 0.1% soda ash) and dried at 350° F. for 2 minutes. The fabrics were tested with the standard test before and after washing and dry-cleaning.

The results are shown in the following table:

CO-APPLICATION OF N,N'-OXYDIMETHYLENEDISTEARAMIDE WITH TEXTILE RESINS

Fabric	Resin Co-Applied	Catalyst (0.6% Applied)	Spray Test			
			Initial	Washed (1)	Dry-Cleaned 2	
					A	B
Cotton Poplin White.....	None	Tartaric Acid.....	100	80+	80	80
Cotton Poplin OD.....	do	Same	90	80	70	70
Cotton Poplin White.....	do	None 4	100	80+	80+	80
Do.....	0.5% methylated methylolmelamine.	A commercial ammonium phosphate catalyst.	100	80+	90+	80
Cotton Poplin OD.....	Same	Same	100	80+	80+	80
Rayon Challis.....	20% dimethylolurea (monomeric)	A commercial ammonium phosphate catalyst.	100	80+	80+	80+
Do.....	4% dimethylolurea (partially condensed).	Same	90	80	80+	80+
Do.....	Same	A commercial amine hydrochloride catalyst.	100	80+	80	80
Rayon Tan Gabardine.....	Same	A commercial ammonium phosphate catalyst.	80+	80	80	80
Do.....	Same	A commercial amine hydrochloride catalyst.	90	80+		
Do.....	20% dimethylolurea (monomeric)	A commercial ammonium phosphate catalyst.	100	90		
Rayon Challis.....	Same	Same	100	70	100	
Nylon.....	None	Tartaric Acid	100	80	80	
Acetate Rayon Taffeta.....	do	do	100	90	100	
Wool Flannel.....	do	do	90	80	100	
Wool Serge.....	do	do	90+			
Polyethylene Terephthalate Continuous Filament Fabric.....	do	do				
Polyacrylonitrile Staple Fabric.....	2.0% Resin (Methylated Methylolmelamine).	do	100	70		
Polyethylene Terephthalate Staple Fabric.....	None	do	100			
Do.....	2.0% Resin (Methylated Methylolmelamine).	do	100	70		

1 3 Washes were done in a laundry wheel at 120° F.; after 9 washes all were 70-80.

2 3 Dry-cleanings were done in Stoddard solvent (a) and perchloroethylene (b) in a Launder-Ometer.

3 A desired stiffening of the fabric also resulted.

4 The stearamidomethylpyridinium chloride was sufficiently acid to catalyze curing at this temperature.

5 3 Standard AATCC No. 3 washes (160° F.).

Very small amounts, of the order of 0.5% to 2.0%, of a film-forming resin such as methylated trimethylol-melamine, when applied with the dispersion of Example III improve the water-repellency of the fabric. This is most noticeable with certain fabrics on which it is difficult to secure high water-repellency, and shows up especially on a determination of the dynamic water-absorption of the treated fabrics according to Federal test method 5500-CCC-T-191-B May 15, 1951 (see AATCC year-book for 1952, p. 139).

The advantages of this invention will now be readily apparent. The water-repellency agents employed in this invention are relatively inexpensive and convenient to prepare. In addition, they are not toxic or noxious in any way and even when decomposed on fabrics no unpleasant odors develop. The usual alkali wash of the treated fabric is not necessary and dispersions of the water-repellent agents are stable in storage and in the application baths. The agents used in the present invention impart a high degree of water-repellency to fabrics and the finish is resistant to washing, dry-cleaning, and the abrasion encountered in normal wear. The agents are compatible with all common resin finishes for textiles. These resins are not necessary for a durable, water-repellent effect, but are useful for improving various other properties of the textiles such as stiffness, crispness, crease-resistance, dimensional stability, etc.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. An aqueous dispersion comprising a N,N'-oxydimethylene-bis-acylamide of a fatty acid having from 9

to 29 carbon atoms in the chain, from 2% to 5% of a protective colloid which forms a protective envelope around the dispersed particles, and from 5% to 8% by weight of a heat-labile transitory dispersing agent which loses its dispersing power after heating, said percentages being based on the weight of the acylamide.

2. The dispersion of claim 1 in which the acylamide is one of stearic acid.

3. The dispersion of claim 1 in which the N,N'-oxydimethylene-bis-acylamide is a mixed ether of the methylol amides of stearic and palmitic acids.

4. The process of treating textile fibers to render them water repellent which comprises the steps of impregnating and heating the said fibers in the presence of a mildly acidic catalyst with an aqueous dispersion comprising a N,N'-oxydimethylene-bis-acylamide of a fatty acid having from 9 to 29 carbon atoms in the chain, from 2% to 5% of a colloid which forms a protective envelope around the dispersed particles of the said amide, and from 5% to 8% by weight of a heat-labile transitory dispersing agent which loses its dispersing power after heating, said percentages being based on the weight of the acylamide.

5. The process of claim 4 in which the acylamide is one of stearic acid.

6. The process of claim 4 in which the acylamide is a mixed ether of the methylol amides of stearic and palmitic acids.

7. The process of claim 4 in which the impregnated fibers are heated to 110° C. to 180° C.

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