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3,051,674

TEXTILE FINISHING COMPOSITION COMPRISING AN AQUEOUS DISPERSION OF THE INTERACTION PRODUCT OF UREA, FORMALDEHYDE, A FATTY ACID AMIDE AND A PRIMARY AMINE

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This invention relates to novel compositions of matter which when applied to fibrous material impart certain durable effects. Such effects as water repellency and softness of hand may be imparted to such materials which may be in the form of textiles, paper, felts, or webs, etc., or as single fibers or yarns. Other effects on textiles may be crease resistance and shrinkage control contributing to "wash-wear" properties. These effects imparted by the compositions of this invention are able to withstand the action of commercial and home laundering procedures and dry cleaning processes.

The compositions of the invention are useful generally in application to cellulosic fibers and materials containing them such as woven and knitted fabrics, paper, and non-woven fabrics. Textiles containing cotton or regenerated cellulose fibers are specially benefited by the application of these compositions. Even mixtures containing non-cellulosic fibers may be benefited by application of these new products: for example, cellulose acetate-cotton, and rayon-polyester mixtures have been treated beneficially.

Compositions of the present invention impart water repellency, as distinct from water proofness, to fibers treated therewith. Accordingly the treated materials retain their air permeability, handle, and drape. The water repellent characteristics as measured by spray rating are excellent and are not greatly reduced by laundering or dry cleaning.

A number of additional valuable properties are imparted to fabrics by these new compositions. The fiber properties are so modified by reaction with these products that the crease resistance of the fabric is increased. This is evident in the rise in crease angle (as measured by the Monsanto crease resistance instrument) obtained on cotton fabrics. This effect is resistant to laundering. This crease resistance is accomplished without an unusual loss in tensile strength of the fabric. Another feature is that the damage to the fabric caused by washing in dilute, chlorine-bleaching solutions and thereafter ironing is very low. Under these conditions there is no color formation.

Application to regenerated cellulose products, e.g. cuprammonium or viscose rayon, imparts a dimensional control to the fabric together with water repellency.

A desirable softening of fabrics is also accomplished by the application of the products of the invention; the effect is imparted in addition to the crease proofing and dimensional control effects mentioned above.

Water repellent properties can be imparted to fabrics by various known compositions. For example, certain silicone liquids may be applied from solution or emulsion. It is well known that although these are very effective they are costly. Similarly various pyridine-containing compositions, although they are less costly than the silicones have the disadvantage of liberating pyridine during the processing of the fabric. This requires special equipment to take care of this bad-smelling by-product. These products because of their chemical nature do not impart the added properties of crease resistance and dimensional control.

Certain heat reactive resins modified by stearamide have also been used for impartation of water repellency. They suffer from the disadvantage of imparting a harsh hand to the fabric and of not yielding wash-wear properties.

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The object of this invention is to provide novel compositions which impart water repellency together with crease resistance and dimensional control to cellulosic fibers.

A further object is to provide novel compositions which are used readily in textile treating equipment without the liberation of undesirable odors.

A still further object is to provide products which can be used together with reactant finishes of the types disclosed in my copending U.S. applications Serial No. 665,138 filed June 12, 1957, now U.S. Patent 2,917,411 and Serial No. 625,241 filed November 30, 1956, now U.S. Patent 2,895,923 to obtain special effects on cellulosic fibers and blends thereof with other fibers.

The compositions of my invention comprise the following ingredients: (a) a long chain fatty acid amide, (b) formaldehyde or a formaldehyde liberating compound such as paraformaldehyde, or methylal, (c) urea and (d) an amine taken from the group consisting of aliphatic mono- and diamines having 1 to 4 carbon atoms for each amino group and having only hydroxy and ether groups attached to the hydrocarbon chain attached to N.

The amides which I may use to prepare my compositions are simple amides having from 8 to 35 carbon atoms. Such substances as stearamide, palmitamide, amides of hydrogenated tallow fatty acids, various commercially produced mixtures of palmitamide and stearamide are specially useful in carrying out my invention. Included in this definition are amides of these fatty acids which have a carboxamide grouping substituted on the beta carbon atom of the fatty amide chain. Thus, dodecyl succinamide is a useful amide for the purposes of this invention.

As formaldehyde, I may use various aqueous solutions of formaldehyde such as formalin or more highly concentrated solutions which may also contain methanol. Various polymers of formaldehyde, such as polyoxy methylene or paraformaldehyde are particularly useful. Formaldehyde containing substances which yield their formaldehyde readily may also be used, such as methylal or methylol urea.

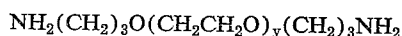
The urea used in my compositions may be introduced as crystal urea or I may use its mixture with formalin.

A number of amines are suitable for the preparation of my compositions. It has been found that primary mono- and diamines with a carbon chain length (for each amino group) not over 4 carbon atoms are suitable. When longer chain amines are tried in my compositions I have experienced difficulty in obtaining suitably stable dispersions for application to fabric. On the other hand, hydroxyalkyl amines containing up to 4 carbon atoms are especially useful in formulating compositions imparting durable crease resistance and low chlorine damage to fabric. Ether and polyether derivatives of these hydroxyalkyl amines containing one or two amino groups have also been found to be especially useful.

As examples of the amines falling within these classifications there are, monomethyl amine, monoethyl amine, monopropyl amine, monoisopropyl amine, monobutyl amine, 1,2-ethylene diamine, 1,2- and 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, ethanolamine, 3-aminopropanol-1, 1-aminopropanol-2, 3-(hydroxyethoxy)-propyl amine, and ether amines of the formula



where x is an integer from 1-10, and the so-called polyglycol diamines of the formula



where y is an integer from 1-5.

The ingredients of my compositions may be combined

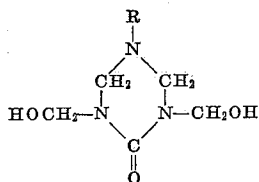
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in a number of ways and under various conditions. It is convenient to put all materials together in a suitable reaction vessel where the mixture is stirred and heated to bring about interaction. If desired the amine, urea and formaldehyde may be reacted followed by addition of the amide and its incorporation with the compositions. When the mixture contains water the reaction may be run at temperatures sufficient to bring about refluxing of the water. When only a small amount of water has been introduced the mixture may be reacted at temperatures of 75 to 150° C.

After a reaction time of 15 minutes to 4 hours depending on conditions and ingredients, the products are conveniently mixed with water to form solutions or dispersions of a pasty, viscous consistency. These aqueous compositions are then diluted further in making up a bath for impregnation of the fibrous material.

It has been found important to use certain restricted ratios of ingredients in order to obtain compositions with optimum properties. The ratio of formaldehyde to urea should be between 3:1 and 5:1 on a molar basis. Similarly 0.25 to 1.0 mole of amine per mole of urea should be reacted and the molar ratio of fatty amide to amine should be between about 0.50 and 2.0.

Certain conjectures have been made concerning the mode of reaction and the structures present in the compositions which are disclosed by this description. The amine, formaldehyde and urea probably interact to form condensation products whose structure may be represented by the following formula:



Urea formaldehyde condensation products are also involved. They probably consist of methylol urea and dimethylol urea or their condensation products with themselves or the amine containing product.

It is known that the fatty acid amide is also combined with formaldehyde and it is believed that the resulting methylol compound has probably condensed with the other condensation products formed from the other ingredients.

Accordingly, it appears impossible to state exactly the structural configuration of the compositions. If the ratios of ingredients are held to those mentioned above it would appear that the proposed structures will be present in the final product in quantities which depend on the ratios of reactants.

It is important that the compositions prepared by the interaction of the ingredients described above be dispersed in water so that they may be readily applied to fibrous materials. Usually this is readily accomplished by mechanical agitation with water at temperatures of about 50–90° C. Adjuvants possessing surface activity may be used in order to aid dispersion. Up to five percent of such materials may be used for this purpose. For example, I may use aryl sulfonic acids, ethylene oxide condensates, fatty esters of polyols and the like. Sometimes I may incorporate a small amount of a fatty acid into my formulation to facilitate the preparation of dispersions of the final products. Such acids as stearic or oleic may be used for this purpose.

In the following examples I have described the preparation of my novel compositions, the parts being given by weight.

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EXAMPLE 1

	Parts
Stearamide -----	234.5
Paraformaldehyde (containing 91% CH ₂ O) -----	154.6
5 Urea -----	70.3
Monisopropanolamine -----	43.3
Stearic acid -----	7.0
Water -----	55.2

All of these ingredients except 53 parts of water are charged to a reaction vessel having a mechanical stirrer and a reflux condenser. The mixture is heated at 220° F., causing slight refluxing, and stirred for 2 hours. The water which has been held out from the mixture is now added slowly with agitation. The resulting paste is smooth and white and after cooling to room temperature is usable in the processing of textile materials as described in later examples.

EXAMPLE 2

	Parts
20 Stearamide -----	234
Paraformaldehyde (containing 91% CH ₂ O) -----	154.6
Urea -----	70.3
Monisopropanolamine -----	86.6
25 Stearic acid -----	7.0
Water -----	55.0

The ingredients are treated as in Example 1. The product is a white paste, dispersible in water.

EXAMPLE 3

	Parts
30 Hydrogenated tallow amide -----	234.0
Paraformaldehyde (containing 91% CH ₂ O) -----	154.0
Urea -----	70.3
35 Monoethanolamine -----	35.3
Stearic acid -----	7.0
Water -----	55.0

The materials of this example are reacted together as in Example 1. The product is a creamy white paste which is dispersible in water.

EXAMPLE 4

	Parts
Stearamide -----	140.7
45 Paraformaldehyde (containing 91% CH ₂ O) -----	93.0
Urea -----	42.22
Monoethylamine -----	21.90
Water -----	21.1
Polyoxyethylene stearate -----	18.00
50 Water -----	267.16

The first five materials are heated under reflux conditions for one hour. Then the polyoxyethylene stearate and water are added with agitation. The product is an easily dispersible paste.

EXAMPLE 5

	Parts
Hydrogenated tallow amide -----	200
Paraformaldehyde (containing 91% CH ₂ O) -----	132
60 Urea -----	60
3-(2-hydroxyethoxy)-propyl amine -----	60
Water -----	47

The ingredients are reacted as in Example 1 except that 40 parts of water are withheld until the reaction has been completed. After addition of this portion of water and cooling the product is a white, dispersible paste.

The following examples illustrate the application of the products of this invention to textile fabrics and describe the effects produced thereon.

70 In general, these products are applied from dilute aqueous dispersions using a padding technique in which the textile material is passed through the aqueous bath, passed through squeeze rolls (this sequence may be done twice if necessary) and then heated to remove water and thereafter cured by further heating. After this curing

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operation the fabric may be afterwashed or treated in any required manner.

The proper application of the products of this invention requires the use of a catalyst in the padding bath. The catalyst remains on the fabric to catalyze (or accelerate) the reactions which take place on the fabric. Sufficient curing is necessary to obtain durable water repellency and this depends on the nature of the fabric, the weight of the fabric, the type and quantity of catalyst, the time and temperature of curing. Catalysts useful in applying these products are acidic or potentially acidic materials such as zinc nitrate, organic acids (e.g. tartaric acid), hydrochlorides of amines, metallic halides (e.g. magnesium chloride), acid salts such as phosphates and the like. Sometimes certain neutral salts are operative, such as for example magnesium sulfate.

The amount of product left on the fabric depends on the concentration in the bath and the amount of this bath picked up by the fabric (wet pickup). Suitable concentrations of my compositions in the pad bath may be from 1% to 50%. Usually high concentrations are not necessary to obtain very satisfactory spray ratings so that concentrations of 3% to 15% are normally applied. Low concentrations, say 0.5 to 3%, are useful if softening without water repellency is desired.

Catalyst concentration may vary considerably depending on the catalyst chosen. When zinc salts are used they are used at about 5 to 25% of the concentration of the product used.

In showing the effectiveness of these applications certain tests have been made:

Water repellency is tested by AATCC Standard Test Method 22-1952. The results are given by spray rating; a spray rating of 100 indicates that under the conditions of the test the fabric is completely repellent to the test spray.

Crease resistance is measured by applying AATCC Tentative Test Method 66-1956. The results reported in the examples below are given as the Monsanto crease angle where the warp and fill figures are added together. Tensile strengths are obtained by a grab tensile test described by ASTM Standard Method D-39-40. Tensile strengths in the warp direction are reported.

EXAMPLE 6

The preparation of Example 1 was dispersed in water. The bath contained the indicated amount of zinc nitrate. Cotton sheeting (80 x 80) was impregnated by passage through a laboratory padder with rolls adjusted to yield 100% wet pickup. The fabric was then dried at 180° F. and cured at 325° F. for 90 seconds. The results of laboratory tests were as follows:

Percent product of Example 1	Percent zinc nitrate	Spray rating			Crease angle (original)
		Original	1 laundering ¹	5 launderings ¹	
0.0	-----	0	0	0	163
5.0	0.5	95-100	80	80	249
10.0	0.75	100	95	80-85	-----

¹ AATCC Standard Test Method 36-1957 No. 3 at 160° F.

EXAMPLE 7

A padding bath was formulated as follows:

	Parts
Product of Example 1 -----	6
Acetic acid (56%) -----	0.1
Zinc nitrate -----	0.8
Water -----	93.1

A viscose rayon challis having a warp tensile strength of 68 lbs. was treated with this bath, applying 115% wet pickup. The impregnated fabric was dried at 180° F.

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and cured at 315° F. for five minutes. Testing of the fabric indicated the following:

Fabric	Tensile strength (lbs.) after 5 launderings.	Spray rating	
		Original	After 5 launderings ¹
Treated -----	70	100	90-100
Untreated -----	50	0	0

¹ Laundered in home washer at 140° F.

EXAMPLE 8

A light weight chlorinated wool challis fabric was padded through a bath (formulated below) at 100% wet pickup, dried at 180° F. and cured at 300° F. for three minutes. Laundering was carried out at 105° F. in an automatic laundry machine.

Pad bath composition:	Parts
Product of Example 1 -----	4
Zinc chloride -----	1
Water -----	95

Fabric	Spray rating		
	Original	1 laundering	5 launderings
Treated -----	100	90	90
Untreated -----	50-70	0	0

EXAMPLE 9

Mixtures of fibers are amenable to treatment as described in this example. A polyester-viscose fabric containing 65% of the former and 35% of the latter was impregnated in a bath containing 8% of the product of Example 1, 0.1% of 56% acetic acid and 1.5% of a zinc nitrate containing catalyst known commercially as "Catalyst H-7." The wet pickup was 80%. The fabric was dried at 180° F. and cured at 305° F. for 90 seconds. The fabric so treated retained a spray rating of 100, even though exposed to 5 automatic launderings at 140° F.

EXAMPLE 10

A cotton-viscose upholstery fabric (35% cotton-65% viscose) was padded through a solution consisting of 10% of the product of Example 3, 0.1% of 56% acetic acid and 1% zinc nitrate (90% wet pickup) dried and cured at 315° F. for 3 minutes.

A spray rating of 80-90 was obtained on treated fabric compared with an untreated fabric showing zero spray rating. In addition, a considerable degree of dimensional control was obtained.

EXAMPLE 11

A cotton drapery fabric was treated in a bath containing 10% of the product of Example 1 and 1% of zinc nitrate catalyst. The wet pickup was 100%. The fabric was dried at 180° F. and cured for 90 seconds at 310° F. The fabric was then tested for water repellency, showing a spray rating of 100. It was then dry-cleaned and washed with water and dried. The spray rating was then 90-100. After three more dry cleanings followed by water washing it had a spray rating of 80.

It is a known fact that commercial dry cleaning tends to leave residual amounts of wetting agents in the cleaned fabric. This obviously lowers the spray rating. If these residual wetting agents are washed out with water or dry cleaning solvent the true water repellent effect of the finish on the fabric is observed. In this way the real durability of the finish is made apparent.

In another experiment 80 x 80 cotton sheeting was treated at 100% wet pickup with a bath containing 8% of the product of Example 1 and 0.8% of zinc nitrate.

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The dried fabric was cured at 310° F. for 90 seconds. The spray rating after curing was 100. After one dry cleaning followed by washing with clean trichloroethylene the spray rating was 70. After 3 commercial drycleanings followed by three 3-minute washes in clean trichloroethylene the spray rating was 50.

In the examples just cited treatment of textile fabric has been by my novel compositions alone. In the examples which follow their conjoint use with various other fabric finishing agents is illustrated.

EXAMPLE 12

A triazone type finishing composition such as that described in my copending application Serial No. 665,138 now U.S. Patent 2,917,411 may be used in conjunction with the novel products of this invention. Such a composition is described as Preparation A.

Preparation A

	Parts
Paraformaldehyde (containing 91% CH ₂ O) -----	132
Urea -----	50
Water -----	128
Monoethanolamine -----	30.5

These materials were heated under a reflux condenser at the reflux temperature (approx. 100° C.) for 2½ hours. A clear solution resulted which was cooled and neutralized to pH 7 with 75% phosphoric acid. This was used with the product of Example 1 in the following amounts and procedure:

	Parts
Product of Example 1 -----	10
Preparation A -----	5
Zinc nitrate -----	0.75
Water -----	84.25

This mixture was used to impregnate 80 x 80 cotton sheeting at 100% wet pickup. The sheeting was cured at 325° F. for 90 seconds after drying at 180° F. The test results were as follows:

Fabric	Spray rating			Crease resistance	Chlorine damage, percent	
	Orig.	1 laund. ¹	5 laund. ¹		After wash	5 laund. ²
Treated -----	100	95	80-85	276	6	10
Untreated -----	0	0	0	163	1	3

¹ AATCC Method 36-57 No. 3 (160° F.).

² AATCC Method 69-52.

It should be noted that the low chlorine damage, even after multiple laundering, is of value in application of these products to white fabrics which ordinarily are bleached in normal washing.

EXAMPLE 13

A melamine modified polyformal, such as those described in my copending application Serial No. 625,241 now U.S. Patent 2,895,923 was prepared (Preparation B) and used with the compositions of my invention in this example.

Preparation B

	Parts
Paraformaldehyde (containing 91% CH ₂ O) -----	79
Diethylene glycol -----	133
Melamine -----	24

The paraformaldehyde and the diethylene glycol were mixed and heated together to form a clear solution. The melamine was added and the mixture stirred and heated until a clear solution resulted.

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Preparation B was used with the novel compositions of this invention as follows:

	Parts
Preparation B -----	8
Product of Example 1 -----	5
Zinc nitrate -----	0.8
Acetic acid -----	0.05
Water -----	86.15

The above mixture was used to impregnate 80 x 80 cotton sheeting at 100% wet pickup. The fabric was cured for 90 seconds at 300° F. after drying at 180° F. The fabric gave the following test results:

Fabric	Orig.	Spray rating			Crease resistance		Tensile strength, lbs.
		1 laund.	5 laund.	10 laund.	Orig.	10 laund.	
Treated -----	90-100	100	80	80	287	266	41
Untreated -----	0	0	0	0	180	172	66

These figures indicate that a durably water repellent, crease-resistant fabric was obtained. The wash-wear appearance of this treated fabric was excellent and durable.

EXAMPLE 14

In this example 80 x 80 cotton sheeting was impregnated with the product of Example 4 alone and with Preparation A. The fabric was padded at 100% wet pickup, dried at 180° F. and cured at 320° F. for 90 seconds. The spray rating, crease resistance and warp tensile strengths were found to be as indicated in the table.

Composition of Bath

	I, percent	II, percent
Product of Example 4 -----	10	5
Preparation A -----	5	5
Acetic acid -----	0.05	0.05
Zinc nitrate -----	0.8	0.8

Properties of Fabric

	I	II	Control
Crease resistance (after 1 laundering) -----	264	259	174
Spray rating—original -----	100	100	0
After 1 laundering -----	95	90	-----
After 5 launderings -----	80	80	-----
Tensile -----	42.4	43.2	65

EXAMPLE 15

The product of Example 5 was dispersed in a bath having the following composition:

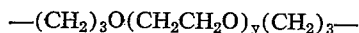
	Parts
Product of Example 5 -----	4
Zinc nitrate -----	0.5
Acetic acid (56%) -----	0.1
Water -----	95.4

Cotton sheeting was impregnated with this bath and treated as in Example 6. The spray rating on the fabric before laundering was 95-100, after five launderings the rating was 80. Cotton sheeting not treated shows a zero spray rating.

The foregoing descriptions and examples show plainly how the products of my invention may be applied to cellulose fabrics such as those made from cotton or regenerated cellulose and combinations thereof. Their application to wool has also been illustrated. They have been found useful when applied to fibers of silk, cellulose acetate, and hydrophobic fibers such as nylon, polyester, saran, acrylic and olefin.

I claim:

1. A textile finishing composition comprising an aqueous dispersion of the products of interaction at reflux temperatures of (a) an amide of a long chain fatty acid having 8 to 35 carbon atoms, (b) formaldehyde, (c) urea and (d) a saturated primary amine containing not more than two amino groups in which the NH_2 groups are attached to a radical selected from the group consisting of monovalent and divalent hydrocarbon radicals having not more than four carbon atoms for each amino group attached thereto, monovalent and divalent radicals having not more than four carbon atoms and having one hydroxyl substituent, radicals having not more than four carbon atoms and having a polyether substituent of the formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x$ —where x is an integer from 1 to 10, and radicals of the formula



where y is an integer from 1 to 5; the molar ratio of reacting substances being taken so that the ratio of formal-

dehyde to urea is between 3:1 and 5:1; the ratio of amine to urea is between 0.25:1 and 1.0:1 and the ratio of amide to amine is between 0.5:1 and 2.0:1.

2. A textile finishing composition as defined in claim 1, wherein the amide is stearamide and the primary amine is a monoalkylamine.

3. A textile finishing composition as defined in claim 1 containing a small amount of a higher fatty acid as a dispersant.

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