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3,074,815 TREATMENT OF CELLULOSIC FIBROUS MATERIALS WITH DIAMIDE QUATERNARIES AND THE RESULTING ARTICLES

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This invention relates to the chemical treatment of cellulosic fibrous materials, such as textiles and paper, whereby desirable physical properties are imparted thereto. The present invention also relates to new organic compounds which are valuable as assistants in the treatment and finishing of textile materials. Particularly, it relates to the method of treating textiles with new chemical softening agents, and lubricants. In another embodiment of the invention, novel and useful chemical compositions have been produced.

Many materials have in the past been used as textile treating assistants for altering the softness or lubricity and imparting easy wettability to textile fibers, but each has some inherent physical or chemical property leading to an undesirable product. Reagents used in the treatment and finishing of textile materials have included silicone oils, sulfated oils and fats, mineral oil emulsions, and polyethylene emulsions. These materials are particularly designed as textile softeners for industrial or home use as rinse washing cycle additives. Each of them has some objectionable characteristic. For example, tallow oils and sulfonated oils do not become sufficiently firmly attached to the goods to survive washing. These materials also impart an objectionable rancid odor to treated materials.

Fatty alcohols, for example, may be used as textile softeners, but these also wash out from the treated fibrous material. Other materials are relatively expensive and some darken the color of textiles. Besides being color darkening and unpleasantly odoriferous, many of the current textile softeners have an objectionable property of softener build-up after repeated treatment, making the treated cloth extremely difficult or, in many cases, impossible to rewet. When the treated textile becomes water-repellant, it is then highly resistant to ordinary laundering and dry cleaning.

Further, many known textile treating materials are unstable with respect to heat and oxidation. The treated cloth becomes yellowed by decomposition of treating agents after heating to dry the cloth or as a result of oxidation incident to storage for a few months.

It therefore becomes an object of the invention to provide textile treating agents and process of treating fiber materials therewith, by means of which the softening, lubricating, and wetting properties of the treated materials are improved without deleterious effect upon their color, odor and launderability.

It is a further object to provide textile softeners and process of treating textiles, the use of which does not tend to "yellow" treated textiles.

Another object is to provide novel compositions of matter which provide excellent textile softening with little or no build-up of softener upon repeated use.

An important object is to provide textile softening compositions and textile treating process, the use of which results in a textile with better rewettability properties than heretofore known in the art.

A still further object is to provide softened textile materials which may be heated or stored for long periods of time without yellowing or visibly aging.

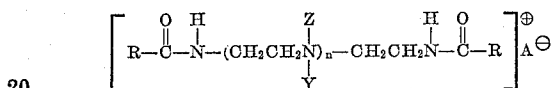
It is a further object of this invention to provide new compositions useful for textile softening that possess low

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dermal toxicity, high chemical and physical stability, light color, easy dispersibility in water and impart no objectionable odor to treated products.

Another important object of the invention is to develop a rinse cycle additive textile softener that excels in the above described properties over those textile treating assistants known in the prior art. Other objects will appear hereinafter.

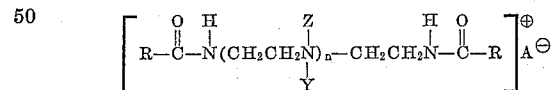
In accordance with the invention, a process of treating cellulosic fibrous materials has been discovered whereby colloiddally dispersible compositions may be easily applied from aqueous solutions to give finishes not only of maximum softness but also of excellent rewettability. The products proposed for use are colloiddally, water dispersible, diamide quaternaries of the general formula:



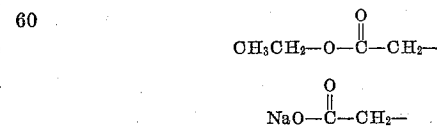
where R is a saturated fatty radical of at least 11 carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms composed of elements from the group consisting of C, H, O, X, and M, where X is halogen and M is an alkali metal, n is an integer of from 1 to 3, and A is an anion.

By the expression "colloiddally dispersible" is meant that the compounds of the above general formula may be suspended in aqueous media up to concentrations of 25% by weight. These suspensions may be either true solutions or colloidal suspensions of the solid colloidal particles in water. The only proviso is that the compositions remain homogeneous over long periods of storage time. The colors of the solid, aqueous, suspended compositions may range from water white or colorless to a very light yellow. Their viscosities may vary over a wide range, but they must remain pourable and ready for instantaneous use. The aqueous suspensions may contain minor portions of other polar solvents, such as lower alkyl alcohols or ketones, which act as solubility promoters.

The cellulosic fibrous materials may be cotton textiles or other cellulose derivative materials, such as paper. A preferred embodiment of the invention is the treatment of cotton textiles. A particularly useful method of treating the cellulosic materials comprises applying and affixing thereto an aqueous colloiddally dispersible diamide quaternary of the formula:



where R is a saturated fatty radical of at least eleven carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and are selected from the group consisting of CH_3 -, CH_3CH_2 -, $\text{CH}_3\text{CH}_2\text{CH}_2$ -, HOCH_2CH_2 -, $\text{HOCH}_2\text{CHOHCH}_2$ -,



$\text{X}-\text{CH}_2-\text{CHOHCH}_2$ -, and $\text{H}-(\text{OCH}_2\text{CH}_2)_y$ -

where X is halogen, n is an integer from 1 to 3, y is an integer from 2 to 12, and A is an anion.

In a preferred species of composition corresponding to the type illustrated, the anion may be selected from the group consisting of halide, sulfate, sulfite, acetate, nitrate, and phosphate. Of these, the most preferred anions are

halides, with chloride being the most preferred specific halide.

PREPARATION OF COMPOSITIONS

In order to prepare the final compositions which are part of this invention, it is first necessary to prepare diamides which are subsequently quaternized with various alkylating and quaternizing groups. The diamides are usually formed by reacting an acid, and in the present instance, preferably a fatty acid of at least 11 carbon atoms, with a polyalkylene polyamine. The polyamines correspond to the formula:

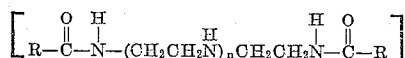


where n is an integer of from 1 to 3. The preferred starting alkylene polyamines may be chosen from among diethylene triamine, tetraethylene pentamine, and triethylene tetramine.

Some of the more readily available and preferred materials for preparing the diamide are the fatty acids or mixtures of such acids that occur in various fats and oils, such as coconut oil, hydrogenated tallow, castor oil, hydrogenated castor oil, etc. Thus, such acids as caprylic, myristic, capric, undecylic, lauric, myristic, palmitic, stearic, behenic, oleic, ricinoleic, and mixtures of these may be used. However, the preferred embodiment of the invention involves the use only of saturated fatty acids which have at least eleven carbon atoms. Examples of these are stearic and palmitic acids.

In order to produce the diamides, it is necessary to heat 1 mol of the polyalkylene polyamine with at least 2 mols of the fatty acid and remove 2 mols of water during the process. The time and temperature of the reaction depends upon the particular long chain fatty acid and polyamine involved, and may vary from 1 to 10 hours at temperatures from 100 to 200° C. However, the preferred time to remove the requisite water may vary from 2 to 6 hours at temperatures from 120 to 180° C. The diamide preparation may be facilitated by the use of azeotropic materials which help to drive out of the reaction system, the water formed in the reaction. These azeotropic materials may be any organic substance capable of forming a suitable azeotrope with water. Preferred azeotropes include benzene, xylene and toluene. The more preferred amides useful for later reactions are bis-(2-alkyl amido ethyl)-amines. These amido amines may also be purified by well known methods such as distillation or recrystallization from polar materials. Such recrystallization agents as isopropyl alcohol and acetone are useful to purify the products. The preferred diamides are white solids which may be recrystallized and then collected by filtration methods.

Such diamides formed by the reaction between a polyalkylene polyamine and a saturated fatty acid may be represented by the general formula:



where R is a saturated fatty acid of at least eleven carbon atoms and preferably from 15 to 17, and n is an integer of from 1 to 3.

The diamides obtained as described above are alkylated and quaternized with various alkylating agents. Any reactive alkylating agent containing a replaceable anion in its structure may be used in the preparation of the quaternaries. Among these quaternizing and alkylating agents are methyl chloride, -chloroethanol, 3-chloro-1, 2-propanediol, ethyl chloroacetate, sodium chloroacetate, polyethylene glycol chloride and epihalohydrins. Other alkylating agents such as ethyl bromide, propyl chloride, and 1-chloro-2,3-dihydroxy propane may also be used. These quaternizing agents may be added directly to the diamides or dissolved in aqueous or organic solvents. In the quaternizing reaction, it is necessary to

add a source of base in order to neutralize the amine salts initially formed from the alkylation. At least 2 mols of quaternizing or alkylating agents must be used for every secondary basic nitrogen atom present in the diamide. Also, at least 1 mol of basic material must be used for every basic nitrogen atom in the diamide in order to neutralize the acid amine salt formed. Basic materials such as sodium hydrogen carbonate, sodium hydroxide, and potassium hydroxide may be used as sources of base.

In a preferred embodiment of the invention, from 5 to 10 mols of alkylating agent are added for every mol of diamide to be reacted. The amount of base may vary from 1 to 5 mols for every mol of diamide, with slightly greater excesses necessary if one uses slightly less basic materials such as sodium bicarbonate. The quaternizing reaction may be run at atmospheric pressures at temperatures from 100 to 200° C. The time of the reaction may take from 1 to 10 hours. Normally, the reaction is completed in from 2 to 6 hours at temperatures from 120 to 180° C.

Contact of the reactants may be effected by solubilizing them with polar solvents. This will expedite the reaction. Solutions may be made from a wide variety of organic solvents, but the preferred solvents are lower alcohols. The diamide quaternaries obtained may also be purified by use of various solvents. A particularly useful combination involves a mixed solvent of acetone and isopropyl alcohol. The diamide quaternaries may be recrystallized from this solvent, filtered, and cooled, in order to obtain a solid product. The product may be collected by such filtration with minimum loss of active ingredient.

Table I refers to the preferred diamides, compositions 1 through 8. These are readily prepared from the condensation reaction of the requisite fatty acids and polyamines listed therein.

Table I

Composition	Fatty acid	Polyalkylene polyamine
1.....	$\text{C}_{15}\text{H}_{31}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Diethylene triamine.
2.....	$\text{C}_{17}\text{H}_{35}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Do.
3.....	$\text{C}_{15}\text{H}_{31}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Do.
4, mixed..	$\text{C}_{15}\text{H}_{31}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}, \text{C}_{17}\text{H}_{35}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Do.
5.....	$\text{C}_{17}\text{H}_{35}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Tetraethylene pentamine.
6.....	$\text{C}_{17}\text{H}_{35}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Triethylene tetramine.
7, mixed..	$\text{C}_{15}\text{H}_{31}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}, \text{C}_{17}\text{H}_{35}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Tetraethylene pentamine.
8.....	$\text{C}_{15}\text{H}_{31}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$	Triethylene tetramine.

Table II recites suitable final reaction products of this invention in terms of listing particular suitable variants of the general final product formulae given above just following statement of objects of invention. These quaternary compounds are formed as outlined above by quaternization of the diamide reaction product of polyamine and fatty acid, using quaternizing agent or agents which contain the requisite Z and Y radicals. If mixed quaternizing agents are used the Z and Y radicals attached to the secondary basic nitrogen atoms of the diamide will differ in molecular structure.

Table II

Composition	R	n	Z	Y	A
I.....	C ₁₃ H ₂₇	1	CH ₃ -----	CH ₃ -----	Cl
II.....	C ₁₇ H ₃₅	1	CH ₃ -----	CH ₃ -----	Cl
III.....	C ₁₅ H ₃₁	1	CH ₃ -----	CH ₃ -----	Cl
IV.....	C ₁₇ H ₃₅	1	HOCH ₂ CH ₂ -----	HOCH ₂ CH ₂ -----	Cl
V.....	C ₁₅ H ₃₁	1	HOCH ₂ CH ₂ -----	HOCH ₂ CH ₂ -----	Cl
VI.....	C ₁₅ H ₃₁	1	HOCH ₂ CHCH ₂ ----- OH	HOCH ₂ CHCH ₂ ----- OH	Cl
VII.....	C ₁₇ H ₃₅	1	HOCH ₂ CHCH ₂ ----- OH	HOCH ₂ CHCH ₂ ----- OH	Cl
VIII.....	C ₁₅ H ₃₁	1	CH ₂ C(=O)OEt-----	CH ₂ C(=O)OEt-----	Cl
IX.....	C ₁₇ H ₃₅	1	CH ₂ C(=O)OEt-----	CH ₂ C(=O)OEt-----	Cl
X.....	C ₁₇ H ₃₅	1	CH ₂ C(=O)ONa-----	CH ₂ C(=O)ONa-----	Cl
XI.....	C ₁₇ H ₃₅	1	H(-OCH ₂ CH ₂ -) ₈₋₁₀ -----	H(-OCH ₂ CH ₂ -) ₈₋₁₀ -----	Cl
XII.....	C ₁₇ H ₃₅	1	H(-OCH ₂ CH ₂ -) ₃₋₅ -----	H(-OCH ₂ CH ₂ -) ₃₋₅ -----	Cl
XIII.....	C ₁₇ H ₃₅	1	CH ₂ CH ₂ OH-----	CH ₂ CH ₂ OH-----	Cl
XIV.....	C ₁₅ H ₃₁	1	CH ₃ -----	H(-OCH ₂ CH ₂ -) ₈₋₁₀ -----	Cl
XV.....	C ₁₇ H ₃₅	1	CH ₃ -----	H(-OCH ₂ CH ₂ -) ₈₋₁₀ -----	Cl
XVI.....	C ₁₇ H ₃₅	1	CH ₃ -----	H(-OCH ₂ CH ₂ -) ₃₋₅ -----	Cl

The above diamide quaternaries may be colloiddally dispersed in aqueous media or polar organic solvents, such as lower alkyl ketones, and lower ethers. They are soluble in pure aqueous media up to 25% based on the weight of the water. The amount that may be suspended or solubilized in liquid aqueous media may be considerably enhanced by minor additions of lower polar organic solvents. Combinations of water and lower alcohols are particularly useful in dispersing the solid compositions.

The described novel products may be marketed as such or in the form of an aqueous dispersion, or in the form of a solvent solution thereof. They may be applied to textile materials by any of the well known methods, e.g., in the form of an aqueous dispersion or solvent solution, and in every case impart excellent softness, drape, flexibility, and "hand" to the textile material. If applied as a solid, it is necessary that they be first incorporated in liquid media in order to be uniformly attached and affixed to the cellulosic fibrous materials to be treated.

An important application is the addition of aqueous suspensions or solutions of the composition to the water rinse cycle of industrial or home laundering processes. Excellent textile softening is accomplished by addition of the compositions in the rinse cycle of baby diaper services. Repeated contact of these textiles with the composition does not result in chemical build-up, but rather softens the textile materials with little or no consequent water-repellency problems of the type commonly encountered.

The amount of chemical that may be applied and affixed to the fibrous materials may vary from .001% to 10% based on the weight of the fibrous materials themselves. However, the amount of active material that is preferably employed is generally from 2% to 7% based on textile weight. These percentage figures are further based upon the amount of active chemical treatment ingredients contained in treating compositions.

EVALUATION OF THE INVENTION

In order to evaluate the compositions described above as textile softeners, the following test method was employed as being found to be the most satisfactory method of screening. This method duplicated as closely as possible home laundry conditions. The test specimens were cotton diapers and cotton wash cloths which were indelibly numbered in one corner for purposes of identification. A portable, four-gallon, 1½ pound capacity washer and spin dryer was used to treat from ¾ to 1 pound of fabrics.

The specimens were washed 3 minutes in 4 gallons of Chicago tap water containing 75 cc. of a commercial anionic detergent. The water was drained and the test cloths spun dry for one minute. The washer was refilled with water to which had been added the treated chemical. The aqueous chemicals were added in a 4% by weight composition, such diluted form being similar to that which a consumer would normally purchase. The rinse cycle was conducted for three minutes, the washer drained, and the specimens again spin-dried for one minute. For purposes of comparison, the various compositions of the invention were directly compared against two well-known commercial textile softeners, composition A and composition B. The treated specimens were then felt by at least 12 persons who gave their opinions as to whether a treated specimen was soft and fluffy, or whether it was relatively rough to the feel. These volunteers were instructed to take into consideration the various factors relating to "hand" of fabrics. These included flexibility, compressibility, softness, pliability, extensibility, and resilience. All these factors are important for evaluating textiles in their various uses. While these subjective performance characteristics may be evaluated only by personal reaction, they are important factors in the traditional concept of fabric performance, particularly in the apparel and household markets. Thus, these subjective criteria such as fabric "hand" or "handle," "drape" and "luster" are all measures of the extremely complex features of the physical properties of the treated fabric as related to their salability to and satisfactory use by the ultimate consumer.

Table III below compares the preferred compositions of the invention to commercial softeners, composition A or composition B, both of which are currently sold in large volume. Each composition of the invention is directly compared to composition A or B after one washing treatment.

Series of pairs of code marked samples of treated fabrics were prepared. One member of each pair had been treated with either composition A or B. The other had been treated with a composition of the invention. The pairs were submitted to a panel of from 11 to 20 people. Each panel member recorded his vote in favor of the sample from each pair which he believed to have superior properties. The number of votes for each treated test specimen was then recorded to measure the quality of the

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treated cloth in regards to the above subjective measures.

To test the reproducibility of the test, series Nos. 1 through 3 were submitted to two different panels. The respective percentage of votes for the test specimens treated with the compositions of the invention or the commercial softener, composition B, remarkably close upon comparing the opinions of the two panels.

Table III

"HAND" TEST COMPARISONS

Series	Treatment composition (4% aqueous solutions)	Number of Panel votes		Percent of total votes cast	
1.	B.	3	2	15	10
	III.	17	18	85	90
2.	B.	2	2	10	11
	50% III, 50% IV.	18	16	90	89
3.	B.	5	3	20	15
	XVI.	19	17	80	85
4.	B.	7		35	
	XV.	13		65	
5.	III.	12		60	
	XVI.	8		40	
6.	XVI.	12		60	
	50% III, 50% IV.	8		40	
7.	XVI.	11		69	
	XV.	5		31	
8.	A.	1		9	
	III.	11		91	
9.	A.	3		27	
	II.	8		73	
10.	A.	4		33	
	XII.	8		67	
11.	III.	4		36	
	IV.	7		64	

From the information in Table III above, it has been shown that the products of the invention, when compared to composition A selected as the standard for softness, are all superior to the market standards with composition III being far superior in softening ability.

In order to further the study of the softening efficiency of the compositions of the invention, two of these, compositions III and IV, were checked against commercial softener, composition B. In this test, direct comparison of each compound was made against composition B on repeated washings and reapplication tests. After each cycle, a number of test specimens were removed and dried. The remainder were washed with detergent, as described above, and softener applied in the rinse cycle again. This procedure was repeated five times. The samples were again checked by the testing panel after each treatment and each member of the panel recorded one vote in favor of the sample he believed to have superior qualities. Table IV below tabulates the number and percentage of votes in favor of the respective compositions.

Table IV

"HAND" TEST COMPARISON AFTER REPEATED WASHINGS

First Treatment		
Composition	Number of votes	Percent of votes
B.	5	28
IV.	13	72
B.	4	25
III.	12	75
Second Treatment		
B.	3	30
IV.	7	70
B.	4	31
III.	9	69

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Third Treatment

B.	4	37
IV.	7	63
B.	4	33
III.	8	67

Fourth Treatment

B.	3	25
IV.	9	75
B.	3	25
III.	9	75

Fifth Treatment

B.	3	21
IV.	11	79
B.	1	10
III.	9	90

From the information in Table IV, it is shown that the selected products of the invention maintain their superiority over the standard for softening effectiveness after repeated washings. Composition III surpasses the standard by a 9 to 1 margin when tested by the "hand" method after the fifth treatment. Composition IV was slightly inferior to composition III, but yet surpassed the standard by nearly a 4 to 1 margin after five successive treatments. In some cases, repeats were made in order to check the results more thoroughly. A combination treatment of composition III and composition IV also shows clear superiority as textile softener treatment over the currently widely used market standard. This combination shows the versatility of the invention and its scope of effective use.

As a conventional softener builds up on a fabric after repeated use, it becomes extremely difficult for the treated fabric to adsorb water. This is a critical drawback to the majority of the softeners on the market today. Thus, re-wettability has become an important factor to be considered in any newly created softener. In order to evaluate the re-wettability of the treated specimens, the following test method was employed.

The cotton diapers were washed as described above and the softeners were added during the rinse cycle in an amount of one ounce of a 4% solution for every 12 diapers. These diapers were again spun-dried in the washer and dried in an automatic dryer. With each series of chemicals of the invention, equal doses of composition A and/or composition B were run for comparison. Blanks were also run in the test. After the test specimens were dried, they were subjected to a re-wettability test known as the dropping method.

This method is performed as follows.

The diaper from each softening treatment is mounted on a 7 inch embroidery hoop. A microburette containing distilled water is adjusted so that it delivers one drop of water approximately every five seconds. The surface of the taut textile is held about $\frac{3}{8}$ inch (1 cm.) below the tip of the burette and a stopwatch is started just as the drop falls on to the cloth. The drop is allowed to fall on to the cloth and the hoop is moved out from under the burette. The watch is stopped when the liquid on the surface of the textile loses its reflective power. The shorter the wetting time, the more readily wettable is the textile.

Four to six samples of each test specimen contacted with the same chemical were tested. Each test specimen was tested by the dropping method in 10 different areas throughout the sample to give an average means.

Table V below shows the results of the re-wettability test when compared to composition A or B, the standards again used for comparison purposes. All the results in Table V are in seconds.

Table V

COMPOSITION A

Test sample.....	1	2	3	4	5	6
Test area:						
1.....	4.5	3.5	4.5	60.5	3.5	4.5
2.....	4.5	3.0	5.0	79.0	4.0	5.0
3.....	4.0	3.5	6.5	37.5	3.5	6.5
4.....	4.0	3.5	7.0	6.0	4.5	7.5
5.....	3.5	4.0	68.5	52.0	8.5	5.5
6.....	4.0	5.0	64.5	58.5	9.5	5.0
7.....	5.0	4.5	36.0	4.0	9.5	4.5
8.....	4.0	4.5	48.0	5.5	6.0	7.5
9.....	4.0	11.0	75.5	75.0	46.5	4.0
10.....	3.5	11.0	10.0	39.0	5.5	3.5
11.....	4.5	27.5	6.0	36.0	5.0	5.0
12.....	5.0	57.0	8.0	32.5	4.0	5.0
Total.....	50.5	138.0	339.5	485.5	110.0	63.5
Mean.....	4.2	11.5	28.3	40.5	9.2	5.3

NOTE.—Average mean, 16.5 seconds.

50% COMPOSITION III, 50% COMPOSITION IV

Test sample.....	1	2	3	4	5	6
Test area:						
1.....	4.0	4.0	4.0	5.5	4.0	6.0
2.....	5.0	4.5	13.0	51.5	5.0	5.0
3.....	5.0	6.0	11.0	8.5	4.5	5.0
4.....	5.0	5.0	16.0	6.0	3.5	4.0
5.....	5.0	4.5	67.0	4.5	5.5	4.5
6.....	5.0	4.5	71.0	5.0	6.0	3.5
7.....	4.0	4.0	66.0	7.5	5.5	3.5
8.....	5.0	4.5	47.0	4.0	5.0	4.5
9.....	43.0	4.0	42.5	3.5	4.5	4.5
10.....	12.5	6.0	73.0	4.0	5.0	7.5
11.....	22.0	4.5	105.0	4.0	62.5	6.5
12.....	16.0	4.5	111.0	4.0	8.0	3.5
Total.....	131.5	56.0	626.5	108.0	119.0	58.0
Mean.....	11.0	4.7	52.2	9.0	9.95	4.8

NOTE.—Average mean, 15.4 seconds.

COMPOSITION XVI

Test sample.....	1	2	3	4	5	6
Test area:						
1.....	4.0	3.0	6.5	5.5	49.0	28.5
2.....	12.0	4.0	10.0	6.5	85.0	80.5
3.....	7.8	5.0	11.5	5.0	-----	28.0
4.....	23.5	5.0	9.5	6.5	-----	34.0
5.....	3.5	6.0	6.0	6.5	4.5	5.0
6.....	4.0	65.0	7.5	10.0	6.0	8.0
7.....	4.5	52.0	5.0	30.5	5.0	6.5
8.....	5.0	4.0	9.0	9.5	4.5	7.5
9.....	3.5	13.5	5.0	7.5	3.0	7.0
10.....	4.5	10.5	5.5	7.0	4.0	8.0
11.....	6.5	29.0	6.5	6.0	5.0	8.5
12.....	14.0	23.0	4.5	6.0	3.0	7.0
Total.....	163.0	220.0	86.5	106.5	169.0	228.5
Mean.....	13.6	18.3	7.2	8.9	16.9	19.0

NOTE.—Average mean, 14 seconds.

COMPOSITION XV

Test sample.....	1	2	3	4	5	6
Test area:						
1.....	65.0	24.0	5.0	2.5	7.5	10.0
2.....	52.0	6.5	4.5	3.5	5.5	27.5
3.....	22.0	8.0	4.0	3.0	12.5	5.0
4.....	15.0	15.0	4.5	3.5	24.0	6.5
5.....	6.0	4.0	6.5	3.5	7.5	32.5
6.....	6.5	5.5	11.0	4.0	6.0	29.0
7.....	5.5	5.0	14.0	3.0	6.5	45.0
8.....	6.5	4.5	9.0	4.0	4.5	7.0
9.....	4.5	5.0	10.0	20.0	8.5	3.0
10.....	4.0	4.0	42.0	4.0	7.5	3.0
11.....	4.5	4.5	43.0	5.0	13.5	4.5
12.....	5.5	4.5	36.0	4.5	8.5	5.5
Total.....	197.0	90.5	189.5	60.5	112.0	178.0
Mean.....	16.4	7.5	15.8	5.0	9.3	14.9

NOTE.—Average mean, 11.5 seconds.

COMPOSITION IV

Test sample.....	1	2	3	4	5	6
Test area:						
1.....	8.5	5.5	5.5	5.0	5.5	4.5
2.....	5.0	7.0	7.0	7.5	6.0	6.0
3.....	8.5	5.0	13.5	6.0	5.0	4.5
4.....	5.0	10.0	8.0	8.0	7.0	5.5
5.....	5.0	14.0	4.5	5.5	6.0	4.5
6.....	5.5	5.5	5.5	6.5	7.0	4.0
7.....	4.5	7.0	6.0	6.5	7.0	4.5
8.....	5.0	15.5	6.0	5.5	6.0	4.0
9.....	5.0	5.5	9.0	5.5	7.5	5.0
10.....	5.5	6.0	9.0	5.0	7.5	5.0
11.....	8.5	6.5	8.0	5.0	5.5	4.5
12.....	8.0	5.0	11.0	5.5	6.5	5.0
Total.....	74.0	92.5	93.0	71.5	76.5	57.0
Mean.....	6.17	7.7	7.75	5.95	6.37	4.75

NOTE.—Average mean, 6.52 seconds.

As is readily apparent from the results tabulated in Table V, all the compositions of the invention are clearly superior to the standard employed. The significant figure, the average mean in seconds, is lower for each composition of the invention tested than is the average mean for the standard. This very important factor of re-wettability is thus inherent in the textiles treated in this case, and their cleanability is left unaffected by treatment over an entire period of useful service during which softness and fluffiness is maintained.

Laboratory tests have shown that fabrics treated in accordance with the invention will not yellow with age or repeated treatment. The inventive compositions are safe for home use when employed in the concentrations suggested herein.

The following examples relate to the preparation of representative compositions of the invention for further illustration, but the invention is not limited in its scope by these examples. The parts given are all parts by weight unless otherwise indicated.

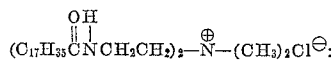
EXAMPLE I

Into a 3-neck 1 liter flask are introduced the reactants. The flask is equipped with a cone-driven stirrer and a thermometer. 552 grams (2 mols) of hydrogenated tallow fatty acid are added to the flask initially, followed by an addition of 103 grams (1 mol) of diethylene triamine. The reactants were vigorously agitated at room temperature and then slowly heated to 150° C. A Dean and Stark trap, coupled with a Friedrich condenser, was then attached to the 3-neck flask, and the temperature of the flask was maintained between 150 and 165° C. for four hours. After this time had elapsed, the temperature was raised to 175° C. and maintained at this temperature for one-half hour. The reaction mass was allowed to cool and the diamide product solidified. During the course of the reaction, 36 ml of water was collected, which corresponds to the theoretical amount of water to be collected from the amide condensation reaction. A neutral equivalent titration of the diamide gave a figure of 580, substantially corresponding to the theoretical neutral equivalent of 619.

62 grams of the above hydrogenated tallow fatty diamide of diethylene triamine ($\frac{1}{10}$ mol) was added to 50 ml. isopropyl alcohol containing 16 grams of sodium bicarbonate. This mixture was added to a pressure vessel capable of being rocked. To the pressure vessel was attached a line leading to a cylinder of methyl chloride gas. The pressure vessel was heated rapidly to 150° C. and maintained between 145 and 150° C. for a period of four hours, during which time the vessel was continuously agitated by rocking. After cooling and venting, the reaction mixture was dissolved in 500 ml. of mixed solvent, acetone-isopropyl alcohol. The reaction product was transferred to a one liter beaker and heated in the mixed solvent at 50° C., at which temperature the product was completely solubilized. The impurities were filtered after

the beaker was cooled and then the filtrate was cooled in a refrigerator for three hours. The product then precipitated from the solvent medium and was collected by such filtration. A fine, white powder was obtained upon which a carbon, hydrogen, nitrogen and chloride microanalysis was done. Oxygen was determined by the difference. The following are the results of the elemental analysis, with corresponding theoretical analysis of the diamide quaternary product of the example.

Microanalysis of

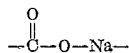


Element	Calculated, percent	Found, percent
Carbon	71.50	69.63
Hydrogen	12.20	12.23
Nitrogen	5.95	6.07
Chlorine	5.07	4.73
Oxygen	5.28	7.34

The product of this example corresponds to composition II of Table II. The overall yield from the reaction was 90%.

EXAMPLE II

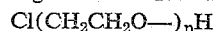
62 grams of the diamide produced from Example I was mixed with 50 grams of sodium chloroacetate in 50 grams of isopropyl alcohol. These weights correspond to $\frac{1}{10}$ mol of diamide and $\frac{2}{10}$ mol of alkylating agent. The reactants were thoroughly mixed and then added to a pressure cylinder and heated at 150° C. for six hours with continuous agitation by rocking. After the reaction was complete, the vessel was cooled and the material was recrystallized from hot methyl alcohol using a procedure similar to that of Example I. The resultant solid was filtered from the solvent by a suction filtration technique. The product obtained was hygroscopic, and infra-red study showed a strong



absorption. This product was composition X of Table II.

EXAMPLE III

Composition XI of Table II, the quaternary from the reaction of polyethylene glycol chloride with hydrogenated tallow diamide, was produced by the following method. 62 grams of the diamide from Example I, 16 grams of sodium bicarbonate, and 200 grams of polyethylene glycol chloride "410" were mixed. The polyethylene glycol chloride "410" is a product of Union Carbide Company and had the following structural formula:



where $n=8$ to 10. The reactants were thoroughly mixed and heated at 150° C. in a pressure vessel for 6 hours, during which time agitation was affected through a rocking mechanism. After cooling and venting the contents of the pressure autoclave, the product was treated with isopropyl alcohol in order to purify it. The solid product was collected on a Buchner funnel by a suction filtration method.

EXAMPLE IV

62 grams of the diamide of Example I ($\frac{1}{10}$ mol), 20 grams of sodium bicarbonate, 80 cc. of isopropyl alcohol, and 100 grams (0.5 mol) of polyethylene glycol chloride "210" were mixed together. The quaternizing agent, polyethylene glycol chloride "210," corresponds to the structure of the glycol compound in Example III with the exception that $n=3$ to 5. As in the previous examples, the quaternization was affected under pressure. The reaction mixture was heated in the pressure vessel at 160 to 180° C. for 10 hours. The crude product was purified by crystallization from isopropyl alcohol. A 2.5% aqueous solution was much more viscous than the corresponding aque-

ous solutions of the previous examples. However, the solution or dispersion was nevertheless readily pourable and capable of effective application for textile softening. The product of this reaction is composition XII in Table II.

EXAMPLE V

In order to demonstrate the scope and versatility of the general reaction of the invention, a product was prepared which contained two different quaternizing agents.

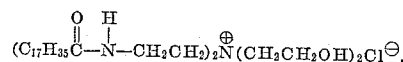
62 grams (0.10 mol) of the diamide of Example I was added to 12 grams (0.15 mol) of 2-chloroethanol in 50 grams of isopropyl alcohol. Since no base was used in the reaction, only 1 mol of the 2-chloroethanol could be added to the nitrogen atom available for quaternization. The reaction was run at 150° C. in a pressure vessel for four hours. The hydrochloride salt of the monoalkylated diamide was produced, and after cooling, the product was further alkylated by the following method:

The entire above impure product was added to 40 grams (0.5 mol) of propyl chloride and 20 grams of sodium bicarbonate in 20 grams of isopropyl alcohol. The reactants were heated at 130 to 140° C. for three hours in the autoclave. After cooling and venting and contents of the autoclave, the crude reaction mixture was dissolved in isopropyl alcohol. The inorganic impurities were removed by crystallization technique and the product was further recrystallized from a 80% acetone-20% isopropyl alcohol solvent. The final product corresponds to composition XIII of Table II.

EXAMPLE VI

62 grams of the diamide of Example I (0.10 mol), 80 grams of 2-chloroethanol (1.0 mol), 16 grams of sodium bicarbonate, and 50 ml. of isopropyl alcohol were mixed and charged into a rocking autoclave. The reaction was run at 150° C. for 4½ hours. After cooling, the crude product was crystallized from isopropyl alcohol and then recrystallized from a 90% acetone-10% isopropyl alcohol solvent mixture. A micro analysis gave the following elemental breakdown, which is compared to the calculated analysis.

Microanalysis of



Element	Calculated, percent	Found, percent
Carbon	69.50	69.57
Hydrogen	11.45	11.96
Nitrogen	5.53	6.62
Chlorine	4.70	5.01

The product of this example corresponds to composition IV, Table II.

EXAMPLE VII

Into a 3-neck, round bottom, 2 liter flask equipped with a stirrer, thermometer and Dean and Stark trap connected between the flask and a condenser, was added 935 grams of the methyl ester of palmitic acid (3.5 mols) and 180 grams of diethylene triamine (1.8 mols). The reactants were thoroughly mixed at room temperature and heated to 150° C. The temperature was maintained with vigorous stirring between 150 and 160° C. for a period of four hours. 72 ml. of methanol was collected, corresponding to a weight of 58 grams, during the course of the reaction. The reaction mixture was cooled and the crude product poured into methyl alcohol, from which it was crystallized. The solid, purified product, after drying in a vacuum oven at 50° C. had a melting point of 100 to 105° C. The yield was quantitative. The white, solid diamide was soluble in various organic solvents such as benzene, chloroform, carbon tetrachloride, but insoluble in lower alcohols and water.

A neutralization equivalent was run on the product and produced a figure of 467 vs. a theoretical figure of 583.

The low neutral equivalent was believed to be due to the presence of some monoamide. Consequently, the resulting product was again crystallized with hot acetone in the hopes of removing monoamide. A white solid with a clear cut melting point of 116 to 118° C. was obtained. The neutral equivalent of this product was 586, corresponding almost exactly to the theoretical neutral equivalent (583) of the desired diamide.

58.3 grams (0.1 mol) of the above pure diamide was added to 16 grams of sodium bicarbonate in 60 ml. of isopropyl alcohol. This mixture was added to a pressure vessel. A continuous supply of methyl chloride gas was passed into the closed pressure system while the temperature was maintained at 140 to 150° C. for four hours. The pressure vessel was cooled and vented, and the crude product was treated with isopropyl alcohol and filtered to remove the inorganic compounds. The filtrate was frozen in a refrigerator overnight. The solid product obtained was filtered and recrystallized from a 90% acetone-10% isopropyl alcohol solvent. The resulting pure white solid was analyzed for its elements and gave the following figures.

Microanalysis for $C_{38}H_{78}N_2ClO_2$:

Element	Calculated, percent	Found, percent
Carbon	72.50	70.23
Hydrogen	12.20	12.15
Nitrogen	6.53	6.62
Chlorine	5.50	4.03

The product of this example corresponds to composition III of Table II.

EXAMPLE VIII

58.3 grams of the diamide of Example VII (0.1 mol) and 50 cc. of isopropyl alcohol were placed in a stainless steel pressure cylinder to which was connected a source of methyl chloride gas. Since no base was present, only 1 mol of methyl chloride gas could be added to the hydrogen available for alkylation. The reaction was run at 150° C. for four hours with continuous agitation by rocking. The monomethylated hydrochloride salt of the diamide was cooled to room temperature and removed from the pressure vessel. The entire contents of the pressure reactor were added to 80 grams of polyethylene glycol chloride "410" and 16 grams of sodium bicarbonate in 10 ml. of isopropyl alcohol. The reactants were thoroughly mixed and placed again in the pressure vessel, and heated at 160° C. for four hours. After cooling and venting, the compound was isolated by recrystallization techniques outlined in Example VI. The final product corresponds to composition XIV of Table II.

EXAMPLE IX

58.3 grams of the diamide of Example VII was added to 16 grams of sodium bicarbonate and 123 grams of ethyl chloroacetate in 10 grams of isopropyl alcohol. The quaternization reaction was run for six hours at 140 to 150° C. The crude solid was recrystallized from an 80% acetone-20% isopropyl alcohol solvent mixture. The quaternary product is composition IX of Table II.

EXAMPLE X

58.3 grams of the diamide of Example VII was added to 16 grams sodium bicarbonate and 110 grams (1.0 mol) of 3-chloro-1,2-propanediol in 10 grams of isopropyl alcohol. The reaction was run in the usual manner at 140 to 150° C. for six hours in a rocking autoclave. The quaternary diamide of this example is composition VI of Table II.

EXAMPLE XI

58.3 grams of the diamide of Example VII was added to 16 grams of sodium bicarbonate and 80 grams of 2-chloroethanol in 10 grams of isopropyl alcohol. The

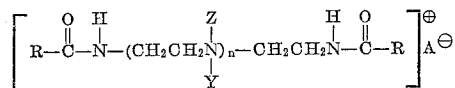
reactants were mixed and added to a pressure vessel and then heated at 140 to 150° C. for six hours. After cooling, the viscous residue was poured into a beaker and washed with isopropyl alcohol. The crude solid was then slurried in isopropyl alcohol and left overnight in a refrigerator. The resultant solid was then filtered and again crystallized from a 20% isopropanol-80% acetone solvent mixture. A 5% aqueous solution prepared from the pure solid remained uniformly dispersed in water over a period of many months. The solid corresponded to composition V of Table II.

The compositions of the invention are especially useful in treating hydratable fibers in cloths or sheets in which such fibers predominate, especially cellulose fibers, such as cottons, or blends of fibers in which cellulose predominates. The invention is applicable to the treatment of wood fibers and cloth. The invention is also applicable to the treatment of wood fibers in cloth, cloth containing glass fibers, synthetic fibers in cloth, blends of synthetic fibers and natural fibers in cloth, e.g., blends of Dacron (polyethylene terephthalate) and wool, blends containing Orlon (acrylic fiber) and the like. In addition to becoming endowed with softness the treated cellulosic textile materials are often crease resistant but yet remain water wettable.

The hand and texture of the textile materials are not only improved but the properties imparted to the fabrics by the chemical assistance may be varied by varying the particular fatty acids used in preparing the diamides, or else changing the particular quaternizing or combination of quaternizing agents used.

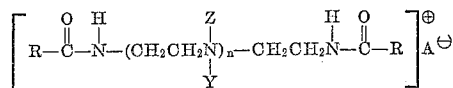
The invention is hereby claimed as follows:

1. The method of treating cellulosic fibrous materials which comprises applying and affixing thereto an aqueous colloiddally dispersible diamide quaternary of the formula:



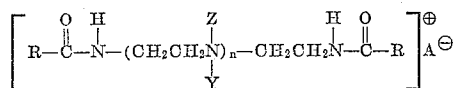
where R is a saturated fatty radical of at least eleven carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and being composed of elements from the group consisting of C, H, O, X and M where X is halogen and M is an alkali metal, n is an integer of from 1 to 3 and A is an anion.

2. The method of treating cellulosic fibrous materials which comprises applying and affixing thereto an aqueous colloiddally dispersible diamide quaternary of the formula:



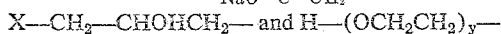
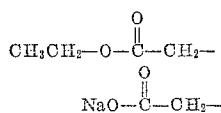
where R is a saturated fatty radical of at least 15 carbon atoms and Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and being composed of elements from the group consisting of C, H, O, X and M where X is halogen and M is an alkali metal, n is an integer of from 1 to 3 and A is an anion of the group consisting of halide, sulfate, phosphate, acetate, sulphite and nitrate.

3. The method of treating cellulosic fibrous materials which comprises applying and affixing thereto an aqueous colloiddally dispersible diamide quaternary of the formula:



where R is a saturated fatty radical of at least eleven carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and each being selected from the group consisting of CH_3- , CH_3CH_2- , $CH_3CH_2CH_2-$, $HOCH_2CH_2-$, $HOCH_2CHOHCH_2-$,

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where X is halogen, n is an integer of from 1 to 3, y is an integer of from 2 to 12 and A is an anion selected from the group consisting of halide, sulfate, sulphite, acetate, nitrate and phosphate.

4. The method of claim 1 where R is a saturated fatty radical derived from hydrogenated tallow, Z and Y are each methyl groups, n is 1 and A is halide.

5. The method of claim 1 where R is a saturated fatty radical derived from hydrogenated tallow, Z and Y are each 2-hydroxy ethyl groups, n is 1 and A is halide.

6. The method of claim 1 where R is a saturated fatty radical containing 17 carbon atoms, Z and Y are each $\text{H}-(\text{OCH}_2\text{CH}_2)_y-$ groups, where y is an integer of from 4 to 12, n is 1 and A is halide.

7. The method of claim 1 wherein the fibrous material is a cotton textile and whereby said textile is softened.

8. The method of claim 2 wherein the fibrous material is a cotton textile and whereby said textile is softened.

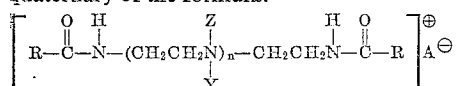
9. The method of claim 3 wherein the fibrous material is a cotton textile and whereby said textile is softened.

10. The method of claim 7 where R is a saturated fatty radical from hydrogenated tallow, Z and Y are each methyl groups, n is 1 and A is halide.

11. The method of claim 7 where R is a saturated fatty radical from hydrogenated tallow, Z and Y are each 2-hydroxy ethyl groups, n is 1 and A is halide.

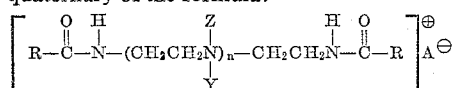
12. The method of claim 7 where R is a saturated fatty radical containing 17 carbon atoms, Z and Y are each $\text{H}-(\text{OCH}_2\text{CH}_2)_y-$ groups where y is an integer of from 4 to 12, n is 1 and A is halide.

13. A cellulosic fibrous material impregnated with a minor amount of an aqueous colloiddally dispersible diamide quaternary of the formula:



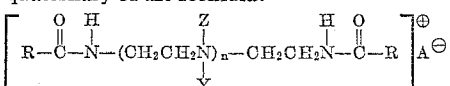
where R is a saturated fatty radical of at least eleven carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and being composed of elements from the group consisting of C, H, O, X and M where X is halogen and M is an alkali metal, n is an integer of from 1 to 3 and A is an anion.

14. A cellulosic fibrous material impregnated with a minor amount of an aqueous colloiddally dispersible diamide quaternary of the formula:



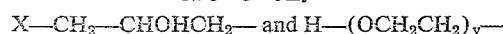
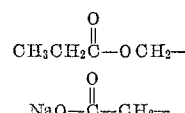
where R is saturated fatty radical of at least 15 carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and being composed of elements from the group consisting of C, H, O, X and M where X is halogen and M is an alkali metal, n is an integer of from 1 to 3 and A is an anion of the group consisting of halide, sulfate, phosphate, acetate, sulphite and nitrate.

15. A cellulosic fibrous material impregnated with a minor amount of an aqueous colloiddally dispersible diamide quaternary of the formula:



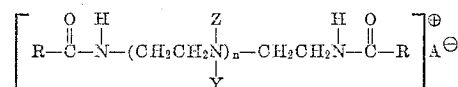
where R is a saturated fatty radical of at least eleven carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and are selected from the group consisting of CH_3- , CH_3CH_2- , $\text{CH}_3\text{CH}_2\text{CH}_2-$, $\text{HOCH}_2\text{CH}_2-$, $\text{HOCH}_2\text{CHOHCH}_2-$,

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where X is halogen, n is an integer of from 1 to 3, y is an integer of from 2 to 12 and A is an anion selected from the group consisting of halide, sulfate, sulphite, acetate, nitrate, and phosphate.

16. A cellulosic fibrous material impregnated with from .001% to 10% based on the weight of said fibrous material of an aqueous colloiddally dispersible diamide quaternary of the formula:



where R is a saturated fatty radical of at least eleven carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and being composed of elements from the group consisting of C, H, O, X and M where X is halogen and M is an alkali metal, n is an integer of from 1 to 3 and A is an anion.

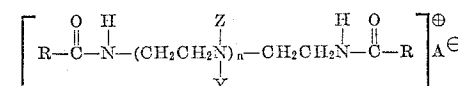
17. A cellulosic fibrous material of claim 13 where R is a saturated fatty radical derived from hydrogenated tallow, Z and Y are each methyl groups, n is 1 and A is halide.

18. A cellulosic fibrous material of claim 13 where R is a saturated fatty radical derived from hydrogenated tallow, Z and Y are each 2-hydroxy ethyl groups, n is 1 and A is halide.

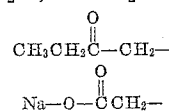
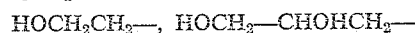
19. A cellulosic fibrous material of claim 13 where R is a saturated fatty radical containing 17 carbon atoms, Z and Y are each $\text{H}-(\text{OCH}_2\text{CH}_2)_y-$ groups where y is an integer of from 4 to 12, n is 1 and A is halide.

20. The cellulosic fibrous material of claim 13 which is further characterized by being water rewettable.

21. A diamide quaternary compound having the formula:



where R is a saturated fatty acid of at least eleven carbon atoms, Z and Y are monovalent organic radicals each containing less than 25 carbon atoms and are selected from the group consisting of



$\text{X}-\text{CH}_2\text{CHOHCH}_2-$, and $\text{H}-(\text{OCH}_2\text{CH}_2)_y-$, where X is halogen, n is an integer of from 1 to 3 and A is an anion selected from the group consisting of halide, sulphate, sulphite, acetate, nitrate and phosphate.

22. The compound of claim 21 where R is a saturated fatty radical derived from hydrogenated tallow, n is 1, Z and Y are each 2-hydroxy ethyl groups and A is halide.

23. The compound of claim 21 where R is a saturated fatty radical containing 17 carbon atoms, Z and Y are each $\text{H}-(\text{OCH}_2\text{CH}_2)_y-$ groups where y is an integer of from 4 to 12, n is 1 and A is halide.

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