United States Patent Office

3,330,770

Patented July 11, 1967

3,330,770

CLEANING COMPOSITIONS CONTAINING SOFTENERS

William Julius van Loo, Jr., Middlesex, George Robert De Paolo, Readington Township, Hunterdon County, and Samuel James O'Brien, Dunellen, N.J., assignors to American Cyanamid Company, Stamford, Conn., a corporation of Maine

No Drawing. Filed Jan. 17, 1964, Ser. No. 338,292
12 Claims. (Cl. 252—152)

This invention relates to cleaning compositions and to the use of such compositions on various substrates, as for example, on textile materials, human hair, and the like. More particularly, the present invention relates to detergent-softener cleaning compositions and to the use of such compositions in the cleaning of various substrates such as are identified above.

At the present time there are commercially available a number of softening agents which may be employed at an appropriate interval in various cleaning operations or procedures, as for example, in home or commercial washing equipment for imparting softness to the washed or laundered material.

Typical of such softeners are those identified as (1) solutions of quaternary ammonium salts, (2) solid urea adducts of the same general chemical type, and (3) emulsions of polyethylene. The first type, when used in the final rinse cycle of a washer, may be highly effective as softeners, depending upon the particular substituents of the quaternary ammonium salt. However, these are ineffective and incompatible when employed in the presence of anionic detergents. Softeners of the second and third types have also been found not to be compatible with anionic detergents and when used in the wash cycle of a home automatic washer do not produce a significant level of softness to the textile materials, particularly cellulosic materials.

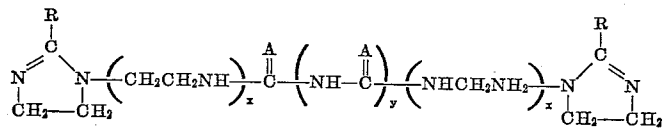
In addition to the cited disadvantages of the softeners referred to above, their use normally adversely affects the absorbency of the substrate softened. In the case of towels and other articles formed of textile material for which absorbency is important, this is a definite disadvantage.

Accordingly, it is an object of the present invention to provide novel cleaning compositions, particularly those containing a detergent and a softener which are compatible in use, thereby permitting their simultaneous use with the avoidance of the necessity for an additional softening step in the cleaning process, as for example, in home or commercial laundering or in shampooing various substrates, such as rugs, slipcovers, or human hair.

It is a further object of the present invention to provide such cleaning compositions which when employed in cleaning textile materials, as for example, in a laundering operation, result in superior absorbency rating when compared with other known softeners, regardless of their method of employment.

These and other objects and advantages of the present invention will become apparent from the detailed description thereof set forth hereinbelow.

According to the present invention, a cleaning composition is provided comprising a detergent selected from the group consisting of anionic and non-ionic types and an acid salt of a composition of matter containing as the desired component a base of the following structure:



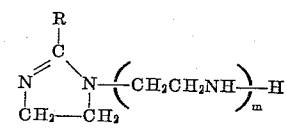
(I)

wherein R is an alkyl group of from 12 to 22 carbon atoms, inclusive, where x is selected from the group consisting of 1 and 2, y is a small integer of from 0 to 3, and where A is selected from the group consisting of O and S.

It has been discovered that the salts of the bases set forth above can be employed in combination with anionic and non-ionic detergents to produce a high degree of softness without affecting the water absorbency of laundered textile materials. This unique advantage is wholly unobvious in view of the fact that the salts are cationic and would not be expected to be compatible with the anionic detergent. This constitutes an advance long sought by detergent manufacturers and others interested in providing textile agents and auxiliaries.

As noted above, R is an alkyl group of from 12 to 22 carbon atoms which can be straight or branched chained and saturated or unsaturated. Dodecyl, tridecyl, pentadecyl, heptadecyl, octadecyl, eicosyl, heneicosyl, 8-heptadecyl, 8,11-heptadecadienyl, and 8,11,14-heptadecatrienyl are examples of such alkyl groups, the heptadecyl product being preferred for economic reasons.

The bases or salt precursors are the reaction products of 1 mole of a fatty acid or the amide thereof and 1 mole of a polyethylene polyamine of the general formula $NH_2(CH_2CH_2NH)_mH$, where m is 2 or 3, the reaction being carried out at for 1–3 hours at atmospheric pressure and a temperature of from 100° C. to 350° C. (preferably 100° C. to 300° C.) to effect the removal of 2 moles of water where the acid is employed or of 1 mole each of water and ammonia where the amide is employed and subsequent condensation to form a 1,2-substituted imidazoline

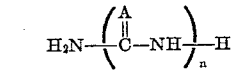


where m is 1 or 2. There follows a heat ageing treatment for an additional 6–14 hours, and preferably 8–12 hours,

which effects a change in the product when the acid is the starting material, the nature of the change is presently unknown but transforms the resulting material from one capable of yielding an inadequate fabric softener to one capable of forming an exceptionally effective softener when employed in the presence of a synthetic detergent.

Such heat ageing is unnecessary where the amide is employed as the starting material.

The said base is then preferably but not necessarily crosslinked with a compound of the formula



where n is 1 or 2 and A is O or S to form a compound of the type represented by Formula I above and subsequently said compound is converted to the acid salt by reaction with an acid.

It should be noted that the structure given (I) is that of the desired reaction product but that such product is not formed exclusively by the preparation process given. A number of side reaction products are possible and are formed, some of which may not contribute to the softening effect observed. By careful control of the various steps in the reaction, however, a successfully performing product is obtained, indicating a favorable concentration of the desired material.

To convert the base to a salt, typically a solution of about 2.5% to 15% or more of solids of the base is prepared in aqueous medium at a pH range of from 2.5 to about 6 or higher by the addition of various acids, whether they be organic or inorganic. Typically, such acids include acetic, lactic, tartaric, citric, formic, boric, oxalic, benzoic, phosphoric, sulfuric, methylsulfuric and the like. Alternatively, the base may be melted with the required amount of appropriate acid to form the salt, subsequently cooled and pulverized to form a dry product.

As noted above, the detergents may be anionic or non-ionic.

The anionic detergents which may be used in the compositions of this invention include alkali metal fatty acid soaps and in addition the well known surface active alkali metal sulfonates and sulfates. The latter group may be employed as the sole detergent base or in admixture with alkali metal fatty acid soaps, as for example, 1 part of fatty acid soap to 0.5 to 2 parts by weight of surface active alkali metal sulfonates or sulfates or mixtures thereof. A preferred group of this class is the long chain alkyl or alkaryl sulfonates, i.e., those wherein the alkyl group is straight or branched in structure, and contains from 8 to 22 carbon atoms but preferably 10 to 16 carbon atoms, examples of which are octyl, decyl, dodecyl, pentadecyl, hexadecyl, octadecyl, mixed long chain alkyl derived from long chain fatty acids such as the lauryl radical, cracked paraffin wax olefins, polymers of low mono-olefins such as propylene tetramer and the like, and wherein the aryl radical is derived from benzene, toluene, xylene, phenol, the cresols, naphthalene and the like. Specific examples of such surface active agents include sodium decylbenzenesulfonate, sodium dodecylbenzenesulfonate, sodium laurylbenzenesulfonate, and sodium hexadecylbenzenesulfonate. Other sulfonate surface active agents are contemplated also, as for example, the long chain alkyl sulfonates such as sodium hexadecylsulfonate and sodium octadecylsulfonate.

The well-known sulfate detergents having 8 to 26 carbon atoms and particularly those having an alkyl radical of about 12 to 22 carbon atoms may be employed as an anionic detergent in the compositions of our invention. Such detergents include sulfuric acid esters of polyhydric alcohols incompletely esterified with fatty acids, e.g., sodium tallow diglyceride monosulfate, the pure and mixed alkyl sulfates, and higher sulfates such as sodium lauryl sulfate and sodium cetyl sulfate.

Additional anionic surface active sulfonates and sulfates contemplated by this invention are the sulfonated and sulfated alkyl acid amides such as Igepon T of the formula

$$C_{17}H_{33}CONH—CH_2CH_2—SO_3Na$$

The sulfated and sulfonated esters such as Igepon AT of the formula

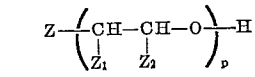
$$R—COO—CH_2SO_3Na$$

in which R is an alkyl radical containing from 12 to 18 carbon atoms, the sodium salt of the sulfonic acid derivative of an aliphatic dialkyl dicarboxylate, disodium sulfosuccinate such as

$$NaOCC—CH_2—CH(SO_3Na)CONHC_{18}H_{37}$$

and the like are also contemplated.

In addition to the anionic surface active agents, non-ionic surface active agents may be used as the base for the compositions of our invention. The non-ionic surface active agents which may be used are viscous liquid, wax-like, water-soluble surface active substances containing a polyglycol ether group of the structure



in which Z_1 and Z_2 are hydrogen or short chain alkyl, p is an integer greater than 3 and Z is a residue of a monomeric organic compound having an active hydrogen, as for example, an alcohol, a phenol, an amide, a secondary amine, a carboxylic acid or the like. These non-ionic detergents are well known (e.g., U.S.P. 1,970,578 and U.S.P. 2,213,477) and may be typified by polyalkylene oxide derivatives (e.g., polyethylene oxide, polypropylene oxide, polybutylene oxide) of water-insoluble higher fatty acids, such as lauric, oleic, palmitic, and stearic and the like or mixtures thereof such as the mixture of fatty acids obtained from animal and vegetable fats and oils and by the oxidation of petroleum fractions such as paraffin wax. They may also be exemplified by the polyalkylene oxide derivatives of such water-insoluble organic hydroxy compounds as higher aliphatic alcohols (i.e., the alcohols corresponding to the fatty acids specified above or mixtures thereof), phenols, particularly alkyl phenols, containing at least 6 alkyl carbon atoms such as isooctyl, di-t-butyl, tri-isopropyl, nonyl, dodecyl, octadecyl phenols or naphthols, or of aralkyl alcohols such as benzyl alcohol, cinnamyl alcohol and the like. They may also be exemplified by the polyalkylene oxide derivatives of such amines as stearyl, lauryl, dicyclohexyl, dibutyl amine and the like. A particularly useful non-ionic detergent is that obtained by condensing 1 mole of tall oil with 5–15 moles of ethylene oxide.

In aqueous laundering conditions, the laundering medium will contain from about .00005% to about 1% and preferably from about .0001% to about .5% of detergent and from .00005% to about .1% and preferably from .0001% to .01% of softener as the salt.

Laundering mediums of the type described above will contain from .0002 to about 2% and preferably from .002 to .2% of softener as the salt based on the dry weight of the substrate such as the textile material is to be laundered.

For formulated softener-detergent compositions, whether they be solid, as for example powdered or formed in bars, or liquid, it has been found that the amount of softener by weight in the complete formulation will vary widely, i.e., from about 1% to about 50% depending upon the recommended use concentrations of the formulation. For most cleaning compositions, however, the range of softener by weight based on the weight of a complete formulation will be from about 5 to about 30%.

Expressed in parts by weight detergent compositions comprising from 5 to 95 parts of a detergent selected from

the group consisting of anionic and non-ionic detergents and from about 0.1 to about 20 parts of the softener are contemplated.

The amount of active detergent substituent in the cleaning composition will vary within wide limits and will depend upon such factors as the nature of the detergent itself as well as other constituents present in the composition. It has been found that from about 5 to about 30% of the total weight of such compositions may advantageously be the detergent constituent with the preferred narrower commercial limits being from about 10 to about 20%.

The cleaning composition may also have added to it various other special additives depending upon the particular end use and physical form in which it is to be employed. Thus, detergent formulations of the type employable as powders may contain hydrotropes or coupling agents, building agents and fillers including soda ash, sodium sesquicarbonate, sodium tetrapyrophosphate, sodium tripolyphosphate, sodium silicate, sodium metasilicate, borax, and the like. In addition, non-alkaline inorganic salts such as sodium sulfate, sodium chloride and the like may be added, as well as scouring abrasives, such as diatomaceous earth, ground pumice, bentonite, and various other clay and clay-like substances. In addition to the above, soil anti-redeposition agents such as carboxymethyl cellulose, cyanoethylated starches, and the like may be employed. The amount of such special purpose additives will naturally vary within wide limits or may even be omitted entirely. However, it has been found that amounts of from about 1% up to as high as 80% by weight based on the formulation weight may be added, depending upon the purpose for which the formulation is intended. Other additives which may be included are germicides, fungicides, bactericides, odorants, colorants, brighteners, and the like.

In liquid detergent formulations, the detergent and the softener will normally be present within the ranges specified above, as is true in the case of bar detergent formulations and detergent formulations employing solvents or the type normally used in dry cleaning.

Aqueous solutions of the softener may be prepared containing as much as 50% or more of active material, though normally solutions containing from 3% up to 25% are employed. When the softener solution is prepared independently of the detergent formulation, it may be added conveniently into most cleaning devices, as for example automatic home washers and the like.

As noted, the process and compositions of this invention are useful in home, institutional and commercial laundering operations. This is so in that the resetting of an automatic home washing machine to the final rinse cycle for the addition of the present commercial softeners is not only time-consuming, laborious, costly with respect to usage of additional hot water, but is also most inconvenient. It is advantageous to the user of an automatic home washer to use a softener with the detergent, either anionic or non-ionic, and thus eliminate the need for resetting the machine for an additional final rinse cycle wherein the softener is added. In coin-operated washing machine establishments such additional rinsing requires additional financial charges which discourage the use of a softener.

As has been described, the most convenient method of employing the softener solutions of this invention is in the wash cycle of the automatic washer, along with the detergent, bleach and other additives. For this use, typically a 6–12% solution of the softener as its acid salt is conveniently employed using one or two ounces of such solutions depending upon the size of the load of textile materials and the degree of softening desired. The softener is added to the wash liquor along with the anionic or non-ionic detergent, bleach, water softener, blueing, etc. and the normal cycles of washing, rinsing, spin-drying are completed. Drying the washed textiles may be accomplished in electric or gas dryers or by air drying on a clothes line. The dried textiles will possess not only a high degree of softness but also will retain their natural water absorbency. Ironing of the textiles when necessary can be accomplished without adverse effect on the softness imparted. No discoloration of the textile will result from the use of the softener, either before or after ironing in the normal manner. It has been found that ironing is improved by the use of the softener in that the iron glides more easily on the treated textile, also less ironing is required. The softener will not interfere with the cleaning action of the detergent or specific action of other washing additives.

Certain automatic washing machines are equipped with a container to which the softener may be added at the beginning of the wash cycle and which automatically dispenses the softener during the final rinse cycle. The softener of this invention may be added to such a container, if desired, or the softener may be added manually to the final rinse cycle, if so desired, without detracting from the utility of the softener.

When some modification of the property of textiles in addition to softening is desired and the compounds producing such effects are not compatible with the wash liquor, use of the softener of this invention in the wash liquor with the detergent will free the built-in dispenser or final rinse cycle for the addition of the desired compounds. Thus, certain compounds, e.g., germicides, water repellents, etc. not compatible with anionic detergents, bleaches, etc. may now be added in the final rinse cycle by the automatic dispenser or manually while the softener has already been added to the detergent wash liquor.

In order that the present invention may be more fully understood, the following examples are given primarily by way of illustration. No specific details or enumerations contained therein should be construed as limitations on the present invention except insofar as they appear in the appended claims. All parts and percentages are by weight unless otherwise specifically designated.

In the following examples, Softeners A, B, C and D are commercially available softeners of the type employed in either home or commercial laundering operations. Softener E is a softener of this invention. These are identified as follows:

A—An aqueous dispersion of approximately 6% solids of a quaternary ammonium softener containing at least one long chain aliphatic group.

B—An aqueous dispersion of approximately 6% solids of a quaternary ammonium softener containing at least one long chain aliphatic group.

C—An aqueous dispersion of approximately 80% solids of a quaternary ammonium softener containing two long chain aliphatic groups diluted to 6% solids for study.

D—A urea-adduct of a quaternary ammonium softener containing one long chain aliphatic group in which the softener is present to approximately 20% of the total.

E—An acid salt of a preparation of 1,3-bis 2-(2-heptadecyl-1-imidazolinyl)ethyl biuret made in accordance with this invention.

A Kenmore automatic washing machine was used for all trials, employing the hot wash-warm rinse setting, the regular wash cycle, and the low water level. A total of six white cotton bath towels comprised a washer load and weighed approximately three pounds or 1360 grams. Since the washing machine contained approximately 9 gallons (34,000 grams) of water, the liquor to cloth ratio was approximately 25 to 1. A commercially available detergent composition containing sodium dodecylbenzene sulfonate was used in all cases, at 18 grams per wash load.

The towels were washed as described in the examples employing the complete washer cycle consisting of washing, rinsing, and spin-drying. In some cases, the final rinse cycle and spin-drying cycle were repeated. The towels were then dried in a Kenmore electric dryer for 40 minutes employing the hot setting and regular cycle. At the end of the first cycle of washing and drying, a towel was re-

moved, properly identified, and held for comparison purposes. It was replaced by a fresh towel of identical construction and the complete washing and drying cycles repeated. This procedure was repeated so that two towels in the load had received a total of ten washing and drying cycles, the others having been removed after 1, 3, 5 and 7 cycles and replaced by fresh towels. Thus, a total of ten towels were involved in each softener evaluation, four of which were replacements and not considered further.

The softness of the laundered towels was rated by a panel of judges experienced in such rating, and the results recorded are the averages of the ratings by individual judges.

Absorbency tests were run by placing a drop of water on the pile surface of the towel and determining the time required for complete disappearance of the water drop by absorbence within the towel. The values reported are the averages of several determinations upon a single towel.

EXAMPLE 1

Washing operations were carried out on four sets of towels using the amounts of softener in the wash liquor as shown in Table I. Another set of towels were washed in the same manner except that no softener was employed. The results are shown in Table I.

TABLE I

Softener Used		Softness Ratings		
Kind	Amount, 100%, g.	1 Wash	5 Washes	10 Washes
None		Standard	Standard	Standard.
A	1.68	Equal	Equal	Equal.
C	1.68	do	do	Do.
D	1.68	do	do	Do.
E [1]	1.68	Much softer	Much softer	Much softer.

[1] 6% stock solution of phosphoric acid salt—pH of 5.0.

Results show that under these conditions of application of softeners in wash liquor with detergent, only a softener of this invention is effective in imparting softness to towels.

Only Softener E gave both softness and absorbency.

EXAMPLE 2

The experiments given in Example 1 were repeated except that the softener was (in each case) added in an additional final rinse cycle, i.e., the regular wash cycle employing 18 grams of a commercially available detergent composition containing sodium dodecylbenzene sulfonate was run followed by the normal rinse and spin-dry cycles, after which the machine was reset to the final rinse cycle in which the softener was added and the machine allowed to complete the additional phases of the normal cycle. The results of softness and absorbency obtained are given in Table II.

TABLE II

Softener Used	Softness Ratings (No. of washes)				
	1	3	5	7	10
None	Standard	Standard	Standard	Standard	Standard.
A	Much softer	Much softer	Much softer	Much softer	Much softer.
C	do	do	do	do	Do.
D	Equal	Equal	Equal	Equal	Equal.
E	Much softer	Much softer	Much softer	Much softer	Much softer.
	Absorbency Ratings—No. of Washes (Wetting time in Seconds)				
None	0	0	0	0	0
A	0	0	1	3	5
C	0	1	3	5	10
D	0	0	0	0	0
E	0	0	0	0	0

0—Instantaneous.

Results show Softeners A, C and E all imparted improved softness to the washed towels when the softeners were added to the final rinse cycle. However, only Softener E imparted *both* softness and instantaneous absorbent properties.

EXAMPLE 3

An experiment was run according to the procedure of Example 1 in which the softener employed was the acetate salt of Softener E, a 6% solution of pH 4.6. Highly desirable softening without change in absorbency was obtained on the washed towels.

EXAMPLE 4

Example 3 was repeated employing two acetate salt solutions of Softener E, one as a 6% solution or dispersion of pH 4.5, the other of pH 6.0.

Both products produced identical results which were equal to those obtained in Example 3.

EXAMPLE 5

Example 3 was repeated employing the sulfate salt of Softener E, the pH of the 6% solution being 2.5. Results equal to those reported in Example 3 were obtained.

EXAMPLE 6

Softeners A, B, D and E were evaluated individually in detergent washing baths wherein swatches of various types of textile fabrics constituted the washer load. Each washer load consisted of the following:

	Grams
Cotton percale	570
Resin-finished cotton percale	1140
Cotton poplin	450
Spun nylon	575
Spun polyester	560
Total	3295

The full level of a Kenmore washer was employed using approximately 16 gallons (60,560 grams) of water. The liquor to cloth ratio was approximately 18 to 1. The regular wash cycle and the hot wash-warm rinse settings were used. The cloth swatches after a wash cycle were dried in a Kenmore electric dryer for 40 minutes at the hot setting and regular cycle. At the end of each complete wash and dry cycle, a sample of each fabric type was removed for reference and replaced by a swatch of familiar fabric or equal weight to maintain constant load composition and weight.

Four such loads and cycles of washes were employed to evaluate the following four softeners:

Softeners used

Kind:	Amount, 100%, g.
A	3.36
B	3.36
D	3.36
E (as the phosphate)	3.36

The above mentioned softeners were evaluated in the wash cycle employing 36 grams of a commercially available anionic detergent composition containing sodium dodecylbenzene sulfonate. After completion of the washing and drying cycles, the cloth swatches were evaluated for softness and absorbency as aforementioned. Results are seen in Table III.

TABLE III

No. of Washes	Softness Ratings		Absorbency Ratings (Wetting time, sec.)		
	1	15	1	5	15
COTTON PERCALE					
Softener:					
None	Standard	Standard	0	0	0
A	Equal	Equal	1	10	>30
B	do	do	1	5	15
D	do	do	0	1	5
E	Much softer	Much softer	0	0	0
COTTON POPLIN					
Softener:					
None	Standard	Standard	0	0	0
A	Equal	Equal	2	15	>30
B	do	do	2	10	>30
D	do	do	0	1	5
E	Much softer	Much softer	0	0	0
RESIN-FINISHED COTTON PERCALE					
Softener:					
None	Standard	Standard			
A	Sl. softer	Sl. softer			
B	Equal	Equal			
D	do	do			
E	Much softer	Much softer			
SPUN NYLON					
Softener:					
None	Standard	Standard			
A	Much softer	Much softer			
B	Sl. softer	Sl. softer			
D	do	do			
E	Much softer	Much softer			
SPUN POLYESTER					
Softener:					
None	Standard	Standard			
A	Much softer	Much softer			
B	Sl. softer	Sl. softer			
D	do	do			
E	Much softer	Much softer			

0—Instantaneous.

Results show that the imidazoline softener used is equally effective on all fabric types tested when employed with anionic detergent in the wash cycle of an automatic home washing machine. The commercial softeners available for use with automatic home washers and used in these trials were not effective as softeners for cellulosic fabrics when employed in the wash cycle with anionic detergent and reduced water absorbency of cellulosic fabrics to some extent.

The commercial softeners do exhibit some softening action on synthetic fibers, however, when employed in this manner.

EXAMPLE 7

Example 6 was repeated as described except that the softeners were added in an additional rinse cycle after completion of the regular wash, rinse and spin-dry cycles with a commercially available anionic detergent composition containing sodium dodecylbenzene sulfonate employed in the wash cycle. Softener E was employed as the phosphate salt.

Results are seen in Table IV.

TABLE IV

No. of Washes	Softness Ratings			Absorbency Ratings		
	1	5	15	1	5	15
COTTON PERCALE						
Softener:						
None	Standard	Standard	Standard	0	0	0
A	Much softer	Much softer	Much softer	5	25	>30
B	Sl. softer	Sl. softer	Sl. softer	2	20	>30
D	V. sl. softer	V. sl. softer	V. sl. softer	0	2	30
E	Much softer	Much softer	Much softer	0	0	0
COTTON POPLIN						
Softener:						
None	Standard	Standard	Standard	0	0	0
A	Much softer	Much softer	Much softer	10	>30	>30
B	Sl. softer	Sl. softer	Sl. softer	5	25	>30
D	V. sl. softer	V. sl. softer	V. sl. softer	0	5	>30
E	Much softer	Much softer	Much softer	0	0	0

TABLE IV—Continued

No. of Washes	Softness Ratings			Absorbency Ratings		
	1	5	15	1	5	15
RESIN-FINISHED COTTON PERCALE						
Softener:						
None	Standard	Standard	Standard			
A	Much softer	Much softer	Much softer			
B	Sl. softer	Sl. softer	Sl. softer			
D	V. sl. softer	V. sl. softer	V. sl. softer			
E	Much softer	Much softer	Much softer			
SPUN NYLON						
Softener:						
None	Standard	Standard	Standard			
A	Much softer	Much softer	Much softer			
B	Sl. softer	Sl. softer	Sl. softer			
D	Sl. softer	Sl. softer	Sl. softer			
E	Much softer	Much softer	Much softer			
SPUN POLYESTER						
Softener:						
None	Standard	Standard	Standard			
A	Much softer	Much softer	Much softer			
B	Sl. softer	Sl. softer	Sl. softer			
D	Sl. softer	Sl. softer	Sl. softer			
E	Much softer	Much softer	Much softer			

0—Instantaneous.

Results indicate that the imidazoline softener is equivalent to the best of the commercial softeners used in softness imparted to all fabric types, without adverse effect on absorbency.

EXAMPLE 8

Two swatches of standard soiled fabric were cut 4" square. Two swatches of the same fabric unsoiled were also cut to the same size. Four reflectance measurements were run on each sample at 455 mμ in different areas and averaged. One soiled and one unsoiled swatch were placed in each of two Launder-Ometer jars, each jar containing ten stainless steel balls of one-quarter inch diameter. In one jar was placed 200 ml. of a 0.25% solution of a commercially available anionic detergent composition containing sodium dodecylbenzene sulfonate. In the other jar was placed 200 ml. of a 0.25% solution of the same detergent also containing 0.75 ml./liter of a 6% solution of the imidazoline softener as the phosphate salt. (This amount of softener corresponds to the amounts recommended for use in the wash cycle of an automatic washer containing a full load of fabric. The closed jars were placed in a Launder-Ometer and allowed to agitate for 12 minutes at 130° F. after preheating. The liquor was then replaced with clean water at 130° F. and the jars were allowed to agitate for an additional three minutes. The swatches were then removed, squeezed to remove excess liquor, and allowed to dry on a clothes line at room temperature.

Reflectances were determined as before and averaged. Soil removal from the soiled fabrics and soil pick-up by the unsoiled fabric were then calculated by the procedure given below.

$$\text{Percent return to origional reflectance}=\frac{R_2-R_1}{R_0-R_1}\times 100$$

R_0=reflectance of original cloth before soiling
R_1=reflectance of artificially soiled cloth before washing
R_2=reflectance of artificially soiled cloth after washing

$$\text{Percent soil pickup}=\frac{R_0-R_3}{R_0}\times 100$$

R_0=reflectance of original cloth before soiling
R_3=reflectance of original cloth after washing

Results are shown in Table V.

TABLE V

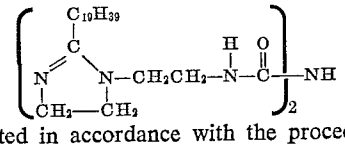
	Percent Return [1]	Percent Soil Pickup [2]
Swatches washed in a commercially available anionic detergent compsoition containing sodium dodecylbenzene sulfonate only	10.6	2.69
Swatches washed in a commercially available anionic detergent composition containing sodium dodecylbenzene sulfontate plus a softener of this invention	15.2	1.05

[1] Of the soiled fabric.
[2] Of the unsoiled fabric.

Results show that the use of the imidazoline type softener of this invention when used in the wash cycle of an automatic washing machine wherein anionic detergent is present does not interfere with the cleaning action and dirt suspending properties of such detergents. The results actually indicate increased efficiency in both effects by the detergent in the presence of the softener and is an unobvious advantage of the softener of this invention.

EXAMPLE 9

A preparation of the imidazoline type of softener from behenic acid, diethylenetriamine and urea in which the desired ingredient had the structure

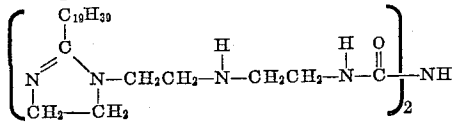


was evaluated in accordance with the procedure of Example 1 as the acetate salt.

Excellent softness properties without change in absorbency was obtained on the washed towels.

EXAMPLE 10

A preparation of the imidazoline type of softener from behenic acid, triethylenetetramine and urea having as the desired component a compound of the structure

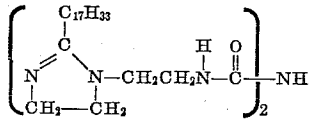


was evaluated in accordance with the procedure of Example 1 as the acetate salt.

Excellent softness properties were obtained without change in absorbency of the washed towels.

EXAMPLE 11

A preparation of the imidazoline type of softener from oleic acid, diethylenetriamine and urea having as the desired component a compound of the structure

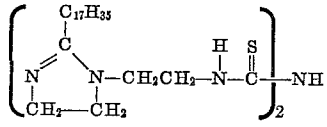


was evaluated in accordance with the procedure of Example 1 as the acetate salt.

Excellent softness properties were obtained without change in absorbency of the washed towels.

EXAMPLE 12

A preparation of the imidazoline type of softener from stearic acid and diethylenetriamine was crosslinked with thiourea instead of urea to give a product which had as the desired component a compound of the following structure:

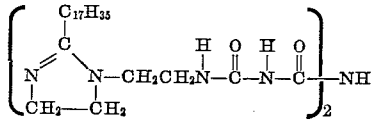


The product was evaluated according to the procedure of Example 1 as the acetate salt.

Excellent softness was obtained without change in absorbency of the washed towels.

EXAMPLE 13

A preparation of the imidazoline type of softener from stearic acid and diethylenetriamine was crosslinked with biuret instead of urea to give a product having as the desired component a compound of the following structure:



The product was evaluated according to the procedure of Example 1 as the acetate salt.

Excellent softness properties were obtained without change in absorbency of the washed towels.

EXAMPLE 14

A preparation of the imidazoline type of softener from stearic acid and diethylenetriamine was crosslinked with double the normal amount of urea to give a product having as the desired component a compound of the structure shown in Example 13. The properties obtained with the softener when evaluated as the acetate in accordance with the procedure of Example 1 were the same as those given in Example 13.

EXAMPLE 15

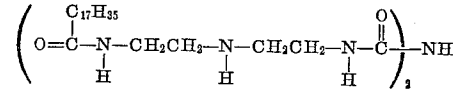
Softener E was evaluated according to the procedure of Example 1 as the following acid salts—

Acid:	Ratio (acid to softener)
Citric	2:1
Sulfamic	2:1
Oxalic	2:1
Formic	2:1
Tartaric	2:1
Succinic	2:1
p-Toluenesulfonic	2:1
p-Toluenesulfonic	1:1
Lactic	2:1
Lactic	1:1
Propionic	2:1
Propionic	1:1

In all cases good softness without change in absorbency of the washed towels was obtained. However, the citric acid salt produced greater softness than the other acid salts.

EXAMPLE 16

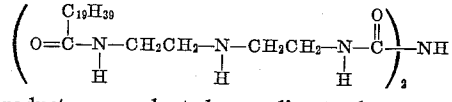
A softener preparation was made employing stearic acid and diethylenetriamine and removing only about 1.7 moles of water during the reaction followed by normal crosslinking with urea to yield a product of the following structure, which is of an amide condensate, not an imidazoline.



The product was evaluated as the acetate salt according to the procedure of Example 1. No softness nor change in absorbency was obtained on the washed towels.

EXAMPLE 17

A preparation similar to that of Example 16 was made employing behenic acid and diethylenetriamine to give a product of the following structure, which is of an amide codensate, not an imidazoline.



The product was evaluated according to the procedure of Example 1 as the acetate salt. No softness nor change in absorbency was obtained on the washed towels.

EXAMPLE 18

The products of Examples 16 and 17 were evaluated according to the process of Example 2, that is, they were added in the final rinse cycle in the absence of detergent. Good softness properties were obtained with some loss of absorbency on the washed towels.

The results of Examples 16, 17 and 18 show that only the imidazoline type of softener of this invention is effective in a detergent composition while the amide condensates are effective in the absence of detergent, in the final rinse cycle.

EXAMPLE 19

A preparation of the imidazoline type of softener from stearamide and diethylenetriamine crosslinked, without the usual ageing prior to crosslinking, with the normal amount of urea and having as the desired component a compound having a structure similar to Softener E was evaluated as the acetate salt according to the procedure of Example 1. Excellent softness without change in absorbency of the washed towels was obtained.

EXAMPLE 20

A preparation similar to that of Example 19 was made from behenamide and diethylenetriamine and had as the desired component a compound of the structure shown in Example 9. The product was evaluated according to the procedure of Example 1, as the acetate salt. Excellent softness properties were obtained without change of absorbency of the washed towels.

EXAMPLE 21

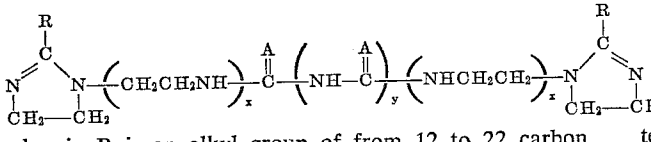
Softener E as the acetate salt was evaluated according to the procedure of Example 1 except that a commercially available non-ionic detergent composition containing an ethylene oxide condensate of tall oil acids was employed instead of the anionic detergent composition. Good softness properties without loss of absorbency of the washed towels were obtained.

EXAMPLE 22

Softener E was prepared as the citrate salt in solid form. 7.9 grams of this solid product were mixed with 18 grams of the commercially available anionic detergent containing sodium dodecylbenzene sulfonate. The mixture was then used to wash towels according to the procedure of Example 1. Excellent softness properties were obtained without loss of absorbency on the washed towels.

What is claimed is:

1. An anionic or non-ionic detergent softener composition which is effective not only to remove soil from textile materials but also to soften said materials comprising a detergent selected from the group consisting of anionic and non-ionic detergents and as a softener an effective amount of an acid salt of a compound of the formula

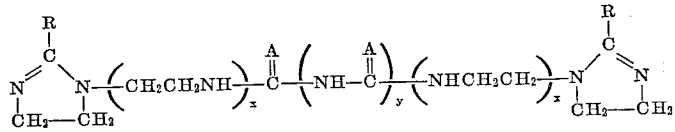


wherein R is an alkyl group of from 12 to 22 carbon atoms, inclusive, where x is selected from the group consisting of 1 and 2, y is a small integer of from 0 to 3, and where A is selected from the group consisting of O and S.

2. An anionic or non-ionic detergent softener composition which is effective not only to remove soil from textile materials but also to soften said materials comprising a detergent selected from the group consisting of anionic and non-ionic detergents and as a softener an effective amount of an acid salt of 1,3-bis[2-(2-heptadecyl-1-imidazolinyl)ethyl]biuret.

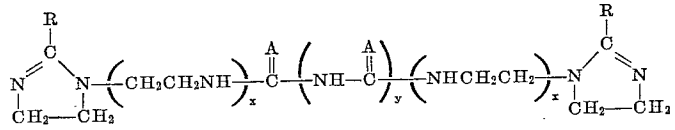
3. An anionic or non-ionic detergent softener composition which is effective not only to remove soil from textile materials but also to soften said materials comprising a detergent selected from the group consisting of anionic and non-ionic detergents and as a softener an effective amount of the acetic acid salt of 1,3-bis[2-(2-heptadecyl-1-imidazolinyl)ethyl]biuret.

4. An anionic or non-ionic detergent softener composition which is effective not only to remove soil from textile materials but also to soften said materials comprising from 5 to 95 parts of a detergent selected from the group consisting of anionic and non-ionic detergents and as a softener from about 0.1 to about 20 parts of an acid salt of a compound of the formula



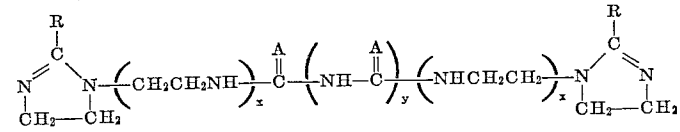
wherein R is an alkyl group of from 12 to 22 carbon atoms, inclusive, where x is selected from the group consisting of 1 and 2, y is a small integer of from 0 to 3, and where A is selected from the group consisting of O and S.

5. A process for cleaning textile materials which comprises having present during the cleaning operation in an amount sufficient to produce a softening effect on the textile materials cleaned therewith, of an acid salt of a compound of the formula



wherein R is an alkyl group of from 12 to 22 carbon atoms, inclusive, where x is selected from the group consisting of 1 and 2, y is a small integer of from 0 to 3, and where A is selected from the group consisting of O and S.

6. A process for laundering textile materials which comprises laundering the textile material in an aqueous medium containing a detergent selected from the group consisting of anionic and non-ionic detergents and an amount sufficient to produce a softening effect on the textile material laundered therewith of an acid salt of a compound of the formula



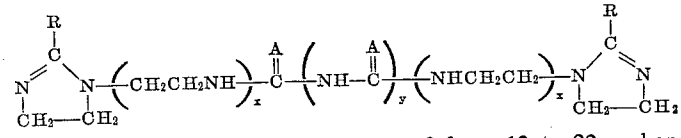
wherein R is an alkyl group of from 12 to 22 carbon atoms, inclusive, where x is selected from the group consisting of 1 and 2, y is a small integer of from 0 to 3, and where A is selected from the group consisting of O and S.

7. A process according to claim 6 in which the acid salt softener is present with the detergent during the wash stage.

8. A process according to claim 6 in which the softener is an acid salt of 1,3-bis[2-(2-heptadecyl-1-imidazolinyl)-ethyl]biuret.

9. A process according to claim 6 in which the softener is the acetic acid salt of 1,3-bis]2-(2-heptadecyl-1-imidazolinyl)ethyl]biuret.

10. A process for laundering textile materials which comprises laundering the textile material in an aqueous medium containing from .00005 and 1% of a detergent selected from the group consisting of anionic and non-ionic detergents and from .0001% to 0.1% of an acid salt of a compound of the formula



wherein R is an alkyl group of from 12 to 22 carbon atoms, inclusive, where x is selected from the group consisting of 1 and 2, y is a small integer of from 0 to 3, and where A is selected from the group consisting of O and S.

11. A process for laundering textile materials which comprises laundering the textile material in an aqueous

medium containing from .0001% to .5% of a detergent selected from the group consisting of anionic and nonionic detergents and from .0001% to 0.1% of an acid salt of 1,3-bis[2-(2-heptadecyl-1-imidazolinyl)ethyl]biuret.

12. A process for laundering textile materials which comprises laundering the textile material in an aqueous medium containing from .0001% to .5% of a detergent selected from the group consisting of anionic and non-

ionic detergents and from .0001% to 0.1% of the acetic acid salt of 1,3-bis[2-(2-heptadecyl-1-imidazolinyl)ethyl]-biuret.

No references cited.

LEON D. ROSDOL, *Primary Examiner.*

SAMUEL H. BLECH, *Examiner.*

S. E. DARDEN, *Assistant Examiner.*