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3,703,480 FABRIC-SOFTENER COMPOSITIONS Paul Sheldon Grand, South Bound Brook, and Harold Eugene Wixon, New Brunswick, N.J., assignors to Colgate-Palmolive Company, New York, N.Y. No Drawing. Filed Nov. 16, 1970, Ser. No. 90,133 Int. Cl. C11d 1/40, 1/50, 1/58

U.S. Cl. 252-524 13 Claims

ABSTRACT OF THE DISCLOSURE

A washing-cycle fabric softener consisting essentially of a cationic quaternary ammonium fabric softener and an amino polyureylene resin wherein the weight ratio of softener to resin is from about 0.16:1 to about 4:1 for 15 di-higher alkyl quaternary ammonium softeners and 0.5:1 to 2:1 for imidazoline softeners. Such compositions effectively soften textiles in the presence of anionic detergent compositions. Another aspect of the invention is detergent-softener compositions containing the washingcycle softener composition in combination with an anionic detergent and, optionally, a water-soluble builder salt. Also within the scope of the invention is a method of softening textiles.

This invention is directed to fabric-softener compositions containing a quaternary ammonium softener material in combination with amino polyureylene (APU) resin and to detergent-softener compositions containing the aforementioned softener composition in combination with an anionic detergent and, optionally, a water-soluble builder salt. The invention is also directed to a process for simultaneously washing and softening fabrics and textiles by laundering in an aqueous medium containing .02-.5% of a mixture of APU resin, softener and anionic detergent.

In recent years, compositions useful for treating fabrics to improve the softness or feel have been widely used. Generally, the softener compositions are liquids which contain as the principal active component a quaternary ammonium softener compound. The quaternary ammonium softener compounds are positively charged and deposit readily on the negatively charged surface 45 of textiles to form a lubricious surface on the textile which feels soft to the touch. However, since a large percentage of the common laundry detergents contain anionic surface active agents which tend to inactivate or neutralize cationic softening agents, the quaternary ammo- 50 nium type fabric-softener compositions have been added to the rinse water during the rinsing cycle. Such addition during the rinse cycle has the disadvantage that the user must monitor the laundering operation to be certain that the softener is added at the proper time and must take 55 special precautions to employ the proper amount to avoid excesses which frequently render the textiles water repellent.

It has now been discovered that the aforementioned problem of compatibility can be substantially reduced by including APU resins in combination with the quaternary ammonium softener compounds. Such fabric-softener compositions can be added simultaneously with the widely used built anionic detergents to the wash cycle to impart a soft texture and feel to the washed textiles. Alterna- 65 tively, the softener compositions may be included as a component of the anionic detergent composition to yield a composition which effectively washes and softens the laundered textile.

Generally, the fabric-softener compositions of this in- 70 vention consist essentially of a cationic quaternary ammonium fabric softener and an APU resin having a molec2

ular weight of about 300 to 100,000, the ratio of softener to resin being from about 0.16:1 to about 4:1 for dihigher alkyl quaternary ammonium softeners and from 0.5:1 to about 2:1 for imidazolinium softeners.

Generally, the cationic fabric softeners consist of at least one hydrophilic functional group bearing a negative charge and a hydrophobic group containing a quaternary ammonium atom which is positively charged. Suitable softeners include the di-higher alkyl quaternary am-10 monium softeners and the di-higher alkyl imidazolinium

One particular class of useful cationic materials may be represented by the general formula

$$\begin{bmatrix} R_1 & R_2 \\ N & R_3 \end{bmatrix}^{\dagger} X^{-1}$$

wherein R and R₁ are higher alkyl or alkenyl radicals each containing between about 12 and 22 carbon atoms and R2 and R3 are independently selected from the group consisting of lower alkyl radicals, lower hydroxy alkyl radicals and the hydroxy polyether radicals formed by the condensation of ethylene oxide, each radical containing 1 to 4 carbon atoms, and X is an anion selected from the group consisting of halogens, such as chloride, bromide, and iodide, methylsulfate and ethylsulfate.

The higher alkyl radicals in the general formula are carbon chains which may be straight or branched and saturated or unsaturated. Preferably, the carbon chains are obtained from long-chain fatty acids such as those derived from tallow, soybean oil or coconut oil. The terms "disoya," "dicoco," and "di-tallow," etc., as used above refer to the source from which the long-chain fatty alkyl chains are derived. Mixtures of the above as well as other quaternary ammonium surface active agents may also be used if desired. Preferably, both R and R₁ are alkyl groups containing about 16 to 20 carbon atoms and R2 and R₃ are methyl groups. Suitable compounds include dilauryl-methyl-ethoxyethanol ammonium chloride; dimyristyl-methyl-ethoxyethanol ammonium methyl sulfate; distearyl di-hydroxyethyl ammonium chloride; and diarachidyl/behenyl dimethyl ammonium bromide.

Still another class of useful fabric softeners include the imidazolines represented by the general formula

$$\begin{bmatrix} \mathbf{R} - \mathbf{C} & & & & \\ \mathbf{R} - \mathbf{C} & & & & \\ & \mathbf{N} - \mathbf{C} \mathbf{H}_2 & \mathbf{0} & & \\ & \mathbf{C} \mathbf{H}_2 \mathbf{C} \mathbf{H}_2 \mathbf{N} \mathbf{H} \mathbf{C} - \mathbf{R}_1 \end{bmatrix} + \mathbf{X} - \mathbf{C} \mathbf{H}_2 \mathbf{C} \mathbf{H}_2 \mathbf{C} \mathbf{H}_2 \mathbf{N} \mathbf{H} \mathbf{C} - \mathbf{R}_1 \end{bmatrix}$$

wherein R and R₁ are higher alkyl or alkenyl radicals each containing between about 12 and 22 carbon atoms, R2 is a lower alkyl radical containing 1 to 4 carbon atoms, and X is an anion selected from the group consisting of halogens such as chloride, bromide, iodide, and methylsulfate, or ethylsulfate.

The higher alkyl radicals in the general formula are carbon chains which may be straight or branched and saturated or unsaturated. Preferably, both R and R1 are alkyl groups containing about 17 carbon atoms and R2 is a methyl group. Suitable compounds include

2-hexadecyl-1-methyl-1[(2-dodecoyl amido)ethyl] imidazolinium methylsulfate,

2-heptadecyl-1-methyl-1[2-stearoyl amido)ethyl] imidazolinium methylsulfate,

2-nonadecyl/heneicosyl-1-methyl-1-[(2-eicosoyl/docosoyl amido)ethyl] imidazolinium methyl chloride.

The amino polyureylene (APU) resins are employed in the softener compositions because of their ability to compatibilize the quaternary ammonium softener component

with anionic organic detergents. APU resins suitable for use in the prescribed compositions are water-soluble polymeric resins characterized by the following repeating unit:

Y is O or S, and n is 2 or 3.

Thus, suitable APU resins include both the polyureaand the polythiourea-containing compounds. Preferred APU resins have a repeating unit where Y is oxygen, n is 35 3, and X is selected from the group consisting of N-C₁₋₈ alkyl and

Generally, the number of repeating units in the resin will be sufficient to yield a polymer having a molecular weight in the range of about 300 to 100,000. Preferred APU resins have an average molecular weight in the range of 1,000 to 20,000; and a particularly preferred resin is the reaction product of equimolar quantities of N-methyl, bis (3-aminopropyl) amine and urea having a molecular weight of about 4,300.

The molecular weight of the APU resins is based upon aqueous gel permeation chromatographic analysis. The separation is carried out in oxalic acid solution, adjusted to pH 3.5 on three Corning controlled-pore glass columns (nominal pore sizes 175, 125, and 75 A.) in series. Detec- 55 tion is by differential refractometer. Reference compounds are dextran polysaccharides of molecular weights of 150,-000, 110,000, 40,000, 20,000, and 10,000 and sucrose and galactose.

The APU resins which can be used in the compositions 60 of this invention are prepared by reacting, for example, 145 grams of N-methyl-bis(3-aminopropyl) amine (1.0 mole) and 60 grams of urea (1.0 mole) in a 3-necked flask equipped with a thermometer, mechanical stirrer, condenser, and nitrogen sparge tube. Nitrogen is bubbled 65 slowly through the solution throughout the course of the reaction. The solution is heated to 140° C. over a 20-minute interval where ammonia begins to evolve. The solution is further heated to 250° C. over a 30 minute interval and allowed to cool. The product is a hard, resinous powder 70 materials, including blends of the foregoing. (Resin A) having a molecular weight of about 4300. The secondary amine analogues can be made by the above process if bis(3-aminopropyl) amine or bis(2-aminoethyl) amine are reacted with urea or thiourea. The piperazine analogues are made by reacting N,N'-di(3-aminopropyl) 75

piperazine or N,N'-di(2-aminoethyl) piperazine with urea or thiourea. The N-C₁ to C₂₂ alkyl analogues are prepared by reacting N-C₁ to C_{22} alkyl-bis(3-aminopropyl) amine or N-C1 to C22 alkyl-bis (2-aminoethyl) amine with urea or thiourea. Additional analogues are prepared by the following reactions:

Thiourea. Additional analogues are prepared by the following reactions:

Resin A + epichlorohydrin
$$\longrightarrow$$
 CH₁

Resin A + epichlorohydrin \longrightarrow N+

CH₂

OH

CH₃

N+

analogues + NaOH

CH₄

The preparation of the remaining analogues is well within the skill of the art following the above techniques.

An important factor herein is the weight ratio of cationic softening material to APU resin. Generally the ratio ranges from 0.16:1 to 4:1, preferably from 0.3:1 to about 3:1 when di-higher alkyl quarternary softeners are used. When imidazolinium softeners are used, satisfactory softener to resin ratios range from 0.5:1 to about 2:1, preferably 1:1 to about 1.5:1.

Another important factor herein is the weight of cationic softening material added to the washer. A minimum weight of about 2.5 grams is needed to achieve a high level of softening performance, especially when the weight of laundry is in the range of 6-12 lbs. and the laundering bath contains 17-20 gallons of water.

It is contemplated that the wash-cycle softener compositions containing a quaternary softener in combination with the APU resin may be in the form of a liquid or a powder. Generally, such compositions contain about 3 to 20% by weight of quarternary softeners and about 3 to 20% by weight of resin. The balance of liquid softener compositions will generally be an aqueous solvent. The aqueous solvent may be water or mixtures of water with a lower mono- or dihydroxy alcohol containing from two to three carbon atoms. The concentration of alcohol is dependent upon the physical characteristics desired in the liquid composition and generally ranges from 2 to 60, preferably 4 to 40%, by weight. Such compositions are prepared by adding the resin and softener ingredients to the aqueous solvent.

In powdered softener compositions, the balance of the compositions will be a substantially dry particulate material. Suitable materials include fillers, such as starch or magnesium silicate and water-soluble inorganic or organic detergent builder salts, such as sodium or potassium sulphate, carbonate, phosphate, nitrolotriacetate, borate or mixtures thereof. The powdered compositions may be prepared by admixing the resin and softener ingredients in either powder or liquid form with the particulate filler or inorganic builder. The softener compositions, whether liquid or powder, may be used on a variety of fabrics, such as cotton, polyester, nylon, acrylic, and other

Other materials may be included in the softener compositions in minor amounts. For example, such compositions can include coloring agents, perfumes, optical dyes, bluing agents, and ethoxylated nonionic detergent as dispersing agents or emulsifiers. Thickening agents such

100.0

as polyvinyl alcohol and sodium carboxymethyl cellulose may also be included. The amount of each such added material may range from 0.1% to 5% by weight.

A particularly satisfactory liquid fabric softener composition is set forth in Example 1.

EXAMPLE 1

Percent by wt., Dimethyl dihydrogenated tallow quaternary am-	ΑI
monium chloride	6.2
Resin A	6.7
Acid Blue #80, 1% solution	1.7
	0.4
Water Bala	nce
and the second	

The foregoing softener composition is prepared by dispersing the quarternary ammonium softener material (an aqueous paste containing 75% of quarternary salt, 5% isopropanol and 20% water) in hot water containing the blue color. A 40.2% aqueous solution of Resin A is added to the mixture with agitation, and a pourable, homogeneous, translucent liquid is obtained. The ratio of softener to resin is 0.9:1.

Compatibility of the liquid softener composition of Example 1 with laundry detergent compositions containing an anionic detergent as the principal surfactant is demonstrated using the "One-Towel Test." In the "One-Towel Test," a single Penney-brand terry cloth towel (16 30 by 26 inches in size) is softened by the following procedure. The terry cloth towel is placed in the bottom of a standard, agitator-type, top-loading, G. E. automatic washing machine. Seventeen gallons of 120° F. tap water of approximately 100 p.p.m. hardness are added. From 35 three-quarters to one-and-one-quarter cups (depending upon the package instructions) of various commercial anionic laundry detergent compositions and sixty grams of the liquid softener composition of Example 1 are added to the washing machine, and the machine agitator is 40 turned on for a ten-minute period. At the end of the ten-minute agitation period, the laundering solution is automatically pumped out of the machine while the towel is spun to a damp-dry condition. The towel is subsequently subjected to a three-minute deep rinse in tap 45 trated in Example 3. water at 80° F. and again spun to a damp-dry condition after the rinsing solution has been pumped from the machine. The towel is then air dried at room temperature and evaluated for softness and whiteness.

The softness of the towel subjected to the foregoing test is reported in terms of values from 1 to 10 based on a tactile rating by an experienced individual. A value of 1 is assigned to a control towel which is subjected to the foregoing test in the absence of a softener composition; whereas, a value of 10 is assigned to the towel 55treated with softener composition A. The softness scale

1	No softness.
2-4	Low softness.
5-7	Fair softness.
8–9	Good softness.
10	Excellent softness.

Whiteness values are determined with a Gardner color difference meter, model No. AC-1, purchased from 65 Gardner Laboratories Inc. at Bethesda, Md., using the +b scale as a measure of the yellow chromaticity. However, higher +b values or whiteness numbers indicate a high amount of yellowness and poor results; whereas low +b values or whiteness numbers denote less yellow- 70 ness or greater whiteness and excellent results. A difference of 0.5 +b unit in the test represents a difference that is visible to the eye.

Results of the tests illustrating the compatibility of the new softener compositions are set forth in Table I. 75 TABLE I

	Detergent amount (cups)	Softner composi- tion	Softness rating	Whiteness value
Detergent:				
A 1	11/4	Yes	10+	−5.9
B 2	11/4	Yes	9	-6.3
C 3	11/4	Yes	9	-6.3
D 4	34	Yes	8	-6.3 -6.8
D	1¼ ¾	No	ī	-6. 1

1 A commercial product which contains about 18% of sodium tridecyl benzene sulfonate and the balance inorganic builder salts.

2 A commercial product which contains 10% of sodium alkyl tridecyl benzene sulfonate, 2% sodium 0.2% nonionic detergent and the balance inorganic builder salts.

3 A commercial product which contains about 7% of sodium dodecylbenzene sulfonate, about 9% of sodium tallow alcohol sulfate, about 1% nonionic detergent, and the balance inorganic builder salts.

4 A commercial product which contains about 3% sodium dodecylbenzene sulfonate, about 3% sodium tallow alcohol sulfate, 1.5% sodium soap, 2% nonionic detergent, and the balance inorganic builder salts.

The tabulation clearly shows that the softener composition containing the quaternary softener-resin mixture effectively softens in the presence of commercial detergentcontaining laundry compositions having water-soluble anionic, organic detergents as the principal detergent ingredient without adversely affecting whiteness. For comparison, use of a similar amount of softener, but no resin, in combination with Detergent D results in a softness rating of 2.

Another suitable liquid softener composition is set forth in Example 2.

EXAMPLE 2

0	Percent by	wt.
•	Dimethyl dihydrogenated tallow quaternary am-	
	monium chloride	7.5
	Resin A 1	2.1
	Isopropyl alcohol	5.3
5		1.4
	Water Bala	nce

The foregoing composition is a readily pourable, homogeneous, translucent liquid wherein the ratio of softener to resin is 0.6:1. Softening results similar to those shown in Table I of Example 1 are obtained when 60 gm. are added to the washer with commercial detergents.

A satisfactory powdered softener composition is illus-

EXAMPLE 3

	Percent 1	by wt.
	Dimethyl dihydrogenated tallow quaternary ammonium chloride	6
0	Resin A	8
	Water	13.6
	Isopropanol	0.4
	Pentasodium tripolyphosphate	72.0
5		100.0

The foregoing powdered composition is prepared by admixing the ingredients in a liquid-solids mixer. When an equivalent amount (on a softener basis) is used in combination with the commercial detergents shown in Table I, Example 1, similar excellent softening results are obtained.

When the N,N'-di(3-aminopropyl) piperazine urea product having a molecular weight of about 5,600 is substituted for Resin A in the composition of Example 3, substantially equivalent softening results are obtained when the powdered softener composition is used in the presence of the commercial detergents of Table I.

EXAMPLE 4

The compatibilizing effect of the APU resins is apparent from the softness results in Table II based upon "One-Towel Test" results in the presence of various combinations of the washing ingredients set forth in the said

TABLE II									
	Test								
Washing ingredient	1	2	3	4	5	6	7	8	6
10 grams of sodium tridecyl benzene sul- fonate					x		x	x	 x
phate					x x		X	x x	x
Resin A (grams):					\mathbf{x}				x
45822.8	-		X			x			
Softness value	i	5	3	10+	10	10++	î	10+++	8

The foregoing tests prove that the softest towels are obtained when the quaternary softeners and APU resin are used in combination with the built anionic detergent. The improved softening results are obtained at quaternarysoftener-to-resin ratios in the range of 0.16:1 to about 4:1.

When 3.8 grams of an aminopolyureylene resin having a molecular weight of about 4600 and containing the repeating unit $f(CH_2)_3N+(CH_3)_2(CH_2)_3NHC(O)NH_7$ are substituted for Resin A in Tests 3 and 4, softness values of 1 and 10 respectively are obtained. These results demonstrate the compatibilizing effectiveness of the APU resin when used in combination with the dihydrogenated tallow dimethyl ammonium chloride softener at a softener-resin weight ratio of approximately 1:1.

EXAMPLE 5

When Tests 3-4 are repeated with the substitution of 35 an aminopolyureylene resin having a molecular weight of about 6600 and containing the repeating unit

$$\frac{-\left\lceil {{\left({{\rm{CH}}_2} \right)}_{\mathfrak{F}}}N+{\left({{\rm{CH}}_3} \right)}{\left({{\rm{CH}}_2}{\rm{CH}}{\rm{CH}}_2}{\rm{Cl}} \right){\left({{\rm{CH}}_2} \right)}_{\mathfrak{F}}NHC(0)NH} \right]}{\left\lceil {{\rm{CH}}_2} \right\rceil_{\mathfrak{F}}NHC(0)NH}$$

for the APU resin therein, softness values of 3 and 10+ are obtained.

EXAMPLE 6

The compatibilizing effect of Resin A on 2-heptadecyl-1-methyl - 1[(2 - stearoyl amido)ethyl]imidazolinium methosulfate is set forth in Table III. The results are obtained by using the same procedure as is used in Example 3.

TABLE III

Washing ingredient	1	2	3	4
10 grams of sodium tridecyl benzene sulfonate 40 grams of pentasodium tripolyphosphate 4.2 grams of imidazolinium softener Resin A (grams):	X X X .	X X	X X	X X X
2		Х.		
5			x	A
Softness.	1	2	3	10

The foregoing results show the effectiveness of using the softener-APU resin combination in a weight ratio of 1.05:1.

EXAMPLE 7

When the "One-Towel Test" is repeated using Detergent D of Table I and a softener composition consisting of 4 grams of the imidazolinium softener of Example 6 in combination with 8 grams of Resin A, the softness of the laundered towel is rated 10.

EXAMPLE 8

When the "One-Towel Test" is repeated using Detergent C of Table I and softener compositions consisting of 3.8 grams of the imidazolinium softener of Example 6 in com- 75 cals.) 8

bination with 3.8 grams and 7.4 grams of Resin A respectively, the softness of the laundered towels is 7 and 6 respectively.

EXAMPLE 9

Table IV sets forth the results of the "One-Towel Test" using the compositions shown therein.

Ψ.	ΔTR	T.E.	TV

			$T\epsilon$	est	
10	Washing ingredient	1	2	3	4
	15 grams of sodium dodecylpentadecyl triethen- oxyether sulfate. 3.8 grams of dihydrogenated tallow dimethyl ammonium chloride.	x	x	x	X
15	3.8 grams of Resin A	<u>i</u>		X 1	X 10+

The foregoing results clearly show that the anionic detergent component inactivates the quaternary ammonium softener. Therefore, it is apparent that the results in Examples 3, 6, and 8 indicate that the inorganic or organic builder salt component has a negligible effect on the softening results.

EXAMPLE 10

Table V sets forth "One-Towel Test" results for compositions containing an organic builder salt, namely sodium nitrilotriacetate.

TABLE V

)		Test					
•	Washing ingredient	1	2	3	4		
	10 grams of sodium tridecylbenzene sulfonate	X	X	X	x		
	30 grams of sodium nitrilotriacetate. 3.8 grams of di-hydrogenated tallow di-methyl ammonium chloride.		X	х	X		
í	3.8 grams of Resin A		A.	×	$\hat{\mathbf{x}}$		
	Softness	1	1	1	10+		

The foregoing results show that the softener-aminopolyureylene resin is effective when used in the presence of anionic detergent and an organic builder.

The foregoing examples clearly demonstrate that softener compositions containing a quaternary ammonium softener in combination with an APU resin are effective when used in the wash cycle in conjunction with a watersoluble anionic organic detergent having a hydrophobic group containing an alkyl group of 8 to 26 carbon atoms and at least one hydrophilic solubilizing radical selected from the group consisting of sulfate, sulfonate and carboxylate. Anionic detergents containing more than one such water-solubilizing group in the molecule may be used or required when inorganic phosphate builder salts are not a component of the laundering composition. These anionic detergents are usually in the form of a water-soluble salt, and the salt-forming ion is generally selected from the 55 group consisting of sodium, potassium, magnesium, ammonium, and alkylol (mono, di, and tri-ethanol) ammonium salts. The most common salts are sodium and potassium.

Examples of suitable anionic detergents within the scope of the anionic detergent class include the water-soluble salts, e.g., the sodium, potassium, ammonium, and alkylolammonium salts, of higher fatty acids containing about 8 to 20 carbon atoms, preferably 10 to 18 carbon atoms. Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, e.g., tallow, grease, coconut oil, tall oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, e.g., sodium coconut soap and potassium tallow soap.

The anionic class of detergents also includes the watersoluble sulfated and sulfonated synthetic detergents having an alkyl radical of 8 to 26, and preferably about 12 to 22 carbon atoms, in their molecular structure. (The term alkyl includes the alkyl portion of the higher acyl radi-

Examples of the sulfonated anionic detergents are the higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, e.g., the sodium, potassium and ammonium salts of higher alkyl benzene sulfonates, higher alkyl toluene sulfonates, higher alkyl phenol sulfonates, and higher naphthalene sulfonates. A preferred sulfonate is linear alkyl benzene sulfonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50%) of 2- (or lower) phenyl isomers, i.e., wherein the benzene ring is preferably attached in large part at the 3 or higher (e.g., 4, 5, 6 or 7) position of the alkyl group and the content of isomers in which the benzene ring is attached at the 2 or 1 position 15 is correspondingly low. Particularly preferred materials are set forth in U.S. Pat. 3,320,174.

Other suitable anionic detergents are the olefin sulfonates, including long-chain alkene sulfonates, long-chain hydroxyalkane sulfonates or mixtures of alkene-sulfonates and hydroxyalkane-sulfonates. These olefin sulfonate detergents may be prepared in a known manner by the reaction of SO₃ with long-chain olefins containing 8 to 25, preferably 12-21, carbon atoms and having the formula RCH=CHR₁ where R is a higher alkyl group of 6 to 23 25 form are set forth in Examples 9-12. carbons and R₁ is an alkyl group of 1 to 17 carbons or hydrogen to form a mixture of sultones and alkenesulfonic acids which is then treated to convert the sultones to sulfonates. Other examples of sulfate or sulfonate detergents are paraffin sulfonates containing about 10-20, 30 preferably about 15-20, carbon atoms, e.g., the primary paraffin sulfonates made by reacting long-chain alpha olefins and bisulfites and paraffin sulfonates having the sulfonate groups distributed along the paraffin chain as shown in U.S. Pats. 2,503,280; 2,507,088; 3,260,741; 36 3,372,188 and German Pat. 735,096; sodium and potassium sulfates of higher alcohols containing 8 to 18 carbon atoms such as sodium lauryl sulfate and sodium tallow alcohol sulfate; sodium and potassium salts of α-sulfofatty acid esters containing about 10 to 20 carbon atoms in 40 the acyl group, e.g., methyl α-sulfomyristate and methyl α-sulfo-tallowate, ammonium sulfates of mono- or diglycerides of higher (C10-C18) fatty acids, e.g., stearic monoglyceride monosulfate; sodium and alkylolammonium salts of alkyl polyethenoxy ether sulfates produced by condensing 1 to 5 moles of ethylene oxide with one mole of higher (C₈-C₁₈) alcohol; sodium higher alkyl (C10-C18) glyceryl ether sulfonates; and sodium or potassium alkyl phenol polyethenoxy ether sulfates with about 1 to 6 oxyethylene groups per molecule and in which 50 the alkyl radicals contain about 8 to about 12 carbon atoms.

The suitable anionic detergents include also the C₈-C₁₈ acyl sarcosinates (e.g. sodium lauroyl sarcosinate), sodium and potassium salts of the reaction product of higher fatty acids containing 8 to 18 carbon atoms in the molecule esterified with isethionic acid, and sodium and potassium salts of the C₈-C₁₈ acyl N-methyl taurides, e.g., sodium cocoyl methyl taurate and potassium stearoyl methyl taurate.

The laundering compositions containing the foregoing anionic detergents may or may not include water-soluble builder salts. Such builders are well known to those skilled in the art and can be either organic or inorganic in character. Laundering compositions containing anionic 65 detergents and builder salts may be prepared in a known manner-by spray drying an aqueous mixture thereof or by dry blending the two components in particulate form-to form a granular laundering composition comprising about 5% to 40%, preferably 8% to 30% by 70 weight of anionic detergent and about 60% to 90% by weight of builder salt. Examples of suitable inorganic builder salts are the soduim and potassium phosphates, sulfates, carbonates, borates and silicates. Included among the suitable phosphates are the sodium or potassium tri- 75 selected from the group consisting of chloride, bromide,

polyphosphates, hexametaphosphates, pyrophosphates, and orthophosphates. Suitable organic builder salts include the trisodium salt of nitrilotriacetic acid and the di, tri, and tetrasodium salts of ethylene diamine tetra-acetic acid, and sodium citrate. Usually, the builder component will comprise a mixture of inorganic builder salts and/or organic builder salts.

Detergent-softener compositions may be prepared by including the qauternary ammonium softener and the APU resin as components in the laundering compositions containing the water-soluble anionic detergent ingredient and, optionally, a detergent builder ingredient. In detergent-softener compositions, the mole ratio of quaternary softener to anionic detergent should not be less than about .12 to 1. In detergent-softener compositions containing builder salts, the general weight proportions of the ingredients will be in the range of 2% to 10% of quaternary ammonium softener, 2% to 16% APU resin, 5% to 35% of water-soluble anionic organic detergent, and about 50% to 85% of detergent builder salt.

The foregoing detergent-softener compositions may be prepared by conventional heat drying or blending techniques known to those skilled in the art.

Suitable detergent-softener compositions in particulate

	Per	cent b	y weig	ht
Example.	9	10	11	12
Sodium tridecylbenzene sulfonate Sodium tallow (C ₁₄ -C ₁₈) alcohol sulfate		8 8 -	10	10
Sodium Ci4-Ci3 soap Ci4-Ci5 alcohol ethoxamer (11 EtO) nonionic			2	
Ethyleneoxide-propylene oxide block copolymer containing 25% ethylene oxide (molecular weight 2300)			2	
Lauramide		1 _		
Sodium sincate (1:2.35)	7	3	7	7
Sodium tripolyphosphate	35	50	45 _	2!
Sodium sulfate	19	12	16	32
chloride	6 .		4	4
methyl imidazolinium methosulfate		4 .		
Resin A	3	ā.	4	8
Water	10	10	10	10

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and spirit of the invention.

What is claimed is:

1. A wash-cycle fabric softener suitable for use simultaneously with anionic detergent-containing laundering compositions consisting essentially of a cationic quaternary fabric softener selected from the group consisting of quaternary ammonium softeners having the general formula

$$\begin{bmatrix} R_1 \\ N \end{bmatrix}$$

wherein R and R₁ are higher alkyl or alkenyl radicals of 12 to 22 carbon atoms and R_2 and R_3 are each selected from the group consisting of \tilde{C}_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl and ethoxyethanol and X is selected from the group consisting of chloride, bromide, iodide, methylsulfate and ethylsulfate, and imidazolinium softeners having the general formula

wherein R and R₁ are higher alkyl or alkenyl radicals of 12 to 22 carbon atoms, R2 is C1-C4 alkyl and X is 11

iodide, methylsulfate and ethylsulfate and an aminopolyureylene resin having the following repeating unit:

$$\frac{\prod_{\text{CCH}_2)_{\text{n}}-\text{X}-(\text{CH}_2)_{\text{n}}\text{NHCNH}}^{\text{Y}}}{\prod_{\text{CH}_2}^{\text{CH}_2)_{\text{n}}}$$

wherein X is NH, N-C₁ to C₂₂ alkyl,

or

Y is O or S, and n is 2 or 3, and a molecular weight in the range of about 300 to 100,000, the weight ratio of 35 said softener to said resin being from about .16:1 to about 4:1 for said quaternary ammonium softeners and about 0.5:1 to about 2:1 for said imidazolinium softeners.

2. A softener composition according to claim 1 wherein the amount of said softener is about 3% to 20% by weight, the amount of said resin is about 3% to 20% by weight, and the balance is a dry particulate starch.

3. A softener composition according to claim 1 wherein the amount of said softener is about 3% to 20% by weight, the amount of said resin is about 3% to 20% by weight and the balance is a dry particulate salt selected from the group consisting of magnesium silicate and sodium or potassium inorganic detergent builder salts.

4. A softener composition according to claim 1 wherein the amount of said softener is about 3% to 20% by 50 weight, the amount of said resin is about 3% to 20% by weight, and the balance is an aqueous solvent containing 2% to 60% by weight of a C_2 - C_3 mono- or dihydroxy alcohol.

5. A fabric softener according to claim 1 wherein the 55 repeating unit of said resin is

{(CH₂)₃N(CH₃)(CH₂)₃NHC(O)NH}

6. A softener according to claim 5 wherein said resin has an average molecular weight in the range of from 60 1,000 to 20,000.

7. A softener composition according to claim 6 wherein said softener is selected from the group consisting of ditallow dimethyl ammonium chloride and 2-heptadecyI-1 methyl-1 [(2-stearoyl amido)ethyl] imidazolinium 65 linium methosulfate.

12. A detergent-

8. A detergent-softener composition consisting essentially of a cationic quaternary ammonium softener selected from the group consisting of quaternary softeners having the general formula

$$\begin{bmatrix} R_1 & R_2 \\ R & R_1 \end{bmatrix} X$$

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wherein R and R_1 are higher alkyl or alkenyl radicals of 12 to 22 carbon atoms and R_2 and R_3 are each selected from the group consisting of C_1 – C_4 alkyl, C_1 – C_4 hydroxyalkyl and ethoxyethanol and X is selected from the group consisting of chloride, bromide, iodide, methylsulfate, and ethylsulfate, and imidazolinium softeners having the general formula

wherein R and R_1 are higher alkyl or alkenyl radicals of 15 12 to 22 carbon atoms, R_2 is C_1 – C_4 alkyl and X is selected from the group consisting of chloride, bromide, iodide, methylsulfate and ethylsulfate; an aminopoly-ureylene resin having the following repeating unit:

$$\frac{\Gamma}{\Gamma}(CH_2)_n - X - (CH_2)_n NHC(Y)NH$$

wherein X is NH, N-C₁ to C₂₂ alkyl,

N+(CH₁)(CH₂CHCH₂Cl) OH

30 or

Y is O or S and n is 2 or 3, and a molecular weight in the range of about 300 to 100,000; and a water-soluble, anionic, organic detergent salt having a hydrophobic group containing an alkyl group of 8 to 26 carbon atoms in its molecular structure and at least one hydrophilic solubilizing radical selected from the group consisting of sulfonate, sulfate, and carboxylate, the weight ratio of said softener to said resin being from about .16:1 to about 4:1 for the quaternary ammonium softeners and 0.5:1 to about 2:1 for the imidazolinium softeners and the mole ratio of said softener to said anionic detergent being greater than about .12:1.

9. A detergent-softener composition according to claim 8 which contains in addition about 50% to 85% by weight of a detergent builder salt.

10. A detergent-softener composition according to claim 9 which consists essentially of

(a) 2% to 10% by weight of said softener;

(b) 2% to 16% by weight of said resin;

(c) 8% to 35% by weight of said anionic detergent;

(d) 50% to 85% by weight of a water-soluble detergent builder salt selected from the group consisting of sodium and potassium salts of nitrilotriacetate, citrate, sulfate, silicate, phosphate, carbonate, and mixtures thereof.

11. A detergent-softener composition according to claim 10 wherein said softener is selected from the group consisting of ditallow dimethyl ammonium chloride and 2-heptadecyl-1 methyl-1[stearoyl amidoethyl] imidazolinium methosulfate

12. A detergent-softener composition according to claim 10 wherein said resin has an average molecular weight of 1000 to 20,000 and said repeating unit is

${\rm f(CH_2)_3N(CH_3)(CH_2)_3NHC(O)NH_3^2}$

13. A process for simultaneously washing and softening fabrics which comprises laundering said fabrics in an aqueous medium containing 0.02% to 0.5% by weight of a mixture consisting essentially of a cationic quaternary ammonium fabric softener selected from the group

consisting of quaternary ammonium softeners having the general formula

wherein R and R_1 are higher alkyl or alkenyl radicals of 12 to 22 carbon atoms and R_2 and R_3 are each selected from the group consisting of C_1 – C_4 alkyl, C_1 – C_4 hydroxyalkyl and ethoxyethanol and X is selected from the group 10 consisting of chloride, bromide, iodide, methylsulfate, and ethylsulfate, and imidazolinium softeners having the general formula

where R and R_1 are higher alkyl or alkenyl radicals of 12 to 22 carbon atoms, R_2 is C_1 – C_4 alkyl and X is selected from the group consisting of chloride, bromide, iodide, methylsulfate and ethylsulfate; an aminopolyureylene resin having the following repeating unit:

$$\frac{\Gamma}{\Gamma}(CH_2)_n - X - (CH_2)_n NHC(Y)NH \frac{1}{\Gamma}$$

wherein X is NH, N-C₁ to C₂₂ alkyl,

 \mathbf{or}

$$N^{+}(CH_{1})$$
 $\left(CH_{2}CH - CH_{2}\right)$

Y is O or S and n is 2 or 3, and a molecular weight in the range of about 300 to 100,000; and a water-soluble, anionic, organic detergent salt having a hydrophobic group containing an alkyl group of 8 to 26 carbon atoms in its molecular structure and at least one hydrophilic solubilizing radical selected from the group consisting of sulfonate, sulfate, and carboxylate, the weight ratio of said softener to said resin being from about .16:1 to about 4:1 for the quaternary ammonium softeners and 0.5:1 to about 2:1 for the imidazolinium softeners and the mole ratio of said softener to said anionic detergent being greater than about 0.12:1.

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