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WASH CYCLE SOFTENER

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No Drawing. Continuation of abandoned application Ser. No. 736,292, June 12, 1968. This application July 21, 1971, Ser. No. 164,827
Int. Cl. C11d *1/00;* **D06m** *13/34*
U.S. Cl. 252—8.8 **5 Claims**

ABSTRACT OF THE DISCLOSURE

Washing and softening of fabrics by including, with the detergent, an N-2-hydroxy higher alkyl amine.

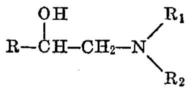
This application is a continuation of application Ser. No. 736,292, filed June 12, 1968, now abandoned.

The softening of fabrics by the addition of certain cationically active quaternary ammonium compounds is well known in the art. It has not, however, been feasible to add these materials when conventional anionic detergents are present in significant amounts in the wash water, since the cationic materials typically react with the anionic detergents to form precipitates which are ineffective to soften the fabric. Accordingly, the housewife must wait until the detergent is substantially removed before adding the softener. This is undesirable for users of automatic washing machines since the required additional personal attention obviously reduces the benefits gained from the use of the automatic machine.

Furthermore, the usual cationic fabric softeners, even when added in the absence of anionic detergents, tend to yellow the fabrics.

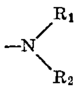
In one aspect of this invention an N-2-hydroxy higher alkyl amine is used as a fabric softener during the washing of the fabric. The amine may be employed in the automatic machine washing of clothes, in which it may be added either during the wash cycle (that is, together with the detergent composition which, as is well known, may comprise an organic detergent, builder salt, etc.) or during the rinse cycle (that is, after the completion of the wash cycle).

The N-2-hydroxy higher alkyl amines used in this invention have the formula:



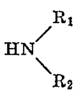
$$R{-}CH(OH){-}CH_2{-}N(R_1)(R_2)$$

where R is a monovalent aliphatic hydrocarbon radical of 8 to 24, preferably 10 to 20, carbon atoms, and



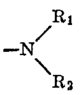
$$-N(R_1)(R_2)$$

is the radical of an amine of the formula



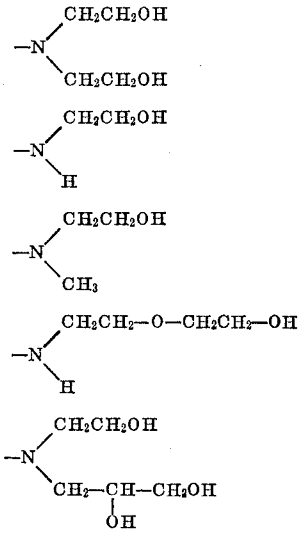
$$HN(R_1)(R_2)$$

In one particularly suitable class, R_1 has an alcoholic hydroxyl group, e.g. it is a hydroxyalkyl radical of the formula $—R_3(OR_4)_nOH$ where *n* is, for example, zero to three, and R_3 and R_4 are alkylene radicals such as ethylene, propylene, isopropylene etc. Examples of



$$-N(R_1)(R_2)$$

radicals of this class are

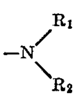


$$-N(CH_2CH_2OH)(CH_2CH_2OH)$$
$$-N(CH_2CH_2OH)(H)$$
$$-N(CH_2CH_2OH)(CH_3)$$
$$-N(CH_2CH_2{-}O{-}CH_2CH_2{-}OH)(H)$$
$$-N(CH_2CH_2OH)(CH_2{-}CH(OH){-}CH_2OH)$$

and related compounds in which the radicals contain more carbon atoms than in the formula shown above, e.g. radicals of

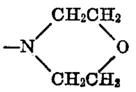
di(isopropanol)amine,
N-methyl-N-isopropanolamine,
N-ethyl-N-ethanolamine,
N-ethyl-N-isopropanolamine,
N-propyl-N-ethanolamine,
N-propyl-N-isopropanolamine,
N-methyl-N-hydroxyethoxyethylamine,
N-butyl-N-hydroxyethoxyethylamine,
N-cyclohexyl-N-hydroxyethoxyethylamine,
N-butyl-N-ethanolamine,
di(hydroxyethoxyethyl)amine,
mono(hydroxyethoxyethoxyethyl)amine,
N-hydroxyethoxyethoxyethyl-N-methylamine,
N-hydroxyethyl-N-hydroxyisopropylamine,
N-benzyl-N-hydroxyethylamine, or
N-cyclohexyl-N-2-hydroxy-2-phenylethylamine.

In another class R_1 and R_2 together constitute part of a heterocyclic ring; examples of

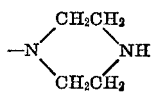


$$-N(R_1)(R_2)$$

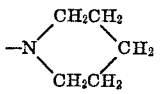
radicals of this type are the radicals of morpholine, i.e.



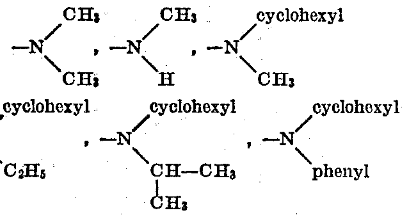
piperazine, i.e.



or piperidine, i.e.

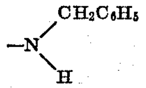


In still another class R_1 is hydrocarbon and R_2 is hydrogen or hydrocarbon; examples of such radicals are



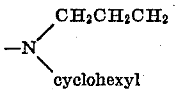
$-N(CH_3)_2$, $-N(CH_3)H$, $-N(\text{cyclohexyl})(CH_3)$, $-N(\text{cyclohexyl})(C_2H_5)$, $-N(\text{cyclohexyl})(CH-CH_3)(CH_3)$, $-N(\text{cyclohexyl})(\text{phenyl})$

and



$-N(CH_2C_6H_5)(H)$

The R_1 (and R_2) radical may carry a substituent other than the alcoholic hydroxyl previously mentioned; for instance it may be an amino group as in



$-N(CH_2CH_2CH_2)(\text{cyclohexyl})$

Generally the ratio of the amount of organic detergent to the amount of hydroxy long chain alkyl amine softener of this invention is in the range of 10:1 to 1:1, preferably about 2:1 to 1.5:1. The amine may be preblended with the entire detergent composition or it may be added separately to the wash water or it may be preblended with a portion of the detergent composition.

One technique of incorporating the amine in a granular washing composition is to form an aqueous slurry containing the organic detergent, the builder salt, the amine and other components (such as agents for preventing soil redeposition, brighteners, bluing agents, bleaching aids, germicidal materials, etc.). The slurry may then be converted to solid form by such methods as spray drying and/or hydration of the builder salt to convert the liquid water to water of crystallization. This hydration operation may be effected while bubbles of gas are dispersed in a mass of the mixture so as to lower the density of the final product and to give a crumbly or granular product; the gas bubbles may result, for example, from the inclusion of hydrogen peroxide to generate oxygen in the mixture, or from the generation of steam in the mixture (as by the exothermic heat of the reaction of sodium trimetaphosphate with NaOH to form sodium tripolyphosphate), or from the dispersing of air in the mixture with violent agitation. In another technique, the amine, when it is a solid, may be mechanically blended, as small particles, with particles of the granular washing composition. Or the amine (e.g. in molten state or in aqueous dispersion) may be sprayed onto the particles of the granular washing composition, or agglomerated with those particles in other ways.

The water-insoluble amine softener may also be incorporated in aqueous liquid washing compositions. For example it may be dispersed in a built aqueous liquid mixture containing dispersed builder salt, organic detergent and hydrotrope (commonly an alkali metal aromatic sulfonate, such as a benzene-, toluene-, or xylene-sulfonate), together with the other components of the types previously mentioned in the discussion of granular compositions.

When the amine is not part of a single washing composition it may be added to the wash water as a liquid or solid. Thus it may be dispersed, emulsified or solubilized in alkaline or neutral aqueous medium; the aqueous medium may contain a hydrotrope (which may be the aromatic sulfonate type mentioned above or water miscible alcohol, such as methanol, ethanol, ethylene glycol, diethylene glycol, etc.). An organic detergent, preferably in minor amount, may also be present in the aqueous medium, the low-foaming nonionic detergents being suitable here. A particularly suitable mixture contains minor proportions of both a long chain alkyl sulfate detergent and a long chain sulfonate detergent, such as an alkylbenzenesulfonate (e.g. in a ratio of sulfate to sulfonate of about 1:10 to 2:1). The amount of the amine present in the liquid may be, for example, in the range of about 2–25%, preferably about 5–20% (e.g. about 10–20%). Preferably the liquid compositions are easily pourable; however, solid gel-like compositions, made with proportions of amine in the above ranges in the presence of aqueous gelling media, may also be used. An acidic aqueous dispersion of the amine, which forms a water-soluble salt with the acid present in the water (e.g. acetic, hydrochloric, lactic, glycollic or phosphoric acid), may be used in place of the neutral or alkaline dispersion; when such an acidic composition is mixed with the alkaline agitated wash water the amine is converted to its water-insoluble form, and is finely dispersed in the wash water. Solid amine-containing compositions for inclusions in the wash water (to which the usual detergent compositions are added) may have the amine distributed on a builder salt or other suitable water-soluble or water-dispersible carrier, preferably one which exerts a beneficial effect on the washing process. Thus the amine in liquid state (e.g. molten) may be sprayed on, or otherwise agglomerated with, particles of such salts as phosphates (e.g. anhydrous or hydrated pentasodium tripolyphosphate), borax or the so-called puffed borax (which is an expanded partial hydrate of sodium tetraborate made, for example, by heating borax or sodium tetraborate pentahydrate in heated air), sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium sulfate, sodium chloride or other carrier materials, to form granular or powdered compositions. The amount of amine present in the solid composition may be, for instance, in the range of about 2–25%, preferably about 5–20%. The foregoing liquid or solid compositions may be added to the wash water in amounts such as to provide, for example, about 30 to 400 parts of the amine per million parts of wash water.

The organic detergent may be a surface-active agent of the anionic, non-ionic, amphoteric or cationic type, or a mixture of such types.

The anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulfonate, sulfate, carboxylate, phosphonate and phosphate. Examples of suitable anionic detergents which fall within the scope of the invention include the soaps, such as the water-soluble salts of higher fatty acids or rosin acids, such as may be derived from fats, oils and waxes of animal, vegetable origin, e.g. the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulfated and sulfonated synthetic detergents, particularly those having about 8 to 26, and preferably about 12 to 22, carbon atoms to the molecule.

As examples of suitable synthetic anionic detergents there may be cited the higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g., the sodium salts of higher alkyl benzene sulfonates or of the higher alkyl toluene, xylene and phenol sulfonates; alkyl naphthalene sulfonate, ammonium diamyl naphthalene sulfonate, and sodium dinonyl naphthalene sulfonate. In one preferred type of composition there is used a 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; in other terminology, 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 is correspondingly low. Particularly preferred materials are set forth in U.S. Pat. 3,320,174, May 16, 1967, of J. Rubinfeld.

Other anionic detergents are the olefin sulfonates, including long chain alkene sulfonates, long chain hydroxyalkane sulfonates or mixtures of alkenesulfonates and hydroxyalkanesulfonates. These olefin sulfonate detergents may be prepared, in known manner, by the reaction of SO_3 with long chain olefins (of 8–25, preferably 12–21 carbon atoms) of the formula $RCH{=}CHR_1$, where R is alkyl and R_1 is alkyl or hydrogen, to produce a mixture of sultones and alkenesulfonic acids, which mixture is then treated to convert the sultones to sulfonates. Examples of other sulfate or sulfonate detergents are paraffin sulfonates, such as the reaction products of alpha olefins and bisulfites (e.g. sodium bisulfite), e.g. primary paraffin sulfonates of about 10–20, preferably about 15–20, carbon atoms; sulfates of higher alcohols; salts of α-sulfofatty esters (e.g. of about 10- to 20-carbon atoms, such as methyl α-sulfomyristate or α-sulfotallowate).

Examples of sulfates of higher alcohols are sodium lauryl sulfate, sodium tallow alcohol sulfate. Turkey Red Oil or other sulfated oils, or sulfates of mono- or diglycerides of fatty acids (e.g. stearic monoglyceride monosulfate), alkyl poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and lauryl alcohol (usually having 1 to 5 ethenoxy groups per molecule); lauryl or other higher alkyl glyceryl ether sulfonates; aromatic poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule).

The suitable anionic detergents include also the acyl sarcosinates (e.g. sodium lauroylsarcosinate), the acyl esters (e.g. oleic acid ester) of isethionates, and the acyl N-methyl taurides (e.g. potassium N-methyl lauroyl- or oleyl tauride).

The most highly preferred water soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di- and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene sulfonates, olefin sulfonates, the higher alkyl sulfates, and the higher fatty acid monoglyceride sulfates. The particular salt will be suitably selected depending upon the particular formulation and the proportions therein.

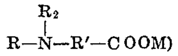
Nonionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylate, hydroxyl, amido or amino with ethylene oxide or with the polyhydration product thereof, polyethylene glycol.

As examples of nonionic surface active agents which may be used there may be noted the condensation products of alkyl phenols with ethylene oxide, e.g., the reaction product of isooctyl phenol with about 6 to 30 ethylene oxide units; condensation products of alkyl thiophenols with 10 to 15 ethylene oxide units; condensation products of higher fatty alcohols such as tridecyl alcohol with ethylene oxide; ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol mono-oleate and mannitan monopalmitate, and the condensation products of polypropylene glycol with ethylene oxide.

Cationic surface active agents may also be employed. Such agents are those surface active detergent compounds which contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and quaternary groups.

As examples of suitable synthetic cationic detergents there may be noted the diamines such as those of the type $RNHC_2H_4NH_2$ wherein R is an alkyl group of about 12 to 22 carbon atoms, such as N-2-aminoethyl stearyl amine and N-2-aminoethyl myristyl amine; amide-linked amines such as those of the type $R^1CONHC_2H_4NH_2$ wherein R^1 is an alkyl group of about 9 to 20 carbon atoms, such as N-2-amino-ethyl stearyl amide and N-aminoethyl myristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group of about 12 to 18 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including such 1 to 3 carbon alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate, methosulfate, etc. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl dilauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulfates and acetates.

Examples of suitable amphoteric detergents are those containing both an anionic and a cationic group and a hydrophobic organic group, which is advantageously a higher aliphatic radical, e.g. of 10–20 carbon atoms. Among these are the N-long chain alkyl aminocarboxylic acids

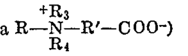


(e.g. of the formula $R-\overset{\overset{R_2}{|}}{N}-R'-COOM$)

the N-long chain alkyl iminodicarboxylic acids

(e.g. of the formula $RN(R'COOM)_2$)

and the N-long chain alkyl betaines



(e.g. of the formula $R-\underset{R_4}{\overset{+R_3}{N}}-R'-COO^-$)

where R is a long chain alkyl group, e.g. of about 10–20 carbons, R′ is a divalent radical joining the amino and carboxyl portions of an amino acid (e.g. an alkylene radical of 1–4 carbon atoms), M is hydrogen or a salt-forming metal, R_2 is a hydrogen or another monovalent substituent (e.g. methyl or other lower alkyl), and R_3 and R_4 are monovalent substituents joined to the nitrogen by carbon-to-nitrogen bonds (e.g. methyl or other lower alkyl substituents). Examples of specific amphoteric detergents are N-alkyl-beta-aminopropionic acid; N-alkyl-beta-iminodipropionic acid, and N-alkyl, N,N-dimethyl glycine; the alkyl group may be, for example, that derived from coco fatty alcohol, lauryl alcohol, myristyl alcohol (or a lauryl-myristyl mixture), hydrogenated tallow alcohol, cetyl, stearyl, or blends of such alcohols. The substituted aminopropionic and iminodipropionic acids are often supplied in the sodium or other salt forms, which may likewise be used in the practice of this invention. Examples of other amphoteric detergents are the fatty imidazolines such as those made by reacting a long chain fatty acid (e.g. of 10 to 20 carbon atoms) with diethylene triamine and monohalocarboxylic acids having 2 to 6 carbon atoms, e.g. 1-coco-5-hydroxethyl-5-carboxymethylimidazoline; betaines containing a sulfonic group instead of the carboxylic group; betaines in which the long chain substituent is joined to the carboxylic group without an intervening nitrogen atom, e.g. inner salts of 2-trimethylamino fatty acids such as 2-trimethylaminolauric acid, and compounds of any of the previously mentioned types but in which the nitrogen atom is replaced by phosphorus.

Examples of water-soluble builder salts which may be used, particularly when heavy duty cleaning is desired, include phosphates and particularly condensed phosphates (e.g. pyrophosphates or tripolyphosphates), silicates, borates and carbonates (including bicarbonates), as well as organic builders such as salts of nitrilotriacetic acid or ethylene diamine tetracetic acid. Sodium and potassium salts are preferred. Specific examples are sodium tripolyphosphate, potassium pyrophosphate, sodium hexametaphosphate, sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium tetraborate, sodium silicate, salts (e.g. Na salt) of methylene diphosphonic acid, trisodium nitrilotriacetate, or mixtures of such builders, including mixtures of pentasodium tripolyphosphate and trisodium nitrilotriacetate in a ratio, of these two builders, of 1:10 to 10:1, e.g. 1:1. The proportions of builders salt may be, for example, 50 parts or more (e.g. 50 to 1000 parts) per 100 parts of detergent.

This invention makes it possible to obtain a high degree of softening in the wash cycle and without the yellowing effects of prior cationic softeners.

The invention has found its greatest utility thus far in the washing of cotton fabrics, but it may be used with fabrics made of other cellulosic fibers, e.g. rayon, or other textile fibers, e.g. nylon, silk, wool, polyethylene terephthalate, cellulose acetate, acrylonitrile polymers or copolymers, or blends of any two or more of these fibers (e.g. cotton-polyester blends).

The following examples are given to illustrate this invention further. In these examples, as in the application as a whole, all parts are by weight unless otherwise indicated.

EXAMPLE 1

A wash cycle softener composition is prepared as follows: A blend is formed from 46.3 parts of water; 12.6 parts of a mixture of N-2 hydroxy higher alkyl diethanolamines in which the higher alkyl radicals have 15 to 18 carbon atoms; 37 parts of an aqueous 43% solution of sodium cumene sulfonate; and 1.5 parts of an aqueous 1% solution of blue dyestuff ("Acid Blue 80," Polar Brilliant Blue). This blend is heated moderately (e.g. to 60° C.) until the amine is fully solubilized. Then 2.5 parts of an aqueous 8% dispersion of polystyrene (which opacifies the mixture) is added to the heated blend, which is then allowed to cool to about 35–40° C. whereupon a small amount (e.g. 0.1 part) of a perfume is added. The resulting mixture is an opaque, homogeneous liquid at room temperature, having a viscosity of about 10–20 cps., a specific gravity of 1.05 and a pH of 10.7.

In use, 60 grams of this composition is mixed, together with 110 grams of a built detergent mixture, with the white cotton fabrics and hot wash water (at 50° C.) in the wash cycle of an automatic washing machine. The built detergent mixture contains 3.3% sodium linear dodecylbenzenesulfonate, 3.8% sodium tallow alcohol sulfate, 1.7% sodium soap of fatty acids (mixed tallow coconut oil fatty acids), 2.1% of nonionic detergent (e.g. a hydrophilic ether of a polyalkylene glycol, which may be of moderately high molecular weight, for example molecular weight about 3,000), 56.5% pentasodium tripolyphosphate, 4.7% tetrasodium pyrophosphate, 0.5% trisodium phosphate, 4.4% sodium silicate (1:2.35 $Na_2O:SiO_2$ mol ratio), 1.6% sodium carbonate, about ½% sodium carboxymethylcellulose, about ½% fluorescent brighteners, 6% water (including water of hydration) and the balance Na_2SO_4. The wash water is New Brunswick, N.J. tap water (whose hardness is 100 p.p.m.), in amount of 17 gallons (35 liters).

The fabrics so washed have a very soft and pleasant feel. They are just as white (and much softer than) similar fabrics washed in an identical manner except that only the built detergent mixture is used.

EXAMPLE 2

In this example there is used a granular softener-detergent composition containing 12% sodium linear tridecylbenzenesulfonate, 2% soap, 6% of the 2-hydroxy higher alkyl diethanolamine of Example 1, 34% of pentasodium tripolyphosphate, 6% sodium silicate (1:2.35 $Na_2O:SiO_2$ mol ratio), 0.5% carboxymethylcellulose, 0.2% polyvinyl alcohol, 0.5% fluorescent brighteners, 0.15% ultramarine blue and 8.5% moisture (including water of hydration) and the balance sodium sulfate.

95 grams of the spray dried composition is used in the automatic machine washing of cotton fabrics under the conditions described in Example 1. Similar excellent performance is obtained, with less foaming in the washer. In using 150 p.p.m. of the spray dried composition in the wash water at 50° C. for the washing of towels and diapers in the wash cycle of an automatic machine, the washed products are found to be noticeably softer than when 95 p.p.m. of a commercial detergent are used together with 60 p.p.m. of a commercial available quaternary ammonium softener product. The absorbency of the washed towels and diapers is excellent.

EXAMPLE 3

Example 1 is repeated (with the wash cycle softener compositions changed to omit the blue dyestuff, polystyrene dispersion and perfume and to use less, or none, of the hydrotrope) using 60 grams of a wash cycle softener composition as follows:

(a) In one case, the composition contains 12.6% of the amine softener, 11% of sodium cumene sulfonate and the balance water. It is a clear single-phase low viscosity liquid at room temperature.

(b) In another case, 45 g. of the composition of (a) above, is blended with 15 g. of a composition containing 12.6% of a long chain alkyl amine oxide having at least 18 carbon atoms in the long chain alkyl, specifically, stearyl dimethyl amine oxide, 16% sodium cumenesulfonate, 1.5% of emulsified polystyrene (emulsifier) and the balance water (containing small amounts of perfume and color).

(c) In still another case, the 60 g. of the composition of (a) above is blended with 2 g. of a nonionic detergent, namely a polyethoxylated long chain alkanol, specifically the condensation product of 10% of ethylene oxide and 90% of an alkanol of 16–20 carbon atoms.

(d) In still another case the 60 grams is a dispersion, in hot water, of 7.6 grams of the amine softener and 2 grams of a sodium olefin sulfonate made in well-known manner by sulfonation (with an SO_3-diluent gas mixture) of an alpha monoolefin of 15–18 carbon atoms followed by alkalinization (as with aqueous NaOH) of the sulfonated product and hydrolysis by heating (giving a mixture containing sodium alkenyl sulfonate and sodium hydroxyalkane sulfonate).

(e) In still another case, the 60 grams is a dispersion, in hot water, of 7.6 of the amine softener and sufficient cumene sulfonate to produce a clear single-phase liquid.

Very good results are obtained in each case, especially good results being obtained with compositions (a), (b) and (e).

EXAMPLE 4

Example 1 is repeated using the following wash cycle softener compositions:

(a) In one case, a mixture of 7.6 g. of the amine softener, 5 g. of trisodium nitrilotriacetate monohydrate and 50 g. of water, which mixture is heated to about 50° C. before being added to the wash water.

(b) In another case, a mixture of 7.6 g. of the amine softener, 5 g. of lactic acid and 50 g. of water; this mixture is heated to about 60° C. and, on cooling, is a clear single-phase low viscosity liquid.

(c) In another case, a mixture of 7.6 g. of the amine softener, 15 g. of sodium dihydrogen phosphate monohydrate and 50 g. of water; this mixture is heated to about 60° C. and, on cooling, is a clear single-phase low viscosity liquid.

(d) In another case, a mixture of 7.6 g. of the amine softener, sufficient of a commercial fabric softener to provide 2 g. of 2-heptadecyl-1-methyl [(2-stearamide) ethyl] imidazolinium methyl sulfate, and 50 g. of water, which mixture is heated to about 60° C. before being added to the wash water.

(e) In another case, a mixture of 7.6 g. of the amine softener, 2 g. of nitrilotriacetic acid and 50 g. of water; this mixture is heated to about 60° C. and, on cooling, is a clear single-phase low viscosity liquid.

(f) In another case, a mixture of 9 g. of the amine softener, 1.5 g. glacial acetic acid and 49.5 g. water. When the amine and water are heated together a viscous opaque gel forms, which becomes a thin and clear liquid (of pH 5.2) when the acetic acid is added.

(g) In another case, a mixture of 9 g. of the amine softener, 3 g. of glacial acetic acid and 48 g. of water. When these three ingredients are heated (at about 50° C.) there is produced a clear low viscosity liquid of pH 4.3 which remains clear on long standing at room temperature.

(h) Example (g) is repeated, using .3 g. of phosphoric acid in place of the acetic acid.

(i) Example (g) is repeated using 3 g. of aqueous concentrated (37.2%) hydrochloric acid in place of the acetic acid.

(j) In another case, a mixture of 9 g. of the amine softener, 1.5 g. of aqueous concentrated (37.2%) hydrochloric acid and 49.5 g. of water. This mixture, when heated and then cooled to room temperature, is a viscous gelatinous blend of pH 6.6. Its viscosity can be reduced by the addition of, for example (I) a water-soluble alcohol, such as $\frac{1}{10}$ its weight of isopropanol, (II) a hydrotrope, such as $\frac{1}{10}$ its weight of sodium xylene sulfonate or (III) a water-soluble salt, such as $\frac{1}{100}$ its weight, or even $\frac{1}{1000}$ its weight or less, of sodium acetate.

The foregoing compositions yield very good results in washing process in terms of fabric softness and detergent power, for example.

EXAMPLE 5

Suitable softener-detergent compositions are prepared according to the following formulations:

(a) 17 parts of an aqueous 47% slurry of sodium linear dodecyl benzenesulfonate; 4.5 parts of the amine softener of Example 1; 20 parts of an aqueous 40% solution of sodium xylene sulfonate; 25 parts of an aqueous 60% solution of tetrapotassium pyrophosphate; and 33.5 parts of added water. The ingredients are blended, heated and stirred at about 60° C. The mixture is a single-phase clear liquid, both when hot and at room temperature; its pH is 10.8 and its specific gravity is 1.19.

(b) Example 5(a) above, is repeated, substituting 23 parts of an aqueous 44% slurry of the sodium olefin sulfonate (of Example 3(d)) for the alkylbenzenesulfonate slurry (giving, in each case, a composition containing 10% detergent). A similar clear liquid is obtained.

(c) 12 grams of sodium alkylbenzenesulfonate (supplied as the 58% slurry of Example 5(a), above), dispersed in hot water with 8 grams of the amine softener of Example 1 and added to the wash water with 40 grams of anhydrous pentasodium tripolyphosphate.

(d) 10 grams of sodium alkylbenzenesulfonate (supplied as the 47% slurry of Example 5(a), above) dispersed in hot water with 5 grams of the amine softener of Example 2 and 5 grams of the sodium sulfate of a long chain alkanol, specifically a mixture of primary alcohols of 16, 18 and 20 carbon atoms.

(e) A slurry formed by dissolving 5 grams of the amine softener of Example 2 in 15 ml. isopropanol, adding about 300 ml. of water and then adding 95 grams of a dry built detergent composition containing 10% sodium linear tridecylbenzenesulfonate, 2% of a nonionic detergent made by reacting a long chain alkanol having 14–15 carbon atoms with an average of 11 mols of ethylene oxide per mol of alkanol, 2% of soap, 35% of anhydrous pentasodium tripolyphosphate, about 8–9% of water together with conventional proportions (as in the built formulations described in Examples 1 and 2) of sodium silicate, sodium carboxymethylcellulose and brighteners, and the balance sodium sulfate.

(f) 10 grams of sodium alkylbenzenesulfonate (supplied as the 58% slurry of Example (a), above), dispersed in hot water with 5 grams of N-2-hydroxydodecylmorpholine, and added to the wash water with 40 grams of anhydrous pentasodium tripolyphosphate.

(g), (h), (i) Formulations identical with 5(f) above, except that the amine softeners are N-2-hydroxytetradecyl-morpholine, N-2-hydroxyhexadecyl - morpholine, N-2-hydroxyheptadecyl, respectively, in place of the N-2-hydroxydodecyl-morpholine.

(j) A formulation identical with 5(a) above, using N-2-hydroxyhexadecyl-morpholine in place of the C15–C18 2-hydroxyalkyldiethanolamine.

(k) A formulation containing 3 grams of sodium linear dodecylbenzenesulfonate (supplied as an aqueous 58% slurry, as in 5(a) above) dispersed in hot water near the boil with 1 gram of N,N-di(2-hydroxydodecyl)-piperazine, and added to the wash water together with 6.6 grams of anhydrous pentasodium tripolyphosphate. The use of this piperazine compound gave only a trace of foam and excellent softness.

(l) A formulation identical with that of 5(c) above, substituting 8 grams of N-2-hydroxyhexadecyl-N-methyl ethanolamine for the 8 grams of N-2-hydroxyalkyl diethanolamine.

(m) A formulation containing 10 grams of sodium linear dodecylbenzenesulfonate (supplied as an aqueous 47% slurry as in 5(a) above) dispersed in hot water (about 60° C.) together with 5 grams of N-2-hydroxyhexadecyl diethanolamine and added to the wash water together with 40 grams of anhydrous pentasodium tripolyphosphate.

(n) A formulation identical with 5(m) above but containing also 10 grams of the sodium sulfate of a higher alkanol, specifically a mixture of 16, 18 and 20 carbon atom primary alkanols (51% C16, 34% C18, 12% C20 and 1% each of C14 and C22).

(o) A formulation as in 5(m) above but containing 5 grams of 2-hydroxyhexadecyl di-isopropanolamine in place of the 2-hydroxyhexadecyl diethanolamine.

(p) A formulation containing 10 parts of sodium linear dodecylbenzenesulfonate (supplied as an aqueous 47% slurry thereof), 5 parts of 2-hydroxydodecyl diethanolamine (supplied as a dispersion thereof in 50° C. water) and 40 parts of anhydrous pentasodium tripolyphosphate.

(q) A formulation containing 5 parts of the amine of Example 1 and 90 parts of a spray-dried composition containing 12% of sodium linear tridecylbenzenesulfonate, 11% of the sodium sulfate of primary alkanols of 16 to 20 carbon atoms, 35% of anhydrous pentasodium tripolyphosphate and amounts of sodium silicate, sodium carboxymethylcellulose brighteners, moisture and sodium sulfate similar to those used in the spray-dried composition of Example 2. The amine and the spray-dried composition are slurried together with 300 parts of water at 60° C.

EXAMPLE 6

The following mixtures are used (in the amounts given below) in the same manner as the wash cycle softener composition of Example 1, with 110 grams of the same detergent composition as in Example 1.

(a) A formulation containing 30 grams of the composition (containing 12.6% stearyl dimethyl amine oxide) referred to in Example 3(b) above, 2 grams of 2-hydroxydodecyl diethanolamine and 25 grams of water.

(b) A clear single phase liquid formulation containing 7.6 grams 2-hydroxyhexadecyl diethanolamine, 50 grams of water, and 10 grams of an aqueous 43% solution of sodium cumene sulfonate.

(c) A formulation containing 30 grams of the composition (containing 12.6% of stearyl dimethylamine oxide) referred to in Example 3(b) above, 5 grams of 2-hydroxyhexadecyl diethanolamine and 25 grams of water.

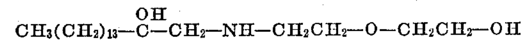
(d) A heated aqueous dispersion containing 12 grams of 2-hydroxyhexadecyl diethanolamine in about 100 grams of water.

(e) A formulation as in 6(b) above in which the amine is 2-hydroxyoctadecyl diethanolamine and only enough of the sodium cumene sulfonate to form a clear dispersion is used.

(f) A formulation as in 6(e) above, in which the amine is 2-hydroxyhexadecyl di-isopropanolamine.

(g) A formulation containing 30 grams of the wash cycle softener composition of Example 1 and 3.8 grams of the amine of 6(f), above.

(h) A formulation as in 6(e) above, in which the amine is N-2-hydroxyhexadecyl diglycolamine of the formula



$$CH_3(CH_2)_{13}-\overset{OH}{C}-CH_2-NH-CH_2CH_2-O-CH_2CH_2-OH$$

(i) A formulation containing 7.6 grams of the amine of 6(f) above, 3 grams of lactic acid and 50 grams of water.

(j) A formulation as in 6(i), above, in which the 3 grams of lactic acid is replaced by 7 grams of sodium dihydrogen phosphate monohydrate.

(k) (l) and (m) formulations containing 7.6 grams of 2-hydroxydodecyl monoethanolamine, 2-hydroxyalkyl monoethanolamine in which the alkyl is a mixture of C15 to C18 chain lengths, and 2-hydroxyhexadecyl monoethanolamine, respectively, in about 100 grams of hot water (at about 60° C.).

(n), (o), (p) and (q) Formulations as in Example 1, replacing its amine softener by respectively, by, N-2-hydroxytetradecyl-morpholine, N-2-hydroxyhexadecyl-morpholine, and N-2-hydroxyheptadecyl-morpholine and N-2-hydroxyalkyl-morpholine in which the alkyl is a mixture of C15 to C18 chain lengths.

(r) A formulation as in Example 1 in which the amount of amine softener is increased to 16% and the amount of added water is decreased to 42.9%.

(s), (t) and (u) Clear one-phase liquid formulation, made by mixing at room temperature, containing 25 grams of water, 25 grams of aqueous 43% sodium cumene sulfonate and 7.6 grams of, respectively 2-hydroxydodecyl methyl ethanolamine, or 2-hydroxyhexadecyl methyl ethanolamine, or 2-hydroxyoctadecyl methyl ethanolamine. Of these, the 2-hydroxyhexadecyl compound gives outstanding results.

(v) A formulation as in 6(s), (t) and (u), above, but using, as the amine softener, N-2-hydroxyhexadecyl N-2-hydroxyethyl N-2,3-dihydroxypropyl amine.

(w) and (x) Formulations which are aqueous dispersions containing 15% of the amine softener of Example 1, 1.5% of aqueous concentrated (37.2%) hydrochloric acid, and 1% of a detergent which is either a sodium linear tridecylbenzenesulfonate of the type disclosed by Rubinfeld U.S. Pat. 3,320,174, or a sodium olefin sulfonate made, for example, by sulfonating hexadecene-1 with air-diluted SO_3 in about 1:1 mol ratio, treating the resulting product with about 9% of its weight of concentrated (e.g. 97%) H_2SO_4, making the product alkaline by adding NaOH (in aqueous solution) in amount of about 1.1–1.2 mols of NaOH per mol of SO_3 used and heat-treating the alkaline mixture at a temperature of about 175° C.

EXAMPLE 7

The following mixtures are used in amounts of 60 grams each, as wash cycle softener compositions, with 110 grams of commercial heavy duty built detergent mixture (such as that of Example 1 or Example 5(e) for washing fabrics as in Example 1.

(a) A mixture of 15% of the amine of Example 1, 3% glacial acetic acid, 3% isopropanol and the balance water (with minor amounts of color and perfume).

(b) A mixture of 15% of the amine of Example 1, 3% glacial acetic acid, 0.8% anionic detergent (sodium primary long chain alkanol sulfate, of a mixture of C16 to C20 alcohols) and the balance water (with minor amounts of color and perfume).

(c) A mixture of 15% of the amine of Example 1, 5% glycolic acid and the balance water (with minor amounts of opacifier, color and perfume), the mixture having a pH of 4.4.

EXAMPLE 8

The N-2-hydroxy higher alkyl diethanolamine used in Example 1 may be prepared by epoxidizing (e.g. with hydrogen peroxide) in conventional manner a mixture of alpha olefins having 15 to 18 carbon atoms and then reacting the resulting 1,2-epoxide mixture with diethanolamine in stoichiometric proportions. The mixture of olefins and the 1,2-epoxide mixture made therefrom each has the following approximate distribution of components: 1.5% of 14 carbon atoms, 28% of 15 carbon atoms, 28% of 16 carbon atoms, 22.9% of 17 carbon atoms and 19.6% of 18 carbon atoms.

In a typical method of preparation 52.5 g. of diethanolamine is heated and about 15 g. of the 1,2-epoxide is added thereto while heating continues with vigorous stirring. When the temperature reaches about 110° C. the mixture becomes homogeneous indicating that reaction has begun. The external source of heat is removed and the epoxide is added in a rapid stream while stirring and adjusting the rate of addition so as to keep the temperature of the mixture in the range of 110–125° C. After a total of 125 g. of epoxide (including the 15 g. initially added) has been added, stirring is continued at 110° C. for 10 minutes, yielding a clear, slightly yellow liquid which solidifies on cooling to 45° C. to form a white waxy solid. Analysis indicates that it contains about 5% long chain hydrocarbon impurities, corresponding to the amount of unepoxidized material present in the 1,2-epoxide used as the starting material.

EXAMPLE 9

The other N-2-hydroxy higher alkyl amines mentioned in the preceding examples, are made in essentially the same manner as described in Example 8 using, of course, the appropriate epoxide and amine. For example, in making the compound in Example 5(f) one employs 1,2-epoxydodecane and morpholine as the reactants. It is preferred to use about equimolar proportions, at a reaction temperature in the range of 90–150° C. under substantially anhydrous conditions. No added catalyst is needed.

EXAMPLE 10

Example 1 is repeated except that the wash cycle softener composition of the first paragraph of that example is replaced by one of the following compositions:

(a) 14% of the mixed N-2-hydroxy higher alkyl diethanolamines having 15 to 18 carbon atoms in the higher alkyl radicals, 0.6% of sodium higher alkyl sulfate having 16 to 20 carbon atoms in its alkyl radicals (as in Example 5(n)), 3% of sodium linear dodecylbenzenesulfonate, 2% of the aqueous blue dyestuff solution described in Example 1, and the balance water with a small amount of perfume. The wash cycle softener composition is a freely flowing liquid homogeneous dispersion, having a pH of 10.8, which remains pourable, without phase separation or precipitation on aging at −1° C. and which gives a highly uniform fabric-softening effect when included in alkaline wash water containing built detergent compositions. It has an opaque appearance without the need for addition of opacifiers.

(b) A mixture as 10(a), containing 1.1% of the sodium alkyl sulfate and 1.8% of sodium linear tridecylbenzenesulfonate. This mixture is a highly viscous, but pourable liquid.

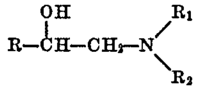
(c) A mixture containing 15% of the same amine mixture as in 10(a), 2.2% of the sodium alkyl sulfate used in 10(a) and the balance water. This mixture is an opaque, highly viscous, gel-like material.

The 2-hydroxy higher alkyl amines described in the foregoing specific examples are insoluble in water, both hot (e.g. at 70° C.) and at room temperature, even at low concentrations (e.g. 0.5% or 1%). They are either solids or, in some cases, oily liquids at room temperature.

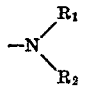
It is understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of the invention. The "Abstract" given above is merely for the convenience of searchers and is not to be given any weight in defining the scope of the invention.

We claim:

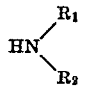
1. A washing and fabric softening composition consisting essentially of a water-soluble organic detergent and an N-2-hydroxy higher alkyl amine of the formula



wherein R is a monovalent alkyl radical of from 8 to 24 carbon atoms and



is a radical of an amine of the formula



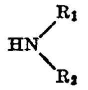
wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, benzyl, C_1 to C_4 alkyl, hydroxyethyl, hydroxypropyl, cyclohexyl and radicals having the formula $—R_3(OR_4)_nOH$, wherein R_3 and R_4 are ethylene, propylene or isopropylene radicals and *n* is an integer of from 0 to 3, and together R_1 and R_2 may constitute the atoms of a morpholine, piperazino or piperidino ring, with the further provision that no more than one of R_1 and R_2 may be hydrogen, wherein said N-2-hydroxy higher alkylamine is present in the range of from about 10:1 to 1:1 with regard to said detergent.

2. The composition of claim **1** which contains additionally a builder salt.

3. The composition of claim **1** wherein R_1 and R_2 are hydroxyalkyl radicals selected from the group consisting of hydroxyethyl and hydroxypropyl radicals.

4. The composition of claim **1** wherein R_1 is a hydroxyalkyl and R_2 is alkyl.

5. A composition as in claim **1** in which said amine of the formula



is selected from the group consisting of diethanolamine, methyl ethanolamine and diisopropanolamine.

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HERBERT B. GUYNN, Primary Examiner

U.S. Cl. X.R.

117—139.5 C.Q.; 252—8.75, 110, 117, 524, 525, 529, 542, 548; 260—584 R, 584 B, 584 C