

[54] SURFACE TREATING COMPOSITIONS CONTAINING SURFACE ACTIVE AMMONIOAMIDATE COMPOUNDS

3,485,806 12/1969 Bloomquist et al. 260/561 X
3,546,115 12/1970 Gill et al. 252/8.8
3,649,569 3/1972 McCarty 252/8.8

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FOREIGN PATENTS OR APPLICATIONS
1,003,926 6/1963 United Kingdom

[73] Assignee: The Procter & Gamble Company, Cincinnati, Ohio

OTHER PUBLICATIONS

[22] Filed: June 27, 1973

Anderson, Ampholytic Detergents, Article in American Perfumer and Aromatics, Documentary Edition, 2-60, pp. 162 and 163.

[21] Appl. No.: 374,148

Related U.S. Application Data

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[63] Continuation-in-part of Ser. No. 243,089, April 11, 1972, abandoned.

[52] U.S. Cl. 252/8.75; 252/8.8; 252/525; 252/529; 252/544; 252/548; 252/DIG. 7; 252/DIG. 13; 260/404.5; 260/561 H; 260/562 H; 424/70

[57] ABSTRACT

Surface-treating compositions containing ammonioamidate surface-active compounds able to exist in either cationic or zwitterionic form are disclosed. The compositions which contain a buffering agent to control pH and the cationic or zwitterionic character of the ammonioamidates are effective in the treatment of fabric or hard surfaces. Hair treating compositions and processes are disclosed. Methods of treating fabric and hard surfaces to provide fabric softening and soil-release properties are also disclosed.

[51] Int. Cl.² D06M 13/40; C11D 1/88

[58] Field of Search 252/8.75, 8.8, 544, 547, 252/525, DIG. 7, 529, 548; 260/561 H, 562 H, 404.5; 117/139.5 CQ

[56] References Cited
UNITED STATES PATENTS

3,410,880 11/1968 Brocklehurst 260/561 X

11 Claims, No Drawings

**SURFACE TREATING COMPOSITIONS
CONTAINING SURFACE ACTIVE
AMMONIOAMIDATE COMPOUNDS**

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of the application of Ronald Edward Atkinson having Ser. No. 243,089, filed Apr. 11, 1972 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to surface-treating compositions comprising certain nitrogen ylides, ammonioamidates, which are surface-active agents and are able to exist in zwitterionic (ylide) form or in cationic form.

Quaternary ammonium compounds having at least one long chain (about C₈ upwards) hydrophobic radical in the molecule have long been known. They are useful as cationic surface-active agents (so called "invert soaps"), as textile softening agents and as bactericides. When intended for use as surface-active agents, the long chain group usually has from about 12 to about 20 carbon atoms. When intended for use as textile softeners, long-chained compounds, for instance having about 16 to 22 or more carbon atoms, are preferred, especially compounds possessing two long chain groups. Typical examples include: octadecyldimethyl benzyl ammonium chloride, octadecyltrimethyl ammonium chloride, distearyl dimethyl ammonium chloride, the corresponding bromides, and many others of similar structure.

These compounds, particularly distearyl dimethyl ammonium chloride, have been used commercially in textile softening compositions intended to be added to the last rinse water after a conventional washing process, and attempts have been made to use them in detergent compositions intended to be combined washing and textile softening agents.

Being cationic, these substances ordinarily react with anionic detergents to form insoluble substances, and so their use in the presence of anionic detergents is not normally practicable. Furthermore, they have a strong affinity for fabrics, especially cotton and wools, a fact which plays an important part in their effectiveness as textile softeners and bactericides, but also has the effect that they are generally not completely washed out of the fabric in a succeeding wash. They therefore tend to build up on repeatedly washed fabrics, and may thus impair the rewetting properties of the fabrics, tend to cause discoloration, fiber snagging and even cause undesirable odors.

Other quaternary ammonium compounds constitute the known zwitterionic surface-active compounds, for example, the long-chain carboxylic betaines, sulphobetaines, sulphato- and sulphito betaines. These compounds are valuable wetting agents and detergents. They are internal salts and, therefore, do not react with the metal ions present in hard water, especially calcium ions, and thus are almost unaffected by water hardness. For the same reason, they are compatible with anionic, cationic and nonionic detergents. Their affinity for and wetting effect upon certain highly hydrophobic fibers, such as polyamine and polyester fibers, renders them particularly valuable for removing certain types of soils, especially greasy soils, from these materials. They are also remarkably effective in cleaning cotton fabrics soiled with dirt which contains clay particles. However,

they are not strongly substantive to fabrics and are not very effective textile softening agents. These known betaine and betaine-like compounds exist in zwitterionic form over a wide range of pH. In relatively strongly acid conditions they do become cationic, but the necessary acidity is outside the practical range for washing fabrics or human beings.

The present invention is concerned with a class of surface-active agents which are cationic under neutral or weakly acid conditions, and are zwitterionic under weakly alkaline conditions. Thus, if present at the ordinary pH of a rinsing operation in an aqueous solution (which need not, of course, necessarily in fact constitute the rinse after a wash) they are largely in cationic form and are effective as textile softening agents substantive to fabrics. Under the ordinarily alkaline conditions of a subsequent conventional washing operation, they convert to a zwitterionic form, and thus are removed from the fabrics. When so removed, they are compatible with the detergent composition and may even enhance its effectiveness.

SUMMARY OF THE INVENTION

The present invention is based in part on the discovery that certain ammonioamidate surface-active compounds are particularly adapted to application to fabric or hard surfaces in a predominantly cationic and substantive form by careful control of the pH of compositions containing them and can, thereafter, by altering pH be removed from the treated surface in a predominantly zwitterionic and relatively non-substantive form. Accordingly, in its composition aspect, the present invention provides a surface-treating composition comprising a substituted ammonioamidate having the formula:



or a cationic adduct thereof having the formula:



where X is an anion; R₁ is an aliphatic (e.g., alkyl), aromatic (e.g., phenyl) or alkaryl (e.g., alkylphenyl) group having from 1 to 25 carbon atoms; each of R₂ and R₃ is a methyl, ethyl, hydroxyethyl or cyanoethyl group; and R₄ is either;



or



wherein R₅ is hydrogen or alkyl of from 1 to 18 carbon atoms and R₆ is hydrogen or an aliphatic group (e.g., alkyl) having 1 to 4 carbon atoms; at least one of R₁ and R₃ having an alkyl chain of at least 6 carbon atoms; and a pH buffering compound.

The surface-treating compositions are suitable for treating textile surfaces such as those of fibers and fabrics, and also hard surfaces, such as those of ceramics, metals and the like.

In its process or method aspect, the present invention provides a method of treating fabric materials whereby the fabrics are improved in softness without undesirable build-up with succeeding washing treatments

which comprise the steps of treating the fabrics with a solution of a predominantly cationic and fabric-substantive compound described hereinbefore thereby to improve softness and, thereafter, washing the fabrics under alkaline conditions to remove the softener in a predominantly zwitterionic form. Also provided is a method of treating hard surfaces whereby the predominantly cationic and substantive form is applied to hard surfaces, said surfaces are subjected to soiling effects and the cationic form is substantially removed by altering the pH of the treated surface to effect conversion to a predominantly zwitterionic form.

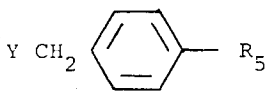
In another process aspect, the ammonioamidate is applied to hair, either in a shampoo or in a rinse or lotion, after washing with a conventional shampoo, leaving the hair glossy, easy to comb when wet or dry and acceptably free from static electricity charges which cause so-called hair "fly".

DETAILED DESCRIPTION OF THE INVENTION

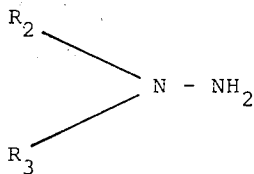
The ammonioamidate compounds of the compositions of the invention can be conveniently prepared. For example, they can be prepared by alkylation of an acyl hydrazide of formula:



by heating it together with either a benzyl halide of the formula



or an allyl halide of the formula $Y \text{ CH}_2 - \text{CH} = \text{CH } R_6$, wherein Y is a chlorine, bromine or iodine atom and the remaining symbols are as defined above. The hydrazide can be prepared, for instance, by reacting an unsymmetrical dialkyl hydrazine



with an acyl chloride $R_1 \text{ COCl}$. The amidates of the invention can suitably be prepared in zwitterionic form by treating the products obtained by the above defined process with an alkali.

Acyl hydrazides can be alkylated by means of alkyl halides as is disclosed in British Pat. No. 1,003,926 but an alkyl iodide must be used to achieve practical yields of the quaternary compound, and the iodides are costly. It is an important advantage of the present invention that the benzyl and allyl halides employed can be the bromides, and more particularly, the much cheaper chlorides. Thus the amidates according to the invention are potentially cheaper than these prior art compounds.

The anion X, in the amidates of the invention in their cationic form, may be any convenient anion, for example halide (e.g., chloride or bromide), sulfate or methosulphate. Other anions include bisulfate, nitrate, perchlorate, and fluoroborate. Often, the anion is the

anion of a buffering agent with which the amidate is associated in a composition, as described hereinafter.

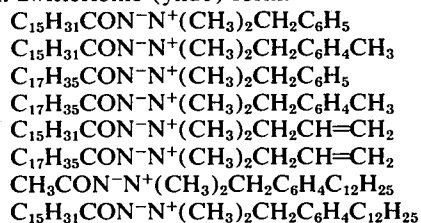
The group R_1 can be an alkyl group of from 1 to 25 carbon atoms. Preferably, the alkyl is either a short-chain alkyl of from 1 to 4 carbon atoms or is a hydrophobic group such as an alkyl of from 9 to 21 carbon atoms. Additionally, R_1 can be an alkaryl group such as an alkylbenzene group where the alkyl has from 8 to 15 carbon atoms. The alkyl benzene group can be derived from detergent alkyl benzenes known in the art. Said alkyl groups can be straight-or branch-chained. Preferably, each of the groups R_2 and R_3 is a methyl or an ethyl group.

The group R_5 is preferably hydrogen, a short-chained alkyl of from 1 to 4 carbon atoms or is a hydrophobic alkyl group having 8 to 15 carbon atoms. In the latter case, again the alkyl benzyl radical constituting R_4 can be derived from a typical detergent alkyl benzene.

The group R_6 is either hydrogen or a lower alkyl group having 1 to 4 carbon atoms, preferably a methyl group. In order that the compounds should be surface-active, at least one of the groups R_1 and R_5 must have at least 6 carbon atoms in the alkyl chain, preferably at least 8, and, particularly when intended for use as textile softeners or hair conditioners, preferably at least 15 carbon atoms.

Compounds of the above formulae deserving special mention are those wherein R_1 is an alkyl group having 10 to 20 carbon atoms and R_5 , if present, is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and R_6 if present is a hydrogen atom; also, those wherein R_1 is an alkyl group having 1 to 4 carbon atoms or an alkyl group having 9 to 21 carbon atoms or an alkyl benzene group having 8 to 15 carbon atoms in the alkyl group and R_5 , if present is an alkyl group having 8 to 15 carbon atoms, and R_6 , if present, is an alkyl group having 1 to 4 carbon atoms.

As suitable compounds, there may be mentioned particularly the compounds having the following formulae, in zwitterionic (ylide) form:



Preferred compounds according to the invention have a pKa value in the range from 5 to 7. The pKa value is the pH at which the compounds are present 50 molar percent in zwitterionic (ylide) form and 50 percent in cationic form. At a pH below the pKa value the compounds are predominantly in cationic form, and at a pH above the pKa value they are predominantly in zwitterionic form. At pH values near the pKa value both forms are present to a considerable extent.

The compositions of the invention can comprise an amidate, as described herein, in its cationic or zwitterionic form together with suitable buffering agents, and may be intended for use in an aqueous liquor of pH less than, equal to, or not more than 2 units higher than the pKa value of the amidate. The pH buffering agent in these compositions is selected to ensure that an aqueous solution of the composition, having a concentration such that 0.1% by weight of said amidate is present, will have a pH in said range. Preferably the pH of the solu-

tion is within 2 units, or more preferably within 1 unit, above or below the pKa value. In solution, the amidate will then be present to a considerable extent in the form of its cationic acid adduct and will be substantive to, and adsorbed upon most surfaces to be treated. In such solutions, the anion of the cationic form of the amidate is often that of the buffering agent. Any effective buffering agent can be used, which is effective at the desired pH, for instance phosphates, polyphosphates, borates, salts of weak organic acids, such as citric, lactic, glycolic, malic, tartaric, acetic, capric, benzoic or adipic, the corresponding glycolic, and mixtures of any of these. Preferred buffering agents are the alkali metal (e.g. sodium and potassium) phosphates, polyphosphates, borates and citrates.

The compositions of the invention can be used to treat surfaces, especially textiles, on any occasion and, in particular they are suitable as rinse additives. Thus they can be added to the rinse liquor after a surface, such as that of a textile fabric, has been washed, to provide the beneficial effects described above. Rinse additive compositions, comprising an ammonioamidate of the invention and a buffering agent effective to provide an aqueous solution of the composition with a pH which ensures the existence of the ammonioamidate in a predominantly cationic and fabric-substantive form, constitute preferred embodiments of the invention.

Suitable rinse additive compositions of the invention are exemplified as follows:

Ingredient	Preferred (% by wt.)	Range (% by wt.)
Ammonioamidate	5.25	1-20
Buffering agent (e.g., glycolic acid)	7	1-20
Emulsifying agent (e.g., Butyl Carbitol)	10	0-15
Water	Balance to 100	Balance to 100

Alternatively, the amidates can form at least part of the active organic detergent of a washing composition or liquor adapted to the washing of textile or other surfaces. A detergent composition, e.g. a conventional heavy-duty laundry detergent, containing an ammonioamidate of the invention will be formulated so that its pH in aqueous solution as used is above the pKa value of the amidate, preferably at least 2 units above it, so that the amidate will be predominantly in Zwitterionic form. Thus, the buffering agent should be such that the pH of a solution of the composition, having a concentration such that there is present 0.1 percent by weight of the said amidate, is at least 1 unit, and preferably at least 2 units, above its pKa value. The amidate will then play its part in the washing action of the detergent composition, and the proportion of it present in the rinse, when dilution with tap water or the like may have reduced the pH to near its pKa value will then be converted to some degree of cationic form and be substantive to the surface being treated. However, the pKa value of these amidates being usually in the range from 5 to 7, often the pH of even a second of third rinse water remains well above the pKa value, owing to the carrying over of alkaline builders from the wash liquor. Accordingly, this method of employing the amidates as detergent-compatible textile softeners and soil release agents would be expected to be less effective than the method of adding them in a rinse or like treatment.

However, it has been found to be more effective than would be expected, and, furthermore, it is often a more convenient method, especially for domestic users.

Generally it is preferred that the amidate, in cationic form, should be present in a treatment solution at a level such as to provide about 0.01 to 5 percent, for example about 0.1 percent, of said cationic form of the amidate, based on the dry weight of a fabric being treated. The concentration of amidate in a treatment solution will depend, for example, on the cloth load, but can suitably be in the range from about 0.001 to 0.5 percent, preferably from about 0.02 to 0.2 percent, by weight of the solution. Correspondingly, the proportion employed in a surface treating composition will depend on the concentration at which it is intended to be used, so as to provide the above concentrations in the working solution. As a guide, an effective composition will contain about 5 percent by weight of the amidate.

The compositions of the invention can contain compatible components commonly included in compositions of the particular type. Thus the "rinse additive" type of compositions can contain inorganic or organic salts (other than those employed as pH buffers), chelating agents, emulsifiers, solvents, coupling agents and the like, provided that they do not displace the pH from the required range. As examples there may be mentioned: sodium sulphate, sodium chloride, and organic acid salts. The detergent compositions can contain watersoluble detergency builder salts such as the inorganic phosphates, polyphosphates, silicates, carbonates or borates, and the organic alkaline sequestrants such as nitrilotriacetates, or polycarboxylates, such as those described in U.S. Pat. No. 3,308,067 (Mar. 7, 1967) including gluconates, polytaconates, and the like. Usually the salts are the sodium salts, but other cations may be used provided that the salts are sufficiently water soluble. Some of the salts can well function both as pH buffers and builders.

In such alkaline detergent compositions, the amidate in zwitterionic form is compatible with all classes of organic detergent including anionic, nonionic and zwitterionic detergents. Most heavy duty built alkaline detergent compositions are based on anionic detergents, either soap or non-soap, and the amidates are compatible with these detergents. In soap compositions, they may act as lime-soap dispersing agents, and for this purpose are generally present at a level of about 10 percent to 20 percent by weight of the soap, but some effect is obtained by as little as 1 percent, and higher levels of up to at least 30 percent can be used. Suitable anionic non-soap detergents include any of those normally used in detergent compositions, such as alkyl benzene sulfonates, alkyl sulfates, alkyl ether sulfates and the like. Anionic surface active agents are preferably avoided in compositions containing the cationic form of the amidates, since they tend to react together to form insoluble substances. However, these insoluble substances if formed on or entrapped in a fabric do have softening properties, and they are soluble in the alkaline condition of a subsequent wash.

Suitable nonionic and zwitterionic detergents include those known in the art. As examples of the nonionics there may be mentioned: polyethylene oxide condensates of long chain fatty acids, fatty alcohols, amines, alkyl phenols and the like, polyethylenimine condensates of fatty acids, amines or amides; polyethoxy-polypropoxy condensates such as the "Pluronic"

(Trade name); and polyethoxy sorbitan esters such as the "Tweens" (Trade name). The zwitterionics include long chain alkyl or alkyl benzyl betaines; sulphobetaines, certain amino acids and the like. Other examples of suitable detergents are provided in U.S. Pat. No. 3,213,030, issued Oct. 19, 1965, lines 53-75 of column 3 lines 1 to 75 of column 4 and lines 1 to 30 of column 5, which disclosure is incorporated herein by reference. Normally, the built detergent compositions of the invention will comprise the ammonioamidate of the invention in an amount of 1 percent to 20 percent, preferably 10 percent to 20 percent, and an admixture of detergent active and builder salt as described above in a ratio of detergent to builder of from about 2:1 to about 1:10 by weight.

The compositions also contain compatible minor ingredients of any of the types commonly used in detergent and softening compositions. These include, for example: perfumes, colors, bactericides, bleaching agents, enzymes, activators or stabilizers for them, foam-enhancing or -suppressing agents, tarnish and corrosion inhibitors, soil-suspending agents and the like.

The compositions of the invention are especially suited to the improvement of the feel or hand of treated textiles and in the treatment of other surfaces. Both on textile and like fibers and on other surfaces, for example hard surfaces, the adsorbed cationic and/or zwitterionic layer provides a surface which tends to repel important classes of soil (or dirt) and to promote their separation from the surface and their dispersion in a subsequent alkaline wash, when the adsorbed layer is rendered non-substantive. These substances can, thus, act as soil-release agents, which are removed to a considerable degree at each wash, and can be reapplied in a rinse or like treatment before the surface is re-exposed to soiling. They also provide anti-static properties for the surfaces treated with them when in their cationic form.

The compositions of the invention have a further benefit, in that they reduce the extent of wrinkling or creasing of fabrics, for instance polyester-cotton fabrics, in the wash, and/or make such wrinkles or creases as are formed more easily removed by ironing. Furthermore, they have a lubricating effect so that there is less frictional resistance to the movement of an iron. Thus the effort of ironing garments treated with these compositions is appreciably lessened.

The compositions are also suitable for treating hard surfaces so as to facilitate cleaning them. By "hard surfaces" are meant principally those exposed to air-borne soiling, such as windows, whether of buildings or of vehicles, motor bodies and metal trim, paintwork, stone or brick work, domestic furniture especially sanitary ware and cookers and the like. The invention is also applicable to crockery, plate and cutlery and the like.

These surfaces often become soiled by air-borne dust, by spray and splashing, for instance on roads or by deposits from smoke and fumes or the like. These soil deposits usually contain grease, as for example, soot, deposits from motor exhaust or cooking fumes. They also often contain clay or like particles for example from wind-borne dust and road spray. Generally, they adhere quite strongly to most surfaces so that the surfaces must be rubbed, preferably in the presence of detergents or wetting agents, in order to clean them. Treatment with the compositions of the invention ren-

ders such surfaces easier to clean, so that if they are sprayed or flushed with water, the adherent soil deposits are mostly carried away without rubbing. Alternatively, surfaces which cannot conveniently be sprayed or flushed with water can be cleaned with a cloth wet with water, with a minimum of rubbing.

The compositions also render the treated surfaces to some degree antistatic, reducing the tendency for dust to adhere to them. They also render windows and like surfaces less liable to condensation of moisture and misting.

The hair treating compositions of this invention include shampoos, and compositions intended to be applied after shampooing, e.g., lotions or rinses. Any effective proportion of the ammonioamidates of this invention can be used in the hair shampooing and conditioning compositions of the invention, together with such conventional components as are desirable to make the product easy to apply and attractive. Usually, shampoo compositions and rinses are liquids intended to be applied in concentrated form to the wetted hair. In such compositions, generally from about 0.01 percent to about 5 percent or more by weight of ammonioamidate is suitable. At a concentration of over about 5 percent, aqueous solutions of the ammonioamidate in nearly neutral solutions which are appropriate for shampoos and the like, may become gelatinous and special precautions or other additives may be necessary to overcome this. As will be understood, quite different proportions would be suitable in compositions intended to be diluted before use.

In addition to the ammonioamidates, the shampoo compositions of this invention can contain organic water-soluble, non-soap, non-cationic surfactants. Cationic surfactants are generally avoided in shampoo compositions because they have little cleaning power on hair and are liable to be harmful to the eyes. The preferred detergents used are anionic detergents of any of the classes which are suitable per se for shampoos such as alkyl sulfate, alkyl ether sulfates, alkyl glyceryl ether sulfonates, sulfosuccinates, and others known in the art containing an alkyl or acyl group having from about 8 to about 18 carbon atoms. These detergents are normally used in the form of their alkali metal, e.g., sodium or potassium, ammonium and substituted ammonium, e.g., triethanolammonium, diethanolammonium and monoethanolammonium salts. The surfactants can be present in the usual concentrations, e.g., from about 5 percent to about 60 percent by weight of the composition, generally from about 20 percent to about 40 percent by weight of the composition in liquid shampoos.

The anionic detergents can be replaced by nonionic, ampholytic, or zwitterionic detergents, or any of these may be present in addition to the anionic detergent. Examples of these detergents may be selected from types known in the art to be suitable for shampoo formulations. Suitable detergents are listed in "Formulation and Function of Cosmetics", J. S. Jellinek, published by Wiley & Sons, 1970, pp. 230-240; and in U.S. Pat. Nos. 3,400,198; 3,580,853; 3,549,542; 3,549,546; 3,313,734; and 3,400,198, said patents being incorporated herein by reference.

The proportion of the ammonioamidates in liquid shampoo compositions can be within the range stated above but is preferably in the upper part of the range, e.g., from about 1 percent to about 3 percent by

weight. It is believed that the ammonioamidates are strongly adsorbed on the keratin of the hair, but that some small degree of desorption may take place during the several rinses to which the hair is subjected after shampooing. The proportion of the ammonioamidate should be high enough to ensure that an effective amount remains on the hair after rinsing.

In addition to a main detergent active compound as referred to above and the ammonioamidate, the shampoo compositions can also contain other ingredients usual in shampoos such as one or more of the following substances: Suds boosters, such as fatty acid amides; emollients, such as lanolin and lecithin; bacteriostats; bactericides; preservatives; dandruff controlling agents such as zinc 2-pyridinethiol-1-oxide; opacifiers, e.g., polyethylene glycol distearate; viscosity controlling agents such as carboxymethylcellulose, alginates, etc.; resins, etc., to impart gloss to the hair; a liquid solvent or dispersing medium, e.g., water, lower alcohol, glycerol, etc.; hormone products; optical brighteners; perfume, colorant matter; etc. Preferred ingredients include bactericides, dandruff control agents, suds boosters and stabilizers, viscosity controllers, opacifiers, preservatives, color, and perfume.

The present invention also includes a method of treating hair which comprises applying thereto a composition as defined above.

The following Examples illustrate the invention:

EXAMPLE I

Ten grams of palmitoyl-N,N-dimethyl hydrazide were heated with 4.2 g. of benzyl chloride for 2 hours at 100°C on a steam bath. The mixture was cooled and the solid obtained was recrystallized from ethanol-ether mixture. Yield: 5.3 g., melting point 107°-108°C. Analysis: C: 71%, H: 11.3%, N: 7.0. Theoretical analysis for $C_{15}H_{31}CONH-N(CH_3)_2CH_2C_6H_5$, Cl^- is C: 70.7%, H: 10.6%, N: 6.6. The pKa value of this compound was 6.1.

EXAMPLE II

Ten grams of palmitoyl-N,N-dimethylhydrazide were refluxed with 10 mls. of allyl chloride for 14 hours. The product was recrystallized from ethanol-ether. Yield: 8 g. Melting point 56°-58°C. Elemental analysis was not carried out. The pKa value of this compound was 6.4

EXAMPLE III

Soil release effect

Test pieces of cotton muslin were washed in a commercial heavy-duty synthetic detergent composition, and half of them (A) were rinsed in water and the other half (B) were rinsed in a solution in water of 0.1 percent by weight of the ylide prepared as in Example I, and 0.036 percent by weight of citric acid. The pH of the latter rinse solution was about 5.5-6. The swatches were stained by immersion in hot, milkless tea, dried and aged at room temperature for 3 days. The swatches were then washed in a miniature washing machine, swatches A and B being washed together in the same vessel in each test. Washing conditions consisted of a three-minute wash in the same synthetic detergent composition as employed above, used at 0.3 percent and 0.5 percent concentration, each at 40°C and 60°C. The washed fabrics were rinsed in water and dried. In every case the test pieces B were clearly visibly whiter than the test pieces A.

Similar results were obtained when the test pieces were of cotton muslin soiled by clay, or polyester-cotton soiled with air-filter dirt or with lanolin/carbon black.

EXAMPLE IV

Textile softening effect

Cotton terry towels were washed under the same conditions as those employed in Example III, and rinsed (A) in water and (B) in the same ylide-citric acid solution. They were then dried. Comparative towels were rinsed in a commercial cationic softener based on ditallowyldimethyl-ammonium chloride. After a single wash and rinse treatment, the softened cloths were similar in feel, and softer than those rinsed in water. After ten washes the cloths washed in the commercial softener had become softer than those washed in the ylide, but had become clearly visibly more yellow and had a greasy feel and had lost absorbency for moisture. The cloths treated with the ylide were softer than those rinsed in water, and remained white and retained their absorbency.

EXAMPLE V

A multi wash and wear test was carried out using an upright-type washing machine (Hoovermatic De Luxe "Twin tub"). The steps of the test were as follows.

A typical mixed laundry load was washed in a conventional alkaline built detergent composition. The load was removed and rinsed, this load playing no further part in the test.

A second mixed laundry load was washed containing new test articles, in the same wash liquor.

Removed, spin dried — 10 seconds.

Rinsed in cold water — 30 seconds.

Spin dried — 10 seconds.

Divided and rinsed in treatment solutions - 30 seconds.

Spin dried — 10 seconds.

Dried in open air.

The test articles were then worn or used (as appropriate) and treated in the same way again, groups of test articles receiving the same rinse treatment at each repeat.

Main wash conditions were:

Detergent composition used — "Daz" (Procter & Gamble Ltd.)

Concentration was 0.25% in 18° Hard water.

Liquor quantity 8 Imperial Gallons (80 lbs.).

Temperature 48°C.

pH of liquor 9-10.

Rinse conditions were:

Cold tap water 4 gallons 12° Hard.

Softener Active/cloth ratio 0.18/100 by weight.

Product concentration 0.36% by weight (treatment (b) and (c)).

Rinse Compositions

(a) Tap water.
Rinsing liquor pH:
7.5-8.

(b) Composition comprising
 $CH_2=CH_2$

5% $C_{15}H_{31}CO-N^+(CH_3)_2-$
3% Citric acid.
2% Trisodium citrate.
90% Water.

Rinsing liquor pH: 5.5-6.5

(c) Composition comprising:

5% Ditallowyldimethyl-
ammonium chloride.

-Continued
95% Water.

Rinsing liquor pH: 7.6-8.2.

Test Articles

1. Cotton, unresinated, white T-vests.
2. Polyester/cotton white shirts.
3. White cotton terry towels.

The shirts and vests were worn for 1 working day between washes.

The towels were used for 1 week between washes.

The treated test articles (three replicates) were evaluated by paired comparison tests by four judges, each judge scoring on a 9 point Scheffe scale, for whiteness preference and for softness preference.

Cotton Vests

From first to 8th cycle those rinsed by (b) and (c) were significantly softer than those water rinsed as under (a), but no difference between (b) and (c) was distinguished with 95 percent confidence in the test; from the 4th cycle onwards, those rinsed by (b) were significantly whiter than those rinsed by (c).

Ratings (9 point Scheffe scale after the eighth cycle) were:

	Whiteness Preference	Softness
(a) Water rinse	+ 0.19	- 0.71
(b) Ylide rinse	+ 1.14	+ 0.08
(c) Cationic rinse	- 1.32	+ 0.64
Least significant difference (95% confidence)	1.80	0.70

Polyester/cotton Shirts

Those rinsed by (b) were significantly whiter than those rinsed by (c), and as white as if water rinsed.

Ratings after the eighth cycle were:

	Whiteness Preference
(a) Water rinse	+ 0.67
(b) Ylide rinse	+ 0.50
(c) Cationic rinse	- 1.16
Least significant difference (95% confidence)	0.75

Softening was not measured on these articles, being deemed to be of little practical importance on shirts of this type.

Cotton terry towels

From first to eighth cycle those rinsed by (b) and (c) were significantly softer than those rinsed by water (a), but no difference between (b) and (c) was distinguished with 95 percent confidence in the test.

Ratings after the fifth cycle were

	Softness
(a) Water rinse	- 1.05
(b) Ylide rinse	0.25
(c) Cationic rinse	0.81
Least significant difference (95% confidence)	1.2

The towels treated by (b) were judged according to the mean ratings to be whiter than those treated by (c) but the difference was not distinguished with 95 percent confidence above the random error of the test.

EXAMPLE VI

Twelve pieces of cotton terry towelling were boiled in a 0.5 percent solution of an anionic detergent-based commercial heavy duty household washing composition for 4 minutes, rinsed in tap water, spin- and then tumble-dried. The pieces were divided into three groups of four.

The first set was rinsed in 10 times their dry weight of cold tap water.

The second and third sets were each rinsed in 10 times their dry weight of cold tap water containing 0.05 percent by weight of, respectively, the compound (i) $C_{15}H_{31}CO NH N(CH_3)_2 CH_2 CH=CH-CH_3$, Br and the compound (ii) $C_{21}H_{42}CO NH N(CH_3)_2 CH-CH=CH_2$, Cl.

In each case the pH of the rinse solution was adjusted to 6 by addition of citric acid.

The test pieces were then spin-dried, and air-dried at room temperature. Their softness was evaluated by a panel of four judges using a Scheffe paired comparison technique.

	Scheffe Scale Score
Water rinse	- 1.45 ± 0.3
Compound (i)	+ 0.48 ± 0.3
Compound (ii)	+ 0.98 ± 0.3

The ± values represent 95% confidence limits.

EXAMPLE VII

Antistatic Effect

A sample of polyacrylonitrile fabric was washed in a conventional built anionic detergent composition in a washing machine, employing a 0.5% concentration by weight of detergent composition, rinsed with water and spin-dried in the machine. The sample was then divided into three parts A, B and C.

Part A was rinsed in tap water, the cloth to water ratio by weight being 1:10, at room temperature.

Part B was rinsed at the same temperature in the same amount of tap water to which had been added 0.2 percent by weight of a 5 percent by weight aqueous solution of ditallowyl dimethyl ammonium chloride.

Part C was rinsed as Part B but there was added, instead of the ditallowyl dimethyl ammonium chloride, 0.2 percent by weight of an aqueous solution of the compound $C_{15}H_{31}CO N^- N^+ (CH_3)_2 CH_2 CH=CH_2$ containing 5 percent of said compound and 5 percent of a sodium citrate/citric acid mixture, such that the pH of said rinse liquor was 6.

The test fabrics were then dried but not ironed.

The samples were then tested. Each sample was held in one hand by an operator and rubbed with a nylon rod held in the other hand. The fabric, after a given number of rubs, was contacted with a gold leaf electroscope.

Sample A gave a full scale deflection (over 5 divisions) after 5 rubs.

Sample B gave a deflection of 1-2 divisions after 20-35 rubs.

Sample C gave nil deflection after 35 rubs.

Thus the ammonioamidate demonstrated better antistatic properties than the cationic softener, and much better antistatic properties than given by simple water rinsing.

EXAMPLE VIII

Antistatic Effect

Four swatches each of Nylon Courtelle (Trade name) polyacrylonitrile fabric were washed in a hot 0.5 percent solution of an anionic detergent-based commercial heavy duty household washing composition for 4 minutes, rinsed, spin-dried and tumble-dried. The swatches were then rinsed in 10 times their dry weight of water, for reference, or in a 0.05 percent solution of an ammonioamidate as indicated below. In each case, the pH of the solution was adjusted by addition of citric acid to 6.0. The swatches were spin-dried and air dried at room temperature. They were then rubbed 10 times on a nylon rod, and the charge in the rod was determined by the deflection of a Gold Leaf Electroscope. Two readings were taken for each of the four cloths and the means and standard deviations calculated, and the latter converted to 95 percent confidence limits.

The following compounds were tested (written in ylide form)

- (a) $C_{15}H_{31}CON^{-}N^{+}(CH_3)_2CH_2CH=CH_2$ having pKa value 5.5
 (b) $CH_3CON^{-}N^{+}(CH_3)_2CH_2C_6H_4C_{12}H_{25}$ " 5.8
 (c) $C_{15}H_{31}CON^{-}N^{+}(CH_3)_2CH_2CH=CHCH_3$ " 5.3
 (d) $C_{21}H_{43}CON^{-}N^{+}(CH_3)_2CH_2CH=CH_2$ " 6.1

The values obtained were:

	Deflection of Electroscope	
	Courtelle Cloth	Nylon Cloth
Water	5.00 ± 1.07	2.13 ± 1.81
Ylide a	3.25 ± 0.46	0.63 ± 0.74
Ylide b	2.50 ± 0.53	0.0
Ylide c	3.75 ± 0.71	0.25 ± 0.46
Ylide d	1.25 ± 0.46	0.88 ± 0.83

These compounds all appeared to have an antistatic effect, though in some cases the test did not demonstrate the effect with 95 percent confidence.

EXAMPLE IX

Soil Release Effect on Hard Surfaces

A number of pieces of window glass were pretreated as follows:

- Cleaned with a commercial window cleaning product.
- Washed with a 5 percent by weight aqueous solution of the compound of formula: $(C_{15}H_{31}CO NH N(CH_3)_2-CH_2CH=CH_2)^+ Cl^-$ the solution being adjusted to pH=6 by addition of a suitable pH buffering compound. This compound had a pK value of 5.8.
- Washed as in (b) but adjusted to pH=7.

The glasses were dried and then stained by impression of a greasy hand ("greased" by a commercial hand cream). The stain was rendered more visible by dusting it lightly with charcoal dust.

Stained glasses from (b) and (c) were then gently sprayed with tap water adjusted, in one test to 2 pH units lower than that of the original solution applied in the pretreatments, and in a second test, with tap water adjusted to 2 pH units higher than the original solution applied. The glasses pretreated as in (a) were sprayed similarly.

It was found that more stain was removed from the glasses pretreated as in (b) or (c) when sprayed with the more alkaline tap water of the second test, than from these glasses when sprayed with less alkaline water of the first test, or than from glasses pretreated as in (a).

EXAMPLE X

In a similar test to that described in Example IX, pieces of glass were pretreated: (d) with aqueous solutions containing 2½ percent of said compound and 2½ percent of dodecyl dimethyl ammonium propane sulphate, a typical zwitterionic surfactant, and (e) with a 5 percent solution of said zwitterionic alone.

When washed as in Example IX with water adjusted to 2 pH units higher than the original solution applied, the stain was largely removed from glasses pretreated as (d), but almost unaffected on glasses pretreated as (e).

EXAMPLE XI

Lime Soap Dispersion

A solution of each of the mixtures defined below was prepared, placed in a water bath to maintain its temperature at 60°C and nitrogen was bubbled through the solution at a fixed rate. The foam produced was carried over for a set time into a vessel containing very hard water (2300 ppm as Ca CO₃), wherein the foam was quenched. The water was filtered through a 200 mesh BSS sieve, and the flocculated lime soaps determined after drying by weighing.

The test solutions each contained 0.5% by weight of the compositions given below, and the weights of undispersed lime soap (flocculated) were as indicated:

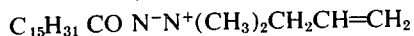
	D	E	F	G
$C_{15}H_{31}CO N^{-}N^{+}(CH_3)_2CH_2CH=CH_2$	—	15	10	5
Sodium coconut soap	100	85	90	95
Floc (grams)	0.134	0.003	0.015	0.045

EXAMPLE XII

Pieces of cotton terry towelling were given a 10 minute wash at 50°C in solutions as indicated below in 18° hard water. They were then squeezed out, given two one-minute rinses in cold water (18° Hard), squeezed and dried in the open air. Their softness was then evaluated by a paired comparison method by a panel of six ladies. Numerical values for softness and the least significant difference (at 95 percent confidence limit based upon the variability of the judgements of the effect of the same treatment), are given below, after one cycle and after 5 cycles of the wash-rinse test.

Compositions of wash liquors were:

- Conventional heavy duty detergent 0.55 percent
- The same with addition of 0.08 percent of the compound



The pH of the wash solutions was 9.7

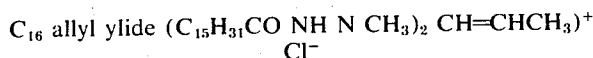
	A	B
Softness results were:		
1 wash	-0.9	+0.91
Least significant difference	0.7	
5 washes	-0.37	+1.0
Least significant difference	1.1	

EXAMPLE XIII

Six swatches of human hair were given a standard preliminary wash in an unbuilt detergent composition based on mixed sodium alkyl benzene sulfonate and sodium alkyl ether sulfate active detergents. The treatment comprised a wash, water rinse, second wash and rinse followed by air drying. The swatches were then treated as follows:

- i. Six swatches were wetted for 5 seconds in running (10 litre/minute) 2°H. water at 40°C (105°F).
- ii. Each swatch was lathered by hand in commercial shampoo (2 ml).
- iii. Each swatch was rinsed for 15 seconds in 2°H. running water (10 litre/minute) at 40°C. (105°F).
- iv. Repeat of (ii).
- v. Three of the swatches were rinsed in water as in (iii).
- vi. The other three swatches were rinsed for 15 seconds in 0.02 percent solution (1 litre) of ammonioamidate, buffered with sodium citrate/citric acid to pH 6.5, the proportions of amidate, citrate and citric acid being 5:2:3 by weight).
- vii. Each swatch was air-dried.

Ammonioamidate Used



Results

The gloss and softness of the treated swatches were evaluated by a panel of ladies using a paired comparison technique. The results are given below in panel score units (psu), with confidence limits based upon the variability of judgements of the same comparisons.

	Gloss	Softness
Water rinse	-0.62	-0.21
treatment mean	psu	psu
Ammonioamidate rinse	+0.63	+0.22
treatment mean	psu	psu
Difference in treatment mean	1.25	0.43
	psu	psu
95% confidence interval	1.04	0.41
	psu	psu

Commercial Shampoo Formulation

Triethanolamine alkyl sulfate	55%
Triethanolamine	2
Coconut monoethanolamide	4
Water and miscellaneous	39
	100%

EXAMPLE XIV

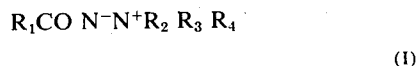
When in the above examples the following ammonioamidates are substituted either wholly or in part, e.g., 1:1 ratios, for the specifically named ammonioamidates, being added in the zwitterionic or cationic (chloride, bromide, phosphate, citrate, etc.) form as is appropriate, substantially equivalent results are obtained in that the surfaces are conditioned:

- 10 $C_{17}H_{35}CON^{-}N^{+}(CH_3)_2-CH_2C_6H_4C_4H_9$;
- $C_{17}H_{35}CON^{-}N^{+}(CH_3)_2-CH_2CH=CHC_6H_{13}$;
- $CH_3CON^{-}N^{+}(CH_3)_2CH_2CH=CHC_{15}H_{31}$;
- $C_{12}H_{25}C_6H_4CON^{-}N^{+}(CH_3)_2-CH_2C_6H_5$;
- $C_{19}H_{39}CON^{-}N^{+}[C_2H_4(OH)]_2-CH_2C_6H_5$;
- 15 $C_{17}H_{35}CON^{-}N^{+}(C_2H_5)_2C_6H_5$;
- $C_{17}H_{35}CON^{-}N^{+}[CH_2(OH)]_2CH=CHC_{17}H_{35}$;
- $C_2H_5CON^{-}N^{+}(CH_3)_2C_6H_4C_{12}H_{25}$;
- $C_2H_5CON^{-}N^{+}(CH_3)_2CH_2-CH=CHC_{18}H_{37}$;
- $C_{17}H_{35}CON^{-}N^{+}(C_2H_4CN)_2CH_2CH=CH_2$;
- 20 $C_{15}H_{31}CON^{-}N^{+}(CH_3)_2CH_2C_6H_5$;
- $C_{15}H_{31}CON^{-}N^{+}(CH_3)_2CH_2C_6H_4CH_3$;
- $C_{17}H_{35}CON^{-}N^{+}(CH_3)_2CH_2C_6H_5$;
- $C_{17}H_{35}CON^{-}N^{+}(CH_3)_2CH_2C_6H_4CH_3$;
- $C_{15}H_{31}CON^{-}N^{+}(CH_3)_2CH_2CH=CH_2$;
- 25 $C_{17}H_{35}CON^{-}N^{+}(CH_3)_2CH_2CH=CH_2$;
- $CH_3CON^{-}N^{+}(CH_3)_2CH_2C_6H_4C_{12}H_{25}$; and
- $C_{15}H_{31}CON^{-}N^{+}(CH_3)_2CH_2C_6H_4C_{12}H_{25}$.

What is claimed is:

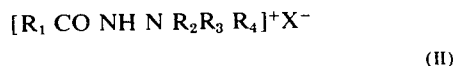
1. A surface-treating composition consisting essentially of:

a. a substituted ammonioamidate having the formula



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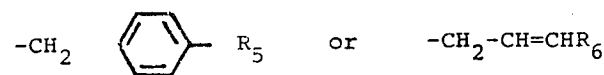
or a cationic adduct thereof having the formula



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wherein X is an anion; R_1 is an alkyl, phenyl, or alkaryl group having 1 to 25 carbon atoms; each of R_2 and R_3 is a methyl, ethyl, hydroxyethyl or cyanoethyl group; and R_4 is either

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wherein R_5 is hydrogen or alkyl of from 1 to 18 carbon atoms and R_6 is hydrogen or an alkyl group having 1 to 4 carbon atoms; at least one of R_1 and R_5 having an alkyl chain of at least 6 carbon atoms; and

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b. a pH buffering compound selected from the group consisting of:

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- i. the alkali metal salts and acid salts of phosphoric acid, the polyphosphoric acids, boric acid, and;
- ii. the acids and corresponding alkali metal salts of citric acid, lactic acid, glycolic acid, malic acid, tartaric acid, acetic acid, capric acid, benzoic acid, and adipic acid;

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or mixtures thereof in an amount sufficient to substantially maintain the pH of a solution containing component (a) at a level of from about 0.001 percent to about 0.5 percent by weight at less than, equal to, or not greater than 2 pH units above the pKa of component (a).

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2. The composition of claim 1 containing one or more non-cationic, nonsoap surface-active agents.

3. The composition of claim 1 wherein X is a halide or a methosulphate.

4. The composition of claim 3 wherein each R₂ and R₃ is methyl or ethyl.

5. The composition of claim 4 wherein R₁ is an alkyl of from 1 to 4 carbon atoms, an alkyl of from 9 to 21 carbon atoms or an alkyl benzene group having from 8 to 15 carbon atoms in the alkyl group.

6. The composition of claim 5 wherein R₄ is



and R₅ is hydrogen, an alkyl of from 1 to 4 carbon atoms or an alkyl of from 8 to 15 carbon atoms.

7. The composition of claim 3 wherein R₅ is -CH₂-CH=CHR₆ and R₆ is hydrogen or methyl.

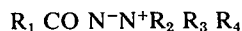
8. The composition of claim 1 wherein the pKa value of the ammonioamidate is in the range of from 5 to 7.

9. The composition of claim 8 wherein the pH of the aqueous solution ranges from 2 units below to 2 units above the pKa value.

10. The composition of claim 9 wherein said buffering agent is a water-soluble buffering agent selected from the group consisting of citrates and borates, the corresponding acids and mixtures thereof.

11. A fabric softening composition consisting essentially of:

a. a substituted ammonioamidate having the formula



(I)

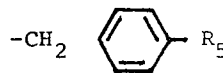
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or a cationic adduct thereof having the formula



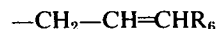
(II)

wherein X is an anion; R₁ is an alkyl, phenyl, or alkaryl group having 1 to 25 carbon atoms; each of R₂ and R₃ is a methyl, ethyl, hydroxyethyl or cyanoethyl group; and R₄ is either



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or



wherein R₅ is hydrogen or alkyl of from 1 to 18 carbon atoms and R₆ is hydrogen or an alkyl group having 1 to 4 carbon atoms; at least one of R₁ and R₅ having an alkyl chain of at least 6 carbon atoms, said compound having a pKa value of from about 5 to about 7; and

b. a pH buffering compound selected from the group consisting of the acids and corresponding alkali metal salts of citric acid, lactic acid, glycolic acid, malic acid, tartaric acid, acetic acid, capric acid, benzoic acid, and adipic acid;

or mixtures thereof wherein the buffering compound is present in amount sufficient to maintain the pH of a solution containing component (a) at a level of from about 0.02 percent to about 0.2 percent by weight at less than, equal to, or not greater than 2 pH units above the pKa of component (a).

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