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NOVEL AMMONIOPHENOLATE COMPOUNDS

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Int. Cl. C07c *87/28;* D06m *13/46*
U.S. Cl. 252—8.8 3 Claims

ABSTRACT OF THE DISCLOSURE

Novel surface-active compounds able to exist in either cationic or zwitterionic form and to compositions containing them. The compounds are effective as textile softening agents substantive to fabrics at the ordinary pH of fabric rinsing operation and removable from fabrics in a zwitterionic form under succeeding alkaline washing conditions.

This invention relates to novel surface-active compounds able to exist in either cationic or zwitterionic form and to compositions containing them.

Quaternary ammonium compounds having at least one long chain (about C_8 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 about 12 to 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 with two long chain groups. Typical examples include dodecyldimethyl benzyl ammonium chloride, dodecyltrimethyl 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, but also has the effect that they generally are not completely washed out of the fabric in a succeeding wash. They therefore tend to build up on repeatedly washed fabrics, where they may impair the re-wetting properties of the fabrics, and where they tend to cause discoloration, fiber snagging, and even undesirable odors.

Other quaternary ammonium compounds constitute the known zwitterionic surface-active compounds, such as long chain carboxylic betaines, sulpho-betaines, sulphato- and sulphito betaines. These compounds are valuable wetting agents and detergents. Being internal salts, they 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,

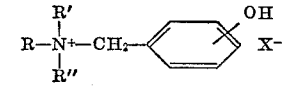
they are not very effective textile softening agents. These known betaine and betaine-like compounds exist in zwitterionic form over a wide range of pH. In relatively strongly acid conditions they do become cationic, but the necessary acidity is outside the practical range for washing fabrics or the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

The present invention is based on the discovery of a novel class of detergents 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, they are in cationic form and are effective as textile softening agents substantive to fabrics. Under the ordinarily alkaline conditions of a succeeding 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. Furthermore, these compounds, which rely upon the acidity of a phenol in the molecule for their zwitterionic property, have two potentially bactericidal functions, namely the phenol and the quaternary ammonium function, and may be strongly bactericidal. They may also impart antistatic properties to fabrics treated with them.

SUMMARY OF THE INVENTION

According to the invention, there is provided novel surface-active compounds having the formula either

(i)



or

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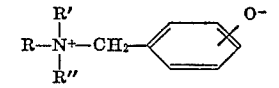

wherein R represents an aliphatic, e.g. alkyl, group of from 6 to 26 carbon atoms, or alkylaryl, e.g. alkylphenyl, group having an alkyl group of from 6 to 26 carbon atoms; R′ represents an alkyl or alkoxy group having from 1 to from 5 carbon atoms, a phenyl or substituted-phenyl group or an R group as hereinbefore defined; R″ represents an alkyl or alkoxy group having from 1 to 5 carbon atoms, a phenyl or substituted-phenyl group; and X^- is a water-soluble anion. The indicated phenyl radical can be further substituted by one or more non-acidic groups.

In its composition aspect, the present invention provides textile softening compositions and detergent compositions comprising a surface-active compound of the formula

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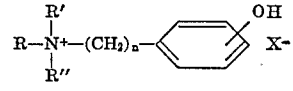

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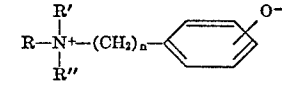
(ii)



where R, R′, R″, and X have the meanings defined hereinbefore and where n is zero or one. The indicated phenyl of the phenolic moiety can be further substituted by one or more non-acidic groups provided that when n is one it is not further substituted by halogen only.

In its process or method aspect, the present invention provides a process of preparing the surface-active compounds described hereinbefore and a method of treating fabric materials whereby the fabrics are improved in softness without undesirable build-up with succeeding washing treatments comprising the steps of treating the fabrics with a solution of a cationic compound described hereinbefore

thereby to improve softness and, thereafter, washing the fabrics under alkaline conditions thereby to remove the softener in a zwitterionic form.

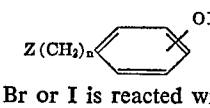
DETAILED DESCRIPTION OF THE INVENTION

When the compounds of the invention contain a single long chain radical, it is preferred that they contain from 16 to 24 carbon atoms in the alkyl chain; if they contain two long chain groups, the groups need not be the same but each has preferably from 12 to 18 carbon atoms. The long chain groups are preferably alkyl groups, or they can be alkylaryl groups, for example C_9- to C_{16}-alkyl benzyl or C_9–C_{16}-alkylphenyl groups derived from typical detergent alkylates, for example alkyl benzenes. The alkyl groups can contain substituents or interrupting atoms or groups. The short chain group R′ is preferably methyl, ethyl, hydroxyethyl or cyanomethyl. The phenolic nucleus can be substituted by one or more other nonacidic groups such as lower-alkyl, lower alkoxy, nitro, amino, amido, keto, cyano, and the like. When there is no $—CH_2—$ group between the phenol and the quaternary nitrogen, i.e. when *n* is zero, or when there is another substituent (other than the phenolic hydroxide), one or more halogen substituents can be present. The choice of substituents, or their absence, may provide various advantages. For example, it may permit control of the solubility of the compounds and of the exact pH at which the compounds change from cationic to zwitterionic form, and thus their special suitability for particular applications, as for instance for softening particular classes of fabrics.

The anion X may be any water-soluble anion which is convenient. The most usual anions, especially in detergent, softening and like compositions, are halides, especially chloride or bromide, sulphate or metho-sulphate. Some others suitable, generally for other purposes, include bisulphate, nitrate, perchlorate, and fluoroborate.

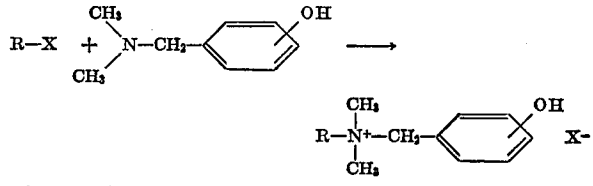
The compounds of the invention preferably have a pKa value in the range of from 10 to 5. If intended to be employed in a detergent composition as described below, the pKa value is preferably in the range from 9.5 to 7.5; if intended to be used in a rinse additive, particularly where pH buffers are incorporated, the preferred range is from about 8 to about 5, for example 8.5 to 5. In each case, the optimum pKa value will depend to some extent upon the intended application. The pKa of a weak acid, such as the present compounds, in aqueous solution is the pH of the solution when the compound is half neutralized, i.e. in the present instance, when it is 50 molar percent in zwitterionic form and 50 molar percent in cationic form.

The compounds of the invention can be prepared by any convenient method, for example, by the reaction of an appropriate halide with an appropriate amine. Thus, the compounds can be prepared in accordance with a method wherein a halide of the formula



wherein Z is Cl, Br or I is reacted with an amine of the formula RNR′R″. R, R′, and R″ and *n* have the definitions set forth hereinbefore. The phenyl group of the phenolic moiety can be optionally substituted as described hereinbefore.

The compounds of the invention can be prepared by reaction of a long-chain alkyl halide with dimethylbenzylaminophenol according to the following scheme:



where R is a long-chain alkyl group and X is halogen.

Ordinarily, the compounds of the invention are applied to fabrics from an aqueous solution, and conveniently at some stage in a washing process. Thus they can be incorporated in compositions intended to be used as rinse additives having textile softening properties and often also bactericidal properties. For this purpose, a compound which is in cationic form at the pH of the rinse is chosen, or optionally the composition contains a pH buffer so that the pH of the rinse is maintained at a sufficiently low level to ensure that the compound present is in cationic form.

Alternatively the compounds, in zwitterionic form, can form part of the active detergent in a washing composition, formulated so that they are in zwitterionic form during the washing step. The proportion of the compound still present in the rinse, when dilution with tap water, or the like, has reduced the alkalinity, is then available in cationic form to act as fabric softener.

When employed as fabric softeners, it is preferred that the compounds of the invention should be present in the rinse water, having a pH at which they are in cationic form suitably at a level to provide about 0.01 to 0.5% of the said compound by dry weight of the fabric being treated.

The compounds can also be employed in bactericidal and disinfectant compositions and in compositions for rendering fabrics anti-static.

These compositions can contain, in addition to the compounds of the invention, other compatible components usually present in such compositions. Thus, textile softening rinse additives can contain other textile softening agents, such as certain polyalkoxy nonionic detergents or long chain tertiary amine oxides; pH buffering compounds such as acid phosphates, phosphoric acid, borates, citric acid, and the like; other bactericides; optical brighteners, dyes, perfume, and the like.

The detergent compositions ordinarily contain alkaline-reacting salts, for example the alkali metal phosphates, polyphosphates, carbonates, silicates, and the organic alkaline sequestering agents, for example the aminopolycarboxylates, such as trisodium nitrilotriacetate and the like. These salts serve as detergency builders, and provide the desirable alkaline reaction when the composition is dissolved in water. Other compatible organic detergents can be employed and these may be members of any of the following classes: soap or non-soap anionic, nonionic, zwitterionic or cationic. Suitable anionic detergents include alkali metal soaps, alkali metal and ammonium alkyl-aryl sulphonates, alkylsulphates, alkyl ether sulphates; suitable nonionic detergents include the polyethylene oxide condensates on long chain (C_8–C_{20}) alcohols, alkyl phenols (alkyl C_6–C_{16}), long chain fatty acids, fatty acylamides and polyethylene oxide—polypropylene oxide condensates and others; tertiary amine oxides and phosphine oxides may be included in this class; suitable zwitterionic detergents include the known betaines, sulpho-betaines and the like, for instance dodecyl dimethyl ammonio propionate, hexadecyl dimethyl ammonio propane sulphonate and dodecyl benzyl dimethyl ammonio propane sulphonate; suitable cationic detergents include compounds such as cetyl pyridinium chloride, dodecyl trimethyl ammonium chloride, and many others. The usual other components of detergent compositions can also be present, such as neutral salts, for example sodium sulphate, sodium chloride; enzymes, especially proteases, amylases or lipases; bleaching agents; stabilizers or activators for the enzymes or the bleaching agents; dust reducing substances; soil suspending agents and like, such as carboxymethyl cellulose, polymers of methylvinylether and maleic anhydride; foam enhancing or limiting agents; optical brighteners, dyes, and perfumes.

The following example illustrates the invention:

EXAMPLE 1

The preparation of a structurally typical compound of the invention is described. This compound, which is yellow

when alkaline, would not normally be suitable in a commercial washing product, but conveniently demonstrates the preparation and some properties of the compounds of the invention.

2-hydroxy-5 nitro benzyl dimethyl octadecyl ammonium chloride was prepared by reacting 1 mole of 2-hydroxy-5-nitro-benzyl chloride with 1 mole of N,N-dimethyl octadecyl amine in acetone. This quaternary ammonium chloride (cationic) was converted to the corresponding zwitterion by elution in methanol through a monobed ion exchange resin. This compound was found to have pKa value 6.1.

0.1% by weight solutions were made up of this zwitterionic compound

(a) in dilute acid, pH 3–4, giving a colorless solution;
(b) in dilute alkali, pH 9–10, giving a yellow solution.

A swatch of cotton terry towelling was dipped in solution (a), rinsed thoroughly in distilled water (pH 6.5). It was then dipped into N/10 caustic soda solution. The cloth turned yellow, indicating that the acid stable form of the compound had been substantive to the fabric. The stained swatch was then washed in a typical built detergent composition containing no chemical bleaching agent, pH about 9, and was decolorized, the yellow color of the alkali-stable form of the compound being visible in the used detergent solution.

Another similar swatch, dipped in the yellow alkaline solution of the compound, lost its yellow color when rinsed in tap water, and remained colorless when it was then dipped in N/10 caustic soda solution, indicating that the alkali stable form of the compound was not substantive to the fabric.

EXAMPLE 2

2.8 g. of p-dodecylmethylaminophenol, 4 mls. of methyliodide, and 0.53 g. of sodium carbonate were heated under reflux in 100 ml. of methanol for 2 hours. The solvent was evaporated and the product isolated by extraction with chloroform, followed by trituration with ethylether. The yield was 2 g. of p-(dodecyl dimethyl ammonio) phenolate. Melting point was 114°–115° C. Analysis: found, C=55.5%; H=8.6%; N=3.3%; theoretical amount, C=55.4%; H=8.3%; N=3.2%. The pKa value was 8.3.

The meta-isomer was made by a similar process. The meta-isomer had a pKa=8.1.

Similar methods starting with the corresponding p-octadecyl-aminophenol gave the p-(octadecyldimethyl ammonio) phenolate (pKa 8.3) and starting with p-di-dodecyl amino phenol, gave the p(didodecylmethyl ammonio) phenolate (pKa=8.7).

Terry towelling test pieces were given a preliminary wash for 5 minutes at 60° C. in a 0.5% solution of a typical conventional heavy duty household detergent, rinsed in tap water (pH 6.5), and dried. 22 g. of these pieces were then steeped in 500 mls. of a 0.20% by weight solution of the octadecyl compound prepared as described above. The pH of the solution was buffered to 7. They were then rinsed in tap water and dried. Half of these pieces were washed again as in the preliminary wash, rinsed, and dried.

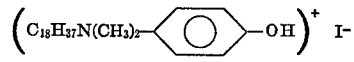
The test pieces after steeping were softer to feel than those which had only received the preliminary wash and than those re-washed.

EXAMPLE 3

Solutions were prepared containing:

(a) Tap water pH 6.5.

(b) A 1% by weight solution of the compound having the formula:



the solution having a pH adjusted to 6. The pKa value of this compound is 8.3.

Cotton muslin swatches were pre-washed in 0.5% solution of a conventional heavy duty synthetic detergent composition at 60° C. for 5 minutes, and then rinsed. The swatches were then divided into two groups, and each group was soaked in one of the above solutions, rinsed in tap water, and dried. All the swatches were then soiled uniformly with a mixture of carbon black and mineral oil, which was rubbed into the fabric. They were then washed in a 0.5% solution of the same heavy duty synthetic detergent composition with pH adjusted to 11.5. The washing procedure consisted of 5 minutes stirring at 80°–100° C., 30 seconds gentle rubbing by hand, followed by 1 minute gentle stirring again.

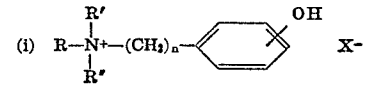
Swatches treated in solution (b) were visibly cleaner than those treated in solution (a) (tap water).

EXAMPLE 4

A detergent composition was prepared comprising 95 parts by weight of a typical heavy duty household detergent and 5 parts of the phenolate compound of Example 3. Terry towelling test pieces were washed in a 0.5% by weight solution of this composition at 68° C. for 5 minutes, and rinsed with tap water (pH 6.5). Comparative test pieces were washed in the same detergent composition (100 parts) omitting the phenolate compound. The test pieces washed in the former composition were softer to feel than the comparative pieces.

What is claimed is:

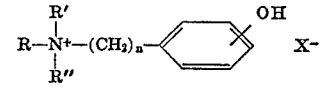
1. A textile softening composition for application in a rinsing step following a washing operation, consisting essentially of a compound having the formula



where R represents an alkyl group of from 6 to 26 carbon atoms, an alkylphenyl group having an alkyl of from 6 to 26 carbon atoms, or an alkylbenzyl group having an alkyl of from 6 to 26 carbon atoms; R′ represents an alkyl group having from 1 to 5 carbon atoms, or an R group as defined herein; R″ represents an alkyl group having from 1 to 5 carbon atoms; and X^- is a water-soluble anion; n is zero or one; the phenyl of the phenolic moiety being optionally substituted by one or more non-acidic groups selected from the group consisting of an alkyl radical with 1 to 6 carbon atoms, an alkoxy radical with 1 to 6 carbon atoms, the nitro radical, the amino radical and the cyano radical, said compound being present in an amount sufficient to provide 0.01% to 0.5% of said compound by dry weight of the fabric being treated; and a buffering agent selected from the group consisting of such that said compound is in cationic form at the pH of the rinsing operation.

2. The textile softening composition of claim 1 where R is an alkyl group with an average of 10 to 20 carbon atoms, R′ and R″ are methyl or ethyl, and X^- is a halide.

3. The textile softening composition of claim 1 wherein the compound having the formula



has a pKa value below 8 and the buffering agent provides a pH between 5 and 8 when said composition is present in an amount sufficient to provide 0.01% to 0.5% of said compound by dry weight of the fabric being treated.

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HERBERT B. GUYNN, Primary Examiner

U.S. Cl. X.R.

117—139.5 CQ; 252—528, 547; 260—567.5

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,809,646 Dated May 7, 1974

Inventor(s) Thomas William Matches Spence

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 56 "0.20%" should read --0.02%--

In the Claims - Claim 1., Column 6, line 56 "such that said compound is in cationic form at the pH of the rinsing operation." should read --acid phosphates, phosphoric acid, borates and citric acid such that said compound is in cationic form at the pH of the rinsing operation.--

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

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