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3,704,320

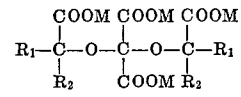
DETERGENT FORMULATIONS

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Int. Cl. C11d 1/38, 1/12
U.S. Cl. 252—546 6 Claims

ABSTRACT OF THE DISCLOSURE

Compounds having the formula



wherein M is an alkali metal or ammonium and R_1 and R_2 are hydrogen or methyl in combination with surfactants provide effective detergent formulations.

BACKGROUND OF THE INVENTION

This invention relates to novel detergent formulations characterized by novel detergency builder ingredients.

Numerous materials are known which, by virtue of sequestering characteristics and/or capability to enhance the cleansing ability of detergent formulations in combination with various surfactants are useful in water treating applications, or as adjuvants, re-enforcers, supplements, augmentors, potentiators, and/or benefactors in detergent formulations wherein such materials are usually referred to as detergency builders. It is noted that although many detergency builders are also sequestrants, the determination of materials which are effective detergency builders is a complex matter empirical in nature and not accurately predictable from known characteristics of the materials.

Many materials of the foregoing type are characterized by high phosphorous content such as the alkali metal tripolyphosphates widely employed as detergency builders. It has recently been suggested by some researchers that such compounds may contribute to the acceleration of eutrophication processes. Accordingly, particularly in the detergent builder field, extensive efforts have been exerted to provide alternate functional compounds free of phosphorus.

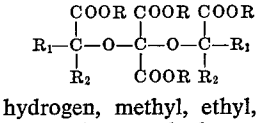
SUMMARY OF THE INVENTION

It is an object of this invention to provide novel detergent formulations characterized by new and effective detergency builders.

The novel formulations of this invention will be understood from the following description of the preferred embodiments.

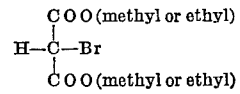
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The detergent formulations of this invention utilize, as detergency builders, the salt forms of novel compounds represented by the formula

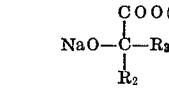


wherein R is hydrogen, methyl, ethyl, alkali metal or ammonium and R_1 and R_2 are hydrogen or methyl.

The compounds are readily prepared reacting the appropriate alkyl bromomalonate



with the sodium salt of the appropriate α-hydroxy ester



in an inert solvent such as 1,2-dimethoxyethane.

This reaction yields the ester forms of the compounds which are saponified by conventional techniques to yield the desired ammonium or alkali metal salts. The acid forms of the compounds of this invention are obtained by acidifying the salts. The acids can be crystallized by conventional techniques to provide useful precursors for high purity salts. It is noted that when R_1 is hydrogen, the acid is relatively unstable due to a tendency to undergo rapid decarboxylation.

In preferred embodiments of the invention, R is sodium and R_1 and R_2 are both methyl or hydrogen. These embodiments are preferred by virtue of availability of raw materials for their manufacture and their excellent performance as detergency builders.

The detergent formulations of this invention will contain from 1 to 75% by weight, preferably from 5 to 50% by weight of the salt, preferably sodium salt forms of the compound described. Such compounds can be utilized as the sole detergency builder in the compositions of this invention or in combination with other known detergency builders such as water soluble inorganic builder salts, for example, alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates or organic builders such as salts of phytic acid, sodium citrate, water soluble polymeric polycarboxylates as described in U.S. Pat. 3,308,067 and the like.

The detergent formulations of this invention will additionally contain at least 8% by weight of a surfactant. Any of the numerous well-known anionic, nonionic, zwitterionic or ampholytic surfactants can be employed.

Examples of suitable anionic surfactants include alkyl ethyl sulfonates, alkyl sulfates, acyl sarcosinates; acyl esters of isocyanates, acyl N-methyl taurides, and alkyl aryl sulfonates. The foregoing materials are used in the form of their water-soluble sodium, potassium, ammonium and alkyl ammonium salts. Specific examples include sodium lauryl sulfate; sodium N-methyl lauryl taurride; sodium dodecyl benzene sulfonate; and triethanol amine undecanol benzene sulfonate.

Examples of suitable nonionic detergents include alkyl phenol and alcohol alkoxylates including condensates of 1-decanol or 1-undecanol with from 3 to 5 molecular proportions of ethylene oxide such as described in U.S. patent application Ser. No. 707,480 filed Feb. 23, 1968 and now abandoned; condensates of monohydroxy or polyhydroxy alcohols such as oleyl alcohol or 1-tridecanol with from 9 to 15 molecular proportions of ethylene oxides; alkyl internal vicinal dialkoxy or hydroxy alkoxy compounds as described in U.S. patent application Ser. No. 852,898 filed Aug. 25, 1969 and now abandoned; and condensates of alkylene oxides with organo amines, for example, ethylene diamine and amides such as N-octadecyl diethanol amide.

Examples of cationic surfactants include octadecyl ammonium chloride; straight chain fatty amines having 8 to 18 carbon atoms; and quaternary ammonium compounds such as octadecyl trimethyl ammonium chloride.

Suitable ampholitic surfactants include the amido alkene sulfonates such as sodium C-pentadecyl, N-methyl amido ethyl sulfonate potassium C-octyl N-naphthalene amido propyl sulfonate; ammonium C-decyl, N-cyclo propyl amido butyl sulfonate, and aliphatic amine derivatives in which the aliphatic substituent contains an anionic water solubilizing substituent such as a carboxy, sulfo, phosphato, or phosphino group, for example, sodium-3-

dodecyl amino propionate and sodium-3-dodecyl amino propane sulfonate.

Examples of zwitterionic surfactants include derivatives of quaternary ammonium phosphonium and sulfonium compounds such as 3-(N,N-dimethyl-N-hexadecyl ammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecyl ammonio-2-hydroxy propane-1-sulfonate).

It will be understood that the above examples of supplementary surfactants are by no means comprehensive. Numerous other surfactants are known to those skilled in the art and are set forth in such familiar references as Surface Active Agents by A. M. Schwarz and James W. Perry. It will be further understood that the use of such surfactants will be in accordance with conventional, well-understood practices of detergent formulation. For example, cationic and anionic detergents will not normally be employed in combination due to recognized problems of precipitation of insoluble products.

In accordance with general practice, the ratio of the detergency building components to the surfactant components will be in the range of from 1:2 to about 12:1 by weight.

In addition to surfactant and builder components, the detergent formulations of this invention may contain fillers such as sodium sulfate and minor amounts of bleaches, dyes, optical brighteners, soil anti-redeposition agents, perfumes and similar conventional detergent formulation additives.

The invention is further illustrated by the following examples wherein all parts and percentages are by weight unless otherwise indicated.

Example I

To a slurry of 68 grams sodium ethyl glycolate in 400 ml. 1,2-dimethoxyethane is added 120 grams diethyl bromomalonate, the temperature being maintained below 5° C. The mixture is allowed to stir for 16 hours at 25° C. Solids are separated by filtration and solvent removed under reduced pressure. The residue is vacuum fractionally distilled, product being collected at 149°–151° C., 0.07 mm. Hg. The product is identified by nuclear magnetic resonance and elemental analyses as tetraethyl 2,4-dioxa-1,3,3,5-pentanetetracarboxylate. The product is saponified in an aqueous ethanol solution of NaOH at 25° C. The salt is precipitated by addition of excess ethanol and isolated by filtration and drying. Acidification of the salt with H_2SO_4 yields the acid form of the product.

Example II

The salt and acid produced according to Example I are tested for sequestration characteristics and are found to effectively sequester Ca^{++} ions.

Example III

Detergent formulations containing 12% linear alkylbenzene sulfonate having an average alkyl chain length of about 12 carbon atoms; from 5 to 75% of the salt form of the product of Example I; 12% sodium silicate having an SiO_2 to Na_2O ratio of about 2:4; and a quantity of sodium sulfate sufficient to equal 100% are found, in conventional laundry operations, to clean soiled samples of cotton and polyester cotton broadcloth substantially better than otherwise identical formulations containing no builder salt. These tests demonstrate that this material is an effective detergency builder material.

Example IV

The tests of Example III above are repeated using a detergent formulation in which Neodole 45–11 (a nonionic surfactant which is an adduct of a modified oxo type C_{14}–C_{15} alcohol with an average of 11 moles of ethylene oxide is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

Example V

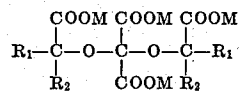
The tests of Example III are repeated with a detergent formulation wherein sodium hydroxyalkyl (C_{14}–C_{16} alkyl chain length) N-methyl taurate, and ampholytic surfactant, is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

Example VI

The tests of Example III are repeated with a detergent formulation wherein cocodimethylsulfopropylbetaine, a zwitterionic surfactant is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

What is claimed is:

1. A detergent composition consisting essentially of at least 8% by weight of a surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and amphoteric surfactants and from 1% to 75% by weight of a detergency builder compound having the formula



wherein M is selected from the group consisting of alkali metals and ammonium and R_1 and R_2 are each selected from the group consisting of hydrogen and methyl substituents.

2. A composition according to claim 1 wherein said detergency builder constitutes from 5% to 50% of the weight of the composition.

3. A composition according to claim 1 wherein the surfactant is a linear alkylbenzene sulfonate surfactant.

4. A composition according to claim 1 wherein M is sodium.

5. A composition according to claim 4 wherein R_1 is hydrogen and R_2 is a methyl substituent.

6. A composition according to claim 4 wherein R_1 and R_2 are hydrogen.

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