United States Patent [19]

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[11] **3,821,115**

[45] **June 28, 1974**

[54] **DETERGENT COMPOSITIONS CONTAINING SALTS OF 4-HYDROXYALKANOIC ACIDS**

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[22] Filed: **Nov. 20, 1972**

[21] Appl. No.: **308,204**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 215,089, Jan. 3, 1972, abandoned.

[52] **U.S. Cl.** **252/89,** 252/117

[51] **Int. Cl.** **C11d 1/04**

[58] **Field of Search** 252/89, 117; 260/413

[56] **References Cited**

UNITED STATES PATENTS

3,305,488	2/1967	Osipow et al.	252/117
3,449,385	6/1969	Muller et al.	260/413

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[57] **ABSTRACT**

Low scum-forming detergent compositions are afforded when salts of C_{14} to C_{20} 4-hydroxyalkanoic acids are employed as the sole detergent active or in combination with another surface active agent.

12 Claims, No Drawings

DETERGENT COMPOSITIONS CONTAINING SALTS OF 4-HYDROXYALKANOIC ACIDS

This application is a continuation-in-part of copending application Ser. No. 215,089, filed Jan. 3, 1972; now abandoned.

BACKGROUND OF THE INVENTION

The use of salts of fatty acids alone or in combination with other organic detergent compounds is well known. For example, washing compositions containing soap derived from fatty acids as the sole active are commercially available. In addition, soaps derived from fatty acids have also been added to detergent compositions containing synthetic surface active agents to control foaming. It is also well known that when used alone or in combination, the chain lengths of the fatty acids from which the soaps are derived serve as important criteria and govern the acceptability or unacceptability of the finished product. More specifically, soaps made from C_{16}–C_{18} natural fatty acids particularly when used alone are not acceptable as laundry detergents because they tend to form objectionable surface scum and/or bulky precipitates which deposit on the objects being washed and other surfaces in contact therewith.

It is also known that soaps of certain hydroxystearic acids are not particularly adaptable to laundry detergents when used alone. For example, U.S. Pat. No. 3,305,488 discloses that soaps of 10 and 12-hydroxystearic acid are relatively poor detergents.

SUMMARY OF THE INVENTION

An object of the invention is to provide detergent compositions containing salts of C_{14} to C_{20} 4-hydroxyalkanoic acids as the main detergent active or detergent compositions containing salts of the 4-hydroxyalkanoic acids in combination with an anionic, nonionic, zwitterionic or ampholytic detergent compound.

Another objective of the present invention is to provide detergent compositions which afford low scum residues in both wash and rinse cycles in laundering processes.

Another object of the present invention is to provide detergent compositions containing soaps which are more readily biodegradable than soaps derived from naturally occurring fatty acids.

DESCRIPTION OF THE INVENTION

I have found that particular hydroxyalkanecarboxylic acids, namely 4-hydroxytetradecanoic acid, 4-hydroxyhexadecanoic, 4-hydroxyoctadecanoic (also known as 4-hydroxystearic acid) and 4-hydroxyeicosanic acid in the form of their alkali metal, ammonium or substituted ammonium salts exhibit properties that render it particularly adaptable in washing compositions and particularly those designed for laundry use.

I have found that the salts of 4-hydroxyalkanoic acids (also known as ν-hydroxyalkanoic acids or 3-hydroxyalkane-1-carboxylic acids) not only act as self-building detergent compounds but perform efficiently as detergent builders and thus increase the efficiency of detergent compositions containing other detergent compounds.

The discovery is suprising in that ordinary soap and the more commonly known 2-hydroxy, 10-hydroxy and 12-hydroxystearates when used alone in the presence of hardness ions, produce a heavy scum and/or precipitates which are not only unsightly but have a pronounced tendency to deposit on surfaces and clothes or other objects being washed.

It is possible to overcome the poor self-dispersing characteristics of hydroxystearates (including the 2-, 3-, and 5-hydroxystearates) by incorporating another detergent compound in the composition. However, in the rinsing step in the conventional washing process the insoluble calcium salts of the hydroxystearates which form tend to produce large aggregates which still tend to deposit on the clothes and washing machine parts. Such deposition on the clothes even in the rinse step can be extremely disadvantageous in that it can nullify the protection of flame retardant finishes that may be present on the clothes. Additionally, of course, such deposits tend to be non-uniform and would be noticeable on clothes, especially colored clothes. In contrast, the uniquely high self-dispersing characteristics of the C_{14} to C_{20} sodium (and potassium) 4-hydroxyalkanoates, particularly 4-hydroxystearates, in the presence of hardness ions enables one to wash and rinse the clothes without forming such troublesome precipitates inasmuch as the precipitated salts remain finely divided and well dispersed in the bulk solution with little tendency to form surface scum. Thus, one mode of the invention is the use of salts of C_{14} to C_{20} 4hydroxyalkanoic acid alone; another mode and the most preferred is the use of a combination of an anionic, nonionic, zwitterionic or ampholytic detergent compound with a salt of C_{14} to C_{20} 4-hydroxyalkanoic acid. The formulations utilizing C_{18} to C_{20} 4-hydroxyalkanoates are especially useful in hot water washing (about 50–90°C) wherein the self-dispersing properties are most pronounced. The lower chain lengths are more useful at lower temperatures (about 25–50°C).

Thus the present invention relates to detergent compositions wherein salt of a C_{14} to C_{20} 4-hydroxyalkanoic acid is used as the sole detergent active compound or a salt of a C_{14} to C_{20} 4-hydroxyalkanoic acid is combined with another detergent compound.

Accordingly, detergent compositions of the present invention comprise:

a. from about 5 to about 100% of salts of C_{14} to C_{20} 4-hydroxyalkanoic acids, and mixtures thereof;

b. from about 0 to about 60% of an anionic, nonionic, zwitterionic or ampholytic detergent compound, and mixtures thereof; and

c. from about 0 to about 90% of a detergent adjuvant (to be defined herein).

The 4-hydroxyalkanoates used in the present invention are preferably the alkali metal salts of the 4-hydroxyalkanoic acids, although the ammonium and substituted ammonium salts such as the mono-, di- and tri-ethanolammonium, tetramethyl ammonium, methyl ammonium and morpholinium salts of the aforementioned acid are also suitable.

The salts of mixtures of the C_{16} to C_{18}, C_{18} to C_{20}, C_{14} to C_{18}, C_{16} to C_{20}, and C_{14} to C_{20} 4-hydroxyalkanoic acids are especially suitable for use in this invention. Also included in the above mentioned mixtures are the 4-hydroxyalkanoic acids containing odd numbered carbon chains, for example C_{15}, C_{17} and C_{19}.

When the 4-hydroxyalkanoates are used as the sole detergent active, they are preferably present in an

amount ranging from about 40 to about 90% or may even comprise 100% of the detergent composition.

When the 4-hydroxyalkanoates are employed in combination with other detergent compounds, the amount present will vary from about 5% to about 60% by weight of the detergent composition.

In regard to the additional detergent compound(s) used in combination with the 4-hydroxyalkanoates, the detergent composition will usually comprise from about 5 to about 60%, preferably about 10 to about 30% of such additional detergent compound. The particular type of organic detergent compound additionally employed in the detergent compositions of the present invention is not important. For example, anionic organic soap and non-soap detergent compounds may be used. Of particular value are the alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals; sodium or potassium alkyl benzene sulfonates in which the alkyl group contains from about nine to about 20 carbon atoms and in which the alkyl group is attached to the benzene ring in either the 1 position or the secondary position as well as many other well known to those skilled in the art and as disclosed in U.S. Pat. No. 3,519,570 incorporated by reference herein.

The nonionic detergent compounds that may be employed in the present invention are those that do not ionize in water and include the polyethylene oxide condensates of alkyl phenols containing six–12 carbons in the alkyl group, the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine, the condensation products of random secondary alcohols derived from C_{10}–C_{18} n-paraffins with ethylene oxide and the condensation products of aliphatic (C_{8-18}) alcohols with ethylene oxide as more fully described in U.S. Pat. No. 3,519,570.

The ampholytic detergent compounds contemplated in the present invention can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about eight to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate and sodium 3-tetradecylaminopropanesulfonate and sodium N-2-hydroxyhexadecyl-N-methyl-taurate.

The zwitterionic detergent compounds which can be used can be broadly described as derivatives of aliphatic quaternary ammonium compounds, sulfonium compounds and phosphonium compounds in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about eight to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate, 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate, 3-(dodecylmethylsulfonium)propane sulfonate, and 3-(cetyl-methylphosphonium)ethane sulfonate.

Mixtures of the above mentioned anionic, nonionic, ampholytic and zwitterionic detergent compounds can also be employed in detergent compositions of this invention. Mixtures of anionic and nonionic detergent compounds are particularly useful in said composition.

Other materials which may be present in the detergent compositions of the invention in minor or major amounts are those components conventionally present in detergent compositions and referred to herein and in the claims as detergent adjuvants. These include such components as well-known soil suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers such as sodium sulfate, buffers such as sodium silicates and carbonate, optical brighteners, bleaches, such as perborates, percarbonates, organic and inorganic chlorine releasing agents, bleach activators, enzymes, detergent boosters and solvents, suds boosters, suds depressants, lime-soap dispersants, germicides, fungicides, anti-tarnishing agents, cationic detergents, fabric softening agents and in the case of liquid compositions, opacifiers and organic solvents. In addition, although any of the conventional well-known detergent builders (phosphate and non-phosphate type) may be employed in the compositions of the present invention in low levels (0–10%) the absence thereof does not adversely affect the cleaning efficiency.

The detergent compositions of the present invention may be in any of the usual physical forms for such compositions such as powders, beads, flakes, bars, tablets, noodles, liquids, pastes and the like. The detergent compositions are prepared and utilized in the conventional manner.

Table 1 illustrates the superior results obtained when soiled test cloths are washed with a detergent composition employing sodium 4-hydroxystearate as the sole detergent active. The detergent formulation was not only equal or superior to a standard detergent formulation containing an anionic detergent compound but did not form a scum and/or undispersed particles as did the compositions containing sodium 2-hydroxy- and sodium 12-hydroxystearate.

Table 2 illustrates the results obtained when soiled test cloths are washed with a detergent composition comprising sodium 4-hydroxystearate and an additional detergent active.

Table 3 illustrates the results obtained when soiled test cloths are washed at 120°F and 160°F with a detergent composition comprising either sodium 4-hydroxytetradecanoate, sodium 4-hydroxyhexadecanoate or sodium 4-hydroxyoctadecanoate and an additional detergent active namely LAS.

Table 4 illustrates the results obtained when soiled test cloths are washed with a detergent composition employing either sodium 4-hydroxytetradecanoate, sodium 4-hydroxyhexadecanoate and sodium 4-hydroxyoctadecanoate as the sole detergent active.

The detergent formulations set forth in Tables 1–4 were prepared by blending together the recited components and tested for detergency or cleansing ability in the Terg-O-Tometer Test using 65% Dacron — 35% cotton VCD (vacuum cleaner dust) cloth as the test cloth and the washing conditions as noted. The pH of the washing solutions were adjusted, where necessary, to pH 10 by the addition of caustic thereto.

The average detergency units (DU) of the formulations is the final reflectance of the washed cloth minus the initial reflectance of the soiled cloth (the average

of two runs), the reflectance being measured with a Gardner Automatic Color Difference Meter.

The following abbreviations have been used in the aforesaid Tables: LAS is an anionic detergent compound which is sodium linear secondary alkyl (C_{10}–C_{15}) secondary benzene sulfonate; Neodol 45-11 is a nonionic detergent compound which is an adduct of a modified Oxo type C_{14}–C_{15} alcohol with an average of 11 moles of ethylene oxide; C_{14}–C_{16} HAMT is an ampholytic detergent compound which is sodium N-2-hydroxy C_{14}–C_{16} alkyl-N-methyltaurate; Sulfobetaine DCH is a zwitterionic detergent compound which is cocodimethylsulfopropyl betaine; Sodium Tripolyphosphate is pentasodium tripolyphosphate; and Sodium Silicate Solids is a water soluble silicate having a SiO_2 : Na_2O ratio of 2.4 : 1.

The sodium 4-hydroxystearate employed in the compositions of the present invention is a known compound and is prepared by saponification of ν-stearolactone which, in turn, may be prepared according to Example 1 of U.S. Pat. No. 3,054,804. The other 4-hydroxyalkanoates are readily prepared by saponification of the corresponding methyl esters or lactones of the 4-hydroxyalkanoic acids which are prepared according to a modification of the method of Lardelli et al., Rec. des Trav. Chim. des Pays-Bas, 86, 481 (1967). The procedure of this reference, which describes a method for preparing the homologous 5-hydroxyalkanoic acids is modified by utilizing succinic anhydride in place of glutaric anhydride in the "Cason" synthetic scheme described on pages 494–495 in the reference. In the case of the C_{18} and C_{20} compounds, the methyl esters of the intermediate 4-oxoalkanoic acids are isolated as solids, reduced with sodium borohydride in methanol/ether to the corresponding hydroxy compounds, which after isolation by acidification and ether extraction, are saponified with alcoholic sodium hydroxide or potassium hydroxide to yield the desired sodium or potassium 4-hydroxyalkanoate.

The ammonium and substituted ammonium salts are prepared by neutralization of the desired 4-hydroxyalkanoic acid with a stoichiometric amount of ammonium hydroxide or the desired organic amine or substituted ammonium hydroxide in alcoholic solution followed by evaporation of the solvent. The free 4-hydroxyalkanoic acids, in turn, are obtained by acidification of an aqueous solution or dispersion of the alkali metal salt of the 4-hydroxyalkanoic acid, extraction of the liberated hydroxy acid with ether and evaporation of the ether layer.

It is intended to cover all changes and modifications of the preferred embodiments of the invention, herein chosen for the purposes of illustration, which do not constitute departures from the spirit and scope of the invention.

Table 1

Component	Formulation (%)			
	1	2	3	4
1. Sodium 2-Hydroxystearate	75	—	—	—
2. Sodium 4-Hydroxystearate	—	75	—	—
3. Sodium 12-Hydroxystearate	—	—	75	—
4. Sodium linear secondary alkyl (C_{10}–C_{15}) benzenesulfonate (LAS)	—	—	—	18
5. Sodium Tripolyphosphate	—	—	—	50
6. Sodium Silicate Solids	10	10	10	10
7. Water	bal.	bal.	bal.	bal.
Detergency (DU's):	30.3	30.0	27.3	29.0
%Efficiency Relative to Standard Formulation (i.e., 1,2,3 vs. 4)	105	104	94	
Clarity of Wash Solution:	undispersed particles	cloudy (dispersed)	greasy scum	cloudy (dispersed)
Washing Conditions:	Terg-O-Tometer, Dacron/Cotton VCD Soil Cloth, 120°F, 180 ppm 2:1 Ca^{++}/Mg^{++} water, pH = 10, formulation concentration, 0.2%			

Table 2

Component	Formulation (%)							
	1	2	3	4	5	6	7	8
1. LAS (anionic)	18	18	—	—	—	—	—	—
2. Neodol 45–11 (nonionic).	—	—	10	10	—	—	—	—
3. C_{14-16} HAMT (ampholytic)	—	—	—	—	18	18	—	—
4. Sulfobetaine DCH (zwitterionic)	—	—	—	—	—	—	18	18
5. Sodium 4-Hydroxystearate	50	—	50	—	50	—	50	—
6. Sodium Tripolyphosphate	—	50	—	50	—	50	—	50
7. Sodium Silicate Solids	10	10	10	10	10	10	10	10
8. Water	balance							
Detergency (DU's)	28.6	29.5	22.4	28.1	23.1	27.6	25.2	29.8
% Efficiency Relative to Control (i.e., 1 vs. 2, 3 vs. 4, 5 vs. 6 and 7 vs. 8).		97		80		88		84
Washing Conditions:	Terg-O-Tometer, Dacron/Cotton VCD Soil Cloth, 120°F, 180 ppm 2/1 Ca^{++}/Mg^{++} water, pH = 10, formulation concentration, 0.2%							

Table 3

Component	Formulation (%)							
	1	2	3	4	5	6	7	8
1. Sodium 4-hydroxytetradecanoate	50	—	—	—	50	—	—	—
2. Sodium 4-hydroxyhexadecanoate	—	50	—	—	—	50	—	—
3. Sodium 4-hydroxyoctadecanoate	—	—	50	—	—	—	50	—
4. LAS	18	18	18	18	18	18	18	18
5. STPP	—	—	—	50	—	—	—	50
6. Sodium Silicate Solids	10	10	10	10	10	10	10	10
7. Water	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.
Detergency (DU's)	13.3	19.6	19.3	19.5	8.1	20.5	23.4	23.2
% Efficiency Relative to Standard Formulation, i.e., 1, 2, 3 vs. 4; 5, 6, 7 vs. 8.	68	100	99		35	88	101	
Appearance of Wash Solution	← dispersed →							
Washing Conditions:	Terg-O-Tometer; Dacron/cotton VCD Soil Cloth, 120°F for formulations 1–4 and 160°F for formulations 180 ppm 2:1 Ca^{++}/Mg^{++} water, pH = 10, formulation concentration, 0.2%							

Table 4

Component	Formulation (%)			
	1	2	3	4
1. Sodium 4-hydroxytetradecanoate	75	—	—	—
2. Sodium 4-hydroxyhexadecanoate	—	75	—	—
3. Sodium 4-hydroxyoctadecanoate	—	—	75	—
4. LAS	—	—	—	18
5. STPP	—	—	—	50
6. Sodium Silicate Solids	10	10	10	10
7. Water	bal.	bal.	bal.	bal.
Detergency (DU's)	11.0	16.4	20.5	23.8
% Efficiency Relative to Standard Formulation, i.e., 1, 2, 3 vs. 4.	46	69	86	
Appearance of Wash Solution	Some scum – C_{18} best dispersed of formulations 1–3.			
Washing Conditions:	Terg-O-Tometer; Dacron/cotton VCD Soil Cloth, 160°F for formulations 1–4; 180 ppm 2:1 Ca^{++}/Mg^{++} water, pH = 10, formulation concentration, 0.2%			

PREPARATION OF SALTS OF 4-HYDROXYALKANOIC ACIDS

EXAMPLES 1–4

Using the Cason procedure [J.A.C.S. 64, 1106 (1942)] for the preparation of methyl 4-keto-1-methyloctoic acid, methyl 4-oxohexadecanoate is prepared from 4.86g of Mg, 49.8g of dodecyl bromide, 19.6g of $CdCl_2$ and 30.1g of β-carbomethoxypropionyl chloride. Yield: 27.0g; b.p. - 115–117°C/0.08mm. Structure confirmed by NMR.

Methyl 4-oxohexadecanoate, 27.0g is saponified by dissolving in 50g of 3A ethyl alcohol and reacting with a solution of 4.2g of sodium hydroxide dissolved in 70g of 3A ethyl alcohol. After standing for two days, the precipated product is filtered, washed with ethanol followed by ether and then air dried. Yield: 26g of sodium 4-oxohexadecanoate.

A solution of 23.2g of sodium 4-oxohexadecanoate in 75ml of water is added dropwise into a stirred solution of 1.2g of sodium borohydride in 20ml of 0.2N NaOH maintained at 28–30°C. After addition is complete, stirring is continued for 1 ½ hours and then the mixture is allowed to stand overnight. The reaction mixture is then acidified with concentrated hydrochloric acid and the precipitated product filtered, washed with water and dried in a vacuum oven. Yield of 4-hydroxyhexadecanoic acid, 21.3g; structure confirmed by NMR.

4-hydroxyhexadecanoic acid, 20.8g is dissolved in 60ml of 3A ethyl alcohol and neutralized with a solution of 3.36g of NaOH dissolved in 30ml of 3A ethyl alcohol. The precipitated product is then filtered, washed with 3A ethyl alcohol and dried in a vacuum oven. Yield of sodium 4-hydroxyhexadecanoate, 20.4g analyzing 98.4% active by titration with standard perchloric acid in acetic acid.

In a similar manner, sodium 4-hydroxytetradecanoate, sodium 4-hydroxyoctadecanoate and sodium 4-elcosanoate are readily prepared from the appropriate alkyl bromide. By utilizing potassium hydroxide in place of sodium hydroxide in the final neutralization steps, the corresponding potassium salts are readily obtained.

What is claimed is:

1. A detergent composition comprising, as components, based on the total weight of said composition, about

a. 5 to about 90% of a salt of a C_{14} to C_{20} 4-hydroxyalkanoic acid and mixtures thereof, the cation of said salt is selected from the group consisting of alkali metal, ammonium and substituted ammonium,

b. 0 to about 60% of a detergent compound selected from the group consisting of anionic, nonionic, zwitterionic, or ampholytic detergent compounds and mixtures thereof, and

c. 0 to about 90% of a detergent adjuvant.

2. The composition of claim **1** wherein said detergent composition consists essentially of

a. 5 to about 90% of said salt of C_{14} to C_{20} 4-hydroxyalkanoic acid, and

b. 10 to about 90% of said detergent adjuvant.

3. The composition of claim **1** wherein the 4-hydroxyalkanoic acid is 4-hydroxytetradecanoic acid.

4. The composition of claim **1** wherein the 4-hydroxyalkanoic acid is 4-hydroxyhexadecanoic acid.

5. The composition of claim **1** wherein the 4-hydroxyalkanoic acid is 4-hydroxyoctadecanoic acid.

6. The composition of claim **1** wherein the 4-hydroxyalkanoic acid is 4-hydroxyeicosanic acid.

7. The composition of claim **1** wherein said detergent compound is present in an amount ranging from about 5 to about 60%.

8. The composition of claim **1** wherein said detergent compound is present in an amount ranging from about 10 to about 30%.

9. The composition of claim **1** wherein said detergent compound is an anionic detergent compound.

10. The composition of claim **1** wherein said detergent compound is a nonionic detergent compound.

11. The composition of claim **1** wherein said detergent compound is a zwitterionic detergent compound.

12. The composition of claim **1** wherein said detergent compound is an ampholytic detergent compound.

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