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[54] **DETERGENT COMPOSITION**

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[63] Continuation-in-part of Ser. No. 103,792, Jan. 4, 1971, abandoned.

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[58] **Field of Search** ..... 252/89, 99, 132, 135, 180, 252/356, DIG. 11, DIG. 15; 260/535 R

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[57] **ABSTRACT**

A detergent composition comprising a cleaner such as a soap or synthetic detergent and a detergent builder corresponding to the general formula:

RO—CHR'—COOM

where R is selected from the group consisting of —CHR'—COOM, $-(-CHR'-CHR'-O-)_n H$ and $-(-CHR'-CHR'-O-)_{n-1}CHR'-COOM$; M is selected from the group of hydrogen, alkali metal and ammonium, R' is selected from the group of hydrogen and lower alkyl having from 1 to 4 carbon atoms and n is a whole integer varying between 1 and 300.

3 Claims, No Drawings

DETERGENT COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my copending U.S. Application Ser. No. 103,792 filed Jan. 4, 1971 now abandoned.

INTRODUCTION

This invention relates to an improvement in detergent compositions and more particularly, to the use of novel detergent builders in a detergent composition.

DESCRIPTION OF THE PRIOR ART

Most common laundering and cleansing compositions contain builder materials that extend and improve the cleaning ability of a detergent composition. One of the principal functions of a builder material in such compositions is to effectively prevent the precipitation of insoluble alkaline earth salts, e.g. those of calcium and magnesium from hard water by sequestering the metal ions. Another function of a builder is to aid in suspending the soil in a washing operation. A third function may be to provide the optimum pH, usually about 8 to 11, in the wash liquid. Among the most widely used builders in common commercial detergent formulations are inorganic alkaline salts such as alkali polyphosphates, phosphates, borates, carbonates and bicarbonates. Similarly, organic materials such as the ammonium, sodium and potassium salts of amino polycarboxylates, e.g. nitrilotriacetate, ethylenediaminetetracetate and N-(2-hydroxyethyl) iminodiacetate, are used as builders. Of the above materials, sodium tripolyphosphate and potassium pyrophosphate command a major part of the builder market and the consumption of sodium tripolyphosphate in detergent applications is in excess of 2 billion pounds per year. Despite its wide use, the tripolyphosphate compounds possess certain disadvantages. Three of the recognized limitations are (1) the tendency of the tripolyphosphates and higher condensed phosphates to hydrolyze to less condensed compounds which are less effective builders, (2) evidence that the presence of phosphates and detergents in sewage discharges can aggravate the growth of algae in lakes and bay areas creating a serious pollution problem, and (3) the low solubility of such phosphates in water, which precludes the use of simple liquid formulations.

The other known builders also have certain disadvantages. Nitrilotriacetic acid, for instance, while it has a high sequestering ability per unit of weight and has not been implicated in pollution problems, lacks the physical properties required of builders and is corrosive to copper and other metals used in plumbing. In addition, nitrilotriacetic acid can cause build-up of nitrates and ammonia which are nutrients fostering the growth of algae in disposal waters.

STATEMENT OF THE INVENTION

The subject invention provides a novel detergent builder which does not present the aforesaid problems and effectively prevents precipitation of insoluble alkaline earth metals in hard water, provides optimum pH and aids the suspension of soil in a washing operation, perhaps to a greater extent than the prior art builders. The detergent builders set forth herein correspond to the following general formula:

RO—CHR'—COOM

where R is selected from the group consisting of —CHR'—COOM, $+CHR'—CHR'—O+_nH$ and $+CHR'—CHR'—O+_{n-1}CHR'—COOM$; M is selected from the group of hydrogen, alkali metals and ammonium, R' is selected from the group of hydrogen and lower alkyl having from 1 to 4 carbon atoms and n is a whole integer varying between 1 and 300.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Some of the detergent builders described above are compounds known in the art and others are novel compounds disclosed in my copending U.S. Pat. Application Ser. No. 123,025 filed Mar. 10, 1971 and incorporated herein by reference. Processes for making all of the aforesaid detergent builders are disclosed in the aforesaid patent application.

Compounds corresponding to the formula:

MOOC—CHR'—O—CHR'—COOM I

comprise substituted and unsubstituted diglycolic acid and its salts. These materials are known in the art. In accordance with my copending U.S. Pat. Application referenced above, such compounds can be formed in a number of ways including (a) reaction of formaldehyde with carbon monoxide in the presence of water or alcohol and an acidic or alkaline catalyst to form diglycolic acid in acid medium and the diglycolate in alkaline medium; (b) reaction of formaldehyde with sodium glycolate and carbon monoxide in the presence of water and preferably an alkaline catalyst; (c) reaction of formaldehyde with esters of glycolic acid and carbon monoxide in the presence of an aliphatic alcohol and an acidic catalyst; (d) hydrolysis of esters of diglycolic acid in a basic medium where the diglycolate is desired; and (e) elimination of one mole of water from 2 moles of a glycolic acid derivative such as glycolonitrile, esters of glycolic acid and sodium glycolate. Elevated temperatures and pressures are desirable for the above reactions, and in this respect, temperatures in excess of 30°C and preferably up to 120°C at higher than atmospheric pressures are preferred. Pressures of up to 200 atmospheres can be employed if desired, especially towards the latter part of the reaction. In the above reactions, where the diglycolic acid is the product, this can be converted to a diglycolate with an alkali metal or ammonium hydroxide. Details for the above reactions can be found in my above referenced copending patent application.

Compounds conforming to the formula:

$H+O—CHR'—CHR'+_nO—CHR'—COOM$ II

comprise polyoxyalkylene acetic acids and polyoxyalkylene glycolates. They may be formed by the condensation of glycolic acid, an alkali metal or ammonium glycolate or an ester of glycolic acid such as methylglycolate with an alkylene oxide such as ethylene oxide, propylene oxide and mixtures of both propylene oxide and ethylene oxide. The reaction is preferably carried out at elevated temperature and pressure, typically at temperatures in excess of 30°C and preferably at temperature up to 120°C. The reaction can be performed anywhere between atmospheric pressure and 200 atmospheres, but preferably, the pressure is maintained between about 10 and 50 atmospheres for the initial portion of the reaction and may be raised to up to 200 atmospheres during the latter part of the reaction. The chain length is determined by the ratio of the alkylene

oxide to its coreactant, the higher the ratio, the longer the chain length and the lower the ratio, the shorter the chain length as would be understood to those skilled in the art. Thus, there may be as many as 300 moles of the alkylene oxide per mole of the glycolic acid, glycolate or ester. If the starting material is the acid and the product of reaction is an acid, the acid can be converted to its corresponding salt with an alkali metal. Again, details for this reaction can be found in my copending U.S. Pat. application referenced above.

Compounds corresponding to the formula:

$$MOOC—CHR'+O—CHR'—CHR'+_{n}O—CHR'—COOM \quad III$$

may be formed by oxidizing the compounds of formula II. The oxidation method would be obvious to one skilled in the art and can comprise, for example, the use of an oxidant such as vanadium pentaoxide mixed with nitric acid and reacted with the compound corresponding to formula II above to form the polyoxyalkylene dioxydiacetic acid which may subsequently be converted to their salts. The oxidation reaction is preferably at elevated temperatures, more preferably at temperatures in excess of 50°C. Details for this reaction can also be found in the above noted copending U.S. Pat. Application.

When using the detergent builders of this invention in a detergent formulation, it is generally desirable to operate in an alkaline medium, usually at a pH of from 8 to 11 so that if the full acid or half acid salt is used, it may be desirable or necessary to add basic components to the cleaning composition containing the builder to attain the desired pH. Use of the full salt will often produce the desired pH without other sources of alkalinity being required.

The detergency and sequestration abilities of the instant builders on a per weight basis have been found to be equal to or better than those of the conventionally used materials. In addition, the salts used herein, unlike sodium tripolyphosphate and other builders, are sufficiently water-soluble to permit their use in liquid formulations. Further, water solutions of the water-soluble salts are substantially less corrosive to metals, such as steel, galvanized (zinc) steel and copper, commonly used to contain detergent-containing water, than builders such as sodium nitrilotriacetate and certain polyphosphates. No water pollution problems such as the algae growth-promoting characteristics of phosphates accumulated in waterways, have been attributed to the materials used herein. Moreover, the materials of the invention biodegrade rapidly in water leaving only the innocuous degradation products, water and carbon dioxide. Therefore, no pollution problems can be seen to arise through the use thereof.

Of the builders defined herein, those represented by formulas II and III above are preferred over those represented by formula I. The reason for this is that they have a greater cleaning ability and are more readily biodegraded.

The builders may be incorporated into laundering or cleansing compositions containing detergents of the anionic, non-ionic, cationic or amphyolytic types. The anionic detergents are exemplified by the (linear or branched) alkyl benzene sulfonates; the alcohol sulfates; the alkane sulfonates such as those made by reacting a paraffin with sulphur dioxide and oxygen or by reacting an olefin with sodium bisulfate; the olefin sulfonates such as the mixture obtained by reacting sulphur trioxide with an olefin; the sulfates of ethoxylated alcohols or alkylphenols; and the sulfonated fatty acids and their esters. The non-ionic detergents are illustrated by the alkanolamides, the ethoxylated alcohols, alkylphenols of fatty acids, and the glycol ethers. Exempliary of the cationic surfactants are amines quaternized with esters of hydrochloric or sulfuric acids. Typical of the ampholytic detergents are the sulfobetaines, N-alkyltaurterates or sarcosinates, and certain protein derivatives. Compilations of detergents with which these builders can be used are given in McCutcheon's "Detergents and Emulsifiers" published by John W. McCutcheon, Incorporated, Morristown, N.J.

Generally, the builder can comprise from about 5 to about 95% by weight of the formulation, but preferably and more usually comprises from about 20 to about 50% by weight of the formulation. The precise amount to be used depends upon the hardness of the available water, the end use intended for the detergent formulation and the amount of soil to be removed.

The builders of this invention may be used alone or in combination with other builders, such as the known phosphate materials. This may be desirable to achieve certain physical or performance properties in a specific formulation; for instance, phosphates may delay or prevent precipitation of soil on the cleansed article.

The builder is generally physically admixed with the other components of the cleansing composition by blending techniques well known to those skilled in the art.

The following examples set forth methods for the formation of certain of the novel detergent builders of this invention.

EXAMPLE 1

Formation of disodium diglycolate.

a. 1 mole of sodium glycolate was mixed with 200 ml of water and 1 mole of formaldehyde in a high pressure autoclave. A carbon monoxide atmosphere was superimposed above the liquid and pressure gradually increased to between 100 and 200 atmospheres. The autoclave and contents were heated at a temperature of between 100° and 110°C for about 3 hours. After cooling, sodium hydroxide solution was added to the reaction mixture and pH was adjusted to about 6. The mixture was evaporated to dryness to obtain the disodium diglycolate along with some sodium formate and some unreacted sodium glycolate.

b. The sodium diglycolate salt may be obtained directly without pH adjustment by repeating the procedure set forth above and including 4 grams of sodium hydroxide in the reaction mixture.

c. 2 moles of formaldehyde were mixed with 2 moles of water and 0.25 moles of hydrochloric acid in a high pressure autoclave. A carbon monoxide atmosphere was superimposed above the solution and the pressure increased to between 2 and 10 atmospheres. The autoclave and contents were heated at a temperature of from 100° to 120°C. During the heating, the pressure decreased and additional carbon monoxide was added. This was continued until the pressure stabilized. After cooling, additional carbon monoxide was added until the pressure increased to between 100 and 200 atmospheres. The autoclave and contents were then heated to a tem-

perature of 100° to 120°C and held at this temperature for 2 hours. Thereafter, the solution was cooled and sodium hydroxide was added until a pH of about 6 was obtained. The mixture was evaporated to dryness to obtain the disodium diglycolate along with some sodium formate and unreacted sodium glycolate.

d. The procedure of paragraph c may be repeated with the substitution of ammonium hydroxide for sodium hydroxide to form the diammonium diglycolate.

e. Methyl alcohol may be used in the procedure of paragraph c to obtain the dimethyl diglycolate ester which may be converted to the disodium diglycolate by hydrolyzing with sodium hydroxide. In this case, 0.10 moles of dimethyl diglycolate are mixed with 50 ml of water followed by the slow addition of 200 ml of 1 normal sodium hydroxide solution. Preferably, the sodium hydroxide solution is added over a period of about 15 minutes. The mixture is then heated at 60° to 70°C and the methanol formed during the hydrolysis reaction distilled off. After about one hour, the hydrolysis reaction is complete. The mixture is then evaporated to dryness to obtain the disodium salt of diglycolic acid.

f. One mole of formaldehyde was mixed with 100 ml of 1 normal sodium hydroxide in a high pressure autoclave. A carbon monoxide atmosphere was superimposed above the liquid and the pressure increased to between 100 and 200 atmospheres. The mixture in the autoclave were heated to a temperature of from 120° to 140°C for 2 to 3 hours. After cooling, the pH of the mixture was adjusted with sodium hydroxide to about 5. The mixture was evaporated to dryness to obtain the disodium diglycolate along with some sodium glycolate and sodium formate.

g. One mole of methylglycolate was mixed with 200 ml of methanol, 0.25 moles of hydrochloric acid and 1 mole of formaldehyde in a high pressure autoclave. A carbon monoxide atmosphere was superimposed above the liquid and the pressure increased to between 100 and 200 atmospheres. The autoclave and contents were heated at a temperature of 100° to 110°C for about 3 hours and dimethyl diglycolate was obtained along with some methyl formate and unreacted methyl glycolate. This material may be hydrolized with a hydroxide such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, and the like in the manner described above.

EXAMPLE 2

Formation of polyoxyalkylene glycolates.

a. A high pressure autoclave equipped with a thermocouple, pressure gauge and reactant inlet tube was charged with 0.10 moles of methyl glycolate and 2 ml of hydrochloric acid. Ethylene oxide gas was superimposed above the mixture and the pressure increased to between about 10 and 20 atmospheres. The autoclave and contents were heated to a temperature of about 80° to 100°C. As the reaction mixture was heated, pressure decreased and it was necessary to add more ethylene oxide gas to maintain the pressure. This was repeated until the pressure remained stable. Thereafter, the reaction mixture was cooled and 200 ml of water were added. Then, sodium hydroxide solution was added and the mixture heated to 50° to 60°C. The mixture was then evaporated to dryness to obtain a product having the formula $H\text{-}(\text{-}O\text{—}CH_2\text{—}CH_2\text{-})_n O\text{—}CH_2\text{—}COONa$ where n is a whole number of about 100. The length of the polymer chain, e.g., n, can be increased or decreased by increasing or decreasing the pressure of the ethylene oxide atmosphere over the reaction mixture.

b. The procedure of paragraph a may be repeated substituting propylene oxide for ethylene oxide to obtain the corresponding sodium polyoxypropylene glycolate. Alternatively a mixture of the ethylene oxide and propylene oxide may be used.

c. The autoclave of paragraph a was charged with 0.10 moles of sodium glycolate mixed with 50 ml of water and 1 gram of sodium hydroxide. Ethylene oxide gas was superimposed above the mixture and the pressure increased to between 10 and 20 atmospheres. The autoclave and contents were heated at a temperature of from 80° to 100°C. During the heating, pressure decreased and it was necessary to add more ethylene oxide. This was repeated until the pressure stabilized. The mixture was then evaporated to dryness to obtain the sodium polyoxyethylene diglycolate.

EXAMPLE 3

Acids of Polyoxyalkylene glycolates

Sodium polyoxyalkylene glycolate of example 2*a* was converted to an acid by oxidation. The acid may be subsequently converted to the di-salt. One part of vanadium pentaoxide was mixed with 200 parts of 60% nitric acid. This mixture was stirred and heated to about 70°C. Then, 60 parts of the polyoxyethylene glycolate were added gradually with stirring for a period of 3 hours. The reaction mixture was maintained between 70° and 80°C for another 2 hours and then water and excess nitric acid evaporated. The corresponding diacetic acid was recovered. This was dissolved in water and sodium hydroxide added in an amount to provide a pH of about 6. The mixture was evaporated to dryness to obtain the corresponding disodium salt.

In formulating cleansers in accordance with the invention, it should be understood that any of the conventional prior art additives to detergents are also useful for the formulations of this invention. For example, there are frequently added inorganic salts for various purposes such as sodium hydroxide, sodium carbonate, sodium bicarbonate, and the like; sanitizer and bleaching compounds such as trichloroisocyanuric acids, chlorinated trisodium phosphate, hydroiodic acid, alkali metal and the alkaline earth metal salts of hypochlorite and the like; various organic materials such as hydroxyacetic acid, citric acid, acetic acid, carboxymethylcellulose, fatty acids and the like; enzymes; optical brighteners; perfumes; pigments; etc.

The following tables illustrate detergent formulations of this invention. The reflectance valves at the bottom of each table were obtained by dissolving 5 grams of each detergent formulation in 2 liters of hard water containing 300 ppm of calcium ions. Cloth swatches (65% dacron/35% cotton) each having a white and gray area were washed with 100 ml of the detergent solution at 60°C. The reflectance values were obtained for the cloth after washing. For purposes of comparison, reflectance of the white area prior to washing was 89.2 and for the gray area 25.1. Quantities of material in the table are set forth in per cent by weight.

TABLE I

Material		Example Number 5	6	7	8	9	10
diglycolic acid		20	20	30	40	40	90
phosphoric acid(75%)		20	20				
iodine		5				5	5
Pluronic P-65		5	5		5	5	5
water		50	55		55	50	
sodium metasilicate				5			
sodium sesquicarbonate				40			
sodium sulphate				13			
linear alkyl aryl sulfonate				10			
sodium carboxymethyl cellulose				0.5			
misc. brighteners pigments etc.				1.5			
reflectance	gray	25.9	n.m.	n.m.	n.m.	n.m.	n.m.
	white	87.9	n.m.	n.m.	n.m.	n.m.	n.m.

From the above, it can be seen that the gray portion of the cloth, considered soiled for purposes of the test described, were considerably cleaned by the formulations of the invention.

I claim:

1. A laundering and cleansing detergent composition consisting essentially of an effective amount of a detergent selected from the group of non-ionic detergents, cationic detergents, anionic detergents and ampholytic detergents and from 5 to 95% by weight of a detergent builder corresponding to the formula

$$H\text{-}(OCH_2\,CH_2)_n\,OCH_2\,COOM$$

where

M is selected from the group of alkali metal and ammonium, and n is a whole integer of from 1 to 100.

2. The composition of claim 1 where the detergent builder is present in an amount of from 10 to 50% by weight.

3. The composition of claim 1 where M is sodium or potassium.

TABLE II

Material		Example Number 11	12	13	14	15	16	17	18
disodium diglycolate		5	10	20	25	25	25	50	50
sodium tripolyphosphate		40	40		25	25	25		
sodium nitrilotriacetate		5		5	5				
sodium metasilicate		5	5	5	5	5	5	5	5
sodium sulfate		23	23	23	18	23	25	23	13
linear alky aryl sulfonate		20	20	20	10	10		20	10
sodium carboxymethyl cellulose		0.5	0.5	0.5	0.5	0.5		0.5	0.5
misc. brighteners, pigments etc.		1.5	1.5	1.5	1.5	1.5		1.5	1.5
sodium sesquicarbonate				25	10	10	20		20
reflectance	gray	38.1	38.7	34.2	38.1	38.3	34.3	34.6	32.6
	white	87.4	87.5	87.2	88.0	87.9	88.1	87.3	81.1

TABLE III

Material		Example Number 19	20	21	22	23	24
sodium polyoxyethylene glycolate		10	25	25	30	50	
sodium polyoxyethylene diacetate							30
sodium tripolyphosphate		25		25			
sodium nitrilotriacetate		10					
sodium metasilicate		5	5	5	5	5	5
sodium sesquicarbonate		10	10	10	30	20	30
sodium sulfate		13	23	23	13	13	13
linear alkyl aryl sulfonate		20	10	10	20	10	20
sodium carboxymethyl cellulose		0.5	0.5	0.5	0.5	0.5	0.5
misc. brighteners, pigments etc.		1.5	1.5	1.5	1.5	1.5	
trisodium phosphate chlorinate			25				1.5
reflectance	gray	43.6	44.8	44.1	41.9	43.7	n.m.
	white	87.6	88.1	88.4	87.2	86.8	n.m.

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