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OXYACETIC ACID COMPOUNDS AS BUILDERS FOR DETERGENT COMPOSITIONS

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U.S. Cl. 252—110 12 Claims

ABSTRACT OF THE DISCLOSURE

A phosphate-free biodegradable detergent builder compatible with various synthetic detergent and soap formulations to produce generally non-eutrophic detergent products. The builder is a water-soluble salt of an aliphatic oxyhydrocarbon carboxylic compound having carboxylic radicals separated from internal oxygen atoms by at least one unsubstituted hydrocarbon radical. A preferred builder is an alkyl metal salt of triglycolic acid and the builders of the invention are combinable in weight ratios with the detergent active surfactants in the formulations ranging from about 20:1 to about 1:10.

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of our copending U.S. Ser. No. 98,887, filed Dec. 16, 1970, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates to organic builders for detergent compositions and more particularly to biodegradable non- or low-eutrophic builders compatible with various organic anionic, nonionic and/or amphoteric surface active compounds which are functional as detergents or cleaners.

Prior art

The use of builders in detergent compositions is well known. Builders are generally considered to be required in detergent formulations to improve detergency levels of the detergent compositions. Due to the complex nature of detergency, i.e., the various and numerous physicochemical and other factors involved, there has been no general basis found with respect to the functional characteristics or the chemical structure of the compounds from which the behavior of a detergent builder could be predicted. In general, detergent builders are believed to affect to various degrees such fatcors in detergent systems as stabilization and/or anti-redeposition of soil suspensions, emulsification of soil particles, surface activity of the aqueous detergent solutions, solubilization of water insoluble materials, foam or suds producing characteristics of the washing solutions, peptization or deflocculation of soil agglomerates, neutralization and/or buffering of acid or basic soils, sequestering of metallic ions, such as mineral hardness constituents which are often present in washing solutions, etc. As will be appreciated from the foregoing exemplary factors, only a relatively few compounds are known that can be classified as effective detergent builders.

However, the mere fact that a compound has been determined to be such a detergent builder, does not necessarily render its use advantageous in detergent compositions. A detergent builder should, among other things, be compatible not only with various available detergent materials but also with the various additives conventionally utilized, be hydrolytically stable in hot or cold alkaline aqueous solutions, be compatible with various bleaching and the like agents and, of course, not corrode and otherwise adversely affect the fabrics being washed or the equipment utilized for such washing operations.

Additionally, a builder should be biodegradable and be generally non-eutrophic (that is, contain a minimum or no elements which cannot be converted into carbon dioxide and water) in various waste water treatment systems, whether man-made or natural. Heretofore, known builders which have found some acceptability include various phosphorous and nitrogen containing compounds, such as for example, sodium tripolyphosphate (STPP) or salts of nitrilotriacetic acid (NTA). While some controversy may exist as to major causes of eutrophication of various bodies of water, in most instances it is generally recognized that phosphorous and nitrogen are most suspect as being the controlling factor; even though carbon has been shown to also contribute to eutrophication. Interested governmental bodies have concluded that phosphorous, and to a certain extent nitrogen, sources of nutrients must be controlled if eutrophication is to be successfully attacked.[1] Accordingly, the term "non-eutrophic" as used herein shall mean materials free from phosphorous and/or nitrogen sources of nutrients. Thus, presently acceptable nitrogen and/or phosphorous containing builders are suspect of contributing to water pollution by providing eutrophication conditions in bodies of water which are conducive to algae and other aquatic plants as well as bacterial growth, eventually rendering such bodies of water unfit for aquatic life or any other use. Phosphorous fertilizes excessive growth of algae and other aquatic weeds. As these plants die and decay they use up the oxygen in the water, cause fish to suffocate, and much of their phosphorous content is redissolved to fertilize yet another cycle or excessive plant growth. Finally, the accumulated masses of decayed vegetation fill the lake and turn it into a noisome bog. Nitrogen based organic builders are also said to contribute a similar fertilizer action, and ideally should be avoided.

Other builder materials are also known, as exemplified by German Display Pat. No. 1,926,422 or by Canadian Pat. No. 853,647 which do not possess the above disadvantage, nevertheless have other disadvantages, either of an economical or a functional nature. To one degree or another, all known builders, organic or inorganic, have certain limitations and disadvantages, such as those previously pointed out, and improved builders are continuously sought which would obviate or at least minimize the limitations and disadvantages of the prior art detergent builders.

SUMMARY OF THE INVENTION

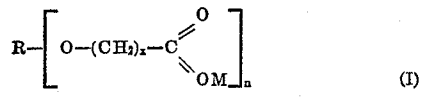
The invention provides in its preferred embodiments a nitrogen and phosphorous-free biodegradable substantially non-toxic organic builder compatible with a wide range of detergent and soap formulations for the production of non-eutrophic detergent and cleanser products.

[1] Environmental Quality.—The First Annual Report on Environmental Control, p. 52; August 1970 (U.S. Government Printing Office, Washington, D.C.).

The builders of the invention generally are water-soluble salts of aliphatic oxy-hydrocarbon carboxylic compounds having carboxylic radicals separated from internal oxygen atoms by at least one unsubstituted hydrocrbon radical (i.e. an alkylene radical). Of these compounds, a preferred embodiment is the alkali metal, NH_4 and amine salts of the oxyacetic acid group and a specific preferred builder is neutralized triglycolic acid. The builders of the invention are compatible in liquid or dry detergent and cleanser formulations in wide weight ratios ranging from about 100:1 to about 1:100.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

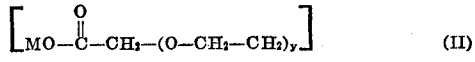
The detergent builders of the invention can be produced by many different organic synthesis methods including the oxidation of polyethylene glycols, ethoxylated glycerines, and ethoxylated polyols and generally comprise carboxyl ether compounds having spatial or steric characeristics for sequestering and/or chelating various metal ions, particularly the Ca and the Mg ions. Such products are utilized as their alkali metal, NH_4 and amine salts and preferably are utilized as the alkali metal salts. Somewhat more specifically, the detergent builders of the invention are salts of aliphatic oxyhydrocarbon carboxylic compounds having carboxylic radicals separated from internal oxygen atoms by at least one unsubstituted hydrocarbon radical and the preferred embodiments are represented by the formula:



(I)

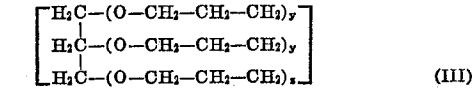
wherein $(CH_2)_x$ is termed the unsubstituted hydrocarbon radical and preferably n and x are whole integers ranging from 1 to 5, M is selected from the group consisting essentially of alkali metals, ammonium and amines, and R is selected from the group consisting essentially of:

(a)



(II)

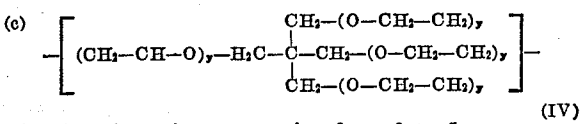
(b)



(III)

and

(c)



(IV)

wherein y is an integer ranging from 0 to 5.

A number of such aliphatic oxy-hydrocarbon carboxylic compounds are oxyacetic acids which exhibit good Ca/Mg chelating properties and detergent building characteristics and include the acids per se and the alkali metal, NH_4 and amine salts of the following:

Diglycolic acid (i.e. oxy-diacetic acid)
Triglycolic acid (i.e. 1,2-bis (carboxy methoxy) ethane)
Tetraglycolic acid (i.e. 1,2-bis (carboxy methoxy) ethyl ether)
Tris (carboxy methoxy ethoxy) propane
Symmetrical tetra(carboxy methoxy) neo-pentane

Preferred non-eutrophic detergent builder compounds are sodium and potassium salts of triglycolic acid and mixtures thereof, i.e., a monosodium and monopotassium salt of triglycolic acid and/or a mixture of disodium salt and dipotassium salt of triglycolic acid. Preferred low eutrophic builder compounds include the ammonium and amine salts of triglycolic and mixtures thereof, i.e., a diammonium salt of triglycolic acid, a di-triethanolamine salt of triglycolic acid and/or a monoammonium monotriethanolamine salt of triglycolic acid. Further, builder compounds of the invention include various mixtures of

the above enumerated acids and salts of the aliphatic oxyhydrocarbon carboxylic compounds, such as a mixture of neutralized or unneutralized diglycolic, triglycolic, tetraglycolic, tris(carboxy methoxy ethoxy) propane and/or tetra(carboxy methoxy)neo-pentane that is attained by certain synthesis route.

The builders of the present invention are not only effective and economical detergent builders but also exhibit many and various advantageous properties, which include hydrolytical stability, i.e., resistance to decomposition or degradation at elevated temperature and/or pH conditions, relative inertness toward various fabrics and equipment associated with laundering operations, low-toxic or irritating characteristics toward humans, compatibility with detergents, soaps, bleaching agents, additives and other various agents customarily in detergent formulations. Additionally, the builders of the invention are biodegradable and generally non-eutrophic, being nitrogen and phosphorous free (or at least having a low proportion thereof) and susceptible to bacteria attack without providing sufficient nutrients for the excessive growth and/or reproduction af algae, aquatic plant life, bacterial growth, and the like.

As mentioned, the builders of the invention are utilizable with any of the conventional detergent classes and mixtures thereof, as synthetic nonsoaps, soaps, anionic, nonionic and/or amphoteric surface active compounds suitable as cleaning agents. These compounds include sulfated or sulfonated alkyl, aryl and alkyl-aryl hydrocarbons and alkali metal salts thereof, for example, sodium salts of long chain alkyl sulfonates, sodium salts of alkyl benzene sulfonates, such as C_8 to C_{24} alkyl-benzol sulfonates, etc. Examples of other detergent materials are shown in pertinent literature sources, such as the book by Schwartz, Perry and Berch entitled "Surface Active Agents and Detergents"; Inter Science Publishers, New York (1949), which is incorporated herein by reference.

The amount of builder of the invention necessary for effective use with a surface active compound or formulation thereof (i.e., active) varies over a wide range and is regulated by a number of factors including the intended end use, the type of active surfactant employed, pH conditions, water hardness, etc. In general, the builders of the invention can be employed in detergent compositions in any desired proportion and include weight ratios of builder to "active" detergent material that range from about 20:1 to about 1:10 and in certain embodiments range from about 5:1 to 1:1.

The builders of the invention are utilizable per se and are often advantageously utilized to replace a portion or all of other builders presently employed in detergent formulations. While for eutrophication reasons and otherwise it is desirable to exclusively use the detergent builders of the invention, they nevertheless can be incorporated into detergent formulations in combination with other builders such as sodium tripolyphosphate (STPP), nitrilotriacetic acid salts (NTA) and/or polyelectrolyte builders. For example, conventional alkali metal polyphosphates, such as tetrasodium polyphosphate, etc., or similar alkali metal and ammonium salts of nitrilotriacetic acid are readily compatible with the builders of the invention in particular detergent formulations. Generally, the weight ratio of the aliphatic oxyhydrocarbon carboxylic builders to such known builders or builder mixtures ranges from about 1:10 to about 10:1.

The builders of the invention are formulated into detergent compositions in any form whatsoever including liquids, powders, flakes, beads, tablets, pellets, pastes, suspensions, aerosols, etc. and utilized in a conventional manner. The manner of formulation is not determinative of the invention and is selected as desired in accordance with the formulation being produced. The builders of the invention are obtainable from a number of known processes and as illustrative thereof, the following are mentioned: air oxidation of diethylene glycol; air-nitric acid

catalytic oxidation of diethylene glycol; reaction of formaldehyde with carbon monoxide and water, reaction of chloroacetic acid with a base, etc.

In order to illustrate, but in no way limit the invention, exemplary synthesis routes for certain of the builders of the invention are set forth:

DEMONSTRATION A

Oxidation of triethylene glycol

A solution of nitric acid comprised of 6 mols (540 grams) of 70% nitric acid in 90 grams of water was prepared and then 0.6 gram of ammonium vanadate was added. The solution was heated to about 68° C. and stirred continuously while approximately 1 gram of triethylene glycol was added. After several minutes, brown fumes started to evolve indicating the initiation of oxidation. Then 1 mol (150 grams) of triethylene glycol was slowly added to the fuming solution over a 70 minute period while maintaining the moderately exothermic reaction at about 67° to 73° C. with continued stirring. After all of the triethylene glycol was added, the reaction mixture was allowed to stand for about 2 hours at about 65° C. to complete the reaction. A clear blue solution resulted, which was concentrated and dried under vacuum and heat to yield about 181.1 grams of a brown solid.

The crude brown solid product was dissolved in water (approximately a 50% solution) and the solution was adjusted to a pH 10 with a sodium hydroxide solution (50%). The solution was then concentrated to a viscous liquid and mixed with a large amount of ethyl alcohol to precipitate a white solid product. After the precipitate was filtered from the solution and dried, it was analyzed as the disodium salt of triglycolic acid, the calcium chelation value of this salt being 197 me./g.

A substantially similar run was made without the use of the vanadate catalyst. The reaction was initiated with brown fumes from another nitric acid oxidation reaction. The reaction yields a crude product having a calcium chelation value of 174.8.

DEMONSTRATION B

Oxidation of tetraethylene glycol

A solution of 1080 grams of 70% nitric acid in 180 grams of water was prepared. 1.29 grams of ammonium vanadate was added to the solution and it was heated to about 68° C., with continuous stirring and a small amount (about 1 gram) of tetraethylene glycol (available from Union Carbide) added. The oxidation reaction started almost immediately. 388.4 grams of tetraethylene glycol was slowly added with continuous stirring in a similar manner as described in Demonstration A. The crude product was neutralized with sodium hydroxide to yield a salt analyzed as disodium tetraglycolic acid. The calcium chelation value of this salt was 78.6 but the acid form exhibited a higher chelation value.

DEMONSTRATION C

Oxidation of ethoxylated pentaerythritol

Pentaerythritol (680 grams, 5 mols) was reacted with ethylene oxide (approximately 20 mols) using potassium hydroxide (3.4 grams) as a catalyst in a 1 gallon autoclave. The reaction temperature was maintained at about 190° C. or less and a pressure of 70 p.s.i. or less.

The ethoxylated pentaerythritol (312 grams) was then oxidized with nitric acid (1080 grams of 70% acid) and ammonium vanadate (0.8 gram) at about 70° C. over a period of about 3 hours. The dried product (318 grams) exhibited an acid value of 8.90 me./g., with the theoretical value for $C[CH_2OCH_2COOH]_4$ being 10.8. The calcium chelation value for this acid product was 171 mg./g.

The acid product was neutralized with sodium hydroxide to a pH 10 and dried to yield the sodium salt thereof, which had a chelation value of 138 mg./g.

DEMONSTRATION D

Ethoxylation of ethylene glycol

Potassium hydroxide (2 grams) was dissolved in ethylene glycol (1240 grams) and charged to a one-gallon autoclave. The autoclave was purged with nitrogen and heated to 100° C. Ethylene oxide was slowly pumped into the autoclave while the reaction temperature was maintained at about 110° to 115° C. and pressure varied from 0 to 50 p.s.i. At intervals the ethylene oxide addition was stopped until all of it that had been added was reacted, as indicated by the decrease of pressure in the autoclave. Periodic samples were removed and analyzed for the number of mols of ethylene oxide added to ethylene glycol. A mixture of homologues was noted with increased additions of ethylene oxide over the reaction time.

The mixed homologues were then oxidized with nitric acid substantially as set forth in the preceding demonstration to yield a mixed oxidate containing the various builders of the invention including diglycolic triglycolic, tetraglycolic, tris (carboxy-methoxy-ethoxy) propane and tetra (carboxy-methoxy) neo-pentane. Such mixture is useful as a builder material and the above synthesized route provides a commercial feasible continuous system of producing the same.

COMPARATIVE CHELATION VALUES

Material:	Calcium chelation value mg./g.
$Na_5P_3O_{10}$ (STPP)	215.
$(NTA)Na_3$	335.
Diglycolic (Na)	177 (235 as acid).
Triglycolic (Na)	163 (197 as acid).
Tetraglycolic (Na)	87 (104 as acid).
Tris (carboxy - methoxy - ethoxy) propane (Na)	95 (110 as acid).
Tetra (carboxy - methoxy) neo-pentane (Na)	138 (117 as acid).

In order to illustrate but in no way limit the invention and compare it with known builders and detergent formulations, a builder of the invention, i.e., disodium diglycolic acid (DSDGA), was formulated into detergent compositions and compared against substantially identical detergent compositions utilizing known builders, i.e., sodium tripolyphosphate (STPP) and sodium nitrilotriacetic acid (NTA), and was studied for building characteristics under laundry operational conditions. The aqueous study solutions had a hardness of 180 p.p.m., a total detergent concentration of about 0.15% (solids), a temperature of 120° F. and a pH of about 9. A standardized Terg-o-Tometer laboratory machine washing procedure was utilized on standard soiled fabric specimens.

The following exemplary embodiment of an ionic detergent composition was used in this study, as set forth below, with the percentages being by weight.

	Percent
Linear sodium alkyl (C_{10}–C_{14}) benzol sulfonate (NaLAS)	18
Alkali metal carboxy methyl cellulose (CMC)	0.5
Builder (STPP; NTA; DSDGA)	30–50
Sodium silicate	5
Sodium sulfate (Na_2SO_4)	Q.S. [1]

[1] Quantity sufficient.

Sodium silicate is available in various combinatons of SO_2 and Na_2O, with each particular combination having, for example, individual toxicity characteristics. A selected sodium silicate may require proper pH adjustment in view of the end use of the detergent composition utilizing the same.

TABLE I.—DETERGENCY TESTS

	Builder	Detergency units [1]
(1)	STPP, 20%	7.5
	STPP, 30%	6.5
	STPP, 40%	3.8
	STPP, 50%	4.0
(2)	(NTA) Na_3, 20%	7.4
	(NTA) Na_3, 30%	6.7
	(NTA) Na_3, 40%	4.5
	(NTA) Na_3, 50%	6.8
(3)	DSDGA, 20%	7.2
	DSDGA, 30%	7.3
	DSDGA, 40%	6.9
	DSDGA, 50%	7.3
(4)	DKDGA,[2] 20%	7.8
	DKDGA, 30%	8.1
	DKDGA, 40%	7.3
	DKDGA, 50%	7.8
(5)	SKDGA,[3] 20%	7.9
	SKDGA, 30%	7.5
	SKDGA, 40%	7.1
	SKDGA, 50%	8.2
(6)	DADGA,[4] 20%	7.8
	DADGA, 30%	6.7
	DADGA, 40%	6.8
	DADGA, 50%	6.6
(7)	DTDGA,[5] 20%	8.3
	DTDGA, 30%	8.6
	DTDGA, 40%	7.3
	DTDGA, 50%	8.5

[1] Detergency units: $D.U.=R_{df}-R_{di}$
where R_{df}=reflectance units after washing, and
R_{di}=reflectance units before washing.
[2] DKDGA: dipotassium salt of diglycolic acid.
[3] SKDGA: monosodium-monopotassium salt of diglycolic acid
[4] DADGA: diammonium salt of diglycolic acid.
[5] DTDGA: ditriethanolamine salt of diglycolic acid.

As shown by the above results the builders of the invention compare very favorable with known builders and in certain instances exceed the known builders, i.e., increased amounts of the builder of the invention do not detract from the detergency characteristics. In addition, the above results demonstrate that certain embodiments of the builders of the invention have advantageous characteristics at lower builder levels over at least some of the known builders. It should be noted that despite their relatively favorable detergency characteristics, the diglycolic builder compounds are not the preferred embodiment of the builder compounds of the invention because of their relatively unfavorable toxicity characteristics.

To further illustrate the ability of the builders of the invention and compare them with known builders, additional detergent formulations were produced, which were identical to each other except for the builder utilized. The hardness of the aqueous solutions under consideration were varied between 350 p.p.m. and 140 p.p.m., the solutions had a total detergent concentration of about 0.2%, a temperature of 120° F. and were utilized on standard soiled fabric specimens in a standardized Terg-o-Tometer washing procedure.

An exemplary embodiment of an ionic detergent composition was utilized in this study, as set forth below, with the percentages being by weight.

	Percent
Linear sodium alkyl (C_{10}–C_{14}) benzol sulfonate (NaLAS) (or other substituted surfactant)	20
Sodium silicate [1]	5
Lauric myristic monoethanol amide (LMMEA)	2
Sodium carboxyl methal cellulose (CMC)	0.5
Builder (STPP; NTA; DSDGA; etc.)	40
Sodium sulfate (Na_2SO_4) QS [1]	

[1] Sodium silicate having a ratio of SiO_2 to Na_2O of about 2.40 was found to have favorable toxicity characteristics.
[2] Ibid.

TABLE II.—DETERGENCY TESTS

Active surfactant, percent by weight	Builder, percent by weight	Average soil removal [1] Water hardness 140 p.p.m.	Water hardness 350 p.p.m.
Ionic:			
NaLAS,[2] 20%	STPP,[3] 40%	26.5	20.6
NaLAS, 20%	DSDGA,[4] 40%	26.0	22.5
NaLAS, 20%	(NTA)Na_3,[5] 40%	24.3	24.5
NaLAS, 20%	Triglycolic oxidate homologue,[6] 40%	22.1	19.4
NaLAS, 20%	Tetraglycolic oxidate homologue,[7] 40%	21.7	21.2
NaLAS, 20%	Glycerine ethoxylated oxidate homologue,[8] 40%	21.5	18.9
NaLAS, 20%	Pentaerythritol ethoxylated oxidate homologue,[9] 40%	24.1	20.2
NaLAS, 20%	DSDGA, 20%; STPP, 20%	22.9	23.5
NaLAS, 20%	DSDGA, 20%; (NTA)Na_3, 20%	25.9	23.5
NaLAS, 20%	DSDGA, 20%; (EDTA)NH_4, [10] 20%	25.2	22.8
NaLAS, 20%	DSDGA, 20%; Na_2CO_3, 20%	23.6	20.8
NaLAS, 20%	DSDGA, 20%; Na_3HCO_3, 20%	22.5	22.2
TMS,[11] 10%	Soap,[12] 20%; DSDGA, 40%	19.7	17.7
TMS, 20%	DSDGA, 40%	20.9	20.4
NaLAS, 10%	NaTAS,[13] 10%; DSDGA, 40%	25.5	21.9
NaαSTA,[14] 13.5%	NaTAS, 6.5%; DSDGA, 40%	25.7	17.7
NaLAS, 20%	DSDGA, 30%	25.7	24.1
NaLAS, 20%	DSDGA, 20%	23.7	23.8
Amphoteric: Deriphat 170–B,[15] 20%	DSDGA, 40%	18.4	20.1

[1] Soil removal percent=(A−B)/(C−B)×100 where A=reflectance of swatch after washing; B=reflectance of swatch before washing; and C=reflectance of swatch before soiling.
These results comprise averages from three test fabrics: (a) commercial "test fabrics"; (b) commercial "U.S. Testing" fabrics; and (c) private laboratory prepared fabrics (carbon black, oily soil, powder-dry application).
[2] Linear sodium alkyl (C_{10}–C_{14}) benzol sulfonate.
[3] Sodium tripolyphosphate.
[4] Disodium diglycolic acid.
[5] Nitrilotriacetic trisodium salt.
[6] 1,2 Bis(carboxy-methoxy-ethane) disodium salt.
[7] 1,2 Bis(carboxy-methoxy-ethyl ether) disodium salt.
[8] Tris(carboxy-methoxy-ethoxy) propane trisodium salt.
[9] Symmetrical tetra(carboxy-methoxy)-neopentane tetrasodium salt.
[10] Ethylene diamine tetraacetic acid tetrasodium salt.
[11] Sodium alpha-sulfo-tallow methyl ester.
[12] 80% tallow, 20% coconut soap.
[13] Sodium tallow alcohol sulfate.
[14] Disodium alpha-sulfo-tallow acid.
[15] Trade name of General Mills for an amphoteric surfactant (N-lauryl myristyl beta-amino propionic acid).

As shown, the builders of the invention compared very favorably with known builders and are, in certain instances advantageously combinable with such known builders and detergent components or adjuvants in detergent compositions for improved soil removal. It will be noted from Table II that the builders of the instant invention can be formulated with a wide range of organic surfactants as well as soap combinations; and that the resulting detergent formulations exhibit detergency characteristics compared to present-day detergents.

To yet additionally illustrate the builders of the invention and compare them with known builders, additional detergent formulations were produced which were nonionic and identical to each other except for the builder and the level of builder in the formulations. Again, standardized aqueous solutions were studied having a hardness of 180 p.p.m., a temperature of 120° F., a total detergent concentration of about 0.15% and again Standard Terg-o-Tometer laboratory detergency tests were conducted using standard soiled cloths.

Those tests were conducted using the following exemplary embodiments of a nonionic detergent formulation; with the percentages being by weight:

	Percent
Tergitol 15–S–9 [1] (a nonionic surfactant)	10
Sodium carboxy methyl cellulose (CMC)	0.5
Sodium silicate	5.0
Builder (STPP; DSDGA; etc.)	20–50
Sodium sulfate (Na_2SO_4) QS [2].	

[1] A trade name of Union Carbide for a linear C_{13-17} alcohol ethoxylated with 9 mols ethylene oxide.
[2] Ibid.

TABLE III.—DETERGENCY TESTS

	Builder	Detergency units
(1)	STPP, 20%	7.4
	STPP, 30%	7.7
	STPP, 40%	7.2
	STPP, 50%	7.8
(2)	(NTA)Na_3, 20%	7.5
	(NTA)Na_3, 30%	7.5
	(NTA)Na_3, 40%	7.9
	(NTA)Na_3, 50%	9.5
(3)	DSGAA, 20%	8.4
	DSDGA, 30%	7.7
	DSDGA, 40%	7.9
	DSDGA, 50%	8.1
(4)	DKDGA,[3] 20%	7.1
	DKDGA, 30%	8.3
	DKDGA, 40%	7.6
	DKDGA, 50%	8.4
(5)	SKDGA,[3] 20%	8.0
	SKDGA, 30%	8.0
	SKDGA, 40%	7.6
	SKDGA, 50%	8.0
(6)	DADGA,[4] 20%	6.7
	DADGA, 30%	7.2
	DADGA, 40%	8.2
	DADGA, 50%	7.8
(7)	DTDGA,[5] 20%	6.4
	DTDGA, 30%	7.9
	DTDGA, 40%	6.7
	DTDGA, 50%	7.8

[2] [3] [4] [5] See footnotes at end of Table I.

The data in Table III shows that the builders of the instant invention also compared favorably with known builders, and appear to have some additional advantage at lower concentration levels, such as at 20% builder level.

To further illustrate additional functional characteristics of the preferred builder of the instant invention, a series of solid detergent formulations were prepared and utilized in Terg-o-Tometer tests in which the solid is added and suspended in the detergent test solution (0.10%) after which clean fabric swatches are immersed for twenty minutes, 90 cycles per minute agitation, at 120° F. liquor temperature. The "wash" cycle is followed by two three-minute rinse cycles using water of comparable temperature and hardness.

This wash/rinse cycle operation was repeated for five cycles, after which the test swatches were dried and their reflectance values recorded.

The detergent formulation used in this study was as follows; with the percentages being by weight:

	Percent
Linear sodium alkyl (C_{10}–C_{14}) benzol sulfonate NaLAS active) (or other substituted surfactant)[14]	20
Sodium carboxy methyl cellulose (CMC)	0.5
Sodium silicate	5.0
Builder (STPP; NTA; DSDGA; etc.)	40
Sodium sulfate (Na_2SO_4) QS [1]	

[1] Quantity sufficient.
[14] See Footnote at end of Table II.

TABLE IV.—REDEPOSITION TESTS

Builder	Redeposition Index [1]	
	Indian head cotton	Terry cloth cotton
No builder	85.5	74.9
STPP, 20%	90.1	81.5
(NTA)Na_3, 20%	87.7	79.5
DSDGA, 20%	88.7	81.6
STPP, 40%	89.2	77.5
(NTA)Na_3, 40%	88.5	81.0
DSDGA, 40%	89.0	79.7

[1] Redeposition Index $=\frac{R_{df} \times 100}{R_{di}}$ where R_{df}=swatch reflectance after washing; R_{di}=swatch reflectance before washing.

The above results show that the DSDGA builder embodiment of the instant invention demonstrates comparable anti-redeposition properties to the other known builders tested in the described detergent formulations.

Similar redeposition tests were conducted on the nonionic based detergent formulation previously described (see Table III). The experimental results are set forth in Table V.

TABLE V.—REDEPOSITION TESTS

Builder	Redeposition Index [1]	
	Indian head cotton	Terry cloth cotton
STPP, 20%	88.7	71.2
(NTA)Na_3, 20%	87.8	79.6
DSDGA, 20%	85.4	80.6
STPP, 40%	88.6	78.7
(NTA)Na_3, 40%	86.7	82.5
DSDGA, 40%	87.2	82.4

[1] See footnote at end of Table IV.

The above results again demonstrate that the preferred builder of the instant invention compares closely with the other known builders and exhibits good anti-redeposition properties for the formulations tested.

Most of the foregoing detergent formulations represented typical solid-type product forms; namely, flakes, beads, tablets, powders, pellets, etc. While in general these formulations can be dissolved in various aqueous and aqueous-solvent systems, such as ethanol and water mixtures, in order to obtain higher liquid concentrates, such formulations will generally be made with little or no inorganic salt filler (such as added sodium sulfate, or sodium chloride), and may use hydrotropic agents and/or co-solvent systems.

The following is an exemplary embodiment of a heavy-duty liquid detergent concentrate prepared with a selected

builder salt of the instant invention; with the percentages being by weight.

	Percent
Bio-Soft EA–10 (LAEO) [a trade name of Stepan Chemical Company for a nonionic 100% active surfactant, a linear alcohol alkoxylate ethoxylated with 10 mols of ethylene oxide]	10.0
Potassium meta silicate (KMS. $5H_2O$)	12.5
Builder (DKTGA)	25.0
Sodium carboxy methyl cellulose (CMC)	0.5
Acrysol stabilizer ASE–95 [a trade name of Rohm & Haas, Inc. for an acrylic polymer]	5.0
TINAPAL RBS [a trade name of Geigy Chemical Co. for an optical brightener]	0.1
Water (H_2O) QS.[1]	
Potassium hydroxide (KOH), QS [1] to pH 10.	

[1] Quantity sufficient.

A clear, stable, liquid floor cleaner formulation was prepared as follows:

	Percent
Ninol 1285 [a trade name of Stepan Chemical Company for a coconut diethanolamide]	7
Builder (DKTGA)	10
Sodium xylane sulfonate	0.5
Water (H_2O)	82.5

The builders of the invention were studied for toxicity and irritancy in accordance with standard procedures to determined the acuate oral toxicity, primary skin irritation and eye irritation potential thereof and compare such properties against at least certain known builders in detergent formulations.

TOXICITY/IRRITANCY RESULTS

Material	LD_{50}, as is	LD_{50}, 100% basis	Irritancy test, 1% active, abraded and unabraded	Draze rabbit eye
DSDGA	2.83	1.23	0.08	0.0
DGA	1.88	0.82		
DSTGA	12.8	5.56	0.0	0.0
Heavy duty form—DSDGA [1]		3.7		
Heavy duty form—STPP [2]		6.2		

[1] 20% NaLAS; 20% DSDGA; 5% Na; 0.5% Na-CMC and 54.5% Na_2SO
[2] Same as above, except 20% STPP used in place ofDSDGA.

An interesting fact of the above study is that the higher homologue, i.e., triglycolic acid compound, is substantially less toxic than diglycolic. The decrease in toxicity by the addition of one mol of ethylene oxide is unexpected. It is presumed that still further addition of ethylene oxide, i.e. higher homologues of diglycolic, are even less toxic, for example, see Gleason et al., Clinical Toxicology of Commercial Products, 3rd Ed. (Williams & Wilkins, Baltimore, Md.) 1969.

The biodegradability of the builders of the invention was studied by a five-day biological oxygen demand test. Using a Madision, Wis. sewage plant "seed" more oxygen was consumed when one of the builders (DSDGA) was incorporated, than when it was absent, and this indicates that the builder can be metabolized by normal, activated sludge. It is expected that other builders of the invention are also biodegradable, for example, see Chemical Abstracts, 1971, 99.399n.

The builders of the invention are compatible with and easily formulated into various light and heavy-duty detergent formulations, dishwashing formulations, "institutional" cleansing formulations, metal cleansing formulations, etc., and are relatively stable in either liquid or dry form over extended periods of time at ambient conditions. The builders of the invention may exhibit some hydroscopic properties somewhat similar to the known builders, and, in certain instances it is advantageous to incorporate various "anti-tacking" agents and the like into detergent formulations utilizing the builders of the invention. Anti-tacking or "anti-caking" agents are utilized in a wide range of amounts, ranging from about 1% to 30% by weight of the detergent composition. Such anti-tacking additives include alkali metal salts of oxalic, maleic, fumaric, thiodisuccinic and sulfonoacetic acids; specially formulated caustic soda; combinations of non-soap synthetic anionic or nonionic surfactants; alkali metal salts of toluenesulfonate in combination with polyvinyl chloride resins or polychloride-butadiene copolymer resins; combinations of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$; dialkali metal salts of benzene-disulfonate or toluenedisulfonate; alkali metal salts of sulfosuccinate; silicones, chlorosilanes, alkoxysilanes, polysiloxanes, alkali metal salts of alkylnaphthalenesulfonates, ethylene glycol-ethylene oxide condensation products having molecular weights of about 1500 to 2500; addition products of ethylene oxide and oleyl alcohol, $Na_5P_3O_{10}$; alkali metal salts of sulfosuccinates, xylenesulfonate or tripolyphosphate; Cab-O-Sil (a registered trademark for a pyrogenic silica), Santocel (a registered trademark for a silica aerogel), alkali metal salts of carbonic acid and alkali metal salts of ortho-, iso or terephthalic acid, etc.

The foregoing illustrations and examples set forth the characteristics of certain specific builders of the invention and it will be appreciated that other builders of the invention yield similar results.

Additives which can be used with the instant detergent builders include tarnish inhibitors (such as benzotriazole, ethylene thiourea, etc., perfumes, coloring agents, optical brighteners, corrosion inhibitors (such as silicates, etc.), hydrotopes (such as benzene, toluene, xylene, cumene, etc., and their sulfonate salts), alkalies (such as caustic carbonate, bicarbonate, etc.), bleaching agents (such as trichlorocarbanilide, etc.), and foam boosters (such as coconut ethanolamides, etc.), and salts (such as Na_2SO_4, NaCl, $MgSO_4$, etc.).

The builders of the invention are readily incorporated into various types of detergent formulations, i.e. free-flowing powders, beads, flakes, pellets, etc. by conventional techniques and finished to a selected form, for example, see J. C. Ingram "Outline of Processes Used in the Drying of Soaps and Detergents," the Journal of the American Oil Chemists' Society, vol. 33, November 1956, pp. 579–585.

Various changes and modifications to the above described embodiments of the invention may be made without departing from the spirit and scope thereof and it is intended that all matters contained in the above description shall be interpreted as illustrative and not as limiting.

We claim as our invention:

1. A washing composition consisting essentially of a synthetic organic detergent selected from the group consisting of non-soap anionics, soaps, nonionics, and amphoteric surface active compounds, and a builder material selected from the group consisting of alkali metal, NH_4 and amine salts of 1,2-bis(carboxy-methoxy-ethane) acid, 1,2 bis(carboxy-methoxy-ethyl-ether) acid, tris-(carboxy-methoxy-ethoxy) propane, symmetrical tetra-(carboxy-methoxy) neo-pentane and mixtures thereof, said builder and said organic detergent being present in said washing composition in a weight ratio ranging from about 20:1 to about 1:10.

2. A washing composition as defined in claim 1 wherein the organic detergent is a non-soap anionic surface active compound.

3. A washing composition as defined in claim 1 which includes a supplemental builder selected from the group consisting of alkali metal polyphosphates, aminopolycarboxylates and mixtures thereof, said aliphatic oxy-hydrocarbon carboxylic compound and said additional builder

being present in said washing composition in a weight ratio ranging from about 1:10 to about 10:1.

4. A washing composition as defined in claim **1** wherein the builder is a water-soluble salt of 1,2-bis(carboxy-methoxy-ethane) acid.

5. A washing composition as defined in claim **1** wherein the builder is a water-soluble salt of 1,2-bis(carboxy-methoxy-ethyl-ether) acid.

6. A washing composition as defined in claim **1** wherein the builder is a water-soluble salt of tris(carboxy-methoxy-ethoxy) propane.

7. A washing composition as defined in claim **1** wherein the builder is a water-soluble salt of symmetrical tetra-(carboxy-methoxy) neo-pentane.

8. A washing composition as defined in claim **1** wherein the builder is 1,2-bis(carboxy-methoxy-ethane) disodium salt.

9. A washing composition as defined in claim **1** wherein the builder is 1,2-bis(carboxy-methoxy-ethyl-ether) disodium salt.

10. A washing composition as defined in claim **1** wherein the builder is tris(carboxy-methoxy-ethoxy) propane trisodium salt.

11. A washing composition as defined in claim **1** wherein the builder is symmetrical tetra(carboxy-methoxy) neo-pentane tetrasodium salt.

12. A washing composition as defined in claim **1** including about 1 to 30% by weight of an anti-caking agent.

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