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DETERGENT FORMULATIONS

Walter E. Foster, and Paul Kobetz, Baton Rouge, La., assignors to Ethyl Corporation, New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

To assist in obviating eutrophication of water, detergent builder systems based on the combination of citrates and nitrilotriacetates are used. Conventional detergent actives may be used with these builder systems.

REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our prior copending application Ser. No. 111,721, filed Feb. 1, 1971 now abandoned.

This invention relates to novel builder compositions for use with synthetic detergents and to the resultant washing compositions and their uses.

BACKGROUND

In the manufacture of detergent formulations for laundering and general purpose washing operations, it is common practice to employ detergent builders—substances used in combination with surface-active compounds to aid in cleansing the articles being washed. The polyphosphates, notably sodium tripolyphosphate and tetrasodium pyrophosphate, are the commonly used detergent builders. However, these materials possess certain shortcomings. In the first place, the polyphosphates are susceptible to hydrolysis and degradation in aqueous solutions (Canadian Pat. 737,422). In addition, the phosphorus residues resulting from the widespread use of synthetic detergent formulations containing these phosphorus-containing builders have been said to contribute to eutrophication of rivers, lakes, underground streams, and other bodies of water. ["Detergent Phosphorus Effect on Algae" by Thomas E. Maloney, *Journal of the Water Pollution Control Federation*, Vol. 38, No. 1, pp. 38–45 (January 1966)].

The desirability of providing an efficacious detergent builder which does not suffer from the foregoing limitations is deemed to be self-evident.

THE INVENTION

This invention involves reducing and preferably eliminating the phosphorus-containing builders in detergent formulations by the use of builder systems based on citric acid and nitrilotriacetic acid salts. More particularly, this invention provides a builder system which comprises an alkali or ammonium salt of citric acid and an alkali or ammonium salt of nitrilotriacetic acid, preferably in a weight ratio (citrate to nitrilotriacetate) ranging from about 1:10 to about 1:1. The most preferred weight ratios fall in the range of from about 1:10 to about 1:3 (citrate:nitrilotriacetate). The preferred salts are the alkali metal salts, potassium and especially sodium being particularly preferred. However, the ammonium and alkyl ammonium salts are suitable.

It is known in the art that NTA (sodium nitrilotriacetate is a substantially better detergent builder than the citric acid salts. It naturally follows that the building capacity of a mixture of the two materials in which a given amount of citrate builder has been replaced by a corresponding amount of NTA will be better than the citrate builder used alone. Likewise, it would naturally follow

that the building capacity of a mixture of the two materials in which a given amount of NTA has been replaced by a corresponding amount of citrate builder should be poorer than the NTA used alone. However, as will be seen from the information presented hereinafter it has been discovered that in the proportions described above this generalization does not hold true.

The builders of this invention can be advantageously used with a wide variety of detergent actives or surfactants, including those known in the art as anionic, cationic, nonionic, ampholytic, and zwitterionic detergents as well as any suitable mixture of such detergents. When the resultant washing compositions are used in aqueous washing systems, the cleaning power of the formulation is enhanced in much the same way as when the commonly used polyphosphate builders are employed. Yet the present builder systems are more resistant to hydrolytic degradation than the polyphosphates and do not contribute to the eutrophication problems characteristic of phosphorus-containing builders.

Accordingly, another embodiment of this invention is a detergent composition comprising (1) a water-soluble organic detergent compound selected from the group consisting of anionic, cationic, nonionic, zwitterionic and ampholytic detergent compounds, (2) a salt of citric acid selected from the group consisting of alkali and ammonium salts thereof and (3) a salt of nitrilotriacetic acid selected from the group consisting of the alkali and ammonium salts thereof, the weight ratio of citrate and nitrilotriacetate salts to detergent compound ranging from about 1:3 to about 10:1 and the weight ratio of citrate to nitrilotriacetate ranging from about 1:10 to about 1:1. The preferred weight ratio of citrate and nitrilotriacetate salts to detergent compound ranges from about 1:10 to about 1:3.

The builder systems and the detergent compositions of this invention preferably additionally contain an alkali metal sulfate or an alkali metal carbonate, or both. Usually the amount of the sulfate and/or carbonate will not exceed about 300 percent by weight of the total weight of the citrate and nitrilotriacetate salts present in the composition. Indeed, amounts considerably less than this are found entirely efficacious in the vast majority of the compositions of this invention. The preferred alkali metal sulfates and alkali metal carbonates are the potassium and especially the sodium salts.

Still another preferred embodiment of this invention involves providing in the builder systems and the detergent compositions a relatively small amount of a water-soluble alkali metal silicate. From the cost effectiveness standpoint the builder system and the detergent composition should contain a water-soluble alkali metal silicate in an amount up to about 25 percent by weight based on the total weight of citrate and nitrilotriaceate salts present in the system. These silicates include the alkali metal metasilicates (e.g., $NaSiO_3$), alkali metal ortho-silicates and related substances containing varying proportions of chemically combined alkali metal oxide and silica. The prime requisite is that the silicate be water-soluble. The sodium silicates are preferred because of their availability and lower cost. However, use may be made of other alkali metal silicates such as the water-soluble silicates of potassium, lithium and the like, or the silicates of a mixture of two or more of the alkali metals. Of the various classes of water-soluble alkali metal silicates, liquid sodium silicate having a $Na_2O:SiO_2$ weight ratio of about 1:2.4 appears to be the most efficacious for use in this invention and thus the use of this silicate constitutes still another preferred embodiment.

As noted above, the builder combinations of this invention are generally employed in the form of water-soluble salts, notably alkali metal salts, ammonium salts

or alkyl ammonium salts. The alkali metal salt of citric acid and of nitrilotriacetic acid can involve one or a mixture of alkali metal salts although the potassium and especially the sodium salts are preferred because of their relatively low cost and enhanced effectiveness. Because the detergent formulations are generally used in alkaline aqueous systems, it is entirely feasible to use in their manufacture citric acid, nitrilotriacetic acid or the partially neutralized free acids. The free acid group(s) will be converted to the appropriate salt at least as soon as the formulations are put to use in an alkaline environment.

As will be apparent from the foregoing, the builder systems of this invention can be used with a wide variety of detergents including those classed in the art as anionic detergents, cationic detergents, nonionic detergents, ampholytic (i.e., amphoteric) detergents, and zwitterionic detergents, and any suitable mixture of two or more of these (whether from the same class or from different classes). Those skilled in the art are thoroughly familiar with the nature of such detergent compounds and the literature is replete with illustrations and exemplifications. Typical of the patents and printed literature which may be consulted in this regard are U.S. Pats. 3,635,829; 3,422,-021 and 2,961,409 as well as "Surface Active Agents" by Schwartz and Perry and "Surface Active Agents and Detergents" by Schwartz, Perry and Berch, the entire disclosure of each of the foregoing references being incorporated by reference herein.

Generally speaking, the preferred detergents for use in this invention are the anionic and the nonionic surface active compounds.

Finished detergent formulations of this invention may contain minor amounts of other commonly used materials in order to enhance the effectiveness or attractiveness of the product. Exemplary of such materials are soluble sodium carboxymethyl cellulose or other soil redeposition inhibitors; benzotriazole, ethylene thiourea, or other tarnish inhibitors; perfume; fluorescers; dyes or pigments; brightening agents; enzymes; water; alcohols; other builder additives, such as the water-soluble salts of ethylenediaminetetraacetic acid, N-(2-hydroxyethyl) - ethylenediaminetriacetic acid and N-(2-hydroxyethyl)-nitrilodiacetic acid and pH adjusters, such as sodium hydroxide and potassium hydroxide. In the built liquid detergent formulations of this invention, the use of hydrotropic agents may be found efficacious. Suitable hydrotropes include the water-soluble alkali metal salts of toluene sulfonic acid, benzene sulfonic acid, and xylene sulfonic acid. Potassium toluene sulfonate and sodium toluene sulfonate are preferred for this use and will normally be employed in concentrates ranging up to about 10 or 12 percent by weight based on the total composition. Foam stabilizers, such as fatty acid alkanolamides (e.g., lauric acid monoethanolamide, lauric acid diethanolamide, etc.) and tertiary amine oxides (e.g., lauryl dimethyl amine oxide, etc.) may also be used in the formulations of this invention. The references incorporated into this disclosure give further illustrations of auxiliary materials which can be used in the compositions of this invention.

It will be apparent from the foregoing that the compositions of this invention may be formulated according to any of the various commercially desirable forms. For example, the formulations of this invention may be provided in granular form, in liquid form, in tablet form, or in the form of flakes or powders.

Except for the proportions of the citrate to the nitrilotriacetate, the relative proportions and absolute quantities of the several ingredients of the finished compositions of this invention are susceptible to considerable variation and in most cases will vary depending upon such factors as the nature of the particular ingredients being utilized, the end use for which the composition is intended to be put, the relative costs of the ingredients, and the like. For example, the total concentration of the detergent formulations of this invention in water will normally range below about 0.3 percent by weight although it is entirely feasible to utilize higher concentrations where the circumstances warrant or justify the use of higher concentrations. In most cases the aqueous washing solutions of this invention will contain from about 0.05 to about 0.25 weight percent of combined detergent active(s) and builder. The preferred compositions of this inventin are phosphorus-free although it may be desired to include therein reduced quantities of conventional phosphorus-containing materials such as sodium tripolyphosphate, tetrasodium pyrophosphate, salts of substituted methylene diphosphonic acids, long chain tertiary phosphine oxides, or the like.

The invention is not to be limited to any particular method of mixing the builder and the detergent. The builder may be mechanically mixed in, crutched in the detergent in the form of a slurry, or dissolved in a solution of the detergent. In addition, the builder system may be admixed with the detergent in any of the forms in which the detergent is manufactured, as well as being added simultaneously or separately to an aqueous solution. In any event, the present builder system is intended to be used with the detergent at the time of application as a cleansing agent.

In order to illustrate the practice and advantages of this invention, the following examples are presented. In these examples a number of detergent formulations were prepared and their cleansing efficacy determined experimentally by means of the standard Launderometer testing procedure. In these tests, use was made of the following detergent formulations in which all percentages are by weight:

	Percent
Ethoxylated alcohols (Neodol 25–9)	9.0
Liquid Sodium Silicate (solids basis)	6.0
Builder (anhydrous basis)	35.0
Na CMC (active basis)	0.6
Na_2SO_4 (anhydrous)	49.4

The surfactant, the ethoxylated alcohols, was a mixture of ethoxylated C_{12}–C_{15} alcohols (primarily linear alcohols) have on the average about nine ethylene oxide units per molecule. This nonionic detergent is available commercially from Shell Chemical Company. The liquid sodium silicate had a $Na_2O:SiO_2$ weight ratio of 1:2.4 and is available from the Philadelphia Quartz Company under the tradename RU Silicate. Na CMC stands for sodium carboxymethyl cellulose.

Four replicate detergency evaluations in duplicate (eight individual evaluations) were made for each builder blend using EMPA No. 101 soiled cloth in the Launderometer. The detergent was used at a concentration of 0.15 percent in water of 150 p.p.m. hardness

$$(3/2Ca^{2+}/Mg^{2+})$$

at 120° F. The average detersive efficiency for each builder blend (100 percent NTA, 75 wt. percent NTA+25 wt. percent sodium citrate, 50 wt. percent NTA+50 wt. percent sodium citrate, 25 wt. percent NTA+75 wt. percent sodium citrate and 100 percent sodium citrate) are reported as percent of the 100 percent NTA builder formulation below.

	Builder (35% of formulation)	Detersive efficiency percent of NTA formulated
Formulation:		
1	100% NTA+0% citrate	100.0
2	75% NTA+25% citrate	98.9±1.4
3	50% NTA+50% citrate	98.5±1.4
4	25% NTA+75% citrate	93.0±1.4
5	0% NTA+100% citrate	93.1±1.4

The data above show that there is no significant difference between formulation (1) with all NTA and formulation (2) with a 3/1 ratio of NTA/Citrate at a 95 percent confidence limit (± 1.4. In the case of formulation (3) the difference at the 95 percent confidence level

is statistically significant, but the magnitude of the difference is not large. On the other hand, replacement of a majority or all of the NTA with citrate as in formulations (4) and (5) gave markedly inferior results. Thus, in accordance with this invention it is possible to replace certain proportions of NTA with the normally less effective citrate builder without incurring any statistically significant loss in detersive efficiency. In other instances, this substitution can be accomplished pursuant to this invention with only a slight loss in detersive efficiency, Hence, this invention makes it possible to achieve all or essentially all of the outstanding builder effectiveness of NTA by means of blends which have reduced amounts of NTA combined with the ecologically desirable citrates.

Some illustrative solid heavy duty laundering formulations of this invention are as follow (percentages being weight percentages):

	Percent
Surface-active agent (See Note 1)	10–25
Sodium citrate and sodium nitrilotriacetate (weight ratio from 1:10 to 1:1)	10–25
Sodium metasilicate (anhydrous)	2–10
Sodium carboxymethylcellulose	1
Optical brightener (fluorescent dye)	0.1
Perfume	0.1
Sodium sulfate (See Note 2)	Balance to 100

NOTES:

1. One or a combination of the following: sodium alkyl aryl sulfonate, sodium alkyl sulfonate, sodium alkane sulfonate, sodium alkenyl sulfonate, octyl phenol ethoxylate, nonyl phenol ethoxylate, fatty alcohol ethoxylate, fatty acid amide, alkanol amide, tall oil ethoxylate.
2. The sodium sulfate may be totally or partially replaced by one or more of the following: borax, soda ash, sodium bicarbonate, sodium chloride, sodium sesquicarbonate.

Typical liquid laundering formulations of this invention are as follows (percentages being weight percentages):

	Percent
Surface-active agent (See Note 1 above)	10–15
Potassium citrate and potassium nitrilotriacetate (weight ratio from 1:10 to 1:1)	10–20
Potassium metasilicate	2–10
Sodium carboxymethylcellulose	1
Sodium benzene sulfonate (See Note 3)	5–10
Optical brightener (fluorescent dye)	0.1
Water	Balance to 100

NOTE:

3. The sodium benzene sulfonate may be totally or partially replaced by potassium benzene sulfonate, sodium toluene sulfonate, sodium xylene sulfonate, etc.

It is not intended that this invention be unduly limited by the exemplifications herein provided. By way of example, although this invention provides compositions which are especially well suited for use as laundry detergents, the compositions can of course be used for other similar cleaning operations, such as washing walls, ceilings, floors, windows, dishes, animals, lawn furniture, bird cages, automobiles, bicycles, patios, sidewalks, fences, railroad cars, ariplanes, gliders, boats, glassware, jewelry, pots, pans, vases and so on, ad infinitum.

What is claimed is:

1. A water-soluble detergent builder composition consisting essentially of (a) a salt of citric acid selected from the group consisting of alkail metal and ammonium salts thereof and (b) a salt of nitrilotriacetic acid selected from the group consisting of the alkali metal and ammonium salts thereof, the weight ratio of citrate to nitrilotriacetate being about 1:1,

2. The composition of Claim **1** wherein said salts are sodium salts.

3. The composition of Claim **1** additionally containing a member selected from the group consisting of alkali metal sulfate, alkali metal carbonate, or mixtures thereof in an amount up to about 300 percent by weight based on the total weight of citrate and nitrilotriacetate salts.

4. The composition of Claim **1** additionally containing a water-soluble alkali metal silicate in an amount up to about 25 percent by weight based on the total weight of citrate and nitrilotriacetate salts.

5. A detergent composition adapted for use with water consisting essentially of (1) a water-soluble organic nonionic detergent compound, (2) a salt of citric acid selected from the group consisting of alkali metal and ammonium salts thereof and (3) a salt of nitrilotriacetic acid selected from the group consisting of the alkali metal and ammonium salts thereof, the weight ratio of citrate and nitrilotriacetate salts to detergent compound ranging from about 1:3 to about 10:1 and the weight ratio of citrate to nitrilotriacetate being about 1:1.

6. The composition of Claim **5** wherein the weight ratio of citrate and nitrilotriacetate salts to detergent compound ranges from about 1:1 to about 5:1.

7. The composition of Claim **5** wherein said salts are sodium salts.

8. The composition of Claim **5** additionally containing a member selected from the group consisting of alkali metal sulfate, alkali metal carbonate, or mixtures thereof in an amount up to about 300 percent by weight based on the total weight of citrate and nitrilotriacetate salts.

9. The composition of Claim **5** additionally containing a water-soluble alkali metal silicate in an amount up to about 25 percent by weight based on the total weight of citrate and nitrilotriacetate salts.

10. A composition according to Claim **5** wherein the citrate and nitrilotriacetate salts are sodium salts, wherein the weight ratio of sodium citrate to sodium nitrilotriacetate is about 1:1, wherein the weight ratio of sodium citrate and sodium nitrilotriacetate to the detergent compound ranges from about 1:1 to about 5:1, wherein the composition additionally contains a member selected from the group consisting of sodium sulfate, sodium carbonate, and mixtures thereof in an amount up to about 300 percent by weight based on the total weight of sodium citrate and sodium nitrilotriacetate salts, and wherein the composition additionally contains sodium silicate having a $Na_2O:SiO_2$ weight ratio of about 1:2.4 in an amount up to about 25 percent by weight based on the total weight of sodium citrate and sodium nitrilotriacetate salts.

References Cited

UNITED STATES PATENTS

3,692,684	9/1972	Hentschel	252—89
2,311,008	2/1943	Tucker	252—89 X

OTHER REFERENCES

"Amine Acid Chelating Agents in Detergent," Robert Pollard, Soap & Chemical Specialties September 1966, pp. 58–62.

LEON D. ROSDOL, Primary Examiner

E. L. ROLLINS, Assistant Examiner