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DETERGENT COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A composition which is soluble in water to form a washing solution which is effective to remove soil from a substrate. The composition comprises an organic surface-active detergent and an aluminate or borate compound of alphahydroxy carboxylic acids.

The present invention relates generally to washing procedures using an improved detergent composition. More particularly, the present invention relates to the use of alpha-hydroxy carboxylic acid complexes as sequestering agents and builders for detergent compositions.

The term "detergency" usually implies cleaning the surfaces of a solid object by means of a liquid bath. Detergency implies that the cleaning process involves a physical chemical action other than simple solutions. Detergency is usually considered to mean an unusually enhanced cleaning effect of a liquid bath, caused primarily by the presence in the bath of a special agent which is called the detergent. The detergent acts by altering the interfacial effects at the various phase boundaries within the system. A typical detersive system consists of a solid object to be cleaned, called the substrate; soil or dirt attached to the substrate which is to be removed in the washing process; and a liquid bath which is applied to the soiled substrate. The bath in a detersive system is invariably a solution, the solute consisting of the detergent. Other solute components may also be present and if these components contribute to the detergent effect they are called "builders."

The modern packaged household cleaners are mixtures of synthetic detergents ad builders. The great majority of detergents belong to a larger and more inclusive group of substances known as surface active agents. The surface active agents, of which the soaps are the oldest and best known, are characterized by the ability of their solutions to promote wetting, spreading, penetration, emulsification and detergency, and under certain conditions to solubilize normally insoluble substances. The most predominant detergents in use in modern packaged household cleaners are synthetic surface active agents.

When synthetic detergent cleaners were first marketed, they consisted of simple mixtures of about 40 percent of a surface active agent and 60 percent sodium sulfate. It has been found, however, that the addition of complex phosphates, silicates and other substances greatly improve the detergency of the mixtures. Caustic soda has been used as a builder, but for the most part builders consist of alkaline salts, such as carbonates, silicates and phosphates.

Desirable functional properties of a detergent builder include the ability to sequester hard water ions, to deflocculate particulate soil, and to provide buffering in the alkaline range. It is also desirable that the builder have good spray drying properties, compatability in detergent formulations, low hygroscopity and moderate cost. The condensed phosphates, such as penta sodium tripolyphosphate, and tetra sodium pyrophosphate, have fulfilled many of these requirements. Modern packaged detergents are formulated to contain from 30 to 50 percent condensed phosphates, such as sodium tripolyphosphate.

Most of the known builders in use in detergent compositions are unsatisfactory in that they are not biodegradable. By the term "biodegradable" is meant the ability of a material to be utilized or broken down by microorganisms in a sewage treatment system and to be disposed of thereby. As a result of the lack of biodegradability in commonly used builders, the builders tend to increase in concentration in the water systems into which the treated sewage may be introduced. As a result of such increased concentration, various deleterious effects have been encountered.

Successful washing operations involve the removal of soil from a soiled substrate and the suspension of the soil in the washing medium so that it will not be redeposited upon the substrate. In general, aqueous washing media containing fatty acid soaps fulfill both of these criteria, as soap is not only a good soil remover but also keeps the removed soil in suspension so that little redeposition takes place. However, synthetic detergents, such as the alkyl benzene sulfonates, have poor suspensing power, and consequently suspending agents are commonly added to the synthetic detergents. Two of the most commonly used suspending agents are sodium carboxymethylcellulose or polyvinylpyrrolidone.

It would be desirable to provide a builder for detergent compositions which is a good sequestering agent for calcium magnesium ions and which is biodegradable in a sewage treatment system.

Consequently, it is the principal object of the present invention to provide a builder for detergent compositions. It is another object of the present invention to provide a detergent composition having a biodegradable builder. It is a further object of the present invention to provide detergent compositions having complexes of alpha hydroxy carboxylic acids as the principal builder. It is a still further object of the invention to provide an improved process for removing soil from a substrate.

These and other objects of the present invention will become more apparent from the following detailed description.

Generally, in accordance with various features of the invention, a composition is provided which is soluble in water to form a washing solution which is effective to remove soil from a substrate. The composition comprises an organic surface-active detergent, and aluminate or borate compounds of alpha-hydroxy carboxylic acids.

It has now been found that aluminate and borate compounds of particular alpha-hydroxy carboxylic acids are useful as sequestering agents and builders in detergent compositions. When these compounds are added to aqueous washing media, their functionality as sequestering agents makes the washing media suitable in hard water conditions wherein substantial calcium and magnesium ions are present.

The alpha-hydroxy carboxylic acids are selected from those alpha-hydroxy carboxylic acids having a carbon chain length of C_2 to C_{12}. In general, as the carbon chain length increases, the aluminate and borate compounds of the invention form calcium and magnesium complexes which are more soluble and the effectiveness of the compounds is increased. Particularly preferred compounds are aluminate and borate compounds of alpha-hydroxy carboxylic acids whose calcium complexes have a solubility that exceeds the maximum calcium hardness in domestic water supplies. The calcium hardness is usually expressed in parts per million and does not usually exceed 400 parts per million. Preferable alpha-hydroxy carboxylic acids are polyhydric alpha-hydroxy carboxylic acids having a carbon chain length of C_2–C_{12}. A preferred polyhydric alpha-hydroxy carboxylic acid is gluconic acid. However, it has been determined that mixtures of alu-

minate or borate compounds of short carbon chain length alpha-hydroxy acids and moderate to long chain length alpha-hydroxy acids are also very suitable as builders. Particularly preferred is a mixture of glycollic acid and gluconic acid, e.g. a C_2 alpha hydroxy acid and a C_6 alpha hydroxy acid.

The compounds of the present invention may be prepared by reacting any alkali metal aluminate or borate with an alpha hydroxy carboxylic acid or mixture of alpha hydroxy carboxylic acids in an aqueous solution. Alkali aluminates or borates may be reacted directly with the alpha hydroxy carboxylic acid in aqueous solution, or with the alkali salt of the hydroxy acid, or with the lactone form of the alpha hydroxy acid which on hydrolysis will elaborate the free carboxylate ion. Aluminum or borate complexes are spontaneously formed when aluminate or borate ions are in contact with an alpha hydroxy carboxylic acid in aqueous solution. The compounds produced depend upon the stoichiometric proportions of the reactants. In general, the sequestering effectiveness of the complexes formed are improved as the stoichiometric proportion of the aluminate or borate is increased up to a molar ratio of 1:1 in proportion to the alpha hydroxy carboxylic acid. No significant improvement results as the stoichiometric ratio of aluminate or borate to acid is increased above a molar ratio of 1:1. However, molar ratios of up to 2:1 of the aluminate or borate to the acid may be used.

The aluminate or borate is introduced as a salt of an alkali metal, i.e., a salt having a monovalent cation. This is to provide coordination bonds upon introduction of the compounds into an aqueous washing solution which are adapted to combining with divalent metal ions, such as calcium or magnesium. Aluminate and borate complexes may also be prepared by dissolving aluminum salts, aluminum hydroxide, or boric acid in an alpha hydroxy carboxylic acid in aqueous solution and adding thereto an alkali metal hydroxide. After preparation, the compounds may be dried and combined with other ingredients in a detergent composition.

In a typical example of the preparation of an equimolar compound of glucono aluminate, 21.8 pounds of sodium gluconate was dissolved in 10 gallons of water, at 25° C., to which was added, with agitation, 8.2 pounds of Nalco 680 sodium aluminate, a commercial brand of sodium aluminate with a Na_2O/Al_2O_3 molecular ratio of 1:12. The resulting alkaline solution of sodium glucono aluminate was then dried by spray atomization in a countercurrent spray drier, to provide a dense, white, free flowing, non-hygroscopic powder. This dry form of the glucono aluminate compound showed full equivalence of divalent metal chelation capacity to that of the original solution, and showed no caking tendency or loss of metal binding capacity on dry heat treatment at 100° C. for 24 hours.

If desired, the compounds of the invention can be incorporated with a detergent so as to form a composition which on dissolving in water furnishes the desired washing solution. In this connection, the composition will usually include from about 30 percent to about 98 percent detergent, and from about 2 percent to about 70 percent of the compounds of the invention.

In carrying out washing operations, a substrate is agitated in the usual manner at elevated temperatures in an aqueous solution containing the compounds of the invention and a detergent. As the detergent, any of the materials commonly used for washing purposes may be used.

The detergent may be of the anionic or non-ionic type. Anionic detergents include ordinary soaps, such as sodium or potassium salts of the higher fatty acids, or mixtures of higher fatty acids, which are derived from naturally occurring oils and fats. Other anionic detergents are of the sulfonate or sulfate type. Such sulfonate or sulfate types include the alkyl (C_8–C_{18}) sulfates, the alkyl (C_8–C_{18}) aromatic sulfonates, the mono- or di-alkyl (C_8–C_{18}) esters of sulpho succinic acid, sulfonated or sulfated amides of the higher fatty acids such as N-sulpho ethyl stearamide and mixtures of these compounds. The detergent compounds are generally employed in the form of sodium, potassium, ammonium or amine salts of the compounds. The commercially available detergents are generally not pure compounds, but mixtures of homologous compounds. Non-ionic detergents include polyalkylene glycol esters, ethers and thio ethers of the following types:

$$RCOO(—C_2H_4O)_n—H$$
$$RO(—C_2H_4O)_n—H$$
$$RS(C_2H_4O)_n—H$$

wherein the R's represent long chain alkyl radicals of 8 to 12 carbon atoms and *n* is an integer of from about 4 to 12. Other non-ionic detergents are the long chain fatty acid esters of anhydro sorbitol or the polyethylene glycol addition products of such esters. The particular detergent used is not critical and a detergent is chosen which is generally useful for the particular application.

It is recognized that gluconic acid is known for use as a sequestering agent or builder in combination with various detergent materials. However, gluconic acid is useful only at high pH where the detergent composition includes caustic materials, such as caustic soda. By high pH is meant a pH above 13. The aluminate and borate complexes of alpha hydroxy carboxylic acids, such as gluconic acid, of the invention, permit the use of these compounds at more useful pH levels in the range of pH 8 to pH 12. This permits more flexible formulation of detergent compositions and also permits the detergent composition to be formulated without the use of excessively caustic materials. The detergent compositions of the invention are also desirable in that they are biodegradable in sewage treatment systems.

The following examples further illustrate various features of the present invention, but are intended to in no way limit the scope of the invention, which is defined in the appended claims.

EXAMPLE

Standardized soiled swatches of a fabric were prepared and were washed in a solution of a detergent composition including an aluminate complex of gluconic acid and also with a detergent composition including tripolyphosphate. The detergent compositions used had the following components:

Component	Detergent composition including— Aluminate complex of alpha hydroxy acid, weight percent	Tripolyphosphate, weight percent
Nacconal 40 F [1]	20.0	20.0
Sodium tripolyphosphate		40.0
Sodium gluconoaluminate, 1:1 mol. ratio of gluconic acid to aluminate	40.0	
Sodium sulphate	38.0	38.0
Carboxy methylcellulose	2.0	2.0

[1] Nacconal 40 F is the trade name for a surfactant manufactured by Allied Chemical Company and identified as a general purpose, flake form, anionic surfactant based on alkylate.

The soiled fabric swatches were prepared from bleached polyester/cotton fabric blends having 60 percent polyester and 40 percent cotton. Swatches measuring 4" x 5" were cut from the fabric and were soiled in a standardized soil by tumbling the swatches in a motorized tumbler. The standardized soil contained 6 percent oleic acid, 6 percent tallow, 8 percent lanolin, 8 percent carbon black and 72 percent bentonite clay.

The soiled swatches were then washed in a detergent solution for .5 minute at 60° C. The detergent solution contained 0.8 gram of each detergent composition, as set forth above, dispersed in 200 ml. of hard water having a mineral hardness of 100 p.p.m. calcium carbonate. The washed swatches were then rinsed twice in hard water for ten minutes and were then air dried. The reflectance

values of the cloth swatches were measured on a reflectometer before soiling and again after washing and drying.

The average light reflectance values for unsoiled fabric swatches was 80.9. The detergent efficiency of the detergent compositions is identified as the percentage recovery of the original light reflectance value after being washed in the respective detergent formulations. The detergent efficiency of the detergent formulation including an aluminate complex of gluconic acid was 94.8 percent. The detergent efficiency of the detergent composition including sodium tripolyphosphate, was 96.9.

The aluminate and borate complexes of alpha hydroxy acids of the present invention provide biodegradable builders for use in detergent composition. Detergent compositions including aluminate and borate complexes of alpha hydroxy acids have detergent efficiency comparable to that of detergent compositions including phosphate builders.

Having described the invention, what is claimed is:

1. A process for removing soil from a substrate which comprises washing the substrate with a solution comprising water, from 30–98% of an organic anionic or nonionic surface active detergent, and from 2–70% of a builder, said builder being a compound selected from aluminate or borate compounds of alpha hydroxy carboxylic acids having a carbon chain length of from C_2 to C_{12} and mixtures thereof.

2. A process in accordance with claim **1** wherein said builder is an aluminate compound of alpha hydroxy carboxylic acids having a carbon chain length of from C_2 to C_{12} and mixtures thereof.

3. A process in accordance with claim **1** wherein said builder is an aluminate compound of gluconic acid.

4. A process in accordance with claim **1** wherein said builder is a mixture of aluminate or borate compounds of glycollic acid and gluconic acid.

5. A process in accordance with claim **1** wherein the pH of said solution is from 8 to 12.

6. A washing solution which is effective to remove soil from a substrate comprising water, from 30–98% of an organic anionic or nonionic surface active detergent and from 2–70% of a builder, said builder being a compound selected from the group consisting of aluminate or borate compounds of alpha hydroxy carboxylic acids having a carbon chain length of from C_2 to C_{12} and mixtures thereof.

7. A washing solution in accordance with claim **6** wherein said builder is an aluminate compound of alpha hydroxy carboxylic acids having a carbon chain length of from C_2 to C_{12} and mixtures thereof.

8. A washing solution in accordance with claim **6** wherein said builder is an aluminate compound of gluconic acid.

9. A washing solution in accordance with claim **6** wherein said builder is a mixture of aluminate or borate compounds of glycollic acid and gluconic acid.

10. A washing solution in accordance with claim **6** wherein the pH of said solution is from 8 to 12.

11. A composition soluble in water to form a washing solution which is effective to remove soil from a substrate comprising from 30–98% of an organic anionic or nonionic surface active detergent and from 2–70% of a builder, said builder being a compound selected from the group consisting of aluminate or borate compounds of alpha hydroxy carboxylic acids having a carbon chain length of from C_2 to C_{12} and mixtures thereof.

12. A composition in accordance with claim **11** wherein said builder is an aluminate compound of alpha hydroxy carboxylic acids having a carbolic chain length of from C_2 to C_{12} and mixtures thereof.

13. A composition in accordance with claim **11** wherein said builder is an aluminate compound of gluconic acid.

14. A composition in accordance with claim **11** wherein said builder is a mixture of aluminate or borate compounds of glycollic acid and gluconic acid.

15. A washing solution in accordance with claim **6** wherein the pH of said solution is from about 8 to about 12.

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