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LAUNDERING COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Laundering compositions, containing a detergent surfactant and, as a builder therefor, an alkali metal or ammonium salt of malic or citric acids together with or in the absence of sodium metasilicate, eliminate the need for using phosphates.

BACKGROUND OF THE INVENTION

(A) Field of the invention

This invention relates to laundering compositions containing a builder material for improving the cleansing action of detergents.

(B) Description of the prior art

In the laundering art, it is known that the detergency of soaps and of synthetic surfactants can be increased by the use of certain materials commonly referred to as builders. Such builders make possible the attainment of superior cleaning performance and at lower cost than can be realized with the so-called non-built detergent compositions.

At the present time there is no completely satisfactory theory to explain the action of these detergent builders, let alone for predicting the performance of candidate materials. The lack of theory is due in part to the complex nature of detergency and the numerous factors which contribute to overall performance.

The beneficial effects of builder compounds appear to be due to improvements in such laundering factors as: stabilization of solid soil particles, emulsification of soil particles, solubilization of water-insoluble materials, increasing the surface activity of aqueous detergent solutions, peptization of soil agglomerates, neutralization of acid soil, and inactivation of mineral constituents in the laundering solution.

Builder materials should have certain other properties to be acceptable in current laundering methods and consumer marketing techniques. A builder should be inexpensive, non-toxic, biodegradable, stable to oxidizers in the dry state, non-corrosive, non-hygroscopic, stable to hot alkaline detergent solutions and stable during the spray drying of detergent formulations.

Known inorganic detergent builders are water-soluble, inorganic alkaline builder salts which can be used alone or in combination, and include alkali metal carbonates, bicarbonates, borates, phosphates, polyphosphates, pyrophosphates and silicates.

Known organic detergent builders are alkali metal, ammonium or substituted ammonium aminopolycarboxylates, such as, sodium or potassium ethylenediaminetetraacetate (EDTA), sodium or potassium N-(2-hydroxyethyl) ethylenediaminetriacetate, sodium or potassium-N-(2-hydroxy-ethyl) nitrilodiacetate.

The condensed inorganic polyphosphates have found the widest commercial acceptance. However, they possess the undesirable property of hydrolyzing into less condensed phosphorus compounds such as orthophosphates which have no builder properties. Further, these hydrolytic derivatives form undesirable precipitates in aqueous washing solutions. They are also plant nutrients which are claimed by some to be one of the major factors in the

eutrophication of lakes, ponds and rivers. Because of the suspected linkage between phosphates in detergents and the eutrophication of our waterways, considerable pressure has been brought to bear by numerous conservation groups and legislative bodies to remove phosphates from detergent formulations. Progress in effecting such a change has been slow because no satisfactory substitute builder has been developed. Alternative inorganic builders have been found wanting in performance. Furthermore, many suggested alternate formulations have been found to be unsafe unless handled with considerable care. Alternate organic builders have been found wanting either because of their non-biodegradability or because of their potential toxicity to humans or to aquatic life.

Accordingly, the detergent industry is still seeking a viable substitute for the present major detergent builder, sodium tripolyphosphate.

SUMMARY OF THE INVENTION

It has now been discovered that excellent builder properties are exhibited by the alkali metal or ammonium salts of malic or citric acids, alone or together with sodium metasilicate. The principal object and purpose of the invention is providing the detergent compositions containing these salts of malic or citric acids. Other objects and purposes will become apparent.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The alkali metal and ammonium salts of malic or citric acids are prepared by neutralizing an aqueous solution of the acid with the respective alkali metal or ammonium hydroxide or with the corresponding alkali metal carbonate or bicarbonate. Malic and citric acids can be purchased commercially. Malic acid can be conveniently prepared in situ by hydrolyzing maleic anhydride, a large volume low-priced commercial chemical, in aqueous solution using sulfuric acid as a catalyst and operating under reflux. Alternatively, the alkali metal malate can be made by neutralizing maleic anhydride, maleic acid or fumaric acid with the corresponding alkali metal hydroxide, carbonate or bicarbonate, and then reacting the resulting salt with water at temperatures of about 150° C. The alkali metal and ammonium malates and citrates are water soluble. I have found it preferable to use the alkali metal malates, and specifically sodium malate because of cost and because the ammonium and potassium salts may not be desirable since they contain plant nutrients (nitrogen and potassium, respectively) which may add to the eutrophication of our waterways.

An important and valuable property of these materials is their total biodegradability to carbon dioxide and water. Thus, use of detergent compositions containing malic or citric acid salts would not result in dangerous toxic materials being discharged into our waterways, and they would be easy to remove completely in conventional sewage treating plants.

I have found that excellent cleansing results can be achieved by using the malate or citrate builder of the invention with a wide range of detergents and mixtures therefor. The malate and citrate builders are effective alone with the detergent. However, it was found that they enhance the building capability of known inorganic builders such as sodium metasilicate and sodium tripolyphosphate.

In the detergent compositions of the invention, the active ingredients are: (1) an organic detergent as defined and illustrated below, and (2) an alkali metal or ammonium salt of malic or citric acid with or without the addition of sodium metasilicate. The ratio of malic or citric salt to detergent is in the range of about 1:3 to about

10:1 by weight. If sodium metasilicate is present, the ratio of malic or citric salt to sodium metasilicate ranges suitably from 10:1 to 1:1 by weight. The pH range of an aqueous solution of the detergent composition is from 8 to 12. The preferred ratio of malic or citric salt to detergent is about 1:2 to about 5:1. The corresponding optimum pH range is from 9.5 to 11.5.

The organic detergent compounds which can be used in the formulations of this invention are anionic, cationic or non-ionic detergents and mixtures thereof as exemplified as follows:

(a) Anionic detergents form negatively charged ions containing the oil-soluble portion of the molecule. The ionizable group is the hydrophilic portion. Examples of this class of detergents include soaps, and sodium salts of synthetic organic sulfonates or sulfates. About 50% of all the synthetic detergents are alkylarylsulfonates (e.g. sodium dodecylbenzene sulfonate); about 20% of the total are sulfates of straight chain primary alcohols (e.g. sodium lauryl sulfate).

(b) Cationic detergents form positively charged ions containing the oil-soluble portion of the molecule. Principal examples of this class are quaternary ammonium halides, e.g. benzethonium chloride. Only about 4% of the synthetic detergents are cationic.

(c) Nonionic detergents do not ionize, and acquire their hydrophilic nature from an oxygenated sidechain, usually polyoxyethylene. The oil-soluble part of the molecule may come from fatty acids, alcohols, amides or amines. The wetting, foaming and detergent properties of the nonionics can be varied by suitable choice of the starting materials and control of the length of the hydrophilic portion. About 24% of all the synthetic detergents are of this class.

In the novel detergent formulations of this invention, the weight ratio of surface active agent to malate salt builder ranges from about 3:1 to 1:10. These two ingredients generally represent at least about 45% of the total detergent formulation.

The formulations may also contain minor amounts of other additives to modify certain properties thereof. Among such optional additives are included: foam builders and stabilizers, anti-redeposition agents such as sodium carboxymethylcellulose, corrosion inhibitors, optical brighteners, bactericides, perfumes, bleaches, enzymes, dyes, blueing agents, inorganic salts, solvents and the like. These total optional ingredients commonly range from about 30% to about 55% by weight of the formulation.

Methods for preparing detergent formulations are well known to those skilled in the art. A typical method involves mixing the ingredients, forming them into an aqueous slurry and then spray drying to a homogenous free flowing solid. Alternatively, the final formulations may be a mixture of dry ingredients, a concentated aqueous solution, or a homogenized non-settleable slurry of the ingredients in water.

Specific embodiments of the invention are illustrated below.

DETERGENT FORMULATION

This example illustrates typical detergent formulations of this invention as well as the excellent laundering properties exhibited by these products.

The detergent formulation (Test Mixture A), which was utilized in this example, is as follows:

	Parts by weight
Sodium dodecylbenzene sulfonate	20.6
Sodium malate	48.5
Sodium metasilicate 5-hydrate	12.4
Sodium carboxymethylcellulose	0.5
Sodium sulfate	18.0

In each instance, the formulation was prepared by slurrying the various ingredients in 30 parts of water for each 100 parts of dry ingredients.

The performance of this formulation was compared with that for commercial products (e.g., "Tide" and "All") and also with formulations in which sodium malate was deleted (Test Mixture B), sodium metasilicate was deleted (Test Mixture C) and sodium malate and sodium metasilicate were deleted (Test Mixture D).

The relative effectiveness of Test Mixture A, above, was evaluated by comparing the relative brightness of launderings of typical bundles of soiled clothes containing mixtures of cotton, nylon, and Dacron-cotton fabrics. Launderings were made in machine washers operating at 120° F. Relative brightness was measured by averaging the reflectance readings on the washed clothes using a Hunter Reflectometer, Model D–10. The results were expressed as percent of the best average reflectance. The results of these tests follow:

Formulation	Size of bundle, lb., dry	Water hardness, p.p.m.Ca^{++}	Number of bundles	Relative brightness of dried laundered-bundle
Test formulation:				
A	15	150	5	100
B	15	150	5	50
C	15	150	5	70
D	15	150	5	30
Tide	15	150	5	90
All	15	150	5	90

These results clearly indicate the effective laundering capabilities of formulations containing sodium malate. As can be seen by comparing Mixtures B and C with Mixture D, there is a significant improvement by adding either sodium metasilicate (Mixture B) or sodium malate (Mixture C), with addition of sodium being somewhat more effective than sodium metasilicate. Surprisingly, sodium malate appears to synergize the performance of sodium metasilicate, and vice versa, as shown by the improvement of Mixture A over both B or C. More importantly, the combined Mixture A shows better performance than the best of today's commercial products, Tide or All, the tested samples of which contained 55% and 50%, respectively, of sodium tripolyphosphates.

What is claimed is:

1. A detergent composition consisting essentially of an organic detergent surfactant selected from the group consisting of anionic and nonionic surfactants and, as a builder therefor, a mixture of sodium metasilicate and an organic salt selected from the group consisting of alkali metal and ammonium salts of malic acid, wherein the ratio of the builder to the surfactant is from about 1:2 to 5:1 by weight, and the ratio of organic salt to sodium metasilicate is 10:1 to 1:1 by weight.

2. A detergent composition according to claim 1 in which said organic salt is sodium malate.

3. A detergent composition according to claim 1 which provides in aqueous solution a pH from about 8 to about 12.

4. A detergent composition according to claim 1 which provides in aqueous solution a pH from about 9.5 to 11.5.

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