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3,697,453

IMINODISUCCINIC ACID SALTS AS DETERGENT BUILDERS

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4 Claims

ABSTRACT OF THE DISCLOSURE

The water-soluble salts of iminodisuccinic acid are used as detergent builders in cleansing and laundering compositions with an organic water-soluble detergent surfactant such as anionic, nonionic, zwitterionic, and amphoteric detergent surfactants or mixtures thereof.

BACKGROUND OF THE INVENTION

The present invention relates to the use of iminodisuccinic acid as a detergent builder in cleansing and laundering compositions.

There is great concern that the phosphate compounds such as sodium tripolyphosphate (STPP) used as detergent builders are causing pollution of natural waters through stimulation of increased plant growth (eutrophication). Consequently, an intensive search is underway for non-phosphate builders. Prior art has shown that the salts of nitrilotriacetic acid (NTA), polyitaconic acid and polymaleic acid are very efficient builders, but each suffers from some disadvantage.

SUMMARY OF THE INVENTION

Chelation of metals, such as calcium or magnesium, and buffering action effective under alkaline conditions are two important functions of builders. It has been discovered that iminodisuccinic acid salts chelate calcium effectively, and also possess buffering action at higher pH's than many organic acid salts. For these reasons, the water soluble salts of iminodisuccinic acid, including among others the alkali metal, ammonium, and alkylammonium salts (or their mixtures) can be used as detergent builders in a variety of formulations without the concomitant undesirable side effects produced by other non-phosphate builders.

Said salts must be used in combination with an organic, water-soluble detergent surfactant which may be anionic, nonionic, zwitterionic, or amphoteric. The use of additional ingredients to make the completed cleansing and laundering composition is not intended to be excluded.

The ratio of total builder to detergent surfactant in the cleansing and laundering composition may vary from about 1:4 to about 10:1 by weight, with a ratio of from about 1:2 to about 5:1 being preferred. Said composition should provide in solution a pH of from about 9 to about 12.

DETAILED DESCRIPTION OF THE INVENTION

The essential ingredients in the detergent composition of this invention are (a) an organic water-soluble detergent surface active substance as defined and illustrated below and (b) water soluble salts of iminodisuccinic acid which served as a detergent builder. Anionic, nonionic, zwitterionic, and amphoteric detergent compounds and mixtures thereof are examples of detergent surface active substances which can be used within the compositions of this invention. The materials are described below in more detail.

(a) Anionic detergent compositions, in this invention, include both soap and non-soap detergent compounds. Examples of suitable soaps are the sodium, potassium, ammonium and alkylolammonium salts of higher fatty

acids (C_{10} – C_{20}). Sodium or potassium salts of the mixtures of fatty acids derived from coconut oil and tallow are particularly useful. Examples of anionic organic non-soap detergent compounds are water-soluble alkali metal salts of organic sulfuric reaction products incorporating an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of anionic synthetic detergent compounds useful in the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 – C_{18} carbon atoms) produced from tallow or coconut oil; sodium or potassium alkyl benzenesulfonates, such as are described in U.S. Letters Patents Nos. 2,220,009 and 2,477,383 in which the alkyl group contains from about 9 to about 15 carbon atoms; alkali metal alkylbenzene sulfonates in which the alkyl radical is a straight chain aliphatic radical (C_{10} – C_{20} carbon atoms); sodium alkyl glyceryl ether sulfonates, especially those derived from tallow and coconut oil; sodium salts of coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfates of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of the sulfates of the reaction products of one mole of an alkylphenol and 1 to about 10 moles of ethylene oxide in which the alkyl radicals contain about 9 to about 12 carbon atoms; the sodium salts of reaction products of fatty acids esterified with isethionic acid where, for example, the fatty acids are derived from coconut oil; and others known in the art, such as those of U.S. Letters Patents Nos. 2,486,921, 2,486,922 and 2,396,278.

(b) Nonionic synthetic detergents are compounds which do not ionize in aqueous solution. Suitable nonionic synthetic detergents include:

(1) The condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol.

(2) The condensation products of aliphatic alcohols having from 8 to 18 carbon atoms with from about 8 to 35 moles of ethylene oxide per mole of alcohol; i.e., a coconut alcohol-ethylene oxide condensate.

(3) The condensation product of ethylene oxide and the hydrophobic product of condensation of propylene oxide with propylene glycol; i.e., the commercially available detergent under the trademark name of "Pluronic."

(4) The condensates of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. For example, compounds containing approximately 40–80% polyoxyethylene by weight and having a molecular weight of about 5,000–11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base formed by reaction of ethylene diamine and excess propylene oxide, said hydrophobic base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

(5) Long chain tertiary amine oxides of the general formula, $R_1R_2R_3N \rightarrow O$, wherein R_1 is an alkyl radical of from about 8 to 18 carbon atoms, and R_2 and R_3 are each methyl or ethyl radicals. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, dimethylhexadecylamine oxide.

(6) Long chain tertiary phosphine oxides corresponding to the following formula $RR'R''P \rightarrow O$, wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R' and

R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. Examples of suitable phosphine oxides are:

dimethyldodecylphosphine oxide
dimethyltetradecylphosphine oxide
dimethylstearylphosphine oxide
cetyl ethylpropylphosphine oxide
diethyltetradecylphosphine oxide
bis(hydroxymethyl)dodecylphosphine oxide
2-hydroxypropylmethyltetradecylphosphine oxide
dimethylolelphosphine oxide
dimethyl-2-hydroxydodecylphosphine oxide

(7) Dialkyl sulfoxides of the formula, $RR'S \rightarrow O$, wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxy-alkyl radical or an alkyl or beta- or gamma-monohydroxy-alkyl radical containing one or two other oxygen atoms in the chain, the R groups ranging from 10 to 18 carbon atoms in chain length, and wherein R' is methyl or ethyl. Examples of suitable sulfoxide compounds are:

dodecyl methyl sulfoxide
tetradecyl methyl sulfoxide
2-hydroxydodecyl methyl sulfoxide
3-hydroxy-4-dodecoxybutyl methyl sulfoxide
dodecyl ethyl sulfoxide
2-hydroxydodecyl ethyl sulfoxide

(c) The class of amphoteric synthetic detergents includes derivatives of aliphatic secondary and tertiary amines, in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of compounds of this group are sodium-3-dodecylaminopropionate and sodium-3-dodecylaminopropanesulfonate.

(d) Zwitterionic synthetic detergents are derivatives of aliphatic quaternary ammonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of such compounds are 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate.

The anionic, nonionic, amphoteric and zwitterionic detergent surfactants described above can be used singly or in combination in the practice of the present invention. The above examples are merely specific illustrations of the numerous detergents which can find application within the scope of this invention.

A variety of water-soluble salts of iminodisuccinic acid, either neutralized or partially neutralized, may be used as builders in the formulations of this invention. The preferred salts include, among others, the alkali metal salts, ammonium salts, and substituted ammonium salts, i.e., the alkylammonium salts. Especially preferred are the tri- and tetrasodium salts.

In addition to the detergents and iminodisuccinic acid salts hereinbefore described, the detergent compositions can also contain from 0% to about 40% by weight of the composition of supplementary builders. Both inorganic and organic supplementary builders may be used. Examples of water-soluble inorganic alkaline detergency builder salts are alkali metal carbonates, bicarbonates, silicates, borates, phosphates, and polyphosphates. Specific examples of such salts are sodium carbonates, silicates ($SiO_2:Na_2O=2:1$), tripolyphosphates, pyrophosphates, phosphates, and hexametaphosphates. Examples of organic alkaline sequestrant builder salts are (1) alkali metal amino polycarboxylates (e.g., sodium and potassium ethylenediaminetetraacetates, N-(2-hydroxyethyl)-ethylenediaminetriacetates, nitrilotriacetates, and N-(2-hydroxyethyl)-nitrilotriacetates); (2) alkali metal citrates; and (3) alkali metal salts of phytic acid (e.g., sodium and potassium phytates—see U.S. Pat. 2,739,942); (4) water-soluble salts of alkylidene 1,1-diphosphonates such as methylene diphosphonates, substituted methylene diphos-

phonates and ethane-1-hydroxy-1,1-diphosphonate; and (5) water soluble salts of polycarboxylic polymers and copolymers as described in U.S. Pat. No. 3,308,067.

In a finished detergent formulation of this invention minor amounts of materials which make the product more effective or more attractive may be added. Examples of such materials include soluble sodium carboxymethylcellulose (to inhibit soil redeposition), benzotriazole or ethylenethiourea (tarnish inhibitors), detergent proteases or amylases, fluorescers, perfumes, and colors. Alkaline materials such as sodium hydroxide or potassium hydroxide can be added in minor amounts as supplementary pH adjusters. In some formulations addition of water, brightening agents, bleaching agents, sodium sulfate, and sodium carbonate may be desirable. Soluble silicates are highly effective corrosion inhibitors and are useful for this function in addition to imparting properties such as alkalinity associated with detergent builders. Alkali metal, preferably potassium or sodium, silicates having a weight ratio of $SiO_2:M_2O$ of from 1:1 to 2.8:1 can be used. M in this ratio refers to sodium or potassium. In built liquid detergents of this invention, a hydrotropic agent may at times be found desirable. Suitable hydrotropes are water soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate.

Cleaning effectiveness of the builders of this invention is dependent upon, and will vary with a number of factors. These include detergent formulation variables such as amount of builder, concentration of formulated detergent in the wash solution, temperature of the solution, hardness of the water, degree and type of soiling, and type of fabric. Detergents using the builders of this invention may be formulated for either general or specialized uses into any of the several commercially desirable composition forms for example, granular, flake, liquid and tablet forms.

The following examples serve to illustrate, but not limit, the novel compositions of the present invention.

PREPARATION A

To a 500 cc. beaker is added 5.0 g. iminodisuccinic acid hydrate and 150 cc. water (pH 2.5). 1 N NaOH is added dropwise with stirring to a total of 80 cc. The solution is then concentrated by drying in vacuo. The product, tetrasodium iminodisuccinate, amounts to 4.5 g. and on heating, decomposes without melting. The pH of a solution of the tetrasodium salt is approximately 11.

The calcium chelation effectiveness of iminodisuccinic acid tetrasodium salt is demonstrated by the following turbimetric titration with calcium acetate. About one gram of iminodisuccinic acid is suspended in about 20 ml. of deionized water and the pH is raised to 10 with 20% sodium hydroxide. Five ml. of 2% sodium carbonate solution is added and the pH is adjusted to 11.5–12.0. After dilution to 50 ml., the solution is titrated to a permanent turbidity with 0.25 M calcium acetate. A 1.35 g. sample of iminodisuccinic acid monohydrate required 19.9 ml. of calcium acetate solution, which is equivalent to 3.95 mmole calcium carbonate/g. (dry basis) or 0.98 mole/mole.

EXAMPLE I

A granular detergent composition giving excellent cleaning when used in laundering applications has the following composition in the percentages indicated:

	Percent
Sodium dodecylbenzenesulfonate (dodecyl group derived from a straight chain hydrocarbon) -----	17.0
Potassium toluene sulfonate -----	2.0
Tetrasodium iminodisuccinate -----	50.0
Sodium silicate (ratio of $SiO_2:Na_2O$ of 2:1) -----	7.0
Sodium sulfate -----	13.0
Coconut fatty acid ethanolamide -----	2.5
Water -----	8.5
	100.0

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The tetrasodium iminodisuccinate builder in Example I can be replaced at an equal iminodisuccinic acid percentage basis by other iminodisuccinic acid salts such as the tetrapotassium salt or a mixture of the tri- and tetrasodium salts.

EXAMPLE II

Another excellent granular detergent composition providing effective cleaning during laundering of a broad variety of soiled fabrics has the following composition:

	Percent
Sodium dodecyl benzenesulfonate (dodecyl group being a straight chain aliphatic radical)	10
Alkyl (C ₉) phenol-11 ethylene oxide condensate ..	4
Tallow fatty acid sodium salt	3.5
Tetrasodium iminodisuccinate	40
Sodium silicate (ratio of SiO ₂ :Na ₂ O of 2:1)	8
Sodium sulfate	24.5
Water	10

EXAMPLE III

Excellent cleaning results are obtained using a granular heavy duty detergent composition prepared according to this invention and having the following ingredients:

	Percent
Sodium dodecylbenzenesulfonate (dodecyl group derived from a straight chain hydrocarbon)	10.0
Tallow alcohol sulfate	6.0
Coconut oil diethanol amide	2.0
Tetrasodium iminodisuccinate	55.0
Sodium silicate (ratio of SiO ₂ :Na ₂ O of 2:1)	6.0
Sodium carboxymethyl cellulose	1.0
Sodium sulfate	14.0
Water	6.0

Any of the other iminodisuccinic acid builder salts given in Example I may be substituted for the above tetrasodium salt.

EXAMPLE IV

A build liquid detergent composition which performs well in either laundering or dishwashing applications has the following composition:

	Percent
Sodium dodecylbenzenesulfonate (the dodecyl radical being a straight chain aliphatic radical)	7.0
Dimethyldodecylamine oxide	5.0
Tetrasodium iminodisuccinate	10.0
Trisodium citrate	10.0
Potassium toluenesulfonate	8.0
Sodium silicate (SiO ₂ :Na ₂ O of 2.45:1)	3.5
Carboxymethyl hydroxyethyl cellulose	0.5
Water	56.0

EXAMPLE V

Excellent cleaning and long term maintenance of whiteness are obtainable with a built liquid heavy duty cool water detergent of the following composition:

	Percent
3(N,N - dimethyl-N-coconutammonio)-2-hydroxypropane-1-sulfonate	12.0
Tetrapotassium iminodisuccinate	20.0
Potassium hydroxide	4.0
Sodium silicate (SiO ₂ :Na ₂ O=1.6:1)	5.0
Potassium toluene sulfonate	8.0
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Fluorescent dye	.10
Perfume	0.20
Benzotriazole	.02
Water	50.18

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EXAMPLE VI

Another effective cool water heavy duty built granular composition consists of the following ingredients:

	Percent
Sodium dodecyl (straight chain) benzenesulfonate ..	18.0
Nonylphenol-ethylene oxide condensate	5.0
Tetrasodium iminodisuccinate	6.0
Sodium tripolyphosphate	12.0
Sodium sesquicarbonate	31.5
Sodium carboxymethylcellulose	1.0
Maxatase (a commercial detergent alkaline protease from a <i>B. subtilis</i> strain—about 3% active enzyme)	0.5
Water	26.0

EXAMPLE VII

A useful, mildly alkaline detergent composition can be formulated from the following ingredients:

	Percent
Sodium 3-dodecylaminopropionate	20
Triethanolamine tris salt of iminodisuccinic acid	55
Sodium sulfate	25

EXAMPLE VIII

An excellent built nonionic liquid detergent of this invention has the following ingredients:

	Percent
Condensation product of dodecylphenol and ethyleneoxide, 11 moles of ethylene oxide per mole of dodecyl phenol	12.0
Tetrapotassium iminodisuccinate	35.0
Sodium silicate (SiO ₂ :Na ₂ O=2.5:1)	8.0
Potassium toluene sulfonate	9.0
Water	36.0

EXAMPLE IX

An effective laundry presoak has the following composition:

	Percent
Sodium dodecylbenzenesulfonate (straight chain dodecyl radical) (40% active)	10.0
Tetrasodium iminodisuccinate	40.0
Borax	12.0
Sodium metasilicate	5.0
Sodium sulfate	32.5
Maxatase (a commercial detergent alkaline protease from a <i>B. subtilis</i> strain—about 3% active enzyme)	0.5

EXAMPLE X

The following low-phosphate formulation is useful for automatic machine dishwashing with hard water:

	Percent
Tetrasodium iminodisuccinate	50
Sodium tripolyphosphate	10
Trisodium phosphate	5
Sodium metasilicate pentahydrate	25
Fatty alcohol (C ₁₀ -C ₁₄)-ethylene ethoxide condensate	3
Hexylene glycol	2
Isopropyl alcohol	1.5
Water	3.5

EXAMPLE XI

An excellent anionic-nonionic laundry detergent has the following composition.

	Percent
Dodecylbenzenesulfonate (40% active LAS)	25
Octylphenol-ethylene oxide condensate (Triton X-100)	10
Sodium metasilicate	8
Tetrasodium iminodisuccinate	40
Sodium sulfate	17

7 EXAMPLE XII

To exemplify the useful detergent building activity of salts of iminodisuccinic acid which is observed when said salts are incorporated into the formulations of Examples I-XI above, results of wash tests using the formulation of Example XI are summarized below. The formulation of Example XI is compared with similar formulations in which the iminodisuccinic acid salt is replaced by sodium tripolyphosphate or inactive sodium sulfate. The Terg-O-tometer (United States Testing Co., Inc., Hoboken, N.J.) was used to wash artificially soiled cotton swatches (B. J. Rutkowski, J. Am. Oil Chem. Soc., 44, 103, 1967) at 50° C. for 10 minutes in water of 150 p.p.m. (CaCO₃) hardness. The detergent formulations were used at the level of 2 g./liter. Cleaning was calculated as percent soil removed (percent SR) or ΔSR in the following manner:

$$\text{Percent SR} = \frac{R_{\text{washed}} - R_{\text{soiled}}}{R_{\text{unsoiled}} - R_{\text{soiled}}} \times 100$$

where

R washed=reflectance of the washed swatches

R soiled=reflectance of the soiled swatches

R unsoiled=reflectance of the cloth before soiling

Reflectance was measured with the Model 670 meter equipped with a 610D search unit, both from the Photovolt Co. of New York, N.Y.

ΔSR=percent SR for built formulation — percent SR unbuilt formulation.

TABLE 1.—CLEANING COMPARISONS FOR EXAMPLE XI FORMULATIONS

	No builder	40% tetrasodium iminodisuccinate	Sodium tripolyphosphate
Percent SR	26.7	49.0	48.7
ΔSR		22.3	22.0

From Table 1 it is seen that the cleaning produced by the phosphate-free formulation containing the iminodi-

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succinate builder is equivalent to the formulation containing 40% phosphate.

Similar cleaning results are observed for the other formulations incorporating the iminodisuccinic acid salts in Examples I-X above.

What is claimed is:

1. A detergent composition consisting essentially of
(a) an organic water-soluble detergent surfactant selected from the group consisting of anionic, nonionic, zwitterionic, and amphoteric detergent surfactants and mixtures thereof, and as a builder a

(b) water-soluble salt of iminodisuccinic acid wherein the ratio of said acid salt to detergent surfactant is from about 1:4 to 10:1, by weight and wherein in solution the pH is from about 9 to about 12.

2. The composition of claim 1 wherein the ratio of said iminodisuccinic acid salt to said detergent surfactant is from about 1:2 to about 5:1 by weight.

3. The composition of claim 1 wherein said surfactant is an alkali metal salt of an alkyl sulfate of from 8 to 18 carbon atoms in the alkyl group.

4. The composition of claim 1 wherein said surfactant is an alkali metal salt of an alkylbenzene sulfonate of from 9 to 15 carbon atoms in the alkyl group.

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