

[54] **DETERGENT COMPOSITIONS**

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[51] **Int. Cl.**..... **C11d 7/54**

[58] **Field of Search**..... 252/99, 95, 135, 252/89, 351

[56] **References Cited**

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3,600,317	8/1971	Lintner	252/99
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[57] **ABSTRACT**

A granular detergent composition containing (a) a granular blend of mixed mono- and di-glycerides of fat-forming fatty acids, said mixture having a melting point of not less than 54°C. with a polyoxyethylene derivative of a higher fatty acid sorbitan ester; and (b) a compound selected from the group consisting of an inorganic water-soluble alkaline detergent salt, an inorganic alkaline sequestering agent, an organic alkaline sequestering agent and mixtures of these compounds. These compositions may contain an oxidizing agent of the oxygen releasing type or the halogen releasing type.

These detergent formulations are useful for washing hard surfaces and are especially suitable for dishwashing machines and the like.

14 Claims, No Drawings

DETERGENT COMPOSITIONS**BACKGROUND OF THE INVENTION**

The invention relates to granular detergent compositions intended primarily for washing hard surfaces, and especially suitable for use in dishwashing and the like machines. Such compositions are hereinafter called dishwashing compositions, and include compositions suitable for washing other hard surfaced articles, for example bottles, plastics articles, cutlery, metal goods, dairy equipment etc.

Known compositions of this type normally comprise a major proportion of alkaline substances such as alkaline inorganic salts, caustic alkalis, sequestering agents and oxidizing and sanitizing agents and the like, together with a minor, but important, proportion of one or more organic wetting agents.

Desirable properties of such dishwashing compositions include:

- they should be free-flowing, even after prolonged storage, for easy handling and dispensing,
- they should effectively remove soil, such as food residues, grease etc., from the surfaces and keep it in suspension during the washing process,
- they should generate little or no foam in use, even in the presence of food residues, grease, etc.,
- they should have bactericidal properties. In addition they should not corrode, tarnish or leave perceptible deposits upon the surfaces even after repeated washings.

If anionic detergents are used in these compositions in an amount sufficient to have appreciable wetting action, they cause excessive foam in use, the foam interfering with the scouring action of the detergent solution on the surfaces to be cleaned, and promoting carry over of soil-laden detergent solution from the washing cycle to the rinsing cycle of the machine. The lower foaming nonionic detergents are therefore more often employed, but most nonionic detergents are liquids or pastes at ordinary temperatures. Hence they tend to make granular compositions containing them sticky and non-freeflowing. Furthermore, for the same reason, they promote intimate contact between any chlorine-releasing oxidizing and sanitizing agents present in the composition, and encourage their decomposition during storage.

BRIEF DESCRIPTION OF THE INVENTION

The present invention is based on the observation that these failings of known anionic and nonionic detergents and wetting agents can be avoided or reduced, and the desired characteristics of a dishwashing composition can be obtained, by using certain emulsifiers which have previously only been considered for use in food preparations, especially in frozen confections such as ice creams.

DETAILED DESCRIPTION OF THE INVENTION

According to the invention there is provided a granular detergent composition comprising:

- a. from 0.1 percent to 20 percent by weight of the composition of an organic surface-active agent which is a granular blend of (1) mixed mono- and di-glycerides of fat-forming fatty acids, said mixtures of glycerides having a melting point of not less than 54°C., with (2) a polyoxyethylene derivative of a higher fatty acid sorbitan ester; and

b. from 80 percent to 99.9 percent by weight of the composition of a compound selected from the group consisting of

1. inorganic water-soluble alkaline detergent salt,
2. an inorganic alkaline sequestering agent,
3. an organic alkaline sequestering agent and
4. mixtures of these compounds.

The above compositions are especially effective when in addition they contain an oxidizing agent. The oxidizing agent may be of the oxygen releasing type or of the halogen releasing type.

The organic surface active agents suitable for the compositions of the invention include those described in British patent specification No. 951,011 of Atlas Chemical Industries, Inc., and marketed under the Trade name "Tween-mos."

Generally, the preferred organic surface active agents comprise a blend of from 95 to 60 percent by weight of mono- and di-glycerides of fat-forming fatty acids, said mixture of glycerides having melting point not less than 54°C., with from 5 to 40 percent of polyoxyethylene sorbitan tristearate containing an average of from 8 to 50 moles of ethylene oxide per mole of sorbitan tristerate. Thus, a preferred organic surface active agent comprises a blend of 60 percent by weight of mono- and di-glycerides of edible fats and oils, containing not less than 22 percent, by weight of the blend of monoglycerides, with 40 percent of a polyoxyethylated sorbitan tristearate containing an average of 20 moles of ethylene oxide per mole of sorbitan tristearate. The composition marketed as Tween-mos 280VS is particularly preferred, and is said to have this constitution. Other suitable agents are Tween-mos 240VS said to comprise a blend of 80 percent mono- and di-glycerides of edible fats or oils containing not less than 30 percent by weight of the blend, of monoglycerides, with 20 percent of a polyoxyethylated sorbitan tristearate containing an average of 20 moles of ethylene oxide per mole of sorbitan tristearate; and a blend of from 97 to 70 percent by weight of mono- and di-glycerides and from 3 to 30 percent by weight of a polyoxyethylene sorbitan monooleate containing an average of from 8 to 50 moles of ethylene oxide per mole of sorbitan monooleate; a preferred agent of this type is Tween-mos 100 VS, said to comprise a blend of 80 percent mono- and di-glycerides of edible fats or oils containing not less than 30 percent by weight of the blend, of monoglycerides, with 20 percent of a polyoxyethylated sorbitan monooleate containing an average of 20 moles of ethylene oxide per mole of sorbitan monooleate.

Normally, the stated organic surface active agent constitutes from about 1 percent to about 10 percent, especially about 2 to about 6 percent, by weight of the dishwashing compositions. Smaller quantities may be effective for some purposes, for instance down to 0.5 percent or as low as 0.1 percent. Larger quantities, up to 20 percent or more may be employed, especially in compositions intended for use at low concentrations. In general, the higher percentages of the organic surface active agent may provide insufficient improved performance to justify their cost.

It is most surprising that these compounds, previously known only as food emulsifiers, have now been found to be effective wetting and cleaning agents, and appear to be even more effective than the well known nonionic detergents, such as Pluronic (trade name), which are

condensates of polypropylene oxide and polyethylene oxides; polyethoxyalkylphenols; polyethoxy alcohols and the like. They have the further advantages of being themselves granular solids at ordinary atmospheric temperatures (melting at 57°C or higher), so that they do not cause stickiness in granular compositions in which they are incorporated. For the same reason, they do not promote intimate contact between oxygen or chlorine releasing agents and the other components of dishwashing compositions containing them. As a result of their limited solubility in water and their high melting point, they are particularly suitable for use in washing processes at relatively high temperature such as are commonly met in dishwashing and like machines, for instance at about 55°C to boiling, preferably about 57°C to 75°C. They may also be used in manual dishwashing provided that temperatures over at least about 50°C can be employed. In these conditions, the compositions of the invention generate little or no foam.

Apart from the small but essential proportion of organic surface active agent, the compositions of the invention comprise inorganic water soluble alkaline detergent salts, especially alkali metal, for example, sodium or potassium (especially sodium) carbonates and silicates; inorganic alkaline sequestering agents such as phosphates and polyphosphates, or borates; organic alkaline sequestering agents such as aminopolycarboxylates, for example, sodium nitrilo-triacetates or sodium ethylenediamine tetra acetates, and polyhydroxycarboxylates may be present. Other organic sequestering agents found to be useful in this invention include mellitates, benzene penta carboxylates, citrates, gluconates, oxydiacetates, oxydisuccinates and mixtures thereof.

The preferred inorganic components are penta sodium tripolyphosphate, tetra sodium pyrophosphate and sodium meta silicate.

Suitable oxidizing and sanitizing agents include peroxy salts such as sodium perborate, percarbonate, peroxy monosulphate and the like, and agents generating hypochlorite or hypobromite ions in solution such as chlorinated tri-sodium or other phosphates, and N-chloro- or N-bromo-organic compounds such as sodium dichloroisocyanurate, trichloroisocyanuric acid, N-chloro- and N-bromo-toluene or -benzene sulphonamide, and the like. These substances serve both to destroy bacteria and to oxidize certain components of the soil so that it is more readily removed in the washing process, and to minimize "spotting" of dishes etc., after drying, for example in heat, without wiping. Generally, preferred compositions contain a chlorine releasing agent, especially chlorinated trisodium phosphate or a chlorinated isocyanuric acid or a salt thereof.

The proportions of these compounds can be varied within wide limits according to the required properties of the composition. Thus very effective compositions contain from about 10 to 80 percent, especially 20 to 50 percent, sodium tripolyphosphate, anhydrous, preferably in granular form (for example such that not more than 20 percent passes a 100 mesh BSS sieve); from 5-60 percent sodium silicate, preferably anhydrous sodium meta silicate, but any solid, optionally hydrated, sodium silicate having weight ratio $\text{SiO}_2:\text{Na}_2\text{O}$ in the range 1:1 to 3.4:1 may be used; from 0 to about 30 percent of anhydrous sodium carbonate, preferably in dense granular form; a source of hypochlorite ion, in amount providing from about 1 to 5 percent of avail-

able chlorine, such as sodium dichloroisocyanurate, trichlorocyanuric acid, or chlorinated trisodium phosphate. From 0 to 20 percent of an oxidizing agent such as the alkali perborates, percarbonates and peroxy monosulphates may be used. Generally the amount of sodium silicate, especially sodium meta silicate, should not exceed about 70 percent and that of sodium carbonate should not exceed about 30 percent, since higher levels may cause some attack on glass or glazed surfaces. This composition should preferably contain insufficient moisture completely to hydrate the hydratable salts present. The remainder comprising from 0 to 30 percent anhydrous sodium sulfate.

The term "available chlorine" as used above and hereinafter presents the level of molecular chlorine (Cl_2) having equal bleaching power. Since one atom of active chlorine in compounds providing hypochlorite ions in solution has the same activity as one molecule (i.e., two atoms) of molecular chlorine, the percentage of "available chlorine" stated, by weight, is double the weight percentage of reactive chlorine. Thus for example pure sodium hypochlorite, having the formula NaOCl would contain 47.7 percent reactive chlorine by weight, expressed as 95.4 percent "available chlorine."

Neutral fillers, such as sodium chloride, sodium sulphate etc. may be present, for instance, from 0 to about 30 percent of sodium sulphate (calculated as anhydrous salt). Various other components may be included for various purposes, such as perfume, colouring matters, tarnish inhibitors such as benzotriazole, iron chelating agents, such as sodium gluconate, which prevent development of stains on aluminum and a haze-like deposit on glazed surfaces after repeated washing. Though not usually necessary or desirable other organic wetting agents and other sanitizing agents may be included in special cases.

The above mentioned inorganic salts may be at least partially hydrated when incorporated in the composition, provided that the free flowing properties of the composition are not impaired. Thus there should normally be sufficient hydrate-forming capacity available to absorb any moisture added during preparation of a product, (as explained below) and to enable the product to remain free flowing despite normal changes of humidity of the atmosphere to which it is exposed.

The compositions may be prepared by any effective method. Conveniently the dry particulate components, for example, salts, Tween-mos compounds, but excluding the oxidizing or chlorine-releasing agent, may be mixed together in any suitable apparatus, such as a rotating drum or cube mixer, inclined pan mixer etc. Liquid components such as perfume and/or an aqueous dispersion of colouring matter are admixed, most conveniently by spraying them on the particular mixture. Any water present or added is absorbed by incompletely hydrated salts in the composition. Finally the oxidizing or chlorine-releasing agent is added as a particulate solid.

The following Examples illustrate the invention:

EXAMPLE I

The following compositions were prepared by dry mixing the first four components listed, spraying on those so indicated, and finally dry mixing the chlorinated trisodium phosphate.

Composition	A	B
	percent	percent

	by weight	by weight
Anhydrous granular sodium tripolyphosphate	45.2	45.5
Anhydrous sodium metasilicate (beads)	11.00	11.00
Sodium Silicate "M" (Crystalline hydrate, SiO ₂ :Na ₂ O:3.3:1 by weight).	11.00	11.00
Tween-mos 280VS	2	—
Pluronic L62	—	2
Perfume sprayed on	0.1	0.1
Dyestuff do.	0.002	0.002
Water do.	0.7	0.4
Chlorinated trisodium phosphate (containing about 3% available chlorine by weight)	30	30

Composition A was according to the invention and was a free flowing dry powder. The reference composition B was a slightly sticky powder, tending to form soft lumps on standing. Their cleaning efficiency was determined by using them in a Kenwood Model A 1212 Dishwashing machine, using its operating cycle II, at a concentration of 0.75 percent by weight in water 12°H (172 ppm hardness as CaCO₃). In the machine, water temperature was 57°–60°C. To provide a representative load for the machine 44 dinner plates, used in a Canteen for a main luncheon course, i.e., meat, fish etc., were obtained and half were washed with each detergent composition. After washing in the machine the number of soil marks remaining was counted. The plates were then carefully hand washed, and dried, for re-use. This was repeated for a total of five washes. In every wash the number of marks on plates washed by the composition A of the invention was less than that on plates washed by the reference composition B, and overall the average values were: Product of the invention 1.1 marks per plate, Reference product 1.8 marks per plate.

EXAMPLE II

Similar washing performance was provided by the following compositions, which also were dry free flowing powders. They contained additives which reduced the tendency of the inorganic components to tarnish cutlery and they reduced the staining of aluminum in the presence of iron-bearing water or soil. The quantities are percentages by weight.

Composition	C	D	E	F
Sodium tripolyphosphate (dense granular)	40	30	50	40
Trisodium orthophosphate	—	—	—	39
Sodium sulfate	—	10	—	—
Sodium metasilicate (beads)	51.9	52.5	36	13
Tween-mos 280 VS	3	3	6	3
Sodium gluconate	1	1	2	1
Benzotriazole	0.1	0.05	0.1	0.05
Color, perfume, water (sprayed on)	1.5	1.0	1.0	1.5
Sodium dichloro (isocyanurate)	2.5	2.5	5	2.5

Products C and D are intended for use at about 1% concentration in the wash liquor; product E, for use at about 0.5% concentration.

EXAMPLE III

Compositions of the following formula were prepared and their cleaning performance tested as in Example I, except that tests were replicated two or three times as indicated below:

	% by weight
Sodium tripolyphosphate	40.4
Sodium metasilicate	13.5
Sodium silicate (SiO ₂ :Na ₂ O by weight 3.3:1)	13.5
Chlorinated trisodiumphosphate	30.1

Color/water/perfume 0.5
Organic detergent 2.0

As organic detergent Tween-mos 100 VS, Tween-mos 240 VS and Tween-mos 280 VS were each compared (on different occasions) with nonylphenol condensed with 9 molar proportions of ethylene oxide (NPE 9). The results were:

Tween-mos 100 VS and NPE 9 — 1.25 and 1.66 spots per plate (two replicates)
Tween-mos 240 VS and NPE 9 — 0.92 and 1.17 spots per plate (three replicates)
Tween-mos 280 VS and NPE 9 — 0.8 and 1.34 spots per plate (two replicates)

EXAMPLE IV

Granular compositions of the formula given in Example III, containing Tween-mos 280 VS as organic detergent, and for comparison Pluronic L 62 (Trade name) were prepared. The products were packed in cardboard sided lever-lid canisters and stored in (1) a constant temperature room maintained at 26.5°C., and (2) in a warehouse whose temperature varied without special control from about 26.5°C. to about 0°C. The percentage losses by weight of available chlorine after the stated times were:

		26.5°C. Room	Warehouse
Tween-mos product	4 months	31%	—
	6 months	46%	7
Pluronic product	4 months	63%	—
	6 months		78% 34

Having fully described the invention, what is claimed is:

1. A granular detergent composition comprising:
 - a. from 0.1% to 20% by weight of the composition of an organic surface-active agent which is a granular blend of (1) mixed mono- and diglycerides of fat-forming fatty acid, said mixtures of glycerides having a melting point of not less than 54°C., with (2) a polyoxyethylene derivative of a higher fatty acid sorbitan ester which contains an average of from 8 to 50 moles of ethylene oxide per mole of sorbitan ester; and
 - b. from 80 percent to 99.9 percent by weight of the composition of a compound selected from the group consisting of (1) inorganic water-soluble alkaline detergent salt, (2) an inorganic alkaline sequestering agent, (3) an organic alkaline sequestering agent and (4) mixtures of these compounds.
2. The composition of claim 1, wherein component (a) is a blend of from 95 to 60 percent by weight of said glycerides and from 5 to 40 percent by weight of a polyoxyethylene sorbitan tristearate containing an average of from 8 to 50 moles of ethylene oxide per mole of sorbitan tristearate.
3. The composition of claim 1, wherein component (a) is a blend of from 97 to 70 percent by weight of said glycerides and from 3 to 30 percent by weight of a polyoxyethylene sorbitan monooleate containing an average of from 8 to 50 moles of ethylene oxide per mole of sorbitan monooleate.
4. The composition of claim 2, wherein component (a) is a blend of 60 percent by weight of mono- and diglycerides of edible fats and oils, containing not less than 22 percent by weight of the blend, of mono-glycerides, with 40 percent of a poly-oxyethylated sor-

bitan tristearate containing an average of 20 moles of ethylene oxide per mole of sorbitan tristearate.

5. The composition of claim 2, wherein component (a) is a blend of 80 percent by weight of mono- and diglycerides of edible fats and oils, containing not less than 30 percent by weight of the blend of mono-glycerides, with 20 percent of polyoxyethylated sorbitan tristearate containing an average of 20 moles ethylene oxide per mole of sorbitan tristearate.

6. The composition of claim 3, wherein component (a) is a blend of 80 percent by weight of mono- and diglycerides of edible fats and oils, containing not less than 30 percent by weight of the blend, of mono-glycerides, with 20 percent of a polyoxyethylated sorbitan monooleate containing an average of 20 moles of ethylene oxide per mole of sorbitan monooleate.

7. The composition of claim 1 which also includes an amount of chlorine releasing agent sufficient to provide from 1 percent to 5 percent available chlorine.

8. The composition of claim 7 wherein the chlorine-releasing agent is a chlorinated isocyanuric acid or salt thereof.

9. A composition as claimed in claim 7 wherein the chlorine-releasing agent is chlorinated trisodium phosphate.

10. The composition of claim 1 which also includes from 0 percent to 20 percent by weight of the composition an oxidizing agent selected from the group consisting of perborates, percarbonates and peroxy monosulfates.

11. The composition of claim 1 wherein component (b) (3) is selected from the group consisting of water soluble citrates, mellitates, benzene penta carboxylates, oxydiacetates, oxydisuccinates, gluconates, and mixtures thereof.

12. The composition of claim 1 wherein component (b) is from 10 to 80 percent of anhydrous sodium tri-polyphosphate, from 5 to 60 percent of sodium silicate having a weight ratio SiO₂ to Na₂O in the range of from 1:1 to 3.4:1, a source of hypochlorite ion in an amount providing from 1 to 5 percent of available chlorine, from 0 to 30 percent of anhydrous sodium carbonate and from 0 to 30 percent anhydrous sodium sulfate.

13. The composition of claim 1 wherein there is present from 1 percent to 10 percent by weight of component (a).

14. The composition of claim 1 wherein there is present from 2 percent to 6 percent of component (a).

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,763,047 Dated October 2, 1973

Inventor(s) Robert Roy Fairs

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 54 "compounds" should read --components--

Column 4, line 15 "presents" should read --represents--

Column 5, line 53 "(isocyanurate" should read --isocyanurate--

Column 6, line 32 "78% under Warehouse column" should read --78% under Room column--

Column 7, line 18, "chlorine" should read --a chlorine--

Signed and sealed this 27th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

UNITED STATES PATENT OFFICE
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