

[54] **PROTEIN SOLUBILIZING WASHING
RINSING AND SOAKING
COMPOSITIONS**

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[58] Field of Search252/89, 137, 138, 161;
260/556 SN

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[57] **ABSTRACT**

A composition for washing, rinsing and soaking comprising (a) a content of at least one compound selected from the group consisting of dialkyldisulfimides and their alkali metal salts, ammonium salts and organic amine salts, wherein the alkyl groups have from 6 to 10 carbon atoms and (b) a content of at least one compound selected from the group consisting of alkali metal and ammonium polyphosphates, alkali metal silicates and alkali metal and ammonium salts of aminopolycarboxylic acids and polyphosphonic acids, wherein said components (a) and (b) are present in amounts of from 0.5:99.5 to 1:3 by weight. These compositions are useful in solubilizing proteinaceous soil when used alone or in combination with other washing agent additives.

3 Claims, No Drawings

PROTEIN SOLUBILIZING WASHING RINSING AND SOAKING COMPOSITIONS

THE PRIOR ART

Protein-containing soil is known to be relatively difficult to remove, and for this reason proteolytically active enzymes are frequently added to washing, rinsing and soaking agents intended for the washing of textiles or the cleaning of dishes. Owing to their complicated production, however, enzyme preparations are relatively expensive and, apart from this, are partially or completely inactivated by high temperatures, long storage times and chemical attack.

OBJECTS OF THE INVENTION

An object of the present invention is the production of washing, rinsing and soaking agents with good protein-solubilizing properties, in which enzymes are wholly or partially replaced by readily available compounds not liable to be rendered inactive.

Another object of the invention is the production of a composition for washing, rinsing and soaking comprising (a) a content of at least one compound selected from the group consisting of dialkyldisulfimides and their alkali metal salts, ammonium salts and organic amine salts, wherein the alkyl groups have from 6 to 10 carbon atoms and (b) a content of at least one compound selected from the group consisting of alkali metal and ammonium polyphosphates, alkali metal silicates and alkali metal and ammonium salts of aminopolycarboxylic acids and polyphosphonic acids, wherein said components (a) and (b) are present in amounts of from 0.5:99.5 to 1:3 by weight.

A further object of the invention is the production of washing, rinsing and soaking compositions containing from 10 to 100 percent by weight on an anhydrous basis of the above composition.

These and other objects of the invention will become more apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

The present invention is directed to a protein-solubilizing washing, rinsing and cleaning agent comprising a content of:

- a. at least one compound from the class of dialkyl-disulfimides or their alkali metal salts, ammonium salts and organic amine salts, in which the preferably straight-chain alkyl groups have from 6 to 10 carbon atoms, and
- b. at least one compound from the class of polymeric alkali metal phosphates, alkali metal silicates and alkali metal salts of aminopolycarboxylic acids and polyphosphonic acids,

wherein the components (a) and (b) are present in amounts from 0.5:99.5 to 1:3 by weight.

The dialkyldisulfimides have a strong acid reaction in the free state and may suitably be used in the form of their alkali metal salts such as the sodium or potassium salts, or ammonium salts or mixtures thereof, the ammonium salts also including the salts of organic bases, preferably organic amines such as mono-, di-, or tri-lower alkylamines or lower alkanolamines such as mono-, di- or tri-ethanolamine. The dialkyldisulfimides may also be utilized in their free state particularly where an inorganic builder is utilized as the component (b). The alkyl residues contained in the dialkyldisulfimides may be the same or different or may be branched. However, dialkyldisulfimides with straight-chain alkyl residues are preferably used, among which di-n-octyl-disulfimide has been found particularly active. The dialkyldisulfimides are selected from the group consisting of (1) dialkyldisulfimide having 6 to 10 carbon atoms in the preferably straight-chain alkyls and (2) their alkali metal salts, ammonium salts and salts with lower alkylamines and lower alkanolamines.

Besides the dialkyldisulfimides, the washing, rinsing and soaking agents according to the invention contain at least one inorganic or organic builder salt from the class of polymeric alkali metal phosphates, alkali metal silicates and the alkali

metal salts of aminopolycarboxylic acids and polyphosphonic acids.

Suitable polymeric phosphates are pyrophosphates, triphosphates, tetraphosphates, trimetaphosphates, tetrametaphosphates, and more highly condensed phosphates, in the form of the neutral or acid sodium, potassium or ammonium salts. Alkali metal triphosphates and their mixtures with pyrophosphates are preferably used. Alkali metal silicates, especially sodium silicate, are also suitable in which the ratio of Na_2O to SiO_2 is from 1:3.5 to 1:1. Suitable organic builder salts are the complex-forming alkali metal or ammonium salts of aminopolycarboxylic acids and/or aminopolyphosphonic acids, especially the sodium or potassium salts of aminotriacetic acid, ethylene diamine tetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid and their higher homologues, ethylenediaminehydroxyethanetriacetic acid, aminotri-(methylenephosphonic acid), ethylenediaminetetra-(methylenephosphonic acid), 1-hydroxyalkane-1,1-diphosphonic acids such as 1-hydroxyethane-1,1-diphosphonic acid, methylenediphosphonic acid, ethylenediphosphonic acid and also the higher homologues of the above polyphosphonic acids.

The protein-solubilizing compositions of the invention may be used as such for the washing, rinsing and soaking of textiles and dishes. They may also contain up to 90 percent on the dry basis of other suitable components of washing, rinsing and soaking agents such as neutral salts, pH regulators, enzymes, detergents, bleaching agents and other usual additives.

Suitable components of the mixtures are neutral salts such as sodium sulfate and sodium chloride, and also substances for regulating the pH value such as bicarbonates, carbonates, borates and hydroxides of sodium or potassium, and acids such as lactic acid and citric acid. The quantity of alkaline-reacting substances including the alkali metal silicates and phosphates should be such that a liquor utilizable for mechanical dishwashing devices has a pH of from 10 to 14; for coarse washing the pH of the washing liquor should be from 9 to 12 and for fine washing, from 6 to 9.

For further improvement of the dirt-loosening properties of the agents according to the invention, these may also contain enzymes from the class of proteases, lipases and amylases. The enzymes may be of animal or vegetable origin, for example, they may be obtained from digestive ferments or yeasts, such as pepsin, pancreatin, trypsin, papain, catalase and diastase. Preferably, enzymic substances obtained from strains of bacteria or fungi, such as *Bacillus subtilis* and *Streptomyces griseus*, are used which are relatively stable towards alkalis, percompounds and anionic detergent substances and even at temperatures between 45° and 70° C are not appreciably inactivated. Their relatively great stability towards oxidizing agents possibly is due to their low content of free sulphydryl groups.

The enzymes represent a valuable addition to the agents of the invention, since they are already active at temperatures at which the dialkyldisulfimides have not yet developed their full activity. On the other hand, the disulfimides are completely stable towards strongly alkaline or active chlorine-containing compounds even at temperatures above 70° C. while most of the known enzymes are already inactivated to a considerable extent under the said conditions. This is of special advantage in that the amount of enzymes required can be considerably reduced by the use of the cheaper dialkyldisulfimides.

The agents according to the invention may contain further detergent substances, oxygen- or chlorine-containing bleaching agents and the usual additives, depending on the purpose for which they are to be used.

Among the surface-active basic detergent substances which may be contained in the agents of the invention, weakly foaming compounds are of primary importance for all fields of application in which the development of foam is to be completely or largely excluded. These are especially the non-ionic polyglycol ether derivatives of alcohols, fatty acids and al-

kyphenols which contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the hydrocarbon residue. Polyglycol ether derivatives in which the number of ethylene glycol ether groups amounts to 5 to 15 and the hydrocarbon residues are derived from straight-chain primary alcohols with 12 to 18 carbon atoms or from alkylphenols with a straight chain alkyl chain containing 6 to 14 carbon atoms, are specially suitable. By adding 3 to 15 mols of propylene oxide on to the last-named polyethyleneglycol ethers or by conversion into the acetals, washing agents are obtained which are marked by a specially low degree of foaming.

Further suitable non-ionic basic detergent substances are the water-soluble adducts containing 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups of polyethylene oxide to polypropylene glycol, ethylenediamine-polypropylene glycol and alkyl-polypropylene glycol with 1 to 10 carbon atoms in the alkyl chain. The said compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Washing and cleaning agents in which the development of foam is not harmful or is desirable, may contain anionic basic detergent substances detergent the sulfonate or sulfate type. Examples of such basic detergent substances are olefinsulfonates such as are obtained, for example, by sulfonation of primary or secondary aliphatic monoolefins with gaseous sulfur trioxide and subsequent alkaline or acid hydrolysis, and also alkylsulfonates such as are obtainable from n-alkanes by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization or by addition of a bisulfite to olefins. In addition, alkylbenzenesulfonates, α -sulfo-fatty acid esters, primary and secondary alkyl sulfates and the sulfates of ethoxylated or propoxylated alcohols are suitable. Further compounds of this class which if desired may be present in the washing agents are the higher molecular weight sulfated partial ethers and partial esters of polyhydric alcohols, such as the alkali metal salts of the monoalkyl ethers or the mono-fatty acid esters of glycerine monosulfuric acid ester or 1,2-dihydroxypropanesulfonic acid. Sulfates of ethoxylated or propoxylated fatty acid amides and alkylphenols as well as fatty acid taurides and fatty acid isothionates are also suitable.

In addition to the said basic detergent substances of the sulfonate and sulfate type, the agents may also contain alkali metal soaps of higher fatty acids, ampholytes such as alkylbetaines and alkylsulfobetaines and nonionic surface-active compounds of the amine oxide and sulfoxide type.

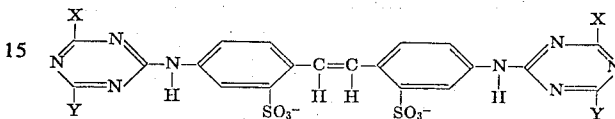
The anionic basic detergent substances may be present in the form of the sodium, potassium and ammonium salts as well as salts of organic bases as, for example, mono-, di- or triethanolamine. Provided the said detergent compounds have an aliphatic hydrocarbon residue, this should preferably have a straight-chain and contain 8 to 22 carbon atoms. In compounds with araliphatic hydrocarbon residues, the preferably unbranched alkyl chains should contain an average of 6 to 16 carbon atoms.

Increases in activity, for example, an improved washing power or a reduced foaming power, can be obtained in many cases by a suitable combination of different surface-active basic detergent substances or builder salts. Such improvements are possible, for example, by combinations of anionic with nonionic and/or amphoteric compounds, by combinations of different anionic compounds with one another, by combinations of different nonionic compounds with one another and by mixing basic detergent substances of the same type which differ with respect to the number of carbon atoms or the number and position of double bonds or the branching of chains in the hydrocarbon residue. Mixtures of inorganic and organic builder salt components with a synergistic action may also be used or combined with the above-mentioned mixtures.

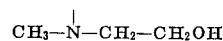
The agents may also contain oxygen-yielding or active chlorine-containing bleaching agents, such as alkali metal perborates, alkali metal percarbonates, alkali metal perphosphates, urea perhydrate, alkali metal hypochlorites,

chlorinated trisodium phosphates and chlorinated cyanuric acid or its alkali metal salts, and bleaching agent activators and stabilizers, such as magnesium silicate.

Further suitable components of the mixture are greying inhibitors such as sodium cellulose glycollate, disinfecting and freshening agents, fillers, e.g., urea, abrasives, dyestuffs and perfumes as well as optical brighteners, for example, of the diaminostilbenedisulfonic acid type according to the following formula

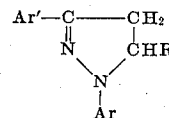


in which X and Y have the following meanings: $-\text{NH}_2$, $-\text{NH}-\text{CH}_3$, $-\text{NH}-\text{CH}_2-\text{CH}_2\text{OH}$,



$-\text{N}(\text{CH}_2-\text{CH}_2\text{OH})_2$, morpholino, dimethylmorpholino, $-\text{NH}-\text{C}_6\text{H}_5$, $-\text{NH}-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$, $-\text{OCH}_3$ and Cl , while X and Y may be the same or different. Compounds in which X represents an anilino group and Y a diethanolamino or morpholino group are particularly suitable.

Further, optical brighteners of the diarylpyrazo-line type according to the following formula may be present:



In this formula, R represents a hydrogen atom or an alkyl or aryl residue which, if desired, may be substituted, Ar and Ar' represent aryl residues such as phenyl, diphenyl or naphthyl, which may carry further substituents such as hydroxy, alkoxy, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, sulfonic acid and sulfonamide groups or halogen atoms.

1,3-diarylpyrazolines in which R represents a hydrogen atom are preferably used.

Agents which are intended for use in drum washing machines or automatic dishwashing machines may contain in addition known anti-foaming agents, for example, saturated fatty acids or their alkali metal soaps with 20 to 24 carbon atoms or triazine derivatives, which are obtainable by reaction of 1 mol of cyanuric chloride with 2 to 3 mols of an aliphatic, straight-chain, branched or cyclic primary monoamine or by propoxylation or butoxylation of melamine.

The washing and cleaning agents may be present in liquid, pasty or solid forms, for example, pulverulent, granulated or lump form. Liquid preparations may contain solvents miscible with water, especially ethanol and isopropanol, and solution aids such as the alkali metal salts of benzene-, toluene-, xylene- or ethylbenzene-sulfonic acids. To increase the foaming power and to improve the compatibility with the skin, alkylolamides, such as fatty acid mono- and di-ethanolamides, may be added.

The preparation of the agents according to the invention may be carried out in the usual way by mixing, granulating or spray drying. When enzymes are used, it is advisable to mix these with nonionic basic detergent substances and possibly perfumes or to disperse them in the melt of a salt containing water of crystallization, for example, Glaubers salt, and then to unite this mixture with the remaining power constituents. The enzymes are thereby cemented with the usual powder

particles, so that the mixtures do not tend to form dust or to separate into their components.

The mixtures of the invention, therefore, may have the following composition, and the following compositions, in weight percent, are based on a water-free recipe:

0.5 to 25 percent, preferably 1 to 15 percent of dialkyldisulfimide or its salts,

10 to 90 percent, preferably 20 to 60 percent, of inorganic and/or organic builders,

0 to 40 percent, preferably 1 to 20 percent, of at least one compound from the class of anionic, nonionic and amphoteric surface-active compounds.

0 to 50 percent, preferably 1 to 30 percent, of a bleaching agent, especially per-compounds and their mixtures with bleaching agent activators or stabilizers, and active-chlorine-containing compounds,

0 to 5 percent, preferably 0.1 to 2.5 percent of enzymes,

0 to 20 percent, preferably 1 to 12 percent, of other washing agent components such as greying inhibitors, anti-foaming agents, skin-protecting agents, biocides, optical brighteners, solution aids, and dyestuffs and perfumes.

Some compositions of the invention are given below which have proved particularly good in practice. The invention is not restricted to the following mixtures. However, on the contrary, these can be varied in a number of ways and/or can be supplemented by the additives mentioned in the specification. The sulfate and sulfonate basic detergent substances and soaps are generally used as the sodium salts. When liquid preparations are concerned, the anionic detergent substances may advantageously be used in the form of the mono-, di- or tri-ethanol-ammonium salts.

COMPOSITIONS

1. Pulverulent, weakly foaming washing agent:
 - 1 to 15 percent of the sodium salt of di-n-octyldisulfimide,
 - 1 to 15 percent of sulfonate basic detergent substances from the class of alkylbenzenesulfonates, olefin-sulfonates and n-alkanesulfonates,
 - 0 to 5 percent of alkylpolyglycol ether ($C_{12}-C_{18}$ -alkyl) or alkylphenolpolyglycol ether (C_8-C_{14} -alkyl) with 5 to 10 ethyleneglycol ether groups,
 - 0 to 5 percent of $C_{12}-C_{18}$ soap,
 - 10 to 50 percent of a condensed alkali metal phosphate from the class of pyro- or tri-phosphates,
 - 0 to 20 percent of complex-forming agents from the class of alkali metal salts of aminopolycarboxylic acids, aminoalkylenepolyphosphonic acids and hydroxyalkylenepolyphosphonic acids,
 - 1 to 5 percent of sodium silicate,
 - 0.1 to 30 percent of an inorganic salt from the class of carbonates, bicarbonates, borates, sulfates and chlorides of alkali metals,
 - 0.5 to 4 percent of magnesium silicate,

10 to 35 percent of sodium perborate tetrahydrate,

0 to 5 percent of enzymes,

0.2 to 5 percent of anti-foaming agent,

0.05 to 1 percent of an optical brightener

0.5 to 3 percent of sodium cellulose glycolate.

2. Dishwashing agent for automatic machines:

0.5 to 3 percent of the sodium salt of di-n-octyl-disulfimide,

0 to 3 percent of alkylpolyglycol ether ($C_{12}-C_{18}$ -alkyl) or alkylphenolpolyglycol ether (C_8-C_{14} -alkyl) with 5 to 30 ethylene glycol ether and 5 to 30 propylene glycol

ether groups,

50 to 95 percent of pentasodium triphosphate,

1 to 40 percent of sodium silicate ($Na_2O:SiO_2 = 1:1$ to $1:3$),

0.5 to 5 percent of anti-foaming agent,

0 to 5 percent of potassium dichloroisocyanurate.

3. Liquid washing, rinsing and cleaning agent:

1 to 15 percent of the sodium salt of di-n-octyl-sulfimide,

0.5 to 10 percent of sulfonate basic detergent,

0 to 10 percent of alkylpolyglycol ether sulfate (C_8-C_{18} -alkyl, 1-5 ethyleneglycol ether groups),

10 to 30 percent of neutral or acid potassium pyrophosphate,

0 to 5 percent of anti-foaming agent,

0.1 to 5 percent of fatty acid amide-ethyleneglycol ether condensate ($C_{10}-C_{18}$ -fatty acid, 1 to 10 ethyleneglycol ether groups),

0 to 10 percent of solution aid from the class of alkali metal salts of benzene-, toluene- or xylene-sulfonic acid,

0 to 10 percent of organic solvent from the class of C_2-C_3 alcohols and ether alcohols,

0 to 1 percent of optical brightener,

Remainder water, perfume, dyestuffs, preservatives.

4. Soaking and pre-washing agent:

1 to 5 percent of the sodium salt of di-n-octyldisulfimide,

0 to 5 percent of sulfonate basic detergent substances,

0 to 3 percent of alkylpolyglycol ether ($C_{12}-C_{18}$ -alkyl) or alkylphenolpolyglycol ether (C_8-C_{12} -alkyl) with 5 to 12 ethyleneglycol ether groups,

10 to 50 percent of soda,

5 to 50 percent of sodium triphosphate and its mixtures with sodium pyrophosphate,

1 to 5 percent of water glass,

0 to 5 percent of magnesium silicate,

0 to 5 percent of enzyme.

The following examples are illustrative of the practice of the invention without being limitative in any respect.

EXAMPLES

A cotton fabric soiled with 14 percent blood-protein standardized EMPA-ferment pollution) was washed in a paddle stirrer washing machine, the washing liquor being heated from 20° to 50° C. in a period of 20 minutes and then kept for a further 10 minutes at 50° C. The proportion by weight of textiles to washing liquor was 1:10, the hardness of the tap water was 16° German hardness and the concentration of the washing agent mixtures, utilized in the following table, was 5 gm per liter. The percentage brightening was determined photometrically. The brightening of the soiled fabrics was 14 percent.

In the Table I the comparative experiments are denoted by A, B and C, and the examples according to the invention by numbers. The numerical values show that the agents according to the invention have an improved dirt-loosening action, especially in combination with enzymes.

TABLE I

	Examples in parts by weight					Comparison		
	1	2	3	4	5	A	B	C
Components of the washing agent:								
Na-di-n-octyldisulfimide	10	10	10	5	15			
Oleyl alcohol polyglycol ether (10 ethyleneglycol ether groups)			5	5	5			5
Pentasodium triphosphate	45	45	45	45	45	45	45	45
Sodium sulfate	45	44.5	40	39.5	40	55	51.5	50
Enzyme		0.5		0.5			0.5	
Percent brightening	47.6	48.8	48.7	61	49	38.1	47.1	43.9

The following examples 6 to 10 were conducted according to the foregoing examples, while the washing period at 50° C was extended to 30 minutes. The washing compositions consisted of

- 10 percent Na-dialkyldisulfimide
- 45 percent pentasodium triphosphate
- 45 percent sodium sulfate

The structure of the dialkyldisulfimides utilized in the experiments and the percentage brightening of the rinsed fabrics are shown in the table II.

TABLE II

Ex.	Dialkyldisulfimide	% Brightening
6	Na-di-n-octyldisulfimide	53.5
7	Na-n-hexyl-n-octyldisulfimide	53.6
8	Na-n-octyl-n-decyldisulfimide	53.7
9	Na-n-heptyl-n-octyldisulfimide	54.2
10	Na-n-heptyl-n-decyldisulfimide	53.8

The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the art may be employed without departing from the spirit of the invention.

We claim:

1. A composition for washing, rinsing and soaking consisting essentially of (a) at least one compound selected from the group consisting of (1) dialkyldisulfimide having straight-chain alkyls with 6 to 10 carbon atoms and (2) alkali metal salts, ammonium salts and lower alkylamine and lower alkanolamine salts of said dialkyldisulfimide and (b) at least one builder salt selected from the group consisting of alkali metal and ammonium polyphosphates, alkali metal silicates and alkali metal and ammonium salts of aminopolycarboxylic acids and polyphosphonic acids, wherein said components (a) and

(b) are present in amounts of from 0.5:99.5 to 1:3 by weight.

2. The composition of claim 1 wherein said dialkyldisulfimide is a salt of di-n-octyldisulfimide selected from the group consisting of the alkali metal salt, ammonium salt and lower alkylamine and lower alkanolamine salts.

3. A protein-solubilizing composition for washing, rinsing and soaking consisting essentially of:

a. from 0.5 to 25 percent by weight of at least one compound selected from the group consisting of (1) dialkyldisulfimide having straight-chain alkyls with 6 to 10 carbon atoms and (2) alkali metal salts, ammonium salts and lower alkylamine and lower alkanolamine salts of said dialkyldisulfimide,

b. from 10 to 90 percent by weight of at least one builder salt selected from the group consisting of alkali metal and ammonium polyphosphates, alkali metal silicates, and alkali metal and ammonium salts of aminopolycarboxylic acids and polyphosphonic acids,

c. from 0 to 80 percent by weight of neutral salts,

d. from 0 to 40 percent by weight of at least one compound selected from the group consisting of anionic, non-ionic and amphoteric surface-active detergent substances,

e. from 0 to 50 percent by weight of bleaching agents,

f. from 0 to 5 percent by weight of enzymes,

g. from 0 to 3 percent by weight of greying inhibitors,

h. from 0 to 5 percent by weight of antifoaming agents,

i. from 0 to 1 percent by weight of optical brighteners

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,673,096

Dated June 27, 1972,

Inventor(s) DIETER WALTER et al

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

Patent Appln.

Col. Line Page Line

3 22 7 13 Please delete "detergent" (second occurrence) and insert -- of --

8 28 Claim 5 of
Claim 3 Amend. "A" After "i. from 0 to 1% by weight of optical brighteners," the following phrase should be inserted -- wherein the percentages are based on a water-free composition and total 100% by weight --

Signed and sealed this 29th day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents