3,679,589 LOW-FOAMING RINSING, WASHING AND CLEANING COMPOSITIONS Harald Schnegelberger, Hilden, Rhineland, and Theodor

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#### ABSTRACT OF THE DISCLOSURE

Low-foaming rinsing, washing and cleaning compositions comprising (a) a content of at least one compound  $^{15}$ having a cleaning action selected from the group consisting of (1) anionic surface-active compounds, amphoteric surface-active compounds, non-ionic surface-active compounds and mixtures thereof, (2) organic builder 20 salts and inorganic builder salts, and (3) mixtures of (1) and (2), and (b) a content of at least one alkoxylated melamine having a molecular weight of from 700 to 20,000 selected from the group consisting of propoxylated melamines, butoxylated melamines and propoxylated- 25 butoxylated melamines, where the weight ratio of components (a) to components (b) is from 999:1 to 3:1.

#### THE PRIOR ART

It is known that non-ionic detergent substances especially those based on polyglycol ethers, have a low-foaming power and beyond that are suitable for suppressing foam formation caused by anionic basic detergent substances. These properties are of particular importance in 35 the case of washing and cleaning agents which are intended for use in automatic dishwashing machines and rotating drum washing machines.

The most active known compounds of this class of nonionic detergent substances include the ethoxylated poly-  $^{40}$ propylene glycols such as the "Pluronics" (registered trademark) and the ethoxylated polypropylene glycol ether derivatives of ethylenediamine such as the "Tetronics" (registered trademark). Their anti-foaming properties, however, are not sufficient in some cases. For ex- 45 ample, when foam-producing impurities, such as protein substances, carbohydrates and other high polymers, such as those from label adhesives, are introduced into the liquor in washing or dishwashing machines or bottlewashing plants by the goods to be cleaned, their foam 50 suppression properties are not sufficient. Moreover, the said compounds possess relatively poor running-off properties. When dishes are rinsed, the rinsing solutions frequently runs off the glass, metal or plastic surface not as a uniform film, but remain in the form of drops or  $^{55}$ streaks and after drying leave a cloudiness and spots.

#### OBJECTS OF THE INVENTION

An object of the present invention is to provide wash- 60 ing, rinsing and cleaning agents which, compared with the known agents, have an improved anti-foaming action and do not have the disadvantages mentioned above.

Another object of the present invention is the obten-

sitions comprising (a) a content of at least one compound having a cleaning action selected from the group consisting of (1) anionic surface-active compounds, amphoteric surface-active compounds, non-ionic surface-active compounds and mixtures thereof, (2) organic builder salts and inorganic builder salts, and (3) mixtures of (1) and (2), and (b) a content of at least one alkoxylated melamine having a molecular weight of from 700 to 20,000 selected from the group consisting of propoxylated melamines, butoxylated melamines and propoxylated-butoxylated melamines, where the weight ratio of components (a) to components (b) is from 999 to 1 to 3 to 1.

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

#### DESCRIPTION OF THE INVENTION

The invention, therefore, comprises low-foaming washing, rinsing and cleaning agents which are characterized in that they contain (a) a content of at least one substance having a cleaning action from the class of (1) anionic, amphoteric and non-ionic surface-active basic detergent substances, (2) inorganic and organic builder salts, and (3) mixtures of (1) and (2), and (b) a content of at least one compound from the class of propoxylated and/or butoxylated melamines having a molecular weight of from 700 to 20,000, where the weight ratio of the compounds mentioned in (a) and (b) is from 999:1 to 3:1.

The preparation of the alkoxylated melamines to be used according to the invention may be carried out in known manner, for example, by reacting melamine, dispersed in water or dissolved in a solvent such as dimethyl sulfoxide, with propylene oxide or butylene oxide or mixtures thereof. The melamine may also first be reacted with one of the two alkylene oxides mentioned, for example, propylene oxide, and the reaction with the other alkylene oxide, for example, butylene oxide, may be carried out until the desired molecular weight is obtained.

Alkoxylated melamines are preferably used whose molecular weight amounts to 1,200 to 12,000. Such compounds preferably contain 20 or more oxypropylene units (abbreviated to PrO groups) or 16 or more oxybutylene units (abbreviated to BO groups), or a corresponding number of PrO and BO groups. As the molecular weight is increased, i.e., to a degree of alkoxylation of 30 units, the increase in activity of the products become insignificant, and with a further increase of the molecular weight, the activity is no longer substantially altered. Alkoxylated melamines have been found specially active in the preparation of which, per mol of melamine, first 4 to 25 mols of propylene oxide and then 10 to 50 mols of butylene oxide are utilized. Mixtures of differently alkoxylated melamines may also be used.

The alkoxylated melamine containing up to 30 PrO groups are water-soluble. More highly propoxylated compounds dissolve in dilute acids such as acetic acid or phosphoric acid. Butoxylated melamines and alkoxylated melamines containing PrO and BO groups are sparingly soluble or insoluble in water and dilute acids, but can be easily dispersed in the usual aqueous concentrates containing the basic basic detergent substances.

In addition to the alkoxylated melamine derivatives, the washing, rinsing and cleaning agents according to the invention contain at least one substance with a cleaning tion of low-foaming rinsing, washing and cleaning compo- 65 action. This may consist of an inorganic or organic build-

er salt or a surface-active basic detergent substance or a combination of these. The agents usually contain several such substances having a cleaning action.

Suitable inorganic builder salt components having a cleaning action are phosphates, such as orthophosphates, pyrophosphates, triphosphates and more highly condensed phosphates in the form of their neutral or acid alkali metal salts such as the sodium or potassium salt, or ammonium salts. Alkali metal silicates are also suitable, especially sodium silicate, in which the ratio of 10 Na<sub>2</sub>O to SiO<sub>2</sub> amounts to 1:3.5 to 1:1. Suitable organic builder salt components having a cleaning action are the complex-forming alkali metal or ammonium salts of aminopolycarboxylic acids and/or aminopolyphosphonic acids, especially the sodium or potassium salts of amino- 15 triacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentacetic acid, triethylenetetraaminehexaacetic acid and higher homologues thereof, ethylenediaminehydroxyethanetriacetic acid, aminotri-(methylenephosphonic acid), ethylenediaminetetra-(methylenephos- 20 phonic acid), 1-hydroxyethane-1,1-diphosphonic acid, methylenediphosphonic acid and the higher homologues of the said polyphosphonic acids.

Further, suitable components of the mixture, in addition to the above, include neutral salts, such as sodium 25 sulfate and sodium chloride, compounds regulating the pH value, such as the bicarbonates, carbonates, borates and hydroxides of the alkali metals, such as sodium or potassium, and acids such as lactic acid and citric acid. The amount of alkaline-reacting substances including the 30 alkali metal silicates and phosphates should be such that the pH of a liquor utilizable for mechanical dishwashing machines amounts to 10 to 14, and in laundry machines for coarse washing, 9 to 12, and for fine washing, 6 to 9. Cleaning and rinsing agents for manual use preferably 35 have a weakly acidic, neutral or weakly basic reaction.

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 phosphate and chlorinated cyanuric acid and its alkali metal salts as well as bleaching agent activator and stabilizers such as magnesium silicate.

Among the surface-active basic detergent substances which may be contained in the agents according to the invention, the most important substances for all fields of application in which development of foam has to be entirely or largely excluded, are weakly foaming compounds, especially the non-ionic polyglycol ether derivatives of alcohols, fatty acids and alkylphenols 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 ethyleneglycol ether groups amounts to 5 to 15 and the hydrocarbon residues of which are derived from straight-chain primary alcohols with 12 to 18 carbon atoms or from alkylphenols with a straight-chain alkyl chain having 6 to 14 carbon atoms, are specially suitable. By adding 3 to 15 mols of propylene oxide to the last-named polyethyleneglycol ethers or by conversion into the acetals, washing agents 60 are obtained which are marked by a particularly lowfoaming power.

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

Washing and cleaning agents in which an insignificant development of foam is not harmful, may also contain anionic basic detergent substances of the sulfonate or sulfate type. Examples of such basic detergent substances are olefin sulfonates, such as are obtained, for example, 75

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by sulfonating primary or secondary aliphatic monoolefins with gaseous sulfur trioxide followed by alkaline or acid hydrolysis, and alkyl sulfonates such as are obtainable from n-alkanes by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization, or by bisulfite addition to olefins. In addition, alkylbenzenesulfonates, α-sulfo-fatty acid esters, primary and secondary alkylsulfates, 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 monofatty acid esters of glycerine monosulfuric acid esters or of 1,2-dihydroxypropanesulfonic acid. Further, sulfates of ethoxylated or propoxylated fatty acid amides and alkylphenols, and fatty acid taurides and fatty acid isothionates are suitable.

Besides the said basic detergent substances of the sulfonate and sulfate type, the agents may also contain alkali metal soaps of fatty acids, amphoteric surfaceactive compounds such as alkylbetaines and alkylsulfobetaines, and non-ionic surface-active compounds of the amineoxide and sulfoxide type.

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

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

The washing and cleaning agents may also contain enzymes from the class of the proteases, lipases and amylases, which may be obtained from animal and vegetable origin, for example, from digestive ferments or yeasts, such as pepsin, pancreatin, trypsin, papain, catalase and diastase. Preferably enzymic active substances are obtained from strains of bacteria or fungi, such as Bacillus subtilis and Streptomyces griseus, which substances are relatively stable towards, alkalis, per-compounds and anionic detergent substances and are not appreciably inactivated even at temperatures between 45° C. and 70° C. Their relatively great stability towards oxidizing agents is possibly due to their low content of free sulfhydryl groups.

Further suitable components of the mixtures are greying inhibitors, such as sodium cellulose glycollate, disinfectant and brightening agents, fillers, such as urea, abrasives, dyestuffs and perfumes, and also optical brighteners, for example, those of the diaminostilbenedisulfonic acid type according to the following formula:

$$\begin{array}{c} X \\ N \\ N \\ N \end{array} \begin{array}{c} -N - \\ H \\ SO_{3^{-}} \end{array} \begin{array}{c} N - N - \\ H \\ SO_{3^{-}} \end{array} \begin{array}{c} X \\ N - \\ N \\ Y \end{array}$$

in which X and Y represent the following: —NH<sub>2</sub>, —NH—CH<sub>3</sub>, —NH—CH<sub>2</sub>—CH<sub>2</sub>OH,

—N(CH<sub>2</sub>—CH<sub>2</sub>OH)<sub>2</sub>, morpholino, dimethylmorpholino, —NH— $C_6H_5$ , —NH— $C_6H_4$ —SO<sub>3</sub>H, —OCH<sub>3</sub>, —Cl, where X and Y are the same or different. Compounds in which X represents an anilino- and Y a diethanolamino- 10 or morpholino-group are specially suitable.

In addition, optical brighteners of the diarylpyrazoline type according to the following formula may be present:

In the 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 acrylamino, carboxyl, sulfonic acid and sulfonamide groups or halogen atoms.

1,3-diarylpyrazolines are preferably used in which R

represents a hydrogen atom.

In some cases it may be expedient to add additionally 30 further known foam-inhibiting agents as, for example, preferably saturated fatty acids having 20 to 24 carbon atoms or their alkali metal soaps or triazine derivatives which are obtainable by reacting 1 mol of cyanuric chloride with 2 to 3 mols of an aliphatic, straight or branched 35 chain, or cyclic primary monoamine.

The washing and cleaning agents may be present in liquid, pasty or solid form, for example, pulverulent, granulated or lump form. For better solubility, liquid preparations may contain solvents miscible with water, especially ethanol and isopropanol, as well as solution aids such as the alkali metal salts of benzene-, toluene-, xylene- or ethylbenzene-sulfonic acids. Skin protecting substances, such as fatty acid mono- and di-alkylolamides may be added to the rinsing and cleaning agents intended for manual use.

The propoxylated and/or butoxylated melamine derivatives to be used according to the invention have to a great extent an anti-foaming action in hard and soft water and solutions containing the same have good run-off properties with respect to glass, ceramic, metal and plastic articles. In this property they considerably surpass the known polyglycol ether derivatives of the type of "Pluronics" (registered trademark) and "Tetronics" (registered trademark). In contrast to anti-foaming agents with a fatty character such as paraffins, fatty acid esters and N-substituted amines, amides and polyamines, they leave behind no fatty film on the rinsed or washed objects and do not lessen the cleaning power of the basic detergent substances.

They can easily be incorporated in liquid or pasty washing agents or concentrates intended for spray drying, if desired, after previous solution in dilute acids, without their anti-foaming action being reduced thereby, such as is frequently observed in the case of known, fatty anti-foaming agents. They may also be mixed with dry, especially pulverulent agents, or sprayed thereon, and the usual mixing, granulating or spraying devices may be employed. The foam inhibitors may first be mixed with a part of the pulverulent components, for example, polymeric phosphates, active-oxygen containing substances, non-ionic basic detergent substances, enzymes or perfumes and then these mixtures may be united with the remaining pulverulent components. Mixing the alkoxylated melamines with the powder or the powder components has the

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advantage that fine-grained constituents and the enzymes are bonded with the other particles of powder, so that the mixtures have no tendency to form dust or to separate into their components.

The following specific embodiments are illustrative of the practice of the invention. They are not, however, to

be deemed limitative in any respect.

The invention, therefore, relates to mixtures which contain surface-active compounds and also those which are free from surface-active compounds. Mixtures containing surface-active compounds may have the following composition. The following figures, in percentages by weight, are based on a water-free recipe.

15 0.1% to 25%, preferably 0.5% to 10%, of alkoxylated melamine.

0.1% to 75%, preferably 1% to 50%, of at least one compound of the class of anionic, non-ionic and amphoteric surface-active compounds,

 $20\,$  0% to 80%, preferably 10% to 60%, of inorganic and/

or organic builder salt components,

0 to 50%, preferably 1% to 30%, of bleaching agents, particularly per-compounds and their mixtures with activators or stabilizers of bleaching agents, as well as active chlorine-containing bleaching compounds,

0 to 20%, preferably 1% to 12%, of other washing agent constituents, such as greying inhibitors, skin-protective substances, biocides, optical brighteners, enzymes, solution aids as well as dyestuffs and perfumes.

Mixtures free from surface-active compounds, also based on a water-free recipe, may contain the following mix components (data in percentage by weight):

0.1% to 25%, preferably 0.2% to 5%, of alkoxylated melamine,

40% to 99.9%, preferably 50 to 90% of inorganic and/or organic builder salt components,

0 to 50% of alkali metal hydroxides,

0 to 30% of active-chlorine-containing bleaching agents,
0 to 10% of other components, such as agents for protecting against corrosion and stabilizers for bleaching

agents.

A few compositions are given below which have proved especially good in practice. The invention is not restricted to the following mixtures, however, and these can be varied in many ways or be supplemented by the additional washing agent substances mentioned in the description.

The sulfate and sulfonate basic surface-active washing components and soaps are generally used as the sodium salts although other alkali metal salts may be employed. If liquid preparations are used, the anionic detergent substances may advantageously be used in the form of the mono-, di- or tri-ethanolammonium salts.

#### (1) Pulverulent, weakly foaming washing agent

3% to 15% of sulfonate basic surface-active washing component from the class of alkylbenzene sulfonates, olefin sulfonates and n-alkanesulfonates,

0 to 5% of alkylpolyglycol ethers ( $C_{12}$  to  $C_{18}$ -alkyl) or alkylphenolpolyglycol ethers ( $C_8$  to  $C_{14}$ -alkyl), with 5 to 10 ethyleneglycol ether groups,

0 to 5% of soap (C<sub>12</sub> to C<sub>18</sub>),

0.5% to 5% of anti-forming agent consisting of propoxylated and/or butoxylated melamine or its mixture with fatty acids or their alkali metal soaps, containing 20 to 24 carbon atoms,

10% to 50% of a condensed alkali metal phosphate from

the class of pyro- and tri-phosphates,

0.1% to 20% of complex-forming agents from the class of alkali metal salts of aminopolycarboxylic acids, aminoalkylene - polyphosphonic acids and hydroxyalkanesphosphonic acids,

1% to 5% of sodium silicate,

10% to 35% of sodium perborate tetrahydrate,

0 to 5% of enzymes

0.05% to 1% of an optical brightener from the class of the diaminostilbenedisulfonic acid derivatives,

0.1% to 30% of an inorganic salt from the class of the carbonates, bicarbonates, borates, sulfates and chlorides of alkali metals,

0.5% to 4% of magnesium silicate,

0.5% to 3% of sodium celluloseglycollate.

#### (2) Mechanical dishwashing agent

0 to 3% of alkylpolyglycol ether ( $C_{12}$  to  $C_{18}$ -alkyl) or alkylphenol polyglycol ether ( $C_8$  to  $C_{14}$ -alkyl) with 5 to 30 ethyleneglycol ether groups and 5 to 30 propylene-  $_{15}$ glycol ether groups,

0.5% to 5% of propoxylated and/or butoxylated mel-

amine,

50% to 95% of pentasodium triphosphate,

1% to 40% of sodium silicate (Na<sub>2</sub>O:SiO<sub>2</sub>=1:1 to 1:3), 200 to 5% of potassium dichloroisocyanurate.

#### (3) Liquid washing, rinsing and cleaning agent

0.5% to 10% of sulfonate basic surface-active washing component.

0 to 10% of alkylpolyglycol ether sulfate (C<sub>8</sub> to C<sub>16</sub>-alkyl,

1 to 5 ethyleneglycol ether groups), 0.1% to 5% of propoxylated and/or butoxylated melamine.

0.1~% to 5% of fatty acid amide-glycol ether condensate  $_{30}$ (C<sub>10</sub> to C<sub>18</sub>-fatty acid, 1 to 10 ethyleneglycol ether groups),

0 to 10% of solution aids from the class of alkali metal salts of benzene-, toluene-, or xylene-sulfonic acids,

0 to 30% of neutral or acid potassium pyrophosphate,

0 to 10% of organic solvents from the class of the C<sub>2</sub> to C<sub>3</sub> alcohols and ether alcohols,

0 to 1% of optical brightener,

Remainder water, perfume, dyestuffs, preservatives.

#### (4) Alkaline cleaning agent

0.2% to 5% of propoxylated and/or butoxylated melamine.

0.5% to 50% of sodium silicate (Na<sub>2</sub>O:SiO<sub>2</sub>=1:1 to 1:3),

0.5% to 80% of sodium hydroxide,

0 to 40% of trisodium phosphate,

0 to 40% of condensed alkali metal phosphates,

0 to 40% of soda,

0 to 10% of hydroxyethanediphosphonate.

#### (5) Pulverulent fine washing agent

1% to 30% of sulfonate basic surface-active washing component.

0 to 10% of alkylpolyglycol ether sulfate ( $C_8$  to  $C_{16}$ -alkyl, 55 1 to 5 ethyleneglycol ether groups),

0 to 20% of alkylpolyglycol ether ( $C_{10}$  to  $C_{18}$ -alkyl) or alkylphenolpolyglycol ether ( $C_8$  to  $C_{12}$ -alkyl) with 5 to 12 ethyleneglycol ether groups,

0.5% to 5% of propoxylated and/or butoxylated mel- 60 amine.

0 to 5% of fatty acid ethanolamide or diethanolamide,

0 to 20% of alkali metal triphosphate,

0 to 20% of complex-forming agents from the class of alkali metal salts of aminotriacetic acid, ethylenediaminetetraacetic acid, hydroxyethanediphosphonic acid and aminoalkylenephosphonic acids,

3% to 70% of sodium sulfate.

#### (6) Soaking and pre-washing agent

0 to 5% of sulfonate basic surface-active washing component,

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

0.1% to 5% of propoxylated and/or butoxylated melamine.

10% to 150% of soda,

5% to 50% of sodium triphosphonate and its mixtures with sodium pyrophosphate,

1% to 5% of waterglass,

0 to 5% of magnesium silicate,

0 to 5% of enzymes.

#### (7) Washing assistant and softening agent

0.2% to 5% of propoxylated and/or butoxylated melamine,

5% to 95% of alkali metal polyphosphates with 4 to 12 phosphoric acid groups in the molecule,

0 to 60% of sodium triphosphate and its mixtures with sodium pyrophosphate,

0 to 30% of soda.

#### EXAMPLES 1-10

A spray-dried washing agent of the following composition was used (data in percent by weight):

13.5% of sodium n-dodecylbenzenesulfonate,

1.5% of oleyl alcohol polyglycol ether (10 ethyleneglycol ether groups),

42% of pentasodium triphosphate,

4% of sodium silicate (Na:SiO<sub>3</sub>=1:3.3),

1.5% of magnesium silicate,

1% of sodium ethylenediamine tetraacetate,

1% of sodium celluloseglycollate,

0.5% of dyestuffs, perfumes, optical brightener,

6.5% of water,

to which were subsequently added:

25% of sodium perborate,

3.5% of alkoxylated melamines of various types.

3.5 kg. of clean laundry were washed with this agent in a drum washing machine with a sight glass (AEG Lavamat Nova 64), at temperatures between 20° and 96° C. and with a washing agent concentration of 5 gm. per liter, a water hardness of 16° German hardness and a weight ratio of textile materials to wash liquor of 1:10, without the liquor foaming over, although the conditions chosen where conducive to a very considerable foam build-up. When the experiments were repeated with normally soiled domestic laundry, only a very little foam build-up occurred. In the following Table I, the results for various alkoxylated melamines are tabulated. The figures given in the values on foaming have the following meaning:

0-no foam

-height of foam ¼ of the sight glass

-height of foam ½ of the sight glass

-height of foam ¾ of the sight glass

4—height of foam ¼ of the sight glass

5—foam visible in the filling tube

-considerable foaming over.

In two further series of expirements, (a) the tap water 65 was replaced by softened water of 3° German hardness, (b) the alkylbenzenesulfonate used in the above formulation was replaced by the same amount of coconut fatty alcohol sulfate (sodium salt).

In both series of experiments the results corresponded 70 with the values in the table within the limits of error.

For comparison, the washing agent was tested once without an anti-foaming agent and once with a commercial anti-foaming agent ("Pluronic L 61," registered trademark) known to be very active. The results show the 75 superiority of the agents according to the invention.

#### TABLE I

		Notes on foaming									
		Clean wash				Dirty wash					
Ex.	Alkoxyl groups in the alkoxylated melamine	30° C.	50° C.	70° C.	90° C.	95° C.	30° C.	56° C.	70° C.	90° C.	95° C.
3	21 PrO	4 4 4 3 3 2 1	3 4 2 0 0 0 0 2	33 33 32 22 22 22 22	4 4 4	5 4 4 4 4 4 4	1 1 1 1.5 1 1 0.5	0.5 0.5 0.5 0.0	0.5 0 0 0 0 1	1 0.5 0 0.5 0 0 0 0	1 1 5 0.1 1 1 5 0.5
10	7.5 Pro plus 35 BO	ĭ	ŏ	Ō	0	1	0. 5		0	0	0. 1
	Without additive	6 6	6 6	6	6	6	5	6	6	6 6	6

#### EXAMPLES 11-16

In the following series of experiments the foaming power of aqueous solutions was determined by the method of DIN 53,902. The apparatus used consisted of several 20 vertical cylinders filled with the solution to be tested up to a predetermined height, and each containing a plunger provided with a perforated plate which, driven by a motor, was periodically immersed in the solution and lifted out again. The height of foam obtained after a 25specified number of oscillating movements is a measure of the foaming tendency of the solution.

The anti-foaming properties of a melamine reacted with 7.5 mols of propylene oxide and then with 34 mols of butylene oxide were investigated in a series of foaming 30 solutions. The cleaner used was a mixture intended for an automatic dishwater and consisted of:

70% of pentasodium triphosphate, 27.9% of sodium metasilicate, 2% of potassium dichloriisocyanurate 0.1% of paraffin oil.

Varying amounts of surface-active compounds were also utilized as indicated. The results are collected in the following Table II. For comparison, the condensation prod- 40 uct from 30 mols of propylene oxide and 4.5 mols of ethylene oxide, known as a foam inhibitor, was again used. The symbol X in the table indicate that the solution foamed over during the experiment.

pounds, non-ionic surface-active compounds and mixtures thereof, and of (2) from 0 to 100% by weight of component (A) of a builder selected from the group consisting of organic builder salts and inorganic builder salts, and components (b) at least one alkoxylated melamine having a molecular weight of from 1,200 to 12,000 selected from the group consisting of propoxylated melamines, butoxylated melamines and propoxylated-butoxylated melamines, where the weight ratio of components (a) to components (b) is from 999:1 to 3:1.

2. A low-foaming rinsing, washing and cleaning composition of claim 1 wherein said alkoxylated melamine of component (b) is a propoxylated melamine having a molecular weight of from 1,200 to 12,000.

3. A low-foaming rinsing, washing and cleaning composition of claim 1 wherein said alkoxylated melamine of component (b) is a butoxylated melamine having a molecular weight of from 1,200 to 12,000.

4. A low-foaming rinsing, washing and cleaning composition of claim 1 wherein said alkoxylated melamine of component (b) is obtained by the reaction of 1 mol of melamine with from 4 to 25 mols of propylene oxide and thereafter with from 10 to 50 mols of butylene oxide.

5. A low-foaming rinsing, washing and cleaning composition of claim 1 having a further content of up to 5% by weight of enzymes selected from the group consisting of proteases, lipases and amylases.

6. A low foaming rinsing, washing and cleaning com-

#### TABLE II

	Height of foam on addition of 60 mg./liter of foam inhibitor			
-	Melamine plus 7.5 PrO plus 34 BO		"Pluronic"® (30 PrO plus 4.5 EO)	
Ex. Forming solution	20° C.	50° C.	20° C.	50° C.
11 12 Antifoamer	1	1	10	1
12{ 13 Cleaner	1	2	8	3
$13 - 13 - 10.06  \text{Cl2 to } \text{C}_{1\text{c}} \text{ alkyldiglycol ether sulfate}.$	1	0.7	x	0. 5
12 Antifoamer	6	6	x	3. 5
15\	6.5	3	x	4
16\begin{cases} 1 & Cleaner.	3	3	х	3

1 Grams per liter.

The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, how- 65 ever, that other expedients known to those skilled in the art may be employed without departing from the spirit of the invention.

We claim:

1. Low-foaming rinsing, washing and cleaning compo- 70 sitions consisting essentially of components (a) at least one compound having a cleaning action of (1) from 0 to 100% by weight of components (a) of a surface-active compound selected from the group consisting of anionic surface-active compounds, amphoteric surface-active com- 75 ponent (b), and additionally containing from 0 to 50% of

position of claim 1 consisting essentially of from 1% to 50% of component (a) (1), from 10% to 60% of component (a) (2), from 0.5% to 10% of component (b), and additionally containing from 1% to 30% of a bleaching agent selected from the group consisting of per-compounds, mixtures of said per-compounds with bleach activators and stabilizers, and active chlorine compounds, and further from 1% to 12% of greying inhibitors.

7. A low-foaming rinsing, washing and cleaning composition of claim 1 consisting essentially of from 40% to 99.9% of component (a) (2), from 0.1% to 25% of com-

### 3,679,589

11	12			
an alkali metal hydroxide, and further from 0 to 30%	2,979,528 4/1961 Lundsted 252—152 X			
of an active chlorine bleaching agent.	3,368,977 2/1968 Tuvell 252—152 X			
8. A low-foaming rinsing, washing and cleaning com-	3,382,178 5/1968 Lissant et al 252—135			
position of claim 7 consisting essentially of from 50% to	3,422,020 1/1969 Schmadel et al 252—152 X			
90% of component (a) (2) and from 0.2% to 5% of 5				
component (b).	LEON D. ROSDOL, Primary Examiner			
References Cited	D. L. ALBRECHT, Assistant Examiner			
UNITED STATES PATENTS	_ · _ · _ · _ · _ · _ · · · · · · · · ·			
2,414,289 1/1947 Ericks 260—2	U.S. Cl. X.R.			
2,674,619 4/1954 Lundsted 252—152 X <sup>10</sup>	U.S. CI. X.R. 252—99, 103, 156, 321, 358, 524, 542; 260—249.6, 249.7			

### UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No.	3,679,589 Dated July 25, 1972
Inventor(s)	Harald Schnegelberger et al.
	ied that error appears in the above-identified patent ters Patent are hereby corrected as shown below:
Column Line 70-75	The formula should appear as follows:
	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
5 26	The line containing the phrase "as hydroxy, alkoxy, hydroxyalkyl, amino, alkylamine," has been omitted in the patent.
5 26	The word "acrylamino" should be acylamino
8 3	The figure "150%" should be 50%
9 & 10 45-0	In the second column of Table II under the heading "Foaming solution" the word "Antifoamer" in each instance i.e., for Examples 11, 12, 13, 14, 15 and 16 should be Foaming agent The first two columns of Table II should read as follows:

## · UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No.	3,679,589	Dated	July 25,	1972
	·			
Inventor(s)	Harald Schneg	gelberger et al	e •	PAGE 2

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

~		
Ex.		Foaming solution
11	<sup>1</sup> 2	Foaming agent
12	1 13 12	Cleaner Foaming agent
13	1 <sub>3</sub> 1 <sub>0.06</sub> 1 <sub>2</sub>	Cleaner Cl2 to Cl4-alkyldiglycol ether sulfate Foaming agent
14	10.06 2	Cleaner Na dodecylbenzenesulfonate Foaming agent
15	10.06 12	Cleaner Nonylphenol + 20 E0 Foaming agent
3,6	1 <sub>0</sub> .06	Cleaner Plurafac A 38 (registered trademark) (alkyl plus E0 plus PrO preparation) Foaming agent

1 Grams per liter

# UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No	3,679,589 Dated July	7 25, 19/2
Inventor(s)	Harald Schnegelberger et al.	PAGE 3
	and the shows it	dontified natent

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

Column 10, line 10, "(A)" should read -- (a) --.

Signed and sealed this 27th day of November 1973.

(SEAL) Attest:

EDWARD M.FLETCHER, JR. Attesting Officer

RENE D. TEGTMEYER Acting Commissioner of Patents