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PROCESS AND AGENTS FOR THE CLEAR-RINSE IN MECHANICAL DISHWASHING

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ABSTRACT OF THE DISCLOSURE

Process for rinsing of dishes in dishwashing machines having one or several clear-rinsing cycles using an aqueous solution of an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to alkanediols with a linear alkane chain of from 10 to 20 carbon atoms and having vicinal, non-terminal hydroxyls, as well as clear-rinsing agent compositions for use in the process.

THE PRIOR ART

In mechanical dishwashing generally two cleaning cycles, usually separated by intermediate rinsing cycles with pure water are used. In the two cleaning cycles, different products are utilized. In the first or true cleaning cycle, alkaline-reacting agents are employed for the loosening and emulsifying of the food residues. In the after-rinsing or clear-rinsing bath, on the other hand, special clear-rinsing agents are employed. The latter should possess a good wetting power and be able to reduce the surface tension of the after-rinsing water to such a degree that it drains in a film-like manner from the dishes and leaves no visible deposits, such as lime spots or other impurities.

Because of the violent agitation of the liquor in the dishwasher, these clear-rinsing agents have to be as low-foaming as possible. It is, however, known that the customary anionic wetting agents, such as higher-molecular-weight alkyl sulfates or alkyl sulfonates or aralkyl sulfonates foam too much. In practice, therefore, mostly non-ionic tensides based on ethylene oxide adducts to fatty alcohols, alkylphenols or polypropylene glycols of higher molecular weights are employed. These products, however, are not sufficiently low foaming in the concentration range, required for a sufficient wetting effect, and disturbances in the rinsing process may occur, because of a too strong foam formation in the dishwasher.

In copending, commonly-assigned U.S. patent application Ser. No. 205,723, filed concurrently herewith, clear-rinsing agents are disclosed based on non-ionic tensides which are characterized by a content of an adduct of from 3 to 30 mols of ethylene oxide to alkanediols with a linear alkane chain of from 10 to 20 carbon atoms and having vicinal, non-terminal hydroxyls. These products, particularly with a content of more than 5 mols of ethylene oxide, are optionally combined with foam-suppressing substances of the type of non-ionic alkylene oxide adducts to higher alkanols, alkanediols and alkylphenols.

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OBJECTS OF THE INVENTION

An object of the invention is the development of low-foaming and biologically degradable clear-rinsing agents for mechanical dishwashing with a good wetting and draining effect toward hard surfaces.

Another object of the invention is the development in the process for the mechanical washing of dishes which comprises subjecting dirty dishes to the action of a washing solution, subjecting the washed dishes to at least one clear-rinsing solution and recovering said washed dishes, the improvement consisting of utilizing an aqueous solution containing from 0.01 to 1.0 gm. per liter of an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, as said at least one clear-rinsing solution.

A further object of the present invention is the development of low-foaming rinsing compositions adapted for dishwashers consisting essentially of (A) an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, and (B) a lower organic carboxylic acid having from 2 to 6 carbon atoms and sequestering properties toward salts causing water hardness, wherein the weight ratio between component (A) and component (B) is from 1:0.2 to 1:3.

A yet further object of the present invention is the development of a clear-rinsing agent concentrate adapted for dishwashers consisting essentially of (1) 20% to 90% by weight of water, (2) from 10% to 60% by weight of an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, (3) from 0 to 40% by weight of a water-miscible lower alcohol and (4) from 0 to 40% by weight of a lower organic carboxylic acid having from 2 to 6 carbon atoms and sequestering properties toward salts causing water hardness.

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

DESCRIPTION OF THE INVENTION

The objects of the invention have been achieved by the development of clear-rinsing agents for automatic dishwashing based on non-ionic, low-foaming tensides that combine the desirable properties to a high degree. The clear-rinsing agents of the invention are adducts of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to alkanediols with linear alkane chains of from 10 to 20 carbon atoms, whose hydroxyl groups are non-terminal and vicinal. By "non-terminal," such diols are designated that do not possess any hydroxyl group on a terminal carbon atom.

Such products are distinguished at concentrations giving good clear-rinsing effects, by extreme low-foaming so that a combination with foam-suppressing substances is not necessary.

For the preparation of the adducts, non-terminal α,β -diols are utilized as the starting materials. Such diols are

prepared in a known way from linear aliphatic olefins with non-terminal double bonds, for instance, by epoxidation with the aid of peracids or hydrogen peroxide and lower carboxylic acids forming peracids and subsequent saponification of the epoxides. The starting materials are preferably such olefins whose double bond is about in the middle of the carbon chain. The products obtained normally are mixtures of different vicinal diols, whose diol groups are distributed statistically around a median value with the main amount in the center of the carbon chain.

The reaction of the ethylene oxide and propylene oxide with the vicinal, non-terminal diols is carried out in a known manner in the presence of acidic or basic catalysts, preferably with the use of elevated temperatures and pressures, first with the desired amount of ethylene oxide and subsequently with the desired amount of propylene oxide. In practice, preferably a two-step process is utilized. In the first step only 1 mol of ethylene oxide is reacted with 1 mol of the diol or diol mixture. The reaction leads substantially to the formation of monoethoxylated diols. The reaction mixture is purified by distilling off the unreacted diol. In the second reaction the monoethoxylated diol is further reacted by addition of the desired amount of ethylene oxide. Subsequently to the addition of ethylene oxide the further reaction with propylene oxide is executed in a conventional and known manner. By this two-step reaction, preferably, each time one polyalkylene glycol chain per diol group is formed, as substantially only the primary hydroxyl groups, deriving from the first reaction step, react further with ethylene oxide and thereafter with the propylene oxide with sufficient speed. The other secondary hydroxyl groups of the vicinal, non-terminal diol remain largely unchanged.

Products, suitable in the sense of the invention, are particularly adducts that contain 5 to 10 mols of ethylene oxide and 3 to 10 mols of propylene oxide and in which the molar amounts of the added ethylene oxide to propylene oxide are in the ratio of 1:0.05 to 2, preferably 1:0.3 to 2. As starting materials diols or diol mixtures of an average alkane chain length of 12 to 18 carbons, preferably 14 to 16 carbons, are preferred. Examples for suitable substances are the adducts of 5 mols of ethylene oxide and 3 mols of propylene oxide or 7 mols of ethylene oxide and 5 mols of propylene oxide or 7 mols of ethylene oxide and 10 mols of propylene oxide to diols or diol mixtures of average chain lengths of 14 to 16 carbons. The claimed products are extremely low foaming and exhibit over large concentration ranges, a good draining and clear-drying effect on various customary kitchenware, such as porcelain plates, cutlery, tableware and particularly on glasses, which are particularly difficult in this respect. They are, therefore, extraordinarily suited for the clear rinsing of dishes after a preceding cleaning cycle, for example, with alkaline cleaners. Already in concentrations of about 0.05 gm./l. a drop-free, filmlike draining of the clear-rinsing liquor from the dishes is attained. A disturbing foam formation does not occur at these concentrations.

The claimed products or combinations are applied in the clear-rinsing bath in concentrations from about 0.01 to 1.0 gm./l., preferably 0.05 to 0.6 gm./l. of active substance. The application concentration depends to a certain degree upon the kind of surface to be cleaned. Particularly, synthetic resin surfaces require a somewhat higher amount of clear-rinsing agents. The application is effected preferably in the form of aqueous or dilute alcoholic concentrates with contents from 10% to 60% by weight of the active components. As alcoholic solvent components, preferably water-miscible lower alcohols such as ethanol, propanol and isopropanol, ethylene glycol, monoethyl ether of ethylene glycol and the like are utilized.

If the adducts themselves are liquid, they can also be applied without solvents. The concentrates are appropriately added with the aid of automatic dosing devices, as

are already customary for such purposes, or manually to the clear-rinsing liquor.

The invention also involves, in the process for the mechanical washing of dishes which comprises subjecting dirty dishes to the action of a washing solution, subjecting the washed dishes to at least one clear-rinsing solution and recovering said washed dishes, the improvement consisting of utilizing an aqueous solution containing from 0.01 to 1.0 gm. per liter of an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, as said at least one clear-rinsing solution.

If the rinsing is effected with hard water, lower organic carboxylic acids with 2 to 6 carbon atoms may be added to the concentrates or the clear-rinsing liquor for the avoidance of lime incrustations and lime hazes on the rinsed dishes. Acids are preferred that are physiologically innocuous and that possess sequestering properties toward the hardness causing salts, such as tartaric acid, lactic acid, glycolic acid and particularly citric acid. The optional addition of acid in the clear-rinsing concentrate amounts to about 10% to 40% by weight.

The low-foaming clear-rinsing agents of the invention are, therefore, optionally low-foaming rinsing compositions adapted for dishwashers consisting essentially of (A) an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, and (B) a lower organic carboxylic acid having from 2 to 6 carbon atoms and sequestering properties toward salts causing water hardness, wherein the weight ratio between component (A) and component (B) is from 1:0.2 to 1:3.

Essentially where a concentrate is employed in accordance with the invention, this is a clear-rinsing agent concentrate adapted for dishwashers consisting essentially of (1) 20% to 90% by weight of water, (2) from 10% to 60% by weight of an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, (3) from 0 to 40% by weight of a water-miscible lower alcohol and (4) from 0 to 40% by weight of a lower organic carboxylic acid having from 2 to 6 carbon atoms and sequestering properties toward salts causing water hardness.

The following specific examples are illustrative of the invention without being limitative in any manner.

EXAMPLES

In a test of foaming caused by the rhythmic insertion and withdrawal of a perforated disk, the foaming behavior of various clear-rinsing agents of the invention was determined. The results of the tests, given in the following Table I, demonstrates the extraordinarily favorable foaming behavior of the claimed agents.

At a dosage level of 1 gm./l. of clear-rinsing agents, aqueous solutions of the compounds listed in Table I were stamped 20 times in a measuring cylinder with a perforated disk and subsequently the foam height in centimeters after 10, 30 and 60 seconds was recorded. Foaming heights above 20 cm. are marked by X. The city water used had a dH (degrees German hardness) of 12°.

The abbreviations used in the table and examples are:

EO=mols of ethylene oxide.

PrO=mols of propylene oxide.

C₁₆-diol=a vicinal, non-terminal alkanediol with carbon chains with 15, 16 and 17 carbon atoms in statistical distribution, average: 16 carbon atoms.

C₁₄-diol=a vicinal, non-terminal alkanediol with carbon chains with 13, 14 and 15 carbon atoms in statistical distribution, average: 14 carbon atoms.

TABLE I

	50° city water			50° C. Permutit treated water		
	10"	30"	60"	10"	30"	60"
1a 20% C ₁₆ -diol plus 7 EO/3 PrO	3.4	1.9	1.2	3.0	1.6	1.2
1b 20% C ₁₆ -diol plus 7 EO/5 PrO	0.7	0.9	0.9	1.1	1.1	1.1
1c 20% C ₁₆ -diol plus 7 EO/10 PrO	0	0	0	0	0	0
1d 20% C ₁₆ -diol plus 7 EO/3 PrO	2.2	1.6	1.6	2.7	1.4	1.4
20% citric acid						
1e 20% C ₁₆ -diol plus 7 EO/5 PrO	0.5	0.5	0.5	1.0	1.0	1.0
20% citric acid						
1f 20% C ₁₆ -diol plus 7 EO/10 PrO	0	0	0	0	0	0
20% citric acid						
2a 20% C ₁₄ -diol plus 5 EO/3 PrO	1.0	1.0	1.0	1.5	1.4	1.4
20% ethanol						
2b 20% C ₁₄ -diol plus 5 EO/5 PrO	0	0	0	0.6	0.5	0.5
20% ethanol						
2c 20% C ₁₄ -diol plus 5 EO/10 PrO	0	0	0	0	0	0

Example 1

A clear-rinsing agent with a good effect for home dishwashing machines as well as for commercial dishwashers has the following composition:

	Percent
C ₁₆ -diol+7EO/5Pro	40
Water	60

The clear-drying effect is very good over a concentration range of 0.1 to 0.7 gm./l. The foaming is at a liquor temperature of 50° C. extraordinarily low, so that the simultaneous use of foam-suppressing substances becomes superfluous.

Example 2

An acidic adjusted after-rinsing agent, particularly for home dishwashers, has the following composition:

	Percent
C ₁₆ -diol+7EO/3Pro	20
Citric acid	28
Water	52

The clear-drying effect is excellent over a concentration range from 0.2 to 1.0 gm./l. Foaming is very low.

Example 3

A neutral clear-rinsing agent that proved particularly suitable in commercial dishwashing machines with a very high water circulation has the following composition:

	Percent
C ₁₄ -diol+5EO/10Pro	53
Ethanol	20
Water	27

In spite of the high water circulation, no disturbing foam is developed. The clear-drying effect is good.

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, or disclosed herein, may be employed without departing from the spirit of the invention or the scope of the claims.

We claim:

1. Low-foaming rinsing concentrates adapted for dishwashers consisting essentially of (A) an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane

chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, and (B) a lower organic carboxylic acid having from 2 to 6 carbon atoms and sequestering properties toward salts causing water hardness, wherein the weight ratio between component (A) and component (B) is from 1:0.2 to 1:3 in an aqueous solution containing from 20% to 90% of water.

2. The low-foaming rinsing concentrates of claim 1 wherein said adduct is an adduct of from 5 to 10 mols of ethylene oxide and from 3 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 12 to 18 carbon atoms and vicinal, non-terminal hydroxyls.

3. A clear-rinsing agent concentrate adapted for dishwashers consisting essentially of (1) 20% to 90% by weight of water, (2) from 10% to 60% by weight of an adduct of from 5 to 20 mols of ethylene oxide and from 1 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 10 to 20 carbon atoms and vicinal, non-terminal hydroxyls, (3) from 0 to 40% by weight of a water-miscible lower alcohol and (4) from 0 to 40% by weight of a lower organic carboxylic acid having from 2 to 6 carbon atoms and sequestering properties toward salts causing water hardness.

4. The clear-rinsing agent concentrate of claim 3 wherein said adduct is an adduct of from 5 to 10 mols of ethylene oxide and from 3 to 10 mols of propylene oxide to an alkanediol having a linear alkane chain with from 12 to 18 carbon atoms and vicinal, non-terminal hydroxyls.

5. The clear-rinsing agent concentrate of claim 3 wherein said component (4) is present in an amount of from 10% to 40% by weight.

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