

Liquid Detergent Composition

The present invention relates to a liquid detergent composition, and more particularly to a neutral liquid detergent composition especially suited for the cleansing of baths and toilets.

Hitherto, ether detergents containing surface active agents, chelating agents and glycol ether solvents have been used for the removal of stains secreted from the human body and attached on the hard surfaces of baths, toilets etc.

It is known that although the liquid detergents are generally adjusted to weak acidity in the pH-value range of 4.5 to 5.5 in order to attain the greatest cleansing effect, they have sufficient cleansing effects even at neutrality depending on compositions. For example, there are disclosed in Japanese Patent Laid-open Sho 53-35710 a detergent composition (pH 4.5-7.5) for baths, which contains an anionic surface active agent, a nonionic surface active agent, a chelating agent such as a citrate or an ethylenediaminetetraacetate, and a glycol ether solvent; and in Japanese Patent Laid-open Sho 63-51500 a neutral detergent composition for baths, which contains a surface active agent, a potassium salt of aminocarboxylic acid, and a glycol ether solvent.

Incidentally, if acid detergents are mixed with chlorine bleaching agents by accident, there is a danger

of chlorine gas harmful to the human body being evolved. The amount of chlorine gas evolved decreases as the pH is changed to weak acidity and then neutrality. In the above-described known examples, however, there is a problem that some amount of chlorine gas is evolved even if the detergent compositions are adjusted to weak acidity or neutrality.

The inventors have made intensive studies in order to solve the above-described problems. As a result, they have found that with a liquid detergent composition in which hydroxycarboxylic acid or a salt thereof is compounded with aminocarboxylic acid, or a salt thereof, in specific proportions and the pH adjusted to neutrality, the evolution of chlorine gas is suppressed completely and an adequate cleansing effect is attained.

Therefore, the invention provides a liquid detergent composition which has a pH-value in the range 6.0 to 8.0, the composition essentially consisting of:

- (a) 0.1 to 20% by weight of an anionic surface active agent and/or a nonionic surface active agent,
 - (b) hydroxycarboxylic acid or a salt thereof,
 - (c) aminocarboxylic acid or a salt thereof, and
 - (d) 0.1 to 20% by weight of an alkylene glycol lower alkyl ether solvent,
- wherein the weight ratio of (b)/(c) is 10/1~1/1, and the amount of (b) + (c) is 0.1 to 20% by weight.

Examples of the component (a), the anionic surface active agent, used in the invention include ordinary sulfonate anionic surface active agents and sulfate anionic surface active agents.

Advantageously, component (a) comprises sulfonate anionic surface active agents such as straight-chain or branched-chain alkyl ($C_8 \sim C_{18}$) benzenesulfonates; long-chain alkyl ($C_8 \sim C_{22}$) sulfonates; long-chain olefin ($C_8 \sim C_{22}$) sulfonates etc. Among them, straight-chain or branched-chain alkyl ($C_8 \sim C_{18}$) benzenesulfonates are especially preferable in view of cleansing effects, etc.

The sulfonate anionic surface active agents being preferable in view of their strong resistance to hydrolysis.

Alternatively, component (a) may comprise sulfate anionic surface active agents such as long-chain monoalkyl ($C_8 \sim C_{22}$) sulfates, polyoxyethylene (1 to 6 moles) long-chain alkyl ($C_8 \sim C_{22}$) ether sulfates, polyoxyethylene (1 to 6 moles) alkyl ($C_8 \sim C_{18}$) phenyl ether sulfates, etc.

Cations used as counter ions to the anionic surface active agents can include ions of alkali metals such as sodium, potassium, etc., and ions of alkanolamines such as monoethanolamine, diethanolamine, triethanolamine, etc.

Component (a) may further include/or comprise a nonionic surface active agent such as polyoxyethylene (6 to 35 moles) long-chain alkyl ($C_8 \sim C_{22}$) ethers,

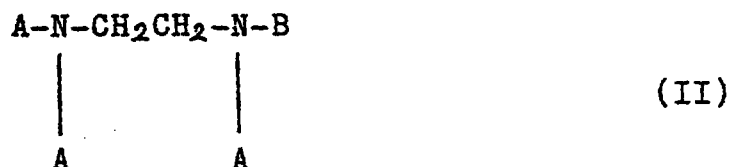
polyoxyethylene (6 to 35 moles) alkyl ($C_8 \sim C_{22}$) phenyl ethers, etc.

The aforesaid surface active agents comprise between 0.1 to 20% by weight, and preferably 0.5 to 10% by weight, of the composition. Simultaneous use of 1 to 7% by weight of the anionic surface active agent and 1 to 7% by weight of the nonionic surface active agent being especially preferable.

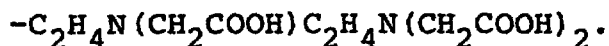
Examples of the hydroxycarboxylic acid comprising component (b) include glycolic acid, lactic acid, gluconic acid, citric acid, malic acid, tartaric acid, etc.

Among them, malic acid, citric acid, tartaric acid, or salts thereof are preferable. Further, examples of the salt of hydroxycarboxylic acid include sodium, potassium, monoethanolamine, diethanolamine and triethanolamine salts of hydroxycarboxylic acid.

Examples of the aminocarboxylic acid or salt thereof as the component (c) include nitrilotriacetic acid, isoserinediacetic acid, and compounds of the general formula



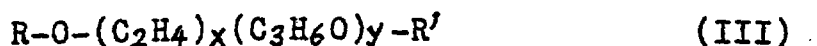
wherein A represents $-\text{CH}_2\text{COOH}$ or $-\text{C}_2\text{H}_4\text{COOH}$, and B represents $-\text{CH}_2\text{COOH}$, $-\text{C}_2\text{H}_4\text{OH}$, $-\text{C}_2\text{H}_4\text{N}(\text{CH}_2\text{COOH})_2$ or



Further examples of the aminocarboxylic acid of the above general formula (II) include ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, N-hydroxyethyl ethylenediaminetriacetic acid, ethylenediaminetetrapropionic acid, triethylenetetraminehexaacetic acid, etc. and sodium, potassium, monoethanolamine, diethanolamine and triethanolamine salts of aminocarboxylic acid.

The aforesaid components (b) and (c) are present in the composition in the weight ratio of (b)/(c), 10/1 ~ 1/1, and preferably 5/1 ~ 1/1, and together (b) + (c) comprise between 0.1 to 20% by weight of the total composition and preferably comprise between 1 to 10% by weight. When the weight ratio and amount of components (b) and (c) are outside the above-described limits, the prevention of chlorine gas evolution from the detergent composition and the maintenance of an adequate cleansing effect cannot be fulfilled simultaneously.

The alkyl glycol lower alkyl ether solvent as the component (d) is represented by the general formula



wherein R and R' independently represent H or an alkyl group having 1 to 4 carbon atoms, provided that R and R' are never H at the same time; x and y may be 0,

respectively, provided that x and y are never 0 at the same time; and $x + y$ is 1 to 10.

Examples of the alkylene glycol lower alkyl ether solvent of the general formula (III) include ethylene glycol monoethyl ether, diethylene glycol monobutyl ether, hexapropylene glycol monoethyl ether, tetrapropylene glycol monomethyl ether, tetrapropylene glycol dimethyl ether, ethylene glycol monobutyl ether, ethylene glycol monoamyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol monobutyl ether, dipropylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monopropyl ether, tripropylene glycol monobutyl ether, polyoxyethylene ($x=1$) polyoxypropylene ($y=4$) glycol monoethyl ether, polyoxyethylene ($x=1$) polyoxypropylene ($y=1.5$) glycol butyl ether, etc.

The alkylene glycol lower alkyl ether solvent (d) comprises between 0.1 to 20% by weight, and preferably between 3 to 10% by weight, of the total detergent composition.

The detergent composition according to the the invention is adjusted to a pH-value in the range 6.0 to 8.0. With a pH-value of less than 6.0, the evolution of chlorine gas can not be suppressed, and with a pH-value of more than 8.0, the cleansing effect is reduced, and

materials such as aluminum sash, may be damaged.

The liquid detergent compositions may also include lower alcohols such as ethyl alcohol, etc., ethylene glycol, and lower alkyl benzenesulfonates such as benzenesulfonates, toluenesulfonates, etc. as low temperature stabilizers. Perfumes, pigments, preservatives, etc. can also be added to the liquid detergent composition in order to render it more desirable to consumers.

Preferred embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawing.

Fig. 1 is a diagrammatic representation of the apparatus for carrying out the chlorine gas evolution test.

Example 1

Detergent compositions for baths, comprising the components shown in Table 1, were prepared and their cleansing effect and the amount of chlorine gas evolved was evaluated by the following method.

Method for Evaluation of the Cleansing Effect

The cleansing effect was evaluated in the following manner. Using a polypropylene plate, to which were attached bath stains that were not easily removed only by scrubbing, the plate was scrubbed by moving an urethane sponge soaked with 5 g of the detergent for evaluation,

back and forth for 5 times with a load of about 1 kg applied to the sponge. After the scrubbing, the state of removal of the stains on the surface of a bath was evaluated visually.

O : Thoroughly cleansed.

△ : Uneven removal of stains observed

× : Almost no effect shown

Chlorine Gas Evolution Test

The chlorine gas evolution test will be explained with reference to Fig. 1.

A 22ℓ covered round plastic container 1 is equipped with a chlorine gas detector tube 2 (SB type manufactured by Komyo Rika Kogyo Co., Ltd.) and a 100 mℓ chlorine gas collector 3. A fan 4 for stirring the inside of the container 1 is provided in the container 1, and a 10 mℓ beaker 5 for admitting the sample detergent composition is placed at the bottom of the container 1.

* Measurement Method

(1) The beaker 5 containing 1 mℓ of the sample detergent composition is placed at the bottom of the container 1.

(2) 1 mℓ chlorine-based standard solution (5.0% of sodium hypochlorite, and 1.0% of sodium hydroxide) is added into the beaker 5.

(3) The container 1 is covered without delay, both the solutions are mixed using a magnetic stirrer 6, and the inside of the container 1 is stirred with the fan 4 at

3000 r.p.m.

(4) At 5 minutes after the mixing of both the solutions, the chlorine gas collector 3 is connected to the rear of the chlorine gas detector tube 2, 100 ml of the gas in the container 1 are sucked and collected once, and the concentration of chlorine gas is measured. Incidentally, room temperature and solution temperature at the time of the test are $20 \pm 5^{\circ}\text{C}$.

The results of the above-described test are shown in Table-1.

Table-1

Components of detergent composition for baths (% by weight)	Comparative composition		Present composition		Comparative composition	
Polyoxyethylene alkyl ether* ¹	3	3	3	3	3	3
Alkyl benzenesulfonate* ²	3	3	3	3	3	3
Propylene glycol monomethyl ether (p = 4.0)	7	7	7	7	7	7
Citric acid	5	5	4	3	2.5	1
Ethylenediaminetetraacetic acid	0	0	1	2	2.5	4
Water	B**	B	B	B	B	B
pH (Adjusted with sodium hydroxide at 25 °C)	5	6.5	6.5	6.5	7.7	6.5
Bath stain cleansing	O	Δ	O	O	O	O
Amount of chlorine gas evolved (ppm)	2.0	-**	-	-	0.5	1.0
						1.5

- Note) * 1 Alkyl chain length: 13 on the average, number of moles of ethylene oxide added: 12.
- * 2 Alkyl chain length: 12 on the average.
- * 3 Abbreviation of balanced amount for making the total 100.
- * 4 Below the detection limit.



Claims:

1. A liquid detergent composition having a pH-value in the range 6.0 to 8.0, the composition essentially consisting of:
(a) 0.1 to 20% by weight of an anionic surface active agent and/or a nonionic surface active agent,
(b) hydroxycarboxylic acid or a salt thereof,
(c) aminocarboxylic acid or a salt thereof, and
(d) 0.1 to 20% by weight of an alkylene glycol lower alkyl ether solvent,
wherein the weight ratio of (b)/(c) is 10/1~1/1, and the amount of (b) + (c) is 0.1 to 20% by weight.
2. A composition as claimed in claim 1, wherein component (a) is a sulfonate anionic surface active agent.
3. A composition as claimed in claim 1 or 2, wherein component (a) comprises straight-chain or branch-chain alkyl benzenesulfonates having 8 to 18 carbon atoms in the alkyl group.
4. A composition as claimed in claim 1 or 2, wherein component (a) comprises a sulfate anionic surface active agent.
5. A composition as claimed in claims 1 or 2,



wherein component (a) comprises a non-ionic surface active agent.

6. A composition as claimed in claim 1, wherein component (a) comprises between 0.5 to 10% by weight of the total composition.

7. A composition as claimed in claim 1, wherein component (a) comprises between 1 to 7% by weight of anionic surface active agent and between 1 to 7% by weight of non-anionic surface active agent.

8. A composition as claimed in any preceding claim, in which the weight ratio of components(b) and (c) is in the range 5/1 to 1/1.

9. A composition as claimed in claim 8, in which components (b) and (c) comprise between 1 to 10% by weight of the total composition.

10. A composition as claimed in any preceding claim, in which component (d) comprises between 3 to 10% by weight of the composition.

11. A composition substantially the same as described herein with reference to examples of the present composition given in Table-1.
