

Detergent composition

The present invention concerns a detergent composition and, in particular, it relates to a liquid detergent composition for hard surfaces.

Existing detergent compositions are selected for use depending on the kind of stain and the degree of contamination or staining. Surface active agent/solvent type detergents have been used mainly for thumb-mark contamination; non-modified oil contaminations with a relatively moderate degree of contamination, surface active agent/solvent/alkali agent-type detergents for oil and fat contamination, etc. denatured under the effect of heat, sunlight and oxygen in air (in kitchen or the like); and surface active agent/solvent/metal chelating-type detergents for metal soap, in particular, calcium salts of fatty acids in bathrooms.

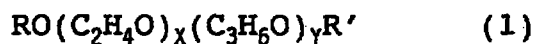
Further, alkylene glycol alkyl ether type solvents prepared by adding ethylene oxide and/or propylene oxide to a lower alcohol are generally used as the solvent as the main ingredient of the detergent in view of damage to substrates.

Although various detergents with satisfactory

detergent power have been proposed which contain such solvents (Japanese Patent Publication Sho 40126, Japanese Patent Laid-Open Sho 54-158408, 61-151300, Japanese Patent Publication Sho 55-9036 and Japanese Patent Laid-Open Hei 1-221497), they release odors inherent to solvents, feel unpleasant and require masking by the addition of perfume ingredients or the like. They have not yet reached a satisfactory level in view of odors, even with addition of perfume ingredients.

Further, although it has been proposed in Japanese Patent Laid-Open Hei 2-132199 to improve an odour by restricting the isomer content in a specific solvent (propylene oxide adduct of a lower alcohol), the solvent odor has not been eliminated completely.

The present inventors have investigated the fundamental cause of solvent odor in alkylene glycol alkyl ether-type solvents represented by the following general formula (1) used in detergent compositions:



where R and R' each represents H or alkyl group with 1 to 8 carbon atoms providing that R and R'

are not simultaneously H, X, Y each represents an integer: $0 \leq X \leq 3$, $0 \leq Y \leq 3$ providing that X and Y are not simultaneously 0; and found that the cause for the unpleasant solvent odor is not an odor possessed by the solvent itself, but is attributable to a slight amount of volatile substance produced as a by-product or derived from raw material.

Further, head space analysis (conditions are to be described later) of solvents has shown that those having the solvent odor contain, in addition to the solvent represented by the general formula (1), by-products or impurities having a molecular weight of 50 to 300 in an amount of from 1 to 3%, more particularly 4 to 20% based on the peak area of the solvent represented by the general formula (1).

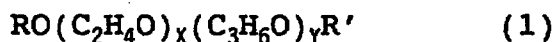
In view of the above, solvent specimens having different impurity contents were obtained by varying the reaction conditions and analysis for the head space in such specimens and odor evaluations were conducted. As a result, it has been found that a solvent having a content of impurities with a molecular weight of 50 to 300 with a peak area in head space analysis of less

than 0.5% relative to the peak area of the solvent is free from odor.

The present inventors have accomplished the present invention based on the finding that an extremely excellent detergent composition can be provided in terms of odor as well as detergent power, by blending a slight amount of impurities having a molecular weight of from 50 to 300 contained in those considered to have a solvent odor with a solvent free from solvent odor, obtained by reducing the peak area ratio by the GC-MS analysis in the head space to less than 0.5%.

The present invention provides a detergent composition comprising:

(A) 0.1 to 20% by weight of an alkylene glycol alkyl ether-type solvent represented by the following general formula:



where R and R' each represents H or an alkyl group with 1 to 8 carbon atoms provided that R and R' are not simultaneously H; X, Y each represents an integer: $0 \leq X \leq 3$, $0 \leq Y \leq 3$ provided that X and Y are not simultaneously 0;

wherein the amount of impurities having a molecular weight of 50 to 300 is limited so that the ratio of the peak area of the impurities to the peak area of solvent (A) is less than 0.5% when determined using a head space gas chromatography-mass spectrometer; and

(B) 0.1 to 20% by weight of a surface active agent.

In the present invention, the head space GC-MS analysis for the compound represented by the general formula (1) in the present invention is carried out as follows:-

(1) Measuring Instrument

Head space sampler

HP 19395 A

manufactured by Hewlett Packard Co

Gas chromatography

HP 5890 SERIES II

Detector HP 5971 A

MASS SELECTIVE DETECTOR

MASS range 10 - 400

(2) Conditions for Gas chromatography

Column --- manufactured by J and W Co. DB-WAX

30m x 0.32 x 50 um

Carrier gas -- He. 1.84 ml/min

Split vent. 20.0 ml/min

Total Split vent. 125 ml/min

Column temperature elevation condition

Time

0 - 2 min --- constant at 40°C

2 - 12 min --- elevated up to 80°C at a
rate of 4°C/min

12 - 19 min --- elevated up to 150°C at a
rate of 10°C/min

19 - 31 min --- constant at 150°C

Specimen charging temperature 230°C

Detector temperature 250°C

(3) Conditions for head space

Sample vessel -- 20 ml vial vessel

Sample amount -- 10 ml

Heating condition -- 90° x 1.5 hr

As the solvent (A) usable in the present invention, there can be mentioned, for example, ethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, tripropylene glycol dimethyl ether,

polyoxyethylene ($X = 1$ in the formula (1))
polyoxypropylene ($Y = 3$ in the formula (1)) glycol
monobutyl ether, etc. It is necessary that the
content of impurities in the solvent is such that
the ratio of the peak area of the impurity to the
peak area of the solvent is less than 0.5% by
weight. If the peak area ratio exceeds 0.5%, a
detergent composition which is satisfactory in
view of the odor cannot be obtained. The solvent
(A) is blended in the composition according to the
present invention by from 0.1 to 20% by weight,
preferably, 3 to 10% by weight.

As the surface active agent (B) used in
the present invention, an anionic surface active
agent and nonionic surface active agent are
preferred but an amphoteric surface active agent
and a cationic surface active agent can also be
used as required.

As the anionic surface active agent,
usual sulfonate-type anionic surface active agents
and sulfate-type anionic surface active agents are
used. As the sulfonate-type anionic surface
active agent, there can be mentioned linear or
branched alkyl ($C_8 - C_{22}$) benzene sulfonate, long-
chained alkyl ($C_8 - C_{22}$) sulfonate and long-chained
olefin ($C_8 - C_{22}$) sulfonate. Further, as the

sulfate-type anionic surface active agent, there can be mentioned, for example, long-chained monoalkyl ($C_8 - C_{22}$) sulfate ester salt, polyoxyethylene (1 - 6 mole) long-chained alkyl ($C_8 - C_{22}$) ether sulfate ester and polyoxyethylene (1 - 6 mole) alkyl ($C_8 - C_{22}$) phenyl ether sulfate ester salt. Cations as pair ions in such anionic surface active agents are, for example, alkali metal ions such as of sodium and potassium and alkanol amine ions such as of monoethanolamine, diethanolamine and triethanolamine. As the anionic surface active agent in the present invention, a sulfonate-type surface active agent is preferred in view of the high resistance to hydrolysis, etc. Further, in view of the detergent power or the like, a linear or branched alkyl benzene sulfonate is preferred.

As the nonionic surface active agent, there can be used, for example, polyethylene (6 - 35 mole) long-chained alkyl (primary or secondary ($C_8 - C_{22}$) ether, polyoxyethylene (6 - 35 mole) alkyl ($C_8 - C_{18}$) phenyl ether and polyoxyethylene polyoxypropylene block copolymer. In view of deterging power, polyoxyethylene (6 - 35 mole) long-chained alkyl (primary or secondary $C_8 - C_{22}$) ether and polyoxyethylene (6 - 35 mole) alkyl ($C_8 - C_{18}$) phenyl ether can be used.

As the amphoteric surface active agent, there can be mentioned, for example, carbobetaine, sulfobetaine or hydroxysulfoxybetaine containing alkyl group with 8 to 22 carbon atoms.

Further, as the cationic surface active agent, there can be mentioned C_{10} - C_{22} mono-long-chained alkyl trimethyl ammonium salt, di-long-chained alkyldimethyl ammonium salt and mono-long-chained alkyldimethyl benzyl ammonium salt.

Such a surface active agent (B) is blended by from 0.1 to 20% by weight in the composition according to the present invention.

An antioxidant may further be added to the detergent composition according to the present invention to prevent aging degradation of odor. As the antioxidant (C) used in the present invention, any of those known so far can be used and there can be preferably mentioned phenolic antioxidant such as 3,5-di-tert-butyl-4-hydroxytoluene and 2,5-di-tert-butylhydroquinone; amine type antioxidant such as N,N'-diphenyl-p-phenylenediamine and phenyl-4-piperidinyl carbonate; sulfur type antioxidant such as didodecyl-3,3'-thiodipropionate, and ditridecyl-3,3'-thiodi proprionate, phosphoric antioxidant

such as tris(isodecyl)phosphite and triphenyl phosphite; a natural antioxidant such as L-ascorbic acid and its sodium salt and DL- α -tocopherol, which may be used alone or as a combination of one or more of them. Among them, 3,5-di-tert-butyl-4-hydroxytoluene, 2,5-di-tert-butylhydroquinone and DL- α -tocopherol are particularly preferred. Such an antioxidant is blended to the solvent (A) in the detergent composition according to the present invention at a ratio of greater than 0.005% by weight, preferably, from 0.005 to 5% by weight and, more preferably, from 0.01 to 0.3% weight. The antioxidant may be added during preparation of the solvent (A) or upon conditioning the detergent composition according to the present invention.

To the detergent composition according to the present invention, there may be blended an alkali agent such as monoethanolamine or diethanolamine, citric acid or metal ion chelating agent such as EDTA depending on the purpose of use, or optionally blended a low temperature stabiliser such as lower alcohol for example, ethanol, ethylene glycol, benzene sulfonate and toluene sulfonate, perfume, dye, corrosion inhibitor and/or antiseptic.

Brief Explanation of the Drawings

Fig. 1 is a chart for the head space GC-MS analysis for butyl carbitol according to the present invention and Fig. 2 is a charge for the head space GC-MS analysis for butyl carbitol in for comparison.

(Example)

The present invention will now be explained with reference to the following illustrative examples.

Examples 1 - 5 and Comparative Examples 1 - 5

Various kinds of detergent compositions or ingredient compositions shown in Table 1 were prepared, the odor for each of which was evaluated by 20 member panel and average values for the sources were determined.

The standards for the evaluation are as shown below.

- 4 ... no unpleasant odor
- 3 ... no substantial unpleasant odor
- 2 ... some unpleasant odor
- 1 unpleasant odor

Charts of the head space GC-MS analysis for butyl carbitol used in the examples and the comparative examples are shown in Fig. 1 and Fig. 2 respectively.

Examples 6 - 9 and Comparative Examples 6 - 9

Various kinds of detergent compositions of the ingredient compositions shown in Table 2 were prepared and odors of specimens were evaluated just after the preparation and after one month storage at 50°C by a ten-member panel and average values for the scores were determined.

The standards for the evaluation are as shown below.

- 4 ... no unpleasant odor
- 3 ... no substantial unpleasant odor
- 2 ... some unpleasant odor
- 1 ... unpleasant odor

Table 1

	Example					Comparative Example				
	1	2	3	4	5	1	2	3	4	5
Polyoxyethylene (P=7) alkyl (C=12) ether	3					3				
Sodium alkyl (C=12) benzene sulfonate		3	3				3	3		
N,N,N-dodecyltrimethyl-N-sulfo propyl ammonium betaine				3	3				5	
Dodecyltrimethyl ammonium chloride										5
Butyl carbitol (peak area ratio: less than 0.1%)	10	10	10	10	10					
Butyl carbitol (peak area ratio: 3%)						10	5	5	5	5
Monoethanolamine		5					5			
Sodium ethylenediamine tetra-acetate			5					5		
Water	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance
pH	7.0	10.8	7.0	7.0	7.0	7.0	10.8	7.0	7.0	7.0
Score for odor	4.0	3.9	4.0	4.0	3.9	1.1	1.2	1.3	1.3	1.3

(1) Balancing amount for making the entire amount to 100

(2) pH was adjusted with NaOH or HCl

Table 2

	Example				Comparative Example			
	6	7	8	9	6	7	8	9
Polyoxyethylene ($\bar{p}=12$) alkyl ($\bar{c}=12$) ether	5	5	5	5	2	2	2	—
Sodium alkyl ($\bar{c}=12$) benzene sulfonate	—	—	—	—	3	3	—	2
Polyoxyethylene ($\bar{p}=3$) alkyl ($\bar{c}=12$) ether sulfonate ester sodium salt	—	—	—	—	—	—	3	2
Butyl carbitol (peak area ratio: less than 0.1%)	5	5	5	5	—	—	—	—
Butyl carbitol (peak area ratio: 3%)	—	—	—	—	5	5	5	5
3,5-di-tert-butyl-4-hydroxytoluene	—	0.05	—	—	—	0.05	—	—
DL- α -tocopherol	—	—	0.05	—	—	—	0.05	—
2,5-di-tert-butylhydroquinone	—	—	—	0.05	—	—	—	0.05
Monoethanolamine	—	—	5	—	—	—	3	—
Sodium ethylenediamine tetracetate	—	—	—	5	—	—	—	3
Water "	balance	balance	balance	balance	balance	balance	balance	balance
pH "	7.0	7.0	10.8	7.0	7.0	7.0	10.8	7.0
Score for odor just after preparation	4.0	4.0	4.0	4.0	1.5	1.4	1.5	1.5
Score for odor after one month storage at 50°C	3.3	3.9	3.9	3.9	1.0	1.1	1.1	1.0

(1) Balancing amount for making the entire amount to 100

(2) pH was adjusted with NaOH or HCl

CLAIMS

1. A detergent composition comprising:
(A) 0.1 to 20% by weight of an alkylene glycol alkyl ether-type solvent represented by the following general formula:



where R and R' each represents H or an alkyl group with 1 to 8 carbon atoms provided that R and R' are not simultaneously H; X, Y each represents an integer: $0 \leq X \leq 3$, $0 \leq Y \leq 3$ provided that X and Y are not simultaneously 0;

wherein the amount of impurities having a molecular weight of 50 to 300 is limited so that the ratio of the peak area of the impurities to the peak area of solvent (A) is less than 0.5% when determined using a head space gas chromatography-mass spectrometer; and

- (B) 0.1 to 20% by weight of a surface active agent.

2. A detergent composition as claimed in Claim 1, wherein solvent (A) includes one or more of the following: ethylene glycol monoethyl ether,



diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, tripropylene glycol dimethyl ether, polyoxyethylene [X = 1 in the formula (1)] polyoxypropylene [Y = 3 in the formula (1)] glycol monobutyl ether.

3. A detergent composition as claimed in Claim 1, wherein the solvent (A) is present in an amount of from 3 to 10% by weight.

4. A detergent composition as defined in any one of Claims 1 to 3 which further contains an antioxidant in an amount of more than 0.005% by weight based on the amount of solvent (A).

5. A detergent composition as claimed in Claim 2, wherein the antioxidant is present in an amount of from 0.005% to 5% by weight.

6. A detergent composition as claimed in Claim 3, wherein the antioxidant is present in an amount of from 0.01 to 0.3% by weight.

7. A detergent composition as defined in Claim 2, wherein the antioxidant is selected from the group consisting of 3,5-di-tert-butyl-4-hydroxytoluene, DL- α -tocopherol and 2,5-di-tert-butylhydroquinone.



8. A detergent composition as claimed in any one of Claims 1 to 7, wherein the surface active agent (B) comprises an anionic and a nonionic surface active agent.

9. A detergent composition substantially as described herein.

10. A detergent composition substantially as described herein with reference to one or more of examples 1 to 5.
