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LIQUID DETERGENT COMPOSITION

Technical Field of the Invention

5 The present invention relates to a liquid detergent composition useful for hard surfaces of kitchens etc. and for the skin and hair, more particularly, relates to a transparent liquid detergent composition having a good low temperature stability and excellent detergent power.

10 Prior Art

 In the past, as a liquid detergent such as a kitchen detergent, it is necessary to possess basic performances such as detergency and lathering property. However, in recent years, due to the trend toward more compactness and the increase in use of wares such as tupperware, 15 which are hard to clean, in the kitchen, detergents capable of removing oil when applied in a small amount have come into demand.

 As such detergents proposed in the past, many have 20 been liquid detergents containing large amounts of various surfactants to improve safety, availability, and cost and oil detergency in a small amount. However, when formulating ingredients for strengthening the detergent power, hard aggregates are easily formed in the system and turbidity is generated. Also, there has been the 25 problem of precipitation at low temperatures in the winter etc. Thus, a detergent composition superior in low temperature stability has been demanded.

Problem to be Solved by the Invention

30 The present invention was made to satisfy the above demands and provides a detergent composition having good storage stability and excellent detergent power.

Means for Solving the Problem

 The present inventors engaged in intensive studies 35 to solve the above problem and, as a result, found that by formulating a surfactant, a metal chelating agent having at least one carboxylic acid group, and at least

one ion selected from the group consisting of manganese, cobalt, nickel, copper, silver, zinc, and tin in the specified amounts and ratio, it was possible to obtain a transparent detergent composition having good low
5 temperature stability and further excellent power and lathering property, whereby the present invention was completed.

That is, in accordance with the present invention, there is provided a transparent liquid detergent
10 composition characterized by comprising the following components (a) to (c) and having a molar ratio of (b)/(c) of 1/100 or more:

- (a) 1 to 60% by weight of a surfactant,
- (b) a metal chelating agent having at least one
15 carboxylic acid group, and
- (c) 0.0001 to 1% by weight of at least one ion selected from the group consisting of manganese, cobalt, nickel, copper, silver, zinc, and tin.

Mode Carrying out the Invention

20 The liquid detergent composition according to the present invention is characterized by comprising the following components (a) to (c) and having a molar ratio of (b)/(c) of 1/100 or more:

- (a) 1 to 60% by weight of a surfactant,
- 25 (b) a metal chelating agent having at least one carboxylic acid group, and
- (c) 0.0001 to 1% by weight of at least one ion selected from the group consisting of manganese, cobalt, nickel, copper, silver, zinc, and tin.

30 As the surfactant usable as the component (a) of the first aspect of the present invention, known surfactants such as anionic surfactants, nonionic surfactants, and amphoteric surfactants may be used.

As anionic surfactants, for example, polyoxyethylene
35 alkyl sulfates, alkyl benzene sulfonates, alkyl sulfates, α -olefin sulfonates, alkyl ether carboxylates, alkane

sulfonates, α -sulfofatty acid salts, soaps, amide ether carboxylates, sulfosuccinates, amino acid-based anionic surfactants, etc. may be mentioned.

5 As nonionic surfactants, for example, fatty acid alkanol amides, alkyl amineoxides, polyoxyethylene alkyl ethers, sorbitan fatty acid esters, polyoxyethylene acyl esters, alkyl polyglycosides, fatty acid glycoside esters, fatty acid methyl glycoside esters, alkyl methyl glucamides, etc. may be mentioned.

10 Further, examples of amphoteric surfactants, for example, alkyl betaines, alkyl hydroxysulfobetaines, alkylamide betaines, imidazolinium betaines, N-alkyl amino acids, etc. may be mentioned.

15 The surfactants are not limited thereto. Further, it may be added alone or in combinations of two or more suitable types. As the amount of the surfactant formulated, 1% by weight or more, based on the total composition, must be formulated. Formulating 2% by weight or more is preferable. If less than 1% by weight, a
20 sufficient detergent power is not obtained, while if formulated in more than 60% by weight, the low temperature stability deteriorates.

The metal chelating agent having at least one carboxylic acid group usable as the component (b) of the
25 present invention is, for example, a hydroxycarboxylic acid such as glycolic acid, lactic acid, malic acid, citric acid, tartaric acid, gluconic acid, etc.; a polyhydric carboxylic acid such as oxalic acid, malonic acid, succinic acid, fumaric acid, etc.; an
30 aminocarboxylic acid such as ethylenediaminetetraacetic acid, nitrilotriacetic acid, hydroxyethyl ethylenediaminetriacetic acid, diethylenetriaminepentacetic acid, triethylenetetraminehexacetic acid, etc., but the present
35 invention is not limited thereto.

The at least one ion selected from the group consisting of manganese, cobalt, nickel, copper, silver,

zinc, and tin usable as the component (c) in the present invention is not particularly limited to the formulation method, but may be added in the form of the chloride, sulfate, hydroxide, phosphate, carbonate, nitrate, salt
5 of an organic substance, etc. thereof. Typically, manganese chloride, cobalt chloride, nickel chloride, copper chloride, silver chloride, zinc chloride, tin chloride, manganese sulfate, cobalt sulfate, copper sulfate, zinc sulfate, copper hydroxide, copper
10 phosphate, copper nitrate, zinc chloride, zinc hydroxide, zinc phosphate, zinc carbonate, zinc nitrate, toluene sulfonate, xylene sulfonate, cumene sulfonate, alkylbenzene sulfonate, etc. may be mentioned. Further, these compounds may be formulated irrespective of
15 anhydrides or hydrates. Further, it is also possible to form ions in the composition after formulating manganese, cobalt, nickel, copper, silver, zinc, or tin compounds by another method.

The total amount of the ions selected from the group
20 consisting of manganese, cobalt, nickel, copper, silver, zinc, and tin must be at least 0.0001% by weight of the total composition, preferably at least 0.001% by weight. If less than 0.0001% by weight, the detergent performance is decreased, while if formulated in an amount of more
25 than 1% by weight, excessive ions are present in the system and the phenomenon of precipitation etc. occur and the detergent power is decreased in this case as well.

Further, if the molar ratio of (b)/(c) is less than 1/100, excessive ions are present with respect to the
30 chelating agent, precipitation of the hydroxides etc. easily occurs, and the low temperature stability becomes poor. Therefore, the molar ratio of (b)/(c) has to be in the range of 1/100 or more, preferably is in the range of 2/100 or more.

35 The liquid detergent composition of the present invention may include other conventionally used additives in any combination within a range so long as the effect

of the present invention is not impaired.

5 The solvent of the liquid detergent composition of the present invention is preferably water and, further, another liquid solvent such as a lower alcohol or glycol may be included.

10 As other preferable components for the formulation, cationic surfactants such as alkyl amine hydrochlorides and quaternary ammonium salts; inorganic salts such as magnesium salts or calcium salts; hydrotropic agents such as aromatic sulfonates; viscosity adjusters; coloring agents; antioxidants; preservatives; bactericides; extinguishing agents; medicinal ingredients, fragrances, and other ordinarily used substances may be mentioned.

15 As the fragrance, a hydrocarbon such as an aliphatic hydrocarbon, terpene hydrocarbon, or aromatic hydrocarbon; an alcohol such as an aliphatic alcohol, terpene alcohol, and aromatic alcohol; an ether such as an aliphatic ether and aromatic ether; an oxide such as an aliphatic oxide or an oxide of a terpene; an aldehyde
20 such as an aliphatic aldehyde, terpene-based aldehyde, alicyclic aldehyde, thioaldehyde, and aromatic aldehyde; a ketone such as an aliphatic ketone, terpene ketone, alicyclic ketone, nonbenzene-based aromatic ketone, and aromatic ketone; an acetal; a ketal; a phenol; a phenol
25 ether; an acid such as a fatty acid, terpene-based carboxylic acid, alicyclic carboxylic acid, and aromatic carboxylic acid; an acid amide; a lactone such as an aliphatic lactone, a macrocyclic lactone, a terpene-based lactone, an alicyclic lactone, and an aromatic lactone;
30 an ester such as an aliphatic ester, a furan-based carboxylic acid ester, an alicyclic carboxylic acid ester, a cyclohexylcarboxylic acid ester, a terpene-based carboxylic acid ester, and an aromatic carboxylic acid ester; a nitrogen-containing compound such as a
35 nitromusk, a nitrile, an amine, a pyridine, a quinoline, pyrrole and indole; and other synthetic fragrances; natural fragrances from plants and animals; and composite

fragrances containing a natural fragrance and/or synthetic fragrance may be used alone or mixed in combinations of two or more types. For example, as the synthetic fragrances, the fragrances described in Gen-
5 ichi Indo, *Gosei Koryo Kagaku to Shohin Chishiki* (*Synthetic Fragrances: Chemical and Product Knowledge*), Kagaku Kogyo Nipposha, 1996; Steffen Arctander, *Perfume and Flavor Chemicals*, Montclair, N.J., 1969, etc. may be used. As the natural fragrances, the fragrances described
10 in *Kaori no Hyakka (Encyclopedia of Fragrances)*, Nippon Koryo Kyokai ed. may be used.

Specifically mentioning the names of the main fragrances, aldehydes C₆ - C₁₂, anisaldehyde, acetal R, acetophenone, acetylcedrene, adoxal, allylamyl glycolate,
15 allylcyclohexane propionate, α-damascone, β-damascone, δ-damascone, anbroxame, amyl cinnamic aldehyde, amyl cinnamic aldehyde dimethylacetal, amyl valerianate, amyl salicylate, isoamyl acetate, isoamyl salicylate, auranliol, acetyl eugenol, bacdanol, benzyl acetate,
20 benzyl alcohol, benzyl salicylate, bergamyl acetate, bornyl acetate, butyl butyrate, p-t-butylcyclohexanol, p-t-butylcyclohexyl acetate, o-t-butylcyclohexanol, o-t-butylcyclohexyl acetate, benzaldehyde, benzyl formate, caryophyllene, cashmeran, carvone, cedroamber, cedryl
25 acetate, cedrol, celestolide, cinnamic alcohol, cinnamic aldehyde, cis-jasmone, citral, citral dimethyl acetal, citrasal, citronellal, citronellol, citronelly acetate, citronellyl formate, citronellyl nitrile, cyclacet, cyclamen aldehyde, cyclaprop, calone, coumarin, cinnamyl
30 acetate, δ-C₆ to C₁₃ lactone, dimethylbenzyl carbinol, dihydrojasmone, dihydrolinalool, dihydro myrcenol, dimetol, dimyrcetol, diphenyl oxide, ethyl vanillin, eugenol, furuitate, phenthyl alcohol, phenylethyl phenylacetate, galaxolide, γ-C₆ to C₁₃ lactone, α-pinene,
35 β-pinene, limonene, myrcene, β-caryophyllene, geraniol, geranyl acetate, geranyl formate, geranyl nitrile,

hedion, helional, heliotropine, cis-3-hexenol, cis-3-hexenyl acetate, cis-3-hexenyl salicylate, hexyl cinnamic aldehyde, hexyl salicylate, hyacinth dimethyl acetal, hydratropic alcohol, hydroxycitronellal, indole, ionone, 5 isobornyl acetate, isocyclocitral, iso E super, isoeugenol, isononyl acetate, isobutyl quinoline, jasmal, jasmolactone, jasmopyran, koavone, ligstral, lilial, lime oxide, linalool, linalool oxide, linalyl acetate, lyral, manzanate, mayyol, menthanyl acetate, menthonate, methyl 10 anthranilate, methyl eugenol, menthol, α -methyl ionone, β -methyl ionone, γ -methyl ionone, methyl isoeugenol, methyl lavender ketone, methyl salicylate, muguet aldehyde, muguol, musk TM-II, musk 781, musk C₁₄, muscone, civetone, cyclopentadecanone, cyclohexadecenone, 15 cyclopentadecanolide, ambrettolide, cyclohexadecanolide, 10-oxahexadecanolide, 11-oxahexadecanolide, 12-oxahexadecanolide, ethylene brassylate, ethylene dodecanedioate, oxahexadecen-2-one, 14-methyl-hexadecenolide, 14-methyl-hexadecanolide, musk ketone, 20 musk tibetene, nopyl alcohol, nopyl acetate, neryl acetate, nerol, methyl phenyl acetate, myrac aldehyde, neobergamate, oakmoss No. 1, orivone, oxyphenylone, p-cresyl methyl ether, pentalide, phenylethyl alcohol, phenylethyl acetate, rhubafurane, damascenone, raspberry 25 ketone, dimethyl benzyl carbonyl acetate, jasmacyclene, methyl naphthyl ketone, rosephenone, rose oxide, sandalore, sandela, santalex, styrallyl acetate, styrallyl propionate, terpeneol, terpinyl acetate, tetrahydrolinalool, tetrahydrolinalyl acetate, tetrahydro 30 geraniol, tetrahydrogeranyl acetate, tonalid, traseolide, triplal, thymol, vanillin, verdox, yara-yara, anis oil, bay oil, bois de rose oil, cananga oil, cardamom oil, cassia oil, cedarwood oil, orange oil, mandarin oil, tangerine oil, basil oil, nutmeg oil, citronella oil, 35 clove oil, coriander oil, elemi oil, eucalyptus oil, fennel oil, galbanum oil, geranium oil, hiba oil, hinoki

oil, jasmin oil, lavandin oil, lavender oil, lemon oil,
lemongrass oil, lime oil, neroli oil, oak moss oil,
ocotea oil, patchouli oil, peppermint oil, perilla oil,
5 petitgrain oil, pine oil, rose oil, rosemary oil, camphor
oil, ho oil, clary sage oil, sandalwood oil, spearmint
oil, spike lavender oil, star anise oil, thyme oil, tonka
bean tincture, turpentine oil, vanilla bean tincture,
vetiver oil, ylang ylang oil, grapefruit oil, citron oil,
10 benzoin, peru balsam, tolu balsam, tuberose oil, musk
tincture, castroium tincture, civet tincture, ambergris
tincture, etc.

As the solvent or the retainer of the fragrance,
diethyl phthalate, dipropylene glycol, benzyl benzoate,
isopropyl myristate, harcholine, isopentane, orange
15 terpene, etc. may be used.

EXAMPLE

The present invention will now be explained in
further detail using the Examples and Comparative
Examples. Note that the present invention is not limited
20 to these Examples.

(Examples 1 to 9 and Comparative Examples 1 to 5)

The liquid detergent compositions having the
formulations shown in the following Tables 1 and 2 were
prepared and evaluated as to detergent power and low
25 temperature stability by the following test methods. The
results are shown in the same Tables. Note that the
amounts of formulation in the Tables are based upon % by
weight. The compositions were adjusted to pH 6.5.

(Evaluation of Detergent Power)

30 1 g of tallow was uniformly spread over a piece of
tupperware having 10 cm x 15 cm size in order to give an
extremely dirty hydrophobic surface grease. 38 g of water
and 2 g of the detergent composition were applied to a
dishwashing sponge of 11.5 cm x 7.5 cm x 3 cm size. This
35 was rubbed several times by the hand, then used to wash
the dirty tupperware at 25°C in the same way as done
normally in the home.

After washing, the tupperware was rinsed well with water and the detergent power was evaluated based on the following criteria by the feeling when touching the previously dirty surface of the tupperware.

5 Evaluation Criteria

O: Feeling of friction giving squeaking sound no matter what location of tupperware touched. No greasy feeling due to residual oil at all.

10 Δ: Feeling of friction when smooth surface of tupperware touched. No residual oil observed, but some greasy feeling remaining at end and corner locations.

x: Greasy feeling at tupperware as a whole. Oil is clearly remained.

(Evaluation of Low Temperature Stability)

15 The liquid detergent composition was packed in a 100 ml glass jar and stored for one day in a -20°C constant temperature chamber to freeze it, then was stored for one day in a 0°C constant temperature chamber to thaw it and restore it to normal. This cycle was repeated three
20 times. Next, the appearance at 0°C was judged according to the following evaluation criteria:

O: Uniform transparency

x: White turbidity or solids present

[Table 1]

[illegible]

[Table 2]

		Comparative Examples				
		1	2	3	4	5
Component a						
Sodium C ₁₂ POE alkyl ether sulfate ester (p=3)		15	15	10	5	
Sodium C ₁₄ alpha olefin sulfonate				5	10	15
C ₁₂ fatty acid diethanol amide		5	5	5	5	5
C ₁₂ alkylamine oxide		5	5	5	5	5
Component b						
Sodium citrate 2 hydrate			0.3			
Glycolic acid						
Sodium lactate				0.005		
Gluconic acid						1
Component c						
Cupric chloride 2 hydrate				0.9		10
Silver nitrate						
Stannic chloride 5 hydrate					0.3	
Zinc sulfate 7 hydrate						
Ethanol		5	5	5	5	5
Polyethylene glycol (M1000)		5	5	5	5	5
p-toluene sulfonic acid		5	5	5	5	5
Fragrance A		0.2	0.2	0.2	0.2	0.2
Fragrance B						
(c) Amount of ions (%)		0	0	0.4	0.1	4.9
(b)/(c) molar ratio		-	-	0.006	0	0.07
Detergent power of detergent composition		Δ	Δ	○	○	○
Low temperature stability of detergent composition		○	○	x	x	x

Note that the following compositions were used as the fragrances formulated (parts by weight)

	Fragrance A	Fragrance B
α-pinene	1.0	0.5
Orange oil, sweet	40.0	40.0
Orange oil, Valencia	12.0	10.0
Coriander oil	2.0	2.0

Citronella oil	2.0	2.0
Sweet fennel oil	1.0	2.0
Mandarin oil	5.0	5.0
Citron oil	1.0	2.0
Lime oil	12.0	13.0
Lemon grass oil	1.0	1.0
Lemon oil	20.0	20.0
Citral	2.0	1.5
Cis-3-hexenol 10% ethanol solution	1.0	1.0

As clear from Tables 1 and 2, Examples 1 to 9
falling within the scope of the present invention all had
a superior detergent performance and good low temperature
5 stability. As opposed thereto, Comparative Examples 1 to
5, which are outside the scope of the present invention,
were all inferior in performance.

CLAIMS

1. A transparent liquid detergent composition characterized by comprising the following components (a) to (c) and having a molar ratio of (b)/(c) of 1/100 or more:

5

(a) 1 to 60% by weight of a surfactant,

(b) a metal chelating agent having at least one carboxylic acid group, and

10

(c) 0.0001 to 1% by weight of at least one ion selected from the group consisting of manganese, cobalt, nickel, copper, silver, zinc, and tin.

