

## DESCRIPTION

Title of Invention: LIQUID DETERGENT COMPOSITION FOR HARD SURFACES

Field of the Invention

[0001]

The present invention relates to a liquid detergent composition for hard surfaces and a method for washing a hard surface.

Background of the Invention

[0002]

In residential environmental facilities surrounding people, there exist various hard surfaces made of materials such as tiles, plastics, and metals, and these hard surfaces are exposed to environments where various stains are adhered in living scenes. Among others, hard surfaces used in bathrooms, kitchens and others are surfaces that come in daily contact with humans; and thus, many stains are likely to remain and accumulate, and further, they have a property of being hard to remove by washing. In general, as a detergent for bathrooms used for bathtubs and bathrooms such as walls and floors of bathrooms, detergents containing a surfactant, a solvent and a sequestering agent are used for removing stains formed of metallic soaps, in particular, calcium salts of fatty acids.

[0003]

For example, JP-A 2015-113455 discloses a sterilizing detergent composition for hard surfaces, which contains: (a) 0.5% by mass or more and 3% by mass or less of a betaine amphoteric surfactant; (b) 0.5% by mass or more and 10% by mass or less of a specific aromatic alcohol; (c) 1% by mass or more and 8% by mass or less of a chelating agent; and (d) water, wherein a ratio of component (a) in the entire surfactants is 65% by mass or more and a pH at 25°C is 2 or higher and 6 or lower.

Further, JP-A 2003-183698 discloses a detergent composition for bathroom, which is characterized by containing at least a surfactant, a chelating agent, a polymer compound, a solvent and a perfume.

#### Summary of the Invention

[0004]

The present invention provides a liquid detergent composition for hard surfaces having high detergency against a stubborn stain generated by combination of soap scum and sebum.

In more detail, the present invention provides a liquid detergent composition for hard surfaces having high detergency against a stubborn stain caused by combination of soap scum and sebum and excellent composition stability.

[0005]

The present invention relates to a liquid detergent

composition for hard surfaces, which contains (a) 0.2% by mass or more and 10% by mass or less of a phosphonic acid-based chelating agent; (b) 0% by mass or more and 10% by mass or less of a chelating agent other than (a); (c) 1% by mass or more of a glycol-based solvent; (d) an amphoteric surfactant; and water,

wherein a mass ratio of anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b) chelating agent other than (a)] is 0.30 or less and a pH at 25°C is 5.8 or higher and 7.5 or lower.

[0006]

In addition, the present invention relates to a method for washing a hard surface, which includes: washing a hard surface with the liquid detergent composition for hard surfaces of the present invention and rinsing the washed hard surface with water.

Further, the present invention relates to a method for removing a calcium salt of a fatty acid on a hard surface, which includes: washing the hard surface with the liquid detergent composition for hard surfaces of the present invention; and rinsing the washed hard surface with water.

[0007]

Hereafter, (a) a phosphonic acid-based chelating agent, (b) a chelating agent other than (a), (c) a glycol-based solvent, and (d) an amphoteric surfactant are explained as components (a), (b), (c) and (d), respectively.

[0008]

According to the present invention, there is provided a liquid detergent composition for hard surfaces having high detergency against a stubborn stain generated by combination of soap scum and sebum.

In more detail, according to the present invention, there is provided a liquid detergent composition for hard surfaces, which has high detergency against a stubborn stain generated by combination of soap scum and sebum and excellent composition stability. The composition according to the present invention exhibits excellent stability in a wide range from a low temperature to a high temperature.

#### Embodiments of the Invention

[0009]

In the present invention, (a) a phosphonic acid-based chelating agent is combined with component (c) and component (d), if necessary, further component (b), and preferably further an organic solvent as component (e) described below, and use of the resultant product in a neutral region at a specific ratio enables more effective removal of a stubborn stain generated by combination of soap scum and sebum. It is speculated that this is because the detergent composition of the present invention having a pH in a neutral region is less likely to generate an acid-based fatty acid from sebum during washing, and as a result, generation or remaining of a

complex of soap scum and the acid-based fatty acid is prevented.

[Liquid detergent composition for hard surfaces]

[0010]

<Component (a)>

Component (a) is a phosphonic acid-based chelating agent.

Examples of the phosphonic acid-based chelating agent include phosphonic acids such as ethane-1,1-diphosphonic acid, ethane-1,1,2-triphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid, ethanehydroxy-1,1,2-triphosphonic acid, ethane-1,2-dicarboxy-1,2-diphosphonic acid, methanehydroxyphosphonic acid; and salts thereof.

Examples of the salts thereof include salts of an alkali metal such as sodium and potassium, ammonium salts and alkanol amine salts such as monoethanol amine and triethanol amine. Preferred are hydroxyphosphonic acids such as ethane-1-hydroxy-1,1-diphosphonic acid and salts thereof.

[0011]

The liquid detergent composition for hard surfaces of the present invention contains component (a) in an amount of, from the viewpoint of the detergency, 0.2% by mass or more, preferably 0.5% by mass or more, further preferably 0.8% by mass or more, and furthermore preferably 1% by mass or more; and from the viewpoint of the stability at high temperatures and the economic efficiency, 10% by mass or less, more preferably 8% by mass or less, further

preferably 6% by mass or less, furthermore preferably 4% by mass or less, and furthermore preferably 3% by mass or less. In the present invention, a value expressed in terms of acid is used as the amount of component (a).

[0012]

<Component (b)>

Component (b) is a chelating agent other than component (a).

As component (b), a carboxylic acid-based chelating agent (hereinafter, also referred to as component (b-1)) is preferred. Examples of the carboxylic acid-based chelating agent include chelating agents selected from hydroxycarboxylic acids and salts thereof, and aminocarboxylic acids and salts thereof.

[0013]

Examples of the hydroxycarboxylic acids and salts thereof include citric acid, lactic acid, tartaric acid, oxalic acid, malic acid, gluconic acid, diglycolic acid, oxydisuccinic acid, carboxymethyl succinic acid, carboxymethyl oxysuccinic acid, carboxymethyl tartaric acid, and salts thereof. Examples of the salts specifically include alkali metal salts or ammonium salts, and alkanolamine salts. Hydroxycarboxylic acids and salts thereof such as citric acid and malic acid are preferred; those having 1 or more carbons are more preferred; those having 3 or more carbons are further preferred; those having 10 or less carbons are preferred; and those having 8 or less carbons are further preferred.

[0014]

Examples of the aminocarboxylic acids and salts thereof include: aminocarboxylic acids such as nitrilotriacetic acid, iminodiacetic acid, ethylenediaminetetraacetic acid, hydroxyethylene diamine acetic acid, diethylene triamine pentaacetic acid, glycol ether diamine tetraacetic acid, hydroxyethyl iminodiacetic acid, triethylene tetramine hexaacetic acid, and Djenkolic acid; and salts thereof. Examples of the salts thereof specifically include alkali metal salts, ammonium salts, and alkanolamine salts.

[0015]

The liquid detergent composition for hard surfaces of the present invention contains component (b) in an amount of, from the viewpoint of the detergency, 0% by mass or more, preferably 0.2% by mass or more, more preferably 0.5% by mass or more, more preferably 1% by mass or more, more preferably 2% by mass or more, and further preferably 3% by mass or more; and from the viewpoint of the economic efficiency, 10% by mass or less, more preferably 8% by mass or less, further preferably 7% by mass or less, and furthermore preferably 6% by mass or less.

In addition, the liquid detergent composition for hard surfaces of the present invention contains component (b-1) in an amount of, from the viewpoint of detergency, preferably 0% by mass or more, more preferably 0.2% by mass or more, more preferably 0.5% by mass or more, more

preferably 1% by mass or more, more preferably 2% by mass or more, further preferably 3% by mass or more; and from the viewpoint of the economic efficiency, 10% by mass or less, more preferably 8% by mass or less, further preferably 7% by mass or less, and furthermore preferably 6% by mass or less.

[0016]

The ratio of component (b-1) in component (b) may be preferably 50% by mass or more, more preferably 70% by mass or more, further preferably 80% by mass or more, and furthermore preferably 90% by mass or more; and preferably 100% by mass or less, and substantially 100% by mass, and further 100% by mass.

[0017]

The liquid detergent composition for hard surfaces of the present invention contains component (a) and component (b), preferably contains component (a) and component (b-1), and thereby, it can provide high detergency while it is low in cost.

[0018]

When component (a) and component (b) are contained, a mass ratio of component (a)/component (b) is, from the viewpoint of the detergency, preferably 0.02 or more, more preferably 0.05 or more, further preferably 0.1 or more, and furthermore preferably 0.15 or more; and from the viewpoint of the high-temperature stability and the economic efficiency, preferably 10 or less, more preferably 8 or less, further preferably 5 or less,

furthermore preferably 3 or less, furthermore preferably 1 or less, furthermore preferably 0.5 or less, furthermore preferably less than 0.5, furthermore preferably 0.4 or less, and furthermore preferably 0.3 or less. This mass ratio is a mass ratio based on a content of component (a) and a content of component (b) in the liquid detergent composition for hard surfaces of the present invention.

When component (a) and component (b-1) are contained, a mass ratio of component (a)/component (b-1) is, from the viewpoint of the detergency, preferably 0.02 or more, more preferably 0.05 or more, further preferably 0.1 or more, and furthermore preferably 0.15 or more; and from the viewpoint of the high-temperature stability and the economic efficiency, preferably 10 or less, more preferably 8 or less, further preferably 5 or less, furthermore preferably 3 or less, furthermore preferably 1 or less, furthermore preferably 0.5 or less, furthermore preferably less than 0.5, furthermore preferably 0.4 or less, and furthermore preferably 0.3 or less. This mass ratio is a mass ratio based on a content of component (a) and a content of component (b-1) in the liquid detergent composition for hard surfaces of the present invention.

[0019]

In the present invention, a value expressed in terms of acid is used as the amount of component (b).

[0020]

<Component (c)>

A glycol-based solvent as component (c) is used from the viewpoint of enhancing the detergency. The term "glycol-based" means that a component belongs to any of a compound having two hydroxyl groups and an ether compound wherein a hydrogen atom of one or both of the hydroxyl groups is substituted by other group. The ether compound is preferably an aliphatic ether compound. In addition, preferred is an ether compound wherein one hydrogen atom of hydroxyl groups possessed by a glycol compound is substituted by other group.

[0021]

Component (c) is preferably a glycol-based water-soluble solvent having 2 to 12 carbons. The term "water-soluble" means that 50 g or more of the component is dissolved in 100 g of water at 20°C. Component (c) has an octanol/water distribution coefficient (LogP) of preferably 3.5 or less and more preferably 0.79 or less; and preferably -5 or more and more preferably -3 or more.

[0022]

Component (c) has a total carbon number of, from the viewpoint of the detergency, preferably 2 or more, more preferably 3 or more, more preferably 4 or more, further preferably 5 or more, and further preferably 6 or more; and from the viewpoint of the detergency, preferably 12 or less, preferably 10 or less, and more preferably 8 or less.

[0023]

From the viewpoint of the detergency, examples of component (c) include ethylene glycol (carbon number: 2), propylene glycol (carbon number: 3), diethylene glycol (carbon number: 4), propylene glycol monomethyl ether (carbon number: 4), isoprene glycol (carbon number: 5), propylene glycol monoethyl ether (carbon number: 5), 3-methyl-3-methoxy butanol (carbon number: 6), ethylene glycol monobutyl ether (carbon number: 6), dipropylene glycol (carbon number: 6), diethylene glycol monobutyl ether (carbon number: 8), dibutylene diglycol (carbon number: 8), and dipropylene glycol monobutyl ether (carbon number: 10).

[0024]

Component (c) is preferably: glycols having 2 or 3 carbons such as ethylene glycol, polyethylene glycol, propylene glycol and polypropylene glycol; polyethers thereof; or monoalkyl ethers thereof. As the alkyl group of these monoalkyl ethers, methyl groups, ethyl groups, various propyl groups and various butyl groups having 1 or more and 4 or less carbons are preferred. The term "various" covers normal, iso and tertiary ones.

[0025]

From the viewpoint of the detergency, component (c) is more preferably one or more selected from the group consisting of propylene glycol (carbon number: 3), ethylene glycol monobutyl ether (carbon number: 6), propylene glycol monobutyl ether (carbon number: 7), diethylene glycol monobutyl ether (carbon number: 8) and

dipropylene glycol monobutyl ether (carbon number: 10).

As component (c), diethylene glycol monobutyl ether (carbon number: 8) is preferably contained.

[0026]

The liquid detergent composition for hard surfaces of the present invention contains component (c) in an amount of, from the viewpoint of the detergency, preferably 1% by mass or more, more preferably 2% by mass or more, and further preferably 3% by mass or more; and preferably 10% by mass or less, more preferably 8% by mass or less, further preferably 6% by mass or less, and furthermore preferably 5% by mass or less.

Further, a mass ratio of component (c)/component (a) in the liquid detergent composition for hard surfaces of the present invention is, from the viewpoint of the detergency, preferably 0.1 or more, and more preferably 0.2 or more; and preferably 10 or less, and more preferably 5 or less. This mass ratio is a mass ratio based on a content of component (a) and a content of component (c) in the liquid detergent composition for hard surfaces of the present invention.

[0027]

<Component (d)>

Examples of component (d) include at least one amphoteric surfactant selected from amine oxides, sulfobetaines and carbobetaines. Component (d) is preferably a carbobetaine. The liquid detergent composition for hard surfaces of the present invention

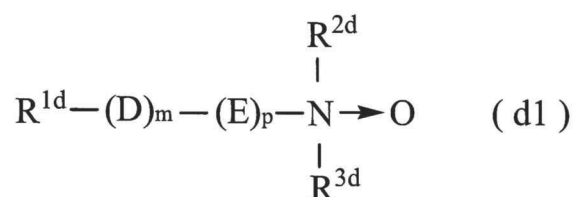
preferably contains a carbobetaine as component (d).

[0028]

As the amine oxides, a compound of the following general formula (d1) is suitable.

[0029]

[Chemical formula 1]



[0030]

In the formula,  $\text{R}^{1\text{d}}$  represents a hydrocarbon group having 8 or more to 22 or less carbons, preferably an alkyl or alkenyl group, more preferably an alkyl group; and  $\text{R}^{2\text{d}}$  and  $\text{R}^{3\text{d}}$  are the same or different and represent an alkyl group having 1 or more to 3 or less carbons. D represents  $-\text{NHC}(=\text{O})-$  group or  $-\text{C}(=\text{O})\text{NH}-$ group, and E represents an alkylene group having 1 or more to 5 or less carbons. m and p represent  $m=0$  and  $p=0$ , or  $m=1$  and  $p=1$ .

[0031]

In the above general formula (d1),  $\text{R}^{1\text{d}}$  is, from the viewpoint of the detergency to solid fat, preferably an alkyl group having 10 or more to 18 or less carbons, more preferably an alkyl group having 12 or more to 16 or less carbons, further preferably an alkyl group having 12 or more to 14 or less carbons, and an alkyl group having 12

carbons.  $R^{2d}$  and  $R^{3d}$  are each, from the viewpoint of the detergency, preferably a methyl group having one carbon.  
[0032]

Examples of the sulfobetaines include: N-alkyl-N,N-dimethyl-N-sulfopropyl ammonium sulfobetaine having an alkyl group with preferably 10 or more carbons, and preferably 18 or less carbons and more preferably 14 or less carbons; N-alkyl-N,N-dimethyl-N-(2-hydroxysulfopropyl)ammonium sulfobetaine having an alkyl group with preferably 10 or more carbons, and preferably 18 or less carbons and more preferably 14 or less carbons; N-alkanoyl amino propyl-N,N-dimethyl-N-sulfopropyl ammonium sulfobetaine having an alkanoyl group with preferably 10 or more carbons, and preferably 18 or less carbons and more preferably 14 or less carbons; and N-alkanoyl aminopropyl-N,N-dimethyl-N-(2-hydroxysulfopropyl)ammonium sulfobetaine having an alkanoyl group with preferably 10 or more carbons, and preferably 18 or less carbons and more preferably 14 or less carbons.

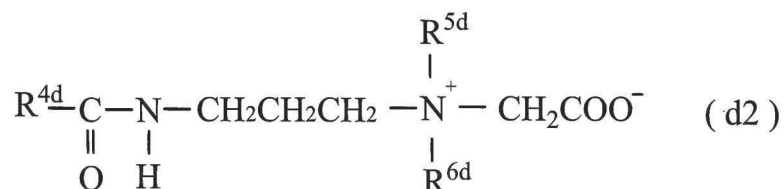
[0033]

Examples of the carbobetaines include: N-alkyl-N,N-dimethyl-N-carboxymethylammonium betaine having an alkyl group with preferably 10 or more carbons, and preferably 18 or less carbons and more preferably 14 or less carbons; and compounds represented by the following general formula (d2). From the viewpoint of the detergency, compounds represented by the following

general formula (d2) are preferred.

[0034]

[Chemical formula 2]



[0035]

In the formula,  $\text{R}^{4\text{d}}$  represents an alkyl or alkenyl group having 7 or more to 21 or less carbons, and  $\text{R}^{5\text{d}}$  and  $\text{R}^{6\text{d}}$  independently represent an alkyl group having 1 or more to 3 or less carbons.

[0036]

In the general formula (d2),  $\text{R}^{4\text{d}}$  is an alkyl or alkenyl group having preferably 9 or more carbons, and more preferably 11 or more carbons; and preferably 15 or less carbons, and more preferably 13 or less carbons; and a nonyl group, a decyl group, an undecyl group, a dodecyl group and a tridecyl group are preferred.

In the general formula (d2),  $\text{R}^{5\text{d}}$  and  $\text{R}^{6\text{d}}$  are independently and preferably a methyl group.

[0037]

The liquid detergent composition for hard surfaces of the present invention contains component (d) in an amount of, from the viewpoint of the detergency, preferably 0.3% by mass or more, more preferably 0.5% by mass or more, and further preferably 0.7% by mass or more; and

preferably 5% by mass or less, more preferably 3% by mass or less, and further preferably 2% by mass or less.

[0038]

<Composition, other components, etc.>

The present invention relates to a liquid detergent composition for hard surfaces, which contains 0.2% by mass or more and 10% by mass or less of component (a), 0% by mass or more and 10% by mass or less of component (b), 1% by mass or more of component (c), component (d) and water, and optionally an anionic surfactant, wherein a mass ratio of the content of the anionic surfactant/[total of the content of component (a) and the content of component (b)] is 0.30 or less and a pH at 25°C is 5.8 or higher and 7.5 or lower.

The liquid detergent composition for hard surfaces of the present invention may contain a surfactant other than component (d). For example, a surfactant such as an anionic surfactant and a nonionic surfactant may be used in such a range that effects of the present invention are not deteriorated.

The liquid detergent composition for hard surfaces of the present invention optionally contains an anionic surfactant. However, in the liquid detergent composition for hard surfaces of the present invention, a mass ratio of the anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b) chelating agent other than component (a)] is, from the viewpoint of the detergency, 0.30 or less, preferably 0.28 or less, more preferably

0.25 or less, further preferably 0.2 or less, furthermore preferably 0.15 or less, furthermore preferably 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.01 or less; and 0 or more and more preferably 0. This mass ratio is a mass ratio based on the content of component (a), the content of component (b) and the content of the anionic surfactant in the liquid detergency composition for hard surfaces of the present invention.

Preferably, a mass ratio of the anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b-1) carboxylic acid-based chelating agent] is, from the viewpoint of the detergency, preferably 0.30 or less, more preferably 0.28 or less, further preferably 0.25 or less, furthermore preferably 0.2 or less, furthermore preferably 0.15 or less, furthermore preferably 0.1 or less, furthermore preferably 0.05 or less, and furthermore preferably 0.01 or less; and preferably 0 or more, and more preferably 0. This mass ratio is a mass ratio based on the content of component (a), the content of component (b-1), and the content of the anionic surfactant in the liquid detergent composition for hard surfaces of the present invention.

That is, the liquid detergent composition for hard surfaces of the present invention may not contain the anionic surfactant. Limiting the content of the anionic surfactant in such a way allows component (c) and component (d) to achieve maximum effect of dissolving a

soap generated after component (a) and component (b) act on soap scum.

[0039]

The liquid detergent composition for hard surfaces of the present invention has a mass ratio of component (d)/[total of component (d) and a surfactant other than component (d)] of preferably 0.50 or more, more preferably 0.55 or more, further preferably 0.60 or more, furthermore preferably 0.65 or more, furthermore preferably 0.70 or more, furthermore preferably 0.75 or more, furthermore preferably 0.80 or more, furthermore preferably 0.85 or more, furthermore preferably 0.90 or more, and furthermore preferably 0.95 or more; and preferably 1 or less; and the mass ratio may be 1. This mass ratio is a mass ratio based on a content of component (d), and a content of the surfactant other than component (d) in the liquid detergent composition for hard surfaces of the present invention.

The liquid detergent composition for hard surfaces of the present invention has a mass ratio of component (d)/[total of component (d) and an anionic surfactant] of preferably 0.60 or more, more preferably 0.65 or more, further preferably 0.70 or more, furthermore preferably 0.75 or more, furthermore preferably 0.80 or more, furthermore preferably 0.85 or more, furthermore preferably 0.90 or more, and furthermore preferably 0.95 or more; and preferably 1 or less, and the mass ratio may be 1. This mass ratio is a mass ratio based on the

content of component (d) and the content of the anionic surfactant in the liquid detergent composition for hard surfaces of the present invention.

[0040]

Here, the anionic surfactant is one which is commonly used by those skilled in the art, and examples thereof include anionic surfactants having a hydrocarbon group having 7 or more to 22 or less carbons; and a sulfuric ester group, a phosphoric ester group, a phosphonic acid group, a sulfonic acid group or a carboxy group.

Specific examples include: alkyl benzene sulfonate, alkane sulfonate, alkyl sulfate ester salt, polyoxyethylene alkyl ether sulfate ester salt,  $\alpha$ -olefin sulfonate,  $\alpha$ -sulfo fatty acid methyl ester salt, polyoxyethylene alkyl (or alkenyl) ether carboxylate, polyoxyethylene amide alkyl (or alkenyl) ether carboxylate, fatty acid salts, alkyl phosphate ester salts, polyoxyethylene alkyl ether phosphate, etc.; and examples of the salts include: alkali metal salts such as sodium, potassium, inorganic salts such as ammonium salt and magnesium salt, and organic salts such as monoethanol ammonium, diethanol ammonium, and triethanol ammonium.

The composition contains an anionic surfactant in an amount of, from the viewpoint of the detergency, preferably 3% by mass or less, more preferably 2% by mass or less, further preferably 1% by mass or less, further preferably 0.5% by mass or less, and further preferably 0.1% by mass or less; and preferably 0% by mass or more;

or 0% by mass.

In the present invention, a value expressed in terms of acid is used as the amount of the anionic surfactant.

[0041]

The liquid detergent composition for hard surfaces of the present invention has a pH at 25°C of, from the viewpoint of the detergency, 5.8 or higher, preferably higher than 6, more preferably 6.1 or higher, further preferably 6.3 or higher, and furthermore preferably 6.5 or higher; and from the viewpoint of the detergency, 7.5 or lower, preferably 7.3 or lower, more preferably 7.0 or lower, and further preferably 6.8 or lower.

[0042]

The liquid detergent composition for hard surfaces of the present invention contains water in an amount of preferably 80% by mass or more, and more preferably 85% by mass or more; and preferably 95% by mass or less, and more preferably 93% by mass or less.

[0043]

The liquid detergent composition for hard surfaces of the present invention preferably has a viscosity at 25°C of 1 mPa·s or more and less than 6 mPa·s. This viscosity is measured as a value obtained by a B-type rotational viscometer with Rotor No. 1 at 60 rpm after 1 minute.

[0044]

The liquid detergent composition for hard surfaces of the present invention preferably contains an organic solvent [hereinafter, referred to as component (e)]

having a LogP of, from the viewpoint of the detergency, 0.80 or more and 1.80 or less. Component (c) is excluded from component (e).

Component (e) has a LogP of, from the viewpoint of the detergency, 0.80 or more, and preferably 0.90 or more; and 1.80 or less, preferably 1.50 or less, and more preferably 1.30 or less. In the present invention, as LogP of component (c) and component (e), used is a value (CLogP) calculated by use of ChemProp of Chem & BioDraw Ultra ver. 11.0.

Component (e) is preferably an aromatic alcohol.

Component (e) is preferably one or more selected from benzyl alcohol (CLogP = 1.08), 2-phenoxy ethanol (CLogP = 1.16), and 2-benzyloxy ethanol (CLogP = 1.2).

The liquid detergent composition for hard surfaces of the present invention contains component (e) in an amount of, from the viewpoint of the detergency, preferably 0.3% by mass or more, more preferably 0.5% by mass or more, and further preferably 1% by mass or more; and from the viewpoint of the high-temperature stability, preferably 10% by mass or less, more preferably 5% by mass or less, further preferably 3% by mass or less, furthermore preferably 2% by mass or less, and furthermore preferably 1.5% by mass or less.

[0045]

With the purpose of increasing an added value of a product, a perfume, a pigment, a preservative, an antioxidant or the like may be optionally formulated into

the liquid detergent composition for hard surfaces of the present invention.

[0046]

The liquid detergent composition for hard surfaces of the present invention is suitably used to wash hard surfaces of bathrooms, bathtubs, washbowls, tiles, powder rooms, washstands, mirrors, and sinks, counter tops and areas around water in kitchens. The composition is suitably used for bathrooms. Bathrooms mentioned herein are directed to not only bathrooms but also other articles having hard surfaces present in bathrooms such as bathtubs and washbowls.

[0047]

[Method for washing hard surfaces]

The present invention provides a method for washing a hard surface, which includes washing a hard surface with the liquid detergent composition for hard surfaces of the present invention, and rinsing the washed hard surface with water.

Further, the present invention provides a method for removing a calcium salt of a fatty acid on a hard surface, which includes washing a hard surface with the liquid detergent composition for hard surfaces of the present invention, and rinsing the washed hard surface with water. That is a method for removing a calcium salt of a fatty acid on a hard surface, which includes washing a hard surface, to which a stain containing a calcium salt of a fatty acid is adhered, with the liquid

detergent composition for hard surfaces, and rinsing the washed hard surface with water. The present invention is effective for removing a stain containing a calcium salt of a fatty acid such as soap scum or a complex stain of soap scum and sebum.

In the present invention, a hard surface may be washed after the liquid detergent composition for hard surfaces of the present invention is sprayed on the hard surface. Further, in the present invention, a hard surface may be washed by a cleaning article having a base carrying the liquid detergent composition for hard surfaces of the present invention thereon.

[0048]

As one example, there is provided a method for washing a hard surface, which includes applying the liquid detergent composition for hard surfaces of the present invention to a hard surface and then, cleaning by wiping. For the cleaning by wiping, a dishcloth, a dustcloth, a nonwoven fabric, or the like is used to remove, from the hard surface, the composition applied to the hard surface.

[0049]

In addition, the liquid detergent composition for hard surfaces of the present invention may be used as a cleaning article having a base impregnated with the composition. The cleaning article having a base impregnated with the liquid detergent composition for hard surfaces of the present invention is preferred from

the viewpoint of the workability of cleaning work.

[0050]

As the base impregnated with the liquid detergent composition for hard surfaces, which is used for a cleaning article, used is a base that has flexibility, can be impregnated with the liquid detergent composition for hard surfaces, has a sufficient strength during use, and has no generation of scraps. It is preferred to use a base that can be impregnated with the liquid detergent composition for hard surfaces in an amount described below under a no-load condition.

[0051]

Examples of such a base include a fibrous structure formed of a fibrous material, for example, various kinds of paper, nonwoven fabric, woven fabric, and knitted fabric. Examples of the fibrous material forming the fibrous structure include a cellulose fiber, a modified cellulose fiber, a synthesized fiber and a mixture of two or more thereof.

[0052]

Further, a porous structure obtained by dispersing air bubbles in a resin (for example, a sponge structure) may also be used as the base.

[0053]

In addition, the method for wiping and cleaning a hard surface using a cleaning article impregnated with the liquid detergent composition for hard surfaces of the present invention is preferred for light cleaning of a

hard surface from the viewpoint of the workability of cleaning work. The cleaning article impregnated with the liquid detergent composition for hard surfaces may be any of:

an article having a base, which is impregnated with the detergent composition in advance; and an article in which a dried base is impregnated with the liquid detergent composition for hard surfaces immediately before use by spraying or the like. Further, a target surface to be cleaned may be cleaned using a cleaning article, onto which the composition has been sprayed. The cleaning article impregnated with the liquid detergent composition for hard surfaces may be fitted to a mop-like cleaning tool, or may be used for wiping by holding the article with a hand.

[0054]

In the case where a base is impregnated with the liquid detergent composition for hard surfaces in advance, a ratio of impregnation of the liquid detergent composition for hard surfaces is, from the viewpoint of the cleaning properties, preferably 100% by mass or more, and more preferably 150% by mass or more; and preferably 1000% by mass or less, more preferably 400% by mass or less, and further preferably 350% by mass or less, relative to a mass of the base [that is, based on a mass of the base in a non-impregnated state (dry state)]. When the ratio of impregnation is 100% by mass or more, sufficient cleaning performances against spot stains or

dusts can be achieved. When the ratio of impregnation is 1000% by mass or less, an appropriate amount of the liquid detergent composition for hard surfaces is released to a surface to be cleaned to prevent stains or dust from remaining on the surface; and the composition may be used without being affected by the cleaning surface made of various material such as wood-based materials. In terms of further enhancing the cleaning properties, when the base is a sheet, a basis weight before impregnation with the liquid detergent composition for hard surfaces is, from the viewpoint of the retentivity of the liquid detergent composition for hard surfaces required to wash a certain size of area and the usability or cost of the sheet, preferably 40 g/m<sup>2</sup> or more, and more preferably 50 g/m<sup>2</sup> or more; and 200 g/m<sup>2</sup> or less, and more preferably 150 g/m<sup>2</sup> or less.

[0055]

During use of a cleaning article impregnated with the liquid detergent composition for hard surfaces, the liquid detergent composition for hard surfaces of the present invention may be separately used for spraying to an object to be cleaned or the cleaning article. This usage method allows a larger size of area to be cleaned.

[0056]

<Embodiments of the present invention>

Hereafter, embodiments of the present invention are exemplified. The matters mentioned for the liquid detergent composition for hard surfaces, the washing

method and the removing method of the present invention are appropriately applied to these embodiments.

<1>

A liquid detergent composition for hard surfaces containing (a) 0.2% by mass or more and 10% by mass or less of a phosphonic acid-based chelating agent [hereafter, referred to as component (a)], (b) 0% by mass or more and 10% by mass or less of a chelating agent other than component (a) [hereafter, referred to as component (b)], (c) 1% by mass or more of a glycol-based solvent [hereafter, referred to as component (c)], (d) an amphoteric surfactant [hereafter, referred to as component (d)], and water, wherein a mass ratio of anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b) chelating agent other than component (a)] is 0.30 or less and a pH at 25°C is 5.8 or higher and 7.5 or lower.

[0057]

<2>

The liquid detergent composition for hard surfaces according to the above <1>, wherein component (a) is a phosphonic acid selected from ethane-1,1-diphosphonic acid, ethane-1,1,2-triphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid, ethanehydroxy-1,1,2-triphosphonic acid, ethane-1,2-dicarboxy-1,2-diphosphonic acid, methanehydroxyphosphonic acid, and salts thereof; or a salt thereof.

[0058]

<3>

The liquid detergent composition for hard surfaces according to the above <1> or <2>, wherein the composition contains component (a) in an amount of 0.2% by mass or more, preferably 0.5% by mass or more, further preferably 0.8% by mass or more, and furthermore preferably 1% by mass or more; and 10% by mass or less, more preferably 8% by mass or less, further preferably 6% by mass or less, furthermore preferably 4% by mass or less, and furthermore preferably 3% by mass or less.

[0059]

<4>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <3>, wherein component (b) includes (b-1) a carboxylic acid-based chelating agent [hereinafter, referred to as component (b-1)].

[0060]

<5>

The liquid detergent composition for hard surfaces according to the above <4>, wherein component (b-1) is a chelating agent selected from hydroxycarboxylic acids and salts thereof, and aminocarboxylic acids and salts thereof.

[0061]

<6>

The liquid detergent composition for hard surfaces according to the above <5>, wherein the hydroxycarboxylic

acids and the salts thereof are compounds selected from citric acid, lactic acid, tartaric acid, oxalic acid, malic acid, gluconic acid, diglycolic acid, oxydisuccinic acid, carboxymethyl succinic acid, carboxymethyl oxysuccinic acid, carboxymethyl tartaric acid, and salts thereof.

[0062]

<7>

The liquid detergent composition for hard surfaces according to any one of the above <4> to <6>, wherein a mass ratio of component (a)/component (b-1) is 0.02 or more and 10 or less.

[0063]

<8>

The liquid detergent composition for hard surfaces according to any one of the above <4> to <7>, wherein the composition contains component (b-1) in an amount of 0% by mass or more, preferably 0.2% by mass or more, more preferably 0.5% by mass or more, more preferably 1% by mass or more, more preferably 2% by mass or more, and further preferably 3% by mass or more; and preferably 10% by mass or less, more preferably 8% by mass or less, further preferably 7% by mass or less, and furthermore preferably 6% by mass or less.

[0064]

<9>

The liquid detergent composition for hard surfaces according to any one of the above <4> to <8>, wherein a

ratio of component (b-1) in component (b) is preferably 50% by mass or more, more preferably 70% by mass or more, further preferably 80% by mass or more, and furthermore preferably 90% by mass or more; and preferably 100% by mass or less, substantially 100% by mass, and further 100% by mass.

[0065]

<10>

The liquid detergent composition for hard surfaces according to any one of the above <4> to <9>, wherein a mass ratio of component (a)/component (b-1) is preferably 0.02 or more, more preferably 0.05 or more, further preferably 0.1 or more, and furthermore preferably 0.15 or more; and preferably 10 or less, more preferably 8 or less, further preferably 5 or less, furthermore preferably 3 or less, furthermore preferably 1 or less, furthermore preferably 0.5 or less, furthermore preferably less than 0.5, furthermore preferably 0.4 or less, and furthermore preferably 0.3 or less.

[0066]

<11>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <10>, wherein the composition contains component (b) in an amount of 0% by mass or more, preferably 0.2% by mass or more, more preferably 0.5% by mass or more, more preferably 1% by mass or more, more preferably 2% by mass or more, and further preferably 3% by mass or more; and 10% by mass or

less, more preferably 8% by mass or less, further preferably 7% by mass or less, and furthermore preferably 6% by mass or less.

[0067]

<12>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <11>, wherein a mass ratio of component (a)/component (b) is preferably 0.02 or more, more preferably 0.05 or more, further preferably 0.1 or more, and furthermore preferably 0.15 or more; and preferably 10 or less, more preferably 8 or less, further preferably 5 or less, furthermore preferably 3 or less, furthermore preferably 1 or less, furthermore preferably 0.5 or less, furthermore preferably less than 0.5, furthermore preferably 0.4 or less, and furthermore preferably 0.3 or less.

[0068]

<13>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <12>, wherein component (c) is a glycol-based water-soluble solvent having 2 or more to 12 or less carbons.

[0069]

<14>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <13>, wherein component (c) has an octanol/water distribution coefficient (LogP) of preferably 3.5 or less and more

preferably 0.79 or less; and preferably -5 or more and more preferably -3 or more.

[0070]

<15>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <14>, wherein component (c) is at least one glycol-based solvent selected from the group consisting of propylene glycol, ethylene glycol monobutyl ether, propylene glycol monobutyl ether, diethylene glycol monobutyl ether, and dipropylene glycol monobutyl ether.

[0071]

<16>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <15>, wherein the composition contains component (c) in an amount of preferably 1% by mass or more, more preferably 2% by mass or more, and further preferably 3% by mass or more; and preferably 10% by mass or less, more preferably 8% by mass or less, further preferably 6% by mass or less, and furthermore preferably 5% by mass or less.

[0072]

<17>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <16>, wherein component (d) is at least one amphoteric surfactant selected from amine oxides, sulfobetaines and carbobetaines.

[0073]

<18>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <17>, wherein the composition contains component (d) in an amount of preferably 0.3% by mass or more, more preferably 0.5% by mass or more, and further preferably 0.7% by mass or more; and preferably 5% by mass or less, more preferably 3% by mass or less, and further preferably 2% by mass or less.

[0074]

<19>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <18>, wherein a mass ratio of the anionic surfactant/[total of component (a) and component (b)] is 0.30 or less, preferably 0.28 or less, more preferably 0.25 or less, further preferably 0.2 or less, furthermore preferably 0.15 or less, furthermore preferably 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.01 or less; and 0 or more and more preferably 0.

[0075]

<20>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <19> dependent from the above <4>, wherein a mass ratio of the anionic surfactant/[total of component (a) and component (b-1)] is preferably 0.30 or less, more preferably 0.28 or less,

further preferably 0.25 or less, furthermore preferably 0.2 or less, furthermore preferably 0.15 or less, furthermore preferably 0.1 or less, furthermore preferably 0.05 or less, and furthermore preferably 0.01 or less; and preferably 0 or more, and more preferably 0.

[0076]

<21>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <20>, wherein a content of the anionic surfactant is preferably 3% by mass or less, more preferably 2% by mass or less, further preferably 1% by mass or less, further preferably 0.5% by mass or less, and further preferably 0.1% by mass or less; and preferably 0% by mass or more, or 0% by mass.

[0077]

<22>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <21>, further containing (e) an organic solvent having a LogP of 0.80 or more and 1.80 or less [hereinafter, referred to as component (e)].

[0078]

<23>

The liquid detergent composition for hard surfaces according to the above <22>, wherein the LogP of component (e) is 0.80 or more, and preferably 0.90 or more; and 1.80 or less, preferably 1.50 or less and more preferably 1.30 or less.

[0079]

<24>

The liquid detergent composition for hard surfaces according to the above <22> or <23>, wherein component (e) is an aromatic alcohol, further at least one aromatic alcohol selected from benzyl alcohol (CLogP = 1.08), 2-phenoxy ethanol (CLogP = 1.16), and 2-benzyloxy ethanol (CLogP = 1.2).

[0080]

<25>

The liquid detergent composition for hard surfaces according to any one of the above <22> to <24>, wherein the composition contains component (e) in an amount of preferably 0.3% by mass or more, more preferably 0.5% by mass or more, and further preferably 1% by mass or more; and preferably 10% by mass or less, more preferably 5% by mass or less, further preferably 3% by mass or less, furthermore preferably 2% by mass or less, and further preferably 1.5% by mass or less.

[0081]

<26>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <25>, wherein the pH is 5.8 or higher, preferably higher than 6, more preferably 6.1 or higher, further preferably 6.3 or higher, and furthermore preferably 6.5 or higher; and 7.5 or lower, preferably 7.3 or lower, more preferably 7.0 or lower, and further preferably 6.8 or lower.

[0082]

<27>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <26>, wherein the composition is for a bathroom.

[0083]

<28>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <27>, wherein a mass ratio of component (d)/[total of component (d) and a surfactant other than component (d)] is preferably 0.50 or more, more preferably 0.55 or more, further preferably 0.60 or more, furthermore preferably 0.65 or more, furthermore preferably 0.70 or more, furthermore preferably 0.75 or more, furthermore preferably 0.80 or more, furthermore preferably 0.85 or more, furthermore preferably 0.90 or more, and furthermore preferably 0.95 or more; and preferably 1 or less, or 1.

[0084]

<29>

The liquid detergent composition for hard surfaces according to any one of the above <1> to <28>, wherein a mass ratio of component (d)/[total of component (d) and the anionic surfactant] is preferably 0.60 or more, more preferably 0.65 or more, further preferably 0.70 or more, furthermore preferably 0.75 or more, furthermore preferably 0.80 or more, furthermore preferably 0.85 or more, furthermore preferably 0.90 or more, and

furthermore preferably 0.95 or more; and preferably 1 or less, or 1.

[0085]

<30>

A method for washing a hard surface including: washing a hard surface with the liquid detergent composition for hard surfaces according to any one of the above <1> to <29>; and rinsing the washed hard surface with water.

[0086]

<31>

A method for removing a calcium salt of a fatty acid on a hard surface including: washing a hard surface with the liquid detergent composition for hard surfaces according to any one of the above <1> to <29>; and rinsing the washed hard surface with water.

[0087]

<32>

Use of a composition containing (a) 0.2% by mass or more and 10% by mass or less of a phosphonic acid-based chelating agent, (b) 0% by mass or more and 10% by mass or less of a chelating agent other than component (a), (c) 1% by mass or more of a glycol-based solvent, (d) an amphoteric surfactant, and water, as a liquid detergent for hard surfaces, wherein a mass ratio of anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b) chelating agent other than component (a)] is 0.30 or less and a pH at 25°C is 5.8 or higher and 7.5

or lower.

The matters mentioned for the liquid detergent composition for hard surfaces of the present invention are appropriately applied to the composition for this use.

#### Examples

[0088]

Liquid detergent compositions for hard surfaces shown in Tables 1 and 2 were prepared, and evaluated in terms of the following items. Results are shown in Tables 1 and 2. Note that pH values of the compositions were adjusted by use of sodium hydroxide in an amount shown in the tables, and if necessary, hydrochloric acid (not shown in the tables). The compositions of Examples had a viscosity of less than 6 mPa·s.

[0089]

#### <Detergency>

Evaluation was made on the detergency against a model bathroom stain in which soap scum and sebum were combined. A method for preparing the model stain is shown below. 90% by mass of a bar soap (KAO White) and 10% by mass of a model sebum stain were mixed at 50 to 60°C, and the resultant solution kept warm was provided as Solution A. The model sebum stain was composed of 40% by mass of linoleic acid, 20% by mass of oleic acid, 20% by mass of palmitic acid, 10% by mass of cholesterol and 10% by mass of liquid paraffin. 6% by mass calcium

chloride aqueous solution kept at a temperature of 20 to 30°C was provided as Solution B. Solution A was applied on a polypropylene plate (50 mm × 100 mm × 2 mm) as uniformly as possible and subjected to air-drying at 20 to 30°C for 5 minutes; and then, Solution B was applied as uniformly as possible and subjected to air-drying at 20 to 30°C for 5 minutes. This procedure including application of Solution A, air-drying, application of Solution B and air-drying in this order was repeated 10 times; and thereafter, drying was conducted at room temperature for 1 month, thereby preparing the model bathroom stain.

[0090]

A cotton puff (manufactured by Marusan Industry Co., Ltd.) cut into a size of 1.5 cm × 1.5 cm was placed on a model bathroom stain; 600 µL of each of liquid detergent compositions for hard surfaces of Tables 1 and 2 was dropped thereon and allowed to stand for 3 minutes; and thereafter, sufficient rinsing was carried out with ion exchanged water. The detergency was determined based on the following standard. As a specific method, used is a method, which includes: capturing images of a plate before stain application, the plate after stain application and before washing, and the plate after washing in a state having the same image-capturing conditions such as brightness; and measuring a gray scale of each plate from the captured image. The washing ratio of the plate before stain washing was taken as 0% while

the washing ratio of the plate before stain application was taken as 100%. Then, the washing ratio of each washed plate was calculated. For the measurement of gray scale, an image processing software ImageJ 1.47v was used.

[0091]

<Appearance of composition>

Appearances of the composition at high- and low-temperatures were evaluated in accordance with the following standard.

30 g of each of the liquid detergent compositions shown in Tables 1 and 2 was charged into a PS-No. 6 standard glass bottle, and allowed to stand for 20 days at -5°C or 50°C; follow-up observation was conducted on appearance changes of each composition; and visual evaluation was conducted. Evaluation standards are as follows.

A: no appearance change

B: semitransparency or partial turbidity occurred

C: separation occurred

[0092]

[0093]

|                                                |                              |                                             |                                           | Example |         |         |         |         |         |         |         |         |         |         |         |         |
|------------------------------------------------|------------------------------|---------------------------------------------|-------------------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|                                                |                              |                                             |                                           | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       | 10      | 11      | 12      |         |
| Liquid detergent composition for hard surfaces | Formulated component (mass%) | (a)                                         | Phosphonic acid-based chelating agent (1) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 3       |         |         |
|                                                |                              | (b)                                         | Carboxylic acid-based chelating agent (1) | 5       | 5       | 5       | 5       | -       | 5       | 5       | 5       | 5       | 3       | 7       | 3       |         |
|                                                |                              |                                             | Carboxylic acid-based chelating agent (2) | -       | -       | -       | -       | 3.7 (5) | -       | -       | -       | -       | -       | -       | -       |         |
|                                                |                              | (c)                                         | Diethylene glycol monobutyl ether         | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     | 3.5     |         |
|                                                |                              | (d)                                         | Amphoteric surfactant (1)                 | 1.3     | 1.3     | 1.3     | 1.3     | 1.3     | 1.3     | 1.3     | 1.3     | -       | 1.3     | 1.3     | 1.3     |         |
|                                                |                              |                                             | Amphoteric surfactant (2)                 | -       | -       | -       | -       | -       | -       | -       | -       | 1.3     | -       | -       | -       |         |
|                                                |                              | Anionic surfactant (1)                      |                                           |         | -       | -       | -       | -       | -       | -       | -       | -       | -       | -       | -       |         |
|                                                |                              | Nonionic surfactant (1)                     |                                           |         | -       | -       | -       | -       | -       | -       | -       | -       | -       | -       | -       |         |
|                                                |                              | (e)                                         | Benzyl alcohol                            | 1       | 2       | -       | -       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |         |
|                                                |                              |                                             | 2-phenoxyethanol                          | -       | -       | 1       | 2       | -       | -       | -       | -       | -       | -       | -       | -       |         |
|                                                |                              | NaOH                                        |                                           |         | 3.152   | 3.216   | 3.184   | 3.072   | -       | 3.056   | 3.344   | 3.392   | 3.152   | 2.08    | 4.288   | 3.056   |
|                                                |                              | Water                                       |                                           |         | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance |
|                                                |                              | Total                                       |                                           |         | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100     |
|                                                |                              | (a)+(b) (% by mass)                         |                                           |         | 6       | 6       | 6       | 6       | 4.7     | 6       | 6       | 6       | 6       | 4       | 8       | 6       |
|                                                |                              | (a)/(b) (mass ratio)                        |                                           |         | 0.2     | 0.2     | 0.2     | 0.2     | 0.27    | 0.2     | 0.2     | 0.2     | 0.2     | 0.33    | 0.14    | 1       |
|                                                |                              | Anionic surfactant/[ (a)+(b) ] (mass ratio) |                                           |         | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0       |
|                                                | pH (25°C)                    |                                             |                                           | 6.5     | 6.5     | 6.5     | 6.5     | 6.5     | 6.0     | 7.0     | 7.2     | 6.5     | 6.5     | 6.5     | 6.5     |         |
| Washing ratio (%)                              |                              |                                             | 95                                        | 98      | 90      | 95      | 90      | 95      | 95      | 90      | 95      | 90      | 95      | 92      |         |         |
| Appearance                                     |                              | 50°C                                        | A                                         | B       | A       | B       | A       | A       | A       | A       | A       | A       | A       | A       |         |         |
|                                                |                              | -5°C                                        | A                                         | A       | A       | A       | A       | A       | A       | A       | A       | A       | A       | A       |         |         |

[Table 1]

[Table 2]

|                                                |                              |                                             |                                           | Example |         |         |         | Comparative Example |         |            |         |         |         |          |         |    |
|------------------------------------------------|------------------------------|---------------------------------------------|-------------------------------------------|---------|---------|---------|---------|---------------------|---------|------------|---------|---------|---------|----------|---------|----|
|                                                |                              |                                             |                                           | 13      | 14      | 15      | 16      | 1                   | 2       | 3          | 4       | 5       | 6       | 7        | 8       |    |
| Liquid detergent composition for hard surfaces | Formulated component (mass%) | (a)                                         | Phosphonic acid-based chelating agent (1) | 5       | 6       | 10      | 1       | 1                   | 1       | 1          | 1       | -       | 1       | 6        |         |    |
|                                                |                              | (b)                                         | Carboxylic acid-based chelating agent (1) | 1       | -       | 1       | 5       | 5                   | 5       | 5          | 5       | 5       | 6       | 5        | -       |    |
|                                                |                              |                                             | Carboxylic acid-based chelating agent (2) | -       | -       | -       | -       | -                   | -       | -          | -       | -       | -       | -        | -       |    |
|                                                |                              | (c)                                         | Diethylene glycol monobutyl ether         | 3.5     | 3.5     | 3.5     | 3.5     | 3.5                 | 3.5     | 3.5        | 3.5     | -       | 3.5     | 3.5      | 3.5     |    |
|                                                |                              | (d)                                         | Amphoteric surfactant (1)                 | 1.3     | 1.3     | 1.3     | 1.3     | 1.3                 | 1.3     | -          | -       | 1.3     | 1.3     | 1.3      | 1.3     |    |
|                                                |                              |                                             | Amphoteric surfactant (2)                 | -       | -       | -       | -       | -                   | -       | -          | -       | -       | -       | -        | -       |    |
|                                                |                              | Anionic surfactant (1)                      |                                           | -       | -       | -       | -       | -                   | -       | 1.22 (1.3) | -       | -       | -       | 1.87 (2) | -       |    |
|                                                |                              | Nonionic surfactant (1)                     |                                           | -       | -       | -       | -       | -                   | -       | -          | 1.3     | -       | -       | -        | -       |    |
|                                                |                              | (e)                                         | Benzyl alcohol                            | 1       | 1       | 1       | -       | 1                   | 1       | 1          | 1       | 1       | -       | 1        | 1       |    |
|                                                |                              |                                             | 2-phenoxy ethanol                         | -       | -       | -       | -       | -                   | -       | -          | -       | -       | -       | -        | -       |    |
|                                                |                              | NaOH                                        |                                           | 2.944   | 2.816   | 1.872   | 3.184   | 3.136               | 3.424   | 3.2        | 3.2     | 3.264   | 3.28    | 3.232    | 2.4     |    |
|                                                |                              | Water                                       |                                           | Balance | Balance | Balance | Balance | Balance             | Balance | Balance    | Balance | Balance | Balance | Balance  | Balance |    |
|                                                |                              | Total                                       |                                           | 100     | 100     | 100     | 100     | 100                 | 100     | 100        | 100     | 100     | 100     | 100      | 100     |    |
|                                                |                              | (a)+(b) (mass%)                             |                                           | 6       | 6       | 11      | 6       | 6                   | 6       | 6          | 6       | 6       | 6       | 6        | 6       |    |
|                                                |                              | (a)/(b) (mass ratio)                        |                                           | 5       | -       | 10      | 0.2     | 0.2                 | 0.2     | 0.2        | 0.2     | 0.2     | 0       | 0.2      | -       |    |
|                                                |                              | Anionic surfactant/[ (a)+(b) ] (mass ratio) |                                           | 0       | 0       | 0       | 0       | 0                   | 0       | 0.20       | 0       | 0       | 0       | 0.31     | 0       |    |
|                                                |                              | pH (25°C)                                   |                                           | 6.5     | 6.5     | 6.5     | 6.5     | 5.5                 | 7.8     | 6.5        | 6.5     | 6.5     | 6.5     | 6.5      | 5.5     |    |
|                                                | Washing ratio (%)            |                                             |                                           |         | 95      | 95      | 99      | 80                  | 70      | 65         | 60      | 65      | 65      | 65       | 55      | 60 |
|                                                | Appearance                   |                                             |                                           | 50°C    |         | A       | A       | B                   | A       | A          | A       | C       | A       | A        | C       | A  |
|                                                |                              |                                             |                                           | -5°C    |         | A       | A       | A                   | A       | A          | A       | C       | C       | A        | A       | C  |

[0094]

In the tables, (a)+(b) is a total of contents of components (a) and (b) . Further, (a)/(b) is a mass ratio of [content of component (a)/content of component (b)] .

In addition, anionic surfactant/[ (a)+(b) ] is a mass ratio of anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b) chelating agent other than (a)] (The same applies hereinafter).

[0095]

Components in the tables are as follows. Note that each component is expressed with % by mass in the tables based on the amount in terms of the active ingredients.

Component (a)

Phosphonic acid-based chelating agent (1): Italmatch Japan Ltd., Dequest 2010CS, 60% 1-hydroxyethylidene-1,1-diphosphonic acid aqueous solution

[0096]

Component (b)

Carboxylic acid-based chelating agent (1): Wako Pure Chemical Industries, Ltd., citric acid, Wako Special Grade

Component (b-1)

Carboxylic acid-based chelating agent (2): Akzo Nobel K.K., Dissolvine GL-PD-S, tetrasodium L-glutamate diacetate (GLDA), component (b-1), in the tables, the percent by mass expressed in terms of acid is shown, and the percent by mass based on the apparent formulation amount is shown in parentheses.

[0097]

Component (c)

Diethylene glycol monobutyl ether: glycol-based solvent, Nippon Nyukazai Co., Ltd., BDG (butyl diglycol), LogP =

0.6

[0098]

Component (d)

Amphoteric surfactant (1): amide propyl betaine laurate, a compound in which, in the general formula (d2),  $R^{4d}$  is an alkyl group having 11 carbons and  $R^{5d}$  and  $R^{6d}$  are a methyl group

Amphoteric surfactant (2): lauryl dimethyl amine oxide, a compound in which, in the general formula (d1),  $R^{1d}$  is an alkyl group having 12 carbons,  $R^{2d}$  and  $R^{3d}$  are a methyl group, and  $m = 0$  and  $p = 0$

[0099]

(Other surfactant)

Anionic surfactant (1): linear alkyl (12 carbons) sodium benzenesulfonate, in the tables, the percent by mass expressed in terms of acid is shown and the percent by mass based on the apparent formulation amount is shown in parentheses.

Nonionic surfactant (1): polyoxyethylene alkyl ether (alkyl group with 12 carbons, average number of moles of ethylene oxide added: 8)

[0100]

Component (e)

Benzyl alcohol: Wako Pure Chemical Industries, Ltd., benzyl alcohol, Wako Special Grade,  $\text{LogP} = 1.08$

2-phenoxy ethanol: Wako Pure Chemical Industries, Ltd.,

2-phenoxy ethanol,  $\text{LogP} = 1.16$

[0101]

From results of Example 14 and Comparative Example 6 in the table, it is found that when being formulated in a liquid detergent composition for hard surfaces having a pH of 5.8 or higher at 25°C, the phosphonic acid-based chelating agent as component (a) exhibits higher detergency than citric acid, which is a chelating agent other than component (a).

In addition, from results of Example 14 and Comparative Example 8 in the tables, it is found that the phosphonic acid-based chelating agent as component (a) exhibits higher detergency in a liquid detergent composition having a pH of 5.8 or higher at 25°C.

Further, from results of Examples 1, 12, 13 and 14 in the tables, it is found that even combined use of components (a) and (b) can maintain high detergency.

Furthermore, from comparison between Example 1 and Comparative Examples 3, 4 and 7 in the tables, it is found that in order for component (a) to provide excellent stability while maintaining higher detergency, it is necessary to use component (d) as a surfactant or to provide a mass ratio of anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b) chelating agent other than (a)] of 0.30 or less.

[0102]

<Formulation examples>

Table 3 shows formulation examples of the liquid detergent composition for hard surfaces of the present invention. All of compositions of the formulation

examples had a viscosity of less than 6 mPa.s.

[0103]

[Table 3]

|                                                |                              |                        |                                               | Formulation example |         |         |         |         |         |         |         |         |         |       |
|------------------------------------------------|------------------------------|------------------------|-----------------------------------------------|---------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|-------|
|                                                |                              |                        |                                               | 1                   | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       | 10      |       |
| Liquid detergent composition for hard surfaces | Formulated component (mass%) | (a)                    | Phosphonic acid-based chelating agent (1)     | 1                   | 1       | 1       | 1       |         | 1       | 1       | 1       | 0.5     | 0.5     |       |
|                                                |                              |                        | Phosphonic acid-based chelating agent (2)     |                     |         |         |         | 1       |         |         |         |         |         |       |
|                                                |                              | (b)                    | Carboxylic acid-based chelating agent (1)     | 5                   | 5       | 5       | 5       | 5       | 5       | 5       | 5       | 5.5     | 9.5     |       |
|                                                |                              | (c)                    | Diethylene glycol monobutyl ether             | 3.5                 | 3.5     |         |         | 3.5     | 3.5     | 10      | 1       | 3.5     | 3.5     |       |
|                                                |                              |                        | Propylene glycol                              |                     |         | 3.5     |         |         |         |         |         |         |         |       |
|                                                |                              |                        | Ethylene glycol monobutyl ether               |                     |         |         | 3.5     |         |         |         |         |         |         |       |
|                                                |                              | (d)                    | Amphoteric surfactant (1)                     | 5                   | 5       | 1.3     | 1.3     | 1.3     | 0.5     | 1.3     | 1.3     | 1.3     | 1.3     |       |
|                                                |                              | Anionic surfactant (1) | 0.937<br>(1)                                  | 1.40<br>(1.5)       | -       | -       | -       | -       | -       | -       | -       | -       |         |       |
|                                                |                              | (e)                    | Benzyl alcohol                                | 1                   | 1       | -       | -       | 1       | 1       | 1       | 1       | -       | -       |       |
|                                                |                              | NaOH                   | Amount for adjusting pH of composition to 6.5 |                     |         |         |         |         |         |         |         |         |         |       |
|                                                |                              | Water                  | Balance                                       | Balance             | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance |       |
|                                                |                              | Total                  |                                               |                     | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100     | 100   |
|                                                |                              | (a)+(b) (mass%)        |                                               |                     | 6       | 6       | 6       | 6       | 6       | 6       | 6       | 6       | 6       | 10    |
|                                                |                              | (a)/(b) (mass ratio)   |                                               |                     | 0.2     | 0.2     | 0.2     | 0.2     | 0.2     | 0.2     | 0.2     | 0.2     | 0.091   | 0.053 |
| Anionic surfactant/ [(a)+(b)] (mass ratio)     |                              |                        | 0.17                                          | 0.23                | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0       |         |       |
| pH (25°C)                                      |                              |                        | 6.5                                           | 6.5                 | 6.5     | 6.5     | 6.5     | 6.5     | 6.5     | 6.5     | 6.5     | 6.5     |         |       |

[0104]

In the tables, phosphonic acid-based chelating agent (2), propylene glycol and ethylene glycol monobutyl ether are shown below while components other than these are the same as in Tables 1 and 2. Note that each component is indicated by the percent by mass in the tables based on the amount in the terms of the active ingredients.

Phosphonic acid-based chelating agent (2): ethylene diamine tetra(methylene phosphonic acid), Italmatch Japan Ltd., model number Dequest 2040

Propylene glycol: glycol-based solvent, Asahi Glass Co., Ltd., LogP = -0.47

Ethylene glycol monobutyl ether: glycol-based solvent, Tokyo Chemical Industry Co., Ltd., LogP = 0.83

## CLAIMS

[Claim 1] A liquid detergent composition for hard surfaces comprising: (a) 0.2% by mass or more and 10% by mass or less of a phosphonic acid-based chelating agent; (b) 0% by mass or more and 10% by mass or less of a chelating agent other than (a); (c) 1% by mass or more of a glycol-based solvent; (d) an amphoteric surfactant; (e) an organic solvent having a LogP of 0.80 or more and 1.80 or less, provided that (c) is excluded from (e); and water,

wherein a mass ratio of anionic surfactant/[total of (a) phosphonic acid-based chelating agent and (b) chelating agent other than (a)] is 0.30 or less and a pH at 25°C is 5.8 or higher and 7.5 or lower.

[Claim 2] The liquid detergent composition for hard surfaces according to Claim 1, wherein the pH is higher than 6.

[Claim 3] The liquid detergent composition for hard surfaces according to Claim 1 or Claim 2, wherein (b) the chelating agent other than (a) includes (b-1) a carboxylic acid-based chelating agent.

[Claim 4] The liquid detergent composition for hard surfaces according to Claim 3, wherein a mass ratio of (a) phosphonic acid-based chelating agent/(b-1) carboxylic acid-based chelating agent is 0.02 or more and 10 or less.

[Claim 5] The liquid detergent composition for hard surfaces according to any one of Claims 1 to 4, wherein the composition is for a bathroom.

[Claim 6] A method for washing a hard surface comprising:  
washing a hard surface with the liquid detergent composition for hard surfaces according to any one of Claims 1 to 5; and  
rinsing the washed hard surface with water.

[Claim 7] A method for removing a calcium salt of a fatty acid on a hard surface, comprising:  
washing a hard surface with the liquid detergent composition for hard surfaces according to any one of Claims 1 to 5; and  
rinsing the washed hard surface with water.