

DESCRIPTION

Title of the 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 removing water scale on hard surfaces.

Background of the Invention

[0002]

In the living environment equipment that surrounds us, various hard surfaces made of tile, plastic, metal, and the like are present and these hard surfaces are exposed to an environment where various kinds of stains adhere to the hard surfaces in the daily life. In particular, the hard surfaces used for bathrooms, kitchens and the like are surfaces that people come into contact with on a daily basis, and therefore tend to have a lot of stains remaining and accumulating which are difficult to be cleaned and removed. In general, as bathroom detergents used in bathrooms for bathtubs, bathroom walls and floors, detergents containing surfactants, solvents, sequestering agents and the like

are used to remove stains of metal soaps, especially fatty acid calcium salts.

[0003]

For example, JP-A 2015-113455 discloses a disinfecting detergent composition for hard surfaces containing (a) 0.5 mass% or more and 3 mass% or less of a betaine type amphoteric surfactant, (b) 0.5 mass% or more and 10 mass% or less of a specific aromatic alcohol, (c) 1 mass% or more and 8 mass% or less of a chelating agent, and (d) water, wherein the ratio of component (a) in the whole surfactant is 65 mass% or more, and having a pH at 25°C of 2 or more and 6 or less. Moreover, JP-A 2003-183698 discloses a bathroom detergent composition containing at least a surfactant, a chelating agent, a polymer compound, a solvent and perfume.

Summary of the Invention

[0004]

In JP-A 2015-113455 and JP-A 2003-183698, the object was to remove fatty acid calcium salts, but it is considered not yet sufficient for water scale. In the present invention, water scale refers to a stain wherein a scaly pattern is deposited by the polymerization and accumulation of silicic acid contained in water on a hard surface.

[0005]

The present invention relates to a liquid detergent composition for hard surfaces that is excellent in detergency against water scale adhered to a hard surface (hereinafter also simply referred to as "detergency"), and a method for removing water scale using the same.

[0006]

The present invention relates to a liquid detergent composition for hard surfaces, containing:

(a) 0.2 mass% or more and 10 mass% or less of one or more chelating agents selected from phosphonic acid-based chelating agents and phosphoric acid-based chelating agents (hereinafter referred to as component (a)), (b) 0 mass% or more and 10 mass% or less of a chelating agent other than component (a) (hereinafter referred to as component (b)), (c) a surfactant (hereinafter referred to as component (c)) and water,

wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less and is used for cleaning where the composition is brought into contact with a hard surface and left for 1 minute or more.

[0007]

In addition, the present invention relates to a liquid detergent composition for hard surfaces, containing:

0.2 mass% or more and 10 mass% or less of component (a),
0.2 mass% or more and 10 mass% or less of (b) (b-1) a carboxylic acid-based chelating agent (provided that

component (a) is excluded) (hereinafter referred to as component (b-1)), component (c) and water, wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less.

[0008]

Moreover, the present invention relates to a method for removing water scale, including bringing a liquid detergent composition for hard surfaces into contact with a hard surface and leaving the composition for 1 minute or more, the liquid detergent composition containing 0.2 mass% or more and 10 mass% or less of component (a), 0 mass% or more and 10 mass% or less of component (b), component (c) and water, wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less.

[0009]

According to the present invention, a liquid detergent composition for hard surfaces that is excellent in detergency against water scale adhered to a hard surface and a method for removing water scale using the same, can be provided.

Brief Description of Drawings

[0010]

[Figure 1] Figure 1 is a photograph of the surface of a stainless steel faucet with water scale adhered thereto before cleaning.

[Figure 2] Figure 2 is a photograph of the surface of the faucet of Figure 1 after cleaning with the liquid detergent composition for hard surfaces of Example 2.

Embodiments of the Invention

[0011]

<Liquid detergent composition for hard surfaces>

The present inventor has found that the cause of water scale is that silicic acid contained in tap water is polymerized and that the polymer is accumulated on hard surfaces in a scaly manner. In addition, the present inventor has found that, to remove this water scale, a liquid detergent composition for hard surfaces with a specific viscosity region, using component (a) of the present invention and combined with component (c) and, as necessary, component (b), is effective for removing water scale by bringing the liquid detergent composition into contact with a hard surface. Such an effect is assumed to be because, although not necessarily exactly known, the liquid detergent composition for hard surfaces of the present invention can separate and remove sequentially silicic acid molecules from the vicinity of the surface of the silicic acid polymer that is causing water scale.

[0012]

<Component (a)>

Component (a) of the present invention is one or more chelating agents selected from phosphonic acid-based chelating agents and phosphoric acid-based chelating agents.

[0013]

Examples of the phosphonic acid-based chelating agents include one or more selected from 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, aminopoly(methylenephosphonic acid), polyethylenepolyaminepoly(methylenephosphonic acid) and salts thereof. Examples of the salts include alkali metal salts such as sodium and potassium, ammonium salts, and alkanolamine salts such as monoethanolamine and triethanolamine.

[0014]

Examples of the phosphoric acid-based chelating agents include one or more selected from orthophosphoric acid, pyrophosphoric acid, tripolyphosphoric acid, tetrapolyphosphoric acid, hexametaphosphoric acid, and salts thereof.

[0015]

From the viewpoint of detergency, component (a) is preferably a phosphonic acid-based chelating agent, more preferably one or more selected from hydroxyphosphonic

acids such as ethane-1-hydroxy-1,1-diphosphonic acid, ethanehydroxy-1,1,2-triphosphonic acid and methanehydroxyphosphonic acid, aminopoly(methylenephosphonic acid), and salts thereof, further preferably one or more selected from hydroxyphosphonic acid and salts thereof, and further preferably ethane-1-hydroxy-1,1-diphosphonic acid or a salt thereof.

[0016]

The liquid detergent composition for hard surfaces of the present invention contains component (a), from the viewpoint of detergency, in an amount of 0.2 mass% or more, preferably 0.3 mass% or more, more preferably 0.4 mass% or more, further preferably 0.5 mass% or more, furthermore preferably 1 mass% or more, furthermore preferably 1.5 mass% or more, and from the viewpoint of economic efficiency, in an amount of 10 mass% or less, preferably 8 mass% or less, more preferably 6 mass% or less, further preferably 4 mass% or less, furthermore preferably 3 mass% or less. In the present invention, the value expressed in terms of acid is used as the content of component (a).

[0017]

<Component (b)>

Component (b) of the present invention is a chelating agent other than component (a). Examples of component (b) preferably include carboxylic acid-based

chelating agents (provided that component (a) is excluded) (hereinafter also referred to as component (b-1)). Examples of the carboxylic acid-based chelating agents more preferably include one or more chelating agents selected from hydroxycarboxylic acids and salts thereof, and aminocarboxylic acids and salts thereof.

[0018]

Examples of the hydroxycarboxylic acids and salts thereof include one or more selected from citric acid, lactic acid, tartaric acid, oxalic acid, malic acid, gluconic acid, diglycolic acid, oxydisuccinic acid, carboxymethylsuccinic acid, carboxymethyloxysuccinic acid, carboxymethyltartaric acid, and salts thereof. Specifically, the salts include alkali metal salts, ammonium salts, and alkanolamine salts.

[0019]

From the viewpoint of detergency, the hydroxycarboxylic acids and salts thereof are preferably one or more selected from hydroxycarboxylic acids and salts thereof having 1 or more, preferably 3 or more carbons, and 10 or less, preferably 8 or less carbons, and more preferably one or more selected from citric acid, malic acid and salts thereof.

[0020]

Examples of the aminocarboxylic acids and salts thereof include one or more selected from nitrilotriacetic acid, iminodiacetic acid,

ethylenediaminetetraacetic acid,
hydroxyethylenediamineacetic acid,
diethylenetriaminepentaacetic acid, glycol-
etherdiaminetetraacetic acid, hydroxyethyliminodiacetic
acid, triethylenetetraminehexaacetic acid, djenkolic acid
and salts thereof. Examples of the salts specifically
include alkali metal salts, ammonium salts, and
alkanolamine salts.

[0021]

From the viewpoint of detergency, component (b-1) is
preferably one or more selected from hydroxycarboxylic
acids having 3 or more and 8 or less carbons and salts
thereof, more preferably one or more selected from citric
acid, malic acid, and salts thereof, and further
preferably citric acid or a salt thereof.

[0022]

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

invention, the value expressed in terms of acid is used as the content of component (b).

[0023]

Moreover, the liquid detergent composition for hard surfaces of the present invention contains component (b-1), from the viewpoint of detergency, in an amount of 0 mass% or more, preferably 0.2 mass% or more, more preferably 0.5 mass% or more, further preferably 1 mass% or more, furthermore preferably 2 mass% or more, furthermore preferably 3 mass% or more, and from the viewpoint of economic efficiency, in an amount of 10 mass% or less, preferably 8 mass% or less, more preferably 7 mass% or less and further preferably 6 mass% or less. In the present invention, the value expressed in terms of acid is used as the content of component (b-1).

[0024]

In the liquid detergent composition for hard surfaces of the present invention, from the viewpoint of detergency, the proportion of component (b-1) in component (b) is preferably 50 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, furthermore preferably 90 mass% or more, and preferably 100 mass% or less, and may be substantially 100 mass%, furthermore 100% by mass.

[0025]

By containing component (a) and component (b), preferably by containing component (a) and component (b-1), the liquid detergent composition for hard surfaces of the present invention is low cost and excellent in economic efficiency, while also allowing to obtain high detergent properties.

[0026]

When component (a) and component (b) are contained in the liquid detergent composition for hard surfaces of the present invention, the mass ratio of the content of component (a) to the content of component (b), $(a)/(b)$ is, from the viewpoint of detergency, preferably 0.02 or more, more preferably 0.05 or more, further preferably 0.1 or more, furthermore preferably 0.15 or more, furthermore preferably 0.2 or more, and from the viewpoint of 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 0.8 or less, furthermore preferably 0.6 or less, and furthermore preferably 0.5 or less.

[0027]

When component (a) and component (b-1) are contained in the liquid detergent composition for hard surfaces of the present invention, the mass ratio of the content of component (a) to the content of component (b-1), $(a)/(b-1)$ is, from the viewpoint of detergency, preferably 0.02

or more, more preferably 0.05 or more, further preferably 0.1 or more, furthermore preferably 0.15 or more, furthermore preferably 0.2 or more, and from the viewpoint of 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 0.8 or less, furthermore preferably 0.6 or less and furthermore preferably 0.5 or less.

[0028]

<Component (c)>

Component (c) of the present invention is a surfactant.

From the viewpoint of detergency, component (c) is preferably one or more selected from amphoteric surfactants and nonionic surfactants, and more preferably one or more selected from amphoteric surfactants.

[0029]

Examples of the amphoteric surfactants include one or more amphoteric surfactants selected from carbobetaines, sulfobetaines, and amine oxides.

It is preferable that the liquid detergent composition for hard surfaces of the present invention contain 1 or more selected from carbobetaines as component (c).

[0030]

tridecyl group is preferable. In general formula (c1), R^{2c} and R^{3c} are preferably methyl groups.

[0034]

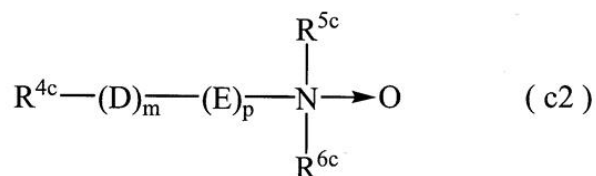
Examples of the sulfobetaines include N-alkyl-N,N-dimethyl-N-sulfopropylammonium sulfobetaine or N-alkenyl-N,N-dimethyl-N-sulfopropylammonium sulfobetaine wherein the alkyl group or alkenyl group has preferably 10 or more carbons, and preferably 18 or less, more preferably 14 or less carbons, N-alkyl-N,N-dimethyl-N-(2-hydroxysulfopropyl) ammonium sulfobetaine or N-alkenyl-N,N-dimethyl-N-(2-hydroxysulfopropyl) ammonium sulfobetaine wherein the alkyl group or alkenyl group has preferably 10 or more carbons, and preferably 18 or less, more preferably 14 or less carbons, N-alkanoylaminoethyl-N,N-dimethyl-N-sulfopropylammonium sulfobetaine wherein the alkanoyl group has preferably 10 or more carbons, and preferably 18 or less, more preferably 14 or less carbons, and N-alkanoylaminoethyl-N,N-dimethyl-N-(2-hydroxysulfopropyl) ammonium sulfobetaine wherein the alkanoyl group has preferably 10 or more carbons, and preferably 18 or less, more preferably 14 or less carbons.

[0035]

As the amine oxide, a compound of the following general formula (c2) is suitable.

[0036]

[Formula 2]



[0037]

In the formula, R^{4c} represents a hydrocarbon group having 8 or more and 22 or less carbons, preferably an alkyl group or an alkenyl group, more preferably an alkyl group, and R^{5c} and R^{6c} are the same or different and represent an alkyl group having 1 or more and 3 or less carbons. D represents an $-\text{NHC}(=\text{O})$ -group or a $-\text{C}(=\text{O})\text{NH}-$ group, and E represents an alkylene group having 1 or more and 5 or less carbons. m and p represent $m = 0$ and $p = 0$ or $m = 1$ and $p = 1$.][0038]

In the above general formula (c2), from the viewpoint of detergency, R^{4c} is preferably an alkyl group having 10 or more and 18 or less carbons, more preferably an alkyl group having 12 or more and 16 or less carbons, further preferably an alkyl group having 12 or more and 14 or less carbons, and furthermore preferably an alkyl group having 12 carbons. From the viewpoint of detergency, R^{5c} and R^{6c} are each preferably a methyl group having 1 carbon.

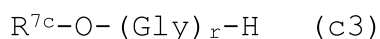
[0039]

Examples of the nonionic surfactants preferably include one or more selected from the group consisting of alkyl monoglyceryl ethers, polyoxyalkylene monoalkyl or

alkenyl ethers, alkyl polyglycosides (glycoside type nonionic surfactants), sorbitan nonionic surfactants, aliphatic alkanolamides, fatty acid monoglycerides and sucrose fatty acid esters, and two or more of these may be used.

[0040]

As the alkyl monoglyceryl ether, a compound represented by the following general formula (c3) is suitable.



In the formula, R^{7c} represents a hydrocarbon group having 6 or more and 18 or less carbons, Gly represents a structural unit derived from glycerin, and preferably represents a residue obtained by removing one hydroxyl group and one hydrogen atom from glycerin, and r represents a number of 1 or more and 4 or less.

[0041]

In general formula (c3), from the viewpoint of detergency, R^{7c} is a hydrocarbon group having preferably 6 or more carbons, more preferably 7 or more, further preferably 8 or more carbons, and preferably 18 or less carbons, more preferably 12 or less and further preferably 10 or less carbons.

[0042]

In general formula (c3), r is preferably 1 or more and preferably 2 or less. r is more preferably a compound of 1. The structure represented by Gly is a

structure represented by $\text{-CH}_2\text{CH(OH)CH}_2\text{-}$ in which the hydroxyl groups at position 1 and position 3 of glycerin are bonded, or a structure represented by $\text{-CH(CH}_2\text{OH)CH}_2\text{-}$ in which the hydroxyl groups at position 1 and position 2 of glycerin are bonded, and this varies depending on the catalyst and reaction conditions.

[0043]

In order to obtain the compound of general formula (c3), for example, a method of producing by using an alkyl alcohol represented by $\text{R}^{7c}\text{-OH}$ as an alcohol having 6 to 10 carbons, and reacting with an epoxy compound such as epihalohydrin or glycidol, using an acid catalyst such as BF_3 or an aluminum catalyst, can be used. For example, when 2-ethylhexanol is used, the obtained 2-ethylhexyl monoglyceryl ether is a mixture that can contain a plurality of products as described in JP-A 2001-49291.

[0044]

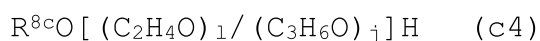
In the polyoxyalkylene monoalkyl or alkenyl ether, the alkyl group or alkenyl group has, from the viewpoint of detergency, preferably 6 or more, more preferably 8 or more, further preferably 10 or more, furthermore preferably 12 or more carbons, and from the same viewpoint, preferably 22 or less, more preferably 18 or less, further preferably 16 or less and furthermore preferably 14 or less carbons.

[0045]

In the polyoxyalkylene monoalkyl or alkenyl ether, the average number of added moles of alkylene oxide is, from the viewpoint of detergency, preferably more than 0, more preferably 1 or more, further preferably 3 or more, and from the same viewpoint, preferably 50 or less, more preferably 30 or less, further preferably 20 or less, and furthermore preferably 10 or less. From the viewpoint of detergency, the alkylene oxide is preferably one or more selected from ethylene oxide, propylene oxide and butylene oxide, more preferably one or more selected from ethylene oxide and propylene oxide, and further preferably ethylene oxide.

[0046]

Preferable examples of the polyoxyalkylene monoalkyl or alkenyl ether include nonionic surfactants represented by the following general formula (c4).



In the formula, R^{8c} represents a hydrocarbon group having 6 or more and 22 or less carbons. l and j represent the average number of added moles, l represents a number that is 0 or more and 30 or less and j represents a number that is 0 or more and 30 or less, and l and j are not 0 at the same time. "/" indicates that the oxyethylene group and the oxypropylene group may be added either randomly or in a block regardless of the order.

[0047]

In the above general formula (c4), from the viewpoint of detergency, R^{8c} has preferably 8 or more, preferably 10 or more, further preferably 12 or more carbons, and from the same viewpoint, preferably 18 or less, more preferably 16 or less and further preferably 14 or less carbons. From the viewpoint of detergency, R^{8c} is preferably an alkyl group or an alkenyl group, more preferably an alkyl group. Specifically, as the alkyl group, exemplified are various octyl groups (including 2-ethylhexyl group), various nonyl groups, various decyl groups, various undecyl groups, various dodecyl groups (lauryl group), various tridecyl groups, various tetradecyl groups, various pentadecyl groups, various hexadecyl groups, various heptadecyl groups, and various octadecyl groups. As the alkenyl group, exemplified are various octanyl groups, various nonanyl groups, various decanyl groups, various undecanyl groups, various dodecanyl groups, various tridecanyl groups, various tetradecanyl groups, various pentadecanyl groups, various hexadecanyl groups, various heptadecanyl groups, and various octadecanyl groups (for example, oleyl groups and linole groups). "Various" means various isomers including n-, sec-, tert-, and iso-.

[0048]

From the viewpoint of storage stability, the total of l and j in the above general formula (c4) is preferably 1 or more, more preferably 2 or more, and from

the same viewpoint, preferably 20 or less, more preferably 10 or less and further preferably 8 or less.

[0049]

From the viewpoint of detergency, the HLB value of the polyoxyalkylene monoalkyl or alkenyl ether, which is component (c4), and further, the nonionic surfactant represented by the general formula (c4) is preferably 5 or more, more preferably 7 or more, and from the same viewpoint, preferably 19 or less, more preferably 15 or less, and further preferably 13 or less.

[0050]

Here, the HLB value is defined by the Griffin's equation shown below.

$$\text{HLB value} = 20 \times \text{Mw}/\text{M}$$

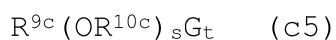
In the formula, M is the molecular weight of the nonionic surfactant, and Mw is the molecular weight of the hydrophilic portion of the nonionic surfactant.

[0051]

In general formula (c4), the hydrophilic portion is the total portion of oxyethylene group and oxypropylene group.

[0052]

As the alkylpolyglycoside (glycoside type nonionic surfactant), a nonionic surfactant represented by the following general formula (c5) is preferable.



In the formula, R^{9c} represents a linear or branched

alkyl group, alkenyl group or alkylphenyl group, preferably an alkyl group, having 8 or more and 18 or less carbons, preferably 12 or more and 14 or less carbons, R^{10c} represents an alkylene group having 2 or more and 4 or less carbons, and G represents a residue derived from a reducing sugar having 5 or 6 carbons. s represents the average number of added moles and is a number of 0 or more and 5 or less. t represents a number whose average value is 1 or more and 5 or less.

[0053]

In general formula (c5), from the viewpoint of detergency, R^{9c} is a linear or branched alkyl group having 8 or more, preferably 10 or more carbons, and 18 or less, preferably 14 or less carbons. From the viewpoint of storage stability, s in general formula (c5) is preferably 0 or more, 2 or less, and more preferably 0. From the viewpoint of storage stability, t is preferably 1.1 or more, and preferably 1.5 or less, more preferably 1.4 or less. Here, t is a value measured by the proton NMR method. In general formula (c5), from the viewpoint of their availability and cost, examples of G include residues derived from one or more monosaccharides selected from glucose and fructose. In addition, examples of G include residues derived from one or more polysaccharides selected from maltose and sucrose. G is preferably a residue derived from a monosaccharide of glucose.

[0054]

The sorbitan nonionic surfactant, aliphatic alkanolamide, fatty acid monoglyceride, and sucrose fatty acid ester preferably have linear or branched alkyl groups with preferably 8 or more and 18 or less carbons, more preferably 12 or more and 14 or less carbons.

[0055]

From the viewpoints of detergency and rinsability, component (c) is preferably one or more selected from carbobetaine and polyoxyalkylene monoalkyl or alkenyl ether, more preferably one or more selected from the compounds represented by general formula (c1) and the compounds represented by general formula (c4), and further preferably a compound represented by general formula (c1).

[0056]

The liquid detergent composition for hard surfaces of the present invention contains a surfactant, component (c), from the viewpoint of detergency, in an amount of preferably 0.05 mass% or more, more preferably 0.1 mass% or more, further preferably 0.2 mass% or more, and from the viewpoint of rinsability, in an amount of preferably 2 mass% or less, more preferably 1.5 mass% or less, further preferably 1 mass% or less and furthermore preferably 0.5 mass% or less.

[0057]

Moreover, the liquid detergent composition for hard surfaces of the present invention may contain an anionic surfactant as component (c) from the viewpoint of improving the foaming property, but from the viewpoint of rinsability, it is preferable that the content be limited.
[0058]

Here, the anionic surfactant is one usually used by those skilled in the art, and for example, exemplified are anionic surfactants having a hydrocarbon group with 7 or more and 22 or less carbons, and a sulfate ester group, a phosphate ester group, a phosphonic acid group, a sulfonic acid group, or a carboxy group. Specifically, examples includes alkylbenzene sulfonates, alkane sulfonates, alkyl sulfates, polyoxyethylene alkyl ether sulfates, α -olefin sulfonates, α -sulfonated fatty acid methyl ester salts, polyoxyethylene alkyl (or alkenyl) ether carboxylates, polyoxyethylene amide alkyl (or alkenyl) ether carboxylates, fatty acid salts, alkyl phosphates, polyoxyethylene alkyl ether phosphate and the like, and examples of the salts include alkali metal salt such as sodium and potassium, inorganic salts such as ammonium salts and magnesium salts, and organic salts such as monoethanolammonium, diethanolammonium and triethanolammonium.
[0059]

In the liquid detergent composition for hard surfaces of the present invention, the mass ratio of the

content of an anionic surfactant to the content of all chelating agents including component (a) and component (b), (anionic surfactant)/chelating agent) is, from the viewpoint of rinsability, 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 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.02 or less, and preferably 0 or more, and may be 0.

[0060]

In the liquid detergent composition for hard surfaces of the present invention, the mass ratio of the content of an anionic surfactant to the total content of component (a) and component (b), [(anionic surfactant)/((a) + (b))] is, from the viewpoint of rinsability, 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 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.01 or less, and preferably 0 or more, and may be 0.

[0061]

In the liquid detergent composition for hard surfaces of the present invention, the mass ratio of the content of an anionic surfactant to the total content of component (a) and component (b-1), [(anionic surfactant)/((a) + (b-1))] is, from the viewpoint of

rinsability, 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 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.01 or less, and preferably 0 or more, and may be 0. In the present invention, a value expressed in terms of acid is used as the content of the anionic surfactant.

[0062]

<Component (d)>

It is preferable that the liquid detergent composition for hard surfaces of the present invention contain a thickener as component (d). The thickener, component (d) is used from a viewpoint of adjusting the viscosity of the composition described later and improving the detergency.

[0063]

Examples of component (d) includes smectite clay minerals mainly composed of montmorillonite, hectorite, permiculite, attapulgite, sepiolite, and a mixture thereof; natural polymers such as nonionic polysaccharides such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose, guar gum and locust bean gum, and anionic polysaccharides such as xanthan gum, carrageenan, and gellan gum; and synthetic polymers such

as polyvinyl alcohol, polyvinylpyrrolidone and polyethylene glycol.

[0064]

From the viewpoint of detergency, component (d) is preferably one or more selected from smectite clay minerals, natural polymers and synthetic polymers, and more preferably one or more selected from nonionic polysaccharides, natural polymers and synthetic polymers, and further preferably one or more selected from nonionic polysaccharides. Specifically, from the viewpoint of detergency, component (d) is preferably one or more selected from hydroxyethyl cellulose, xanthan gum, and polyvinylpyrrolidone and further preferably hydroxyethyl cellulose.

[0065]

The liquid detergent composition for hard surfaces of the present invention contains component (d), from the viewpoint of improving the detergency by improving the viscosity, in an amount of preferably 0.01 mass% or more, more preferably 0.05 mass% or more, further preferably 0.1 mass% or more, furthermore preferably 0.2 mass% or more, and from the viewpoint of detergency and rinsability, in an amount of preferably 3 mass% or less, more preferably 2 mass% or less, further preferably 1 mass% or less, furthermore preferably 0.9 mass% or less, furthermore preferably 0.8 mass% or less, and from the

viewpoint of low cost and excellent economic efficiency, furthermore preferably 0.5 mass% or less.

[0066]

<Component (e)>

It is preferable that the liquid detergent composition for hard surfaces of the present invention contain a glycol solvent as component (e). The glycol solvent, component (e), is used from the viewpoint of cleanability of soap residue and sebum stains. In the present invention, glycol type means that it belongs to either a compound having two hydroxyl groups or an ether compound in which one or both hydrogen atoms of the hydroxyl groups is substituted with another group. As an ether compound, an aliphatic ether compound is preferable. Moreover, an ether compound in which one hydrogen atom of the hydroxyl group of the glycol compound is substituted with another group, is preferable.

[0067]

Component (e) is preferably a glycol water-soluble solvent having 2 or more and 12 or less carbons. In the present invention, "water-soluble" means that 50 g or more dissolves in 100 g of water at 20°C.

[0068]

From the viewpoint of detergency, component (e) has preferably 2 or more, more preferably 3 or more, further preferably 4 or more, furthermore preferably 5 or more, furthermore preferably 6 or more carbons in total, and

from the viewpoint of detergency, preferably 12 or less, more preferably 10 or less and further preferably 8 or less carbons in total.

[0069]

From the viewpoint of detergency, examples of component (e) includes one or more selected from ethylene glycol (2 carbons), propylene glycol (3 carbons), diethylene glycol (4 carbons), propylene glycol monomethyl ether (4 carbons), isoprene glycol (5 carbons), propylene glycol monoethyl ether (5 carbons), 3-methyl-3-methoxybutanol (6 carbons), ethylene glycol monobutyl ether (6 carbons), dipropylene glycol (6 carbons), diethylene glycol monobutyl ether (8 carbons), dibutylene glycol (8 carbons), and dipropylene glycol monobutyl ether (10 carbons).

[0070]

Component (e) is preferably a glycol having 2 or 3 carbons such as ethylene glycol, polyethylene glycol, propylene glycol and polypropylene glycol, a polyether thereof, or a monoalkyl ether thereof. The alkyl group of the monoalkyl ether has preferably 1 or more and 4 or less carbons, and is a methyl group, an ethyl group, various propyl groups, or various butyl groups.

"Various" includes normal, iso, and tertiary.

[0071]

From the viewpoint of detergency, component (e) is more preferably one or more selected from the group

consisting of propylene glycol (3 carbons), ethylene glycol monobutyl ether (6 carbons), propylene glycol monobutyl ether (7 carbons), diethylene glycol monobutyl ether (8 carbons) and dipropylene glycol monobutyl ether (10 carbons). As component (e), it is particularly preferable to include diethylene glycol monobutyl ether (8 carbons).

[0072]

The liquid detergent composition for hard surfaces of the present invention contains component (e), from the viewpoint of cleanability of soap residue and sebum stains, in an amount of preferably 1 mass% or more, more preferably 1.5 mass% or more, further preferably 2 mass% or more, and preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 6 mass% or less and furthermore preferably 5 mass% or less.

[0073]

<Component (f)>

From the viewpoint of detergency of soap residue, it is preferable that the liquid detergent composition for hard surfaces of the present invention contain an aromatic alcohol (hereinafter referred to as component (f)).

[0074]

Component (f) is preferably one or more selected from benzyl alcohol, 2-phenoxyethanol, and 2-benzyloxyethanol.

[0075]

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

[0076]

In order to increase the added value of the product, the liquid detergent composition for hard surfaces of the present invention can optionally be formulated with perfume, pigments, preservatives, antioxidants and the like (provided that components (a) to (f) are excluded).

[0077]

The liquid detergent composition for hard surfaces of the present invention contains water. That is, the balance other than components (a) to (c) and the optional components is water. The liquid detergent composition for hard surfaces of the present invention contains water in an amount of preferably 60 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, furthermore preferably 85 mass% or more, and preferably 95 mass% or less and more preferably 93 mass% or less. As the water, it is preferable to use ion

exchange water, sterilized ion exchange water, or the like.

[0078]

From the viewpoint of detergency, the liquid detergent composition for hard surfaces of the present invention has a pH at 25°C of preferably more than 6, more preferably 6.3 or more, further preferably 6.5 or more, furthermore preferably 6.8 or more, and from the viewpoint of low irritation to the skin, preferably 9.5 or less, more preferably 9 or less and further preferably 8.5 or less.

[0079]

From the viewpoint of detergency, the viscosity at 25°C of the liquid detergent composition for hard surfaces of the present invention is more than 6 mPa·s, preferably 10 mPa·s or more, more preferably 15 mPa·s or more, and from the viewpoint of detergency and rinsability, 1000 mPa·s or less, preferably 800 mPa·s or less, and furthermore, from the viewpoint of reducing the formulation amount of component (d) and being low cost and excellent in economic efficiency, more preferably 600 mPa·s or less, further preferably 400 mPa·s or less, furthermore preferably 200 mPa·s or less and furthermore preferably 100 mPa·s or less. The viscosity can be adjusted by component (d) or component (e). The viscosity in the liquid detergent composition for hard surfaces of the present invention was measured as a value

after 1 minute at 60 rpm using a B-type rotational viscometer, and for low viscosity, rotor No.1 was used and, if necessary, the rotor No.2 or 3 was used in order to fall within the viscosity measurement range.

[0080]

The liquid detergent composition for hard surfaces of the present invention is suitably used for cleaning hard surfaces for bathrooms, bathtubs, wash-basins, tiles, restrooms, washstands, mirrors, kitchen sinks, countertops, and water sections, and the like, and furthermore, it is suitably used for bathrooms. Here, "for bathrooms" applies not only for bathroom itself but also for other objects having a hard surface that are present in the bathroom such as bathtubs and wash-basins. Moreover, the liquid detergent composition is suitable for cleaning hard surfaces such as tile, glass, stainless steel, plastic, or ceramic.

[0081]

<Method for cleaning hard surfaces and method for removing water scale>

The present invention is a method for cleaning hard surfaces, including bringing a liquid detergent composition for hard surfaces into contact with a hard surface and leaving the composition for 1 minute or more, the liquid detergent composition containing 0.2 mass% or more and 10 mass% or less of component (a), 0 mass% or more and 10 mass% or less of component (b), component (c)

and water, wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less.

[0082]

In the method for cleaning hard surfaces of the present invention, the liquid detergent composition for hard surfaces of the present invention is used. The preferable aspect of this composition is the same as the above liquid detergent composition for hard surfaces of the present invention. That is, the liquid detergent composition for hard surfaces of the present invention is a liquid detergent composition for hard surfaces used for cleaning by being left in contact with a hard surface for 1 minute or more.

[0083]

Moreover, the present invention is also a method for removing water scale, including bringing a liquid detergent composition for hard surfaces into contact with a hard surface and leaving the composition for 1 minute or more, the liquid detergent composition containing 0.2 mass% or more and 10 mass% or less of component (a), 0 mass% or more and 10 mass% or less of component (b), component (c) and water, wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less. Water scale can be removed by cleaning the hard surface by the method of the present invention.

[0084]

Specifically, preferably exemplified as the cleaning method of the present invention is a cleaning method which includes bringing the liquid detergent composition for hard surfaces into contact with a hard surface as a stock solution, or bringing the liquid detergent composition for hard surfaces into contact with a hard surface as a stock solution without diluting, that is, bringing the liquid detergent composition for hard surfaces into contact with a hard surface without diluting. Furthermore, exemplified as the cleaning method of the present invention is a cleaning method which includes bringing the liquid detergent composition for hard surfaces into contact with a hard surface to which water scale has adhered, without diluting. As a method for bringing the liquid detergent composition for hard surfaces into contact with a hard surface, the method of coating the hard surface with the liquid detergent composition is preferable.

[0085]

Bringing the liquid detergent composition for hard surfaces into contact with a hard surface without diluting means that the detergent composition is not brought into contact with the hard surface after intentionally diluting with water or the like. For example, when the liquid detergent composition for hard surfaces is brought into contact with a hard surface to which water droplets or the like are adhered, or when

water droplets adhere to the hard surface after bringing the liquid detergent composition for hard surfaces into contact with the hard surface, it can be considered that the liquid detergent composition for hard surfaces is brought into contact with the hard surface without diluting.

[0086]

In the present invention, the stock solution of the liquid detergent composition for hard surfaces is adhered to the hard surface as it is, that is, without changing the composition. For example, the liquid detergent composition for hard surfaces is brought into contact with a hard surface to which water scale has adhered without adhering the liquid detergent composition to an absorbent cotton containing water. The composition of the liquid detergent composition for hard surfaces may vary after bringing the liquid detergent composition into contact with the hard surface. That is, after bringing the liquid detergent composition into contact with the hard surface, the composition of the liquid detergent composition for hard surfaces may be diluted or concentrated.

[0087]

In the cleaning method of the present invention, the liquid detergent composition for hard surfaces may be applied directly from a bottle in order to bring the liquid detergent composition into contact with the hard

surface as a stock solution, and examples of the bottle include a squeeze bottle.

[0088]

However, a concentrated composition containing components (a), (b) and (c) of the present invention may be prepared, and the concentrated composition may be diluted with water to prepare the liquid detergent composition for hard surfaces of the present invention and brought into contact with a hard surface. That is, the cleaning method of the present invention may be a method for cleaning hard surfaces, in which a concentrated composition containing components (a), (b) and (c) of the present invention is diluted with water to prepare the liquid detergent composition for hard surfaces of the present invention and the liquid detergent composition for hard surfaces is brought into contact with a hard surface without diluting.

[0089]

From the viewpoint of detergency, the standing time after coating on the hard surface is preferably 1 minute or more, preferably 2 minutes or more, more preferably 3 minutes or more, further preferably more than 3 minutes, furthermore preferably 4 minutes or more, furthermore preferably 5 minutes or more, and from the viewpoint of efficiently cleaning, preferably 60 minutes or less, more preferably 30 minutes or less, further preferably 15

minutes or less and furthermore preferably 10 minutes or less.

[0090]

After being left to stand, the liquid detergent composition for hard surfaces is usually rinsed with water. When rinsing, an external force (physical force) may be applied by hand or the like, or it may simply be rinsed with a flow of water. The temperature when being left to stand may be room temperature, and examples include 10°C or more and 30°C or less. Moreover, in the present invention, a hard surface can be cleaned with a cleaning article carrying the liquid detergent composition for hard surfaces of the present invention on a substrate.

[0091]

As an example, a method for cleaning hard surfaces in which the liquid detergent composition for hard surfaces of the present invention is applied to a hard surface and then wipe-cleaned, is provided. When wipe-cleaning, it is preferable to remove the composition applied to the hard surface from the hard surface using a dishcloth, a dustcloth, a nonwoven fabric or the like.

[0092]

Moreover, the liquid detergent composition for hard surfaces of the present invention can also be used as a cleaning article by impregnating on a substrate. The cleaning article in which the liquid detergent

composition for hard surfaces of the present invention has been impregnated on a substrate is preferable from the viewpoint of work efficiency of the cleaning work.

[0093]

As the substrate used in the cleaning article impregnated with the liquid detergent composition for hard surfaces, one that is flexible, that can be impregnated with the liquid detergent composition for hard surfaces, has sufficient strength during use, and does not generate waste or the like is used. It is preferable to use a substrate that can be impregnated with the following amount of liquid detergent composition for hard surfaces under no load.

[0094]

Examples of such a substrate include fiber structures composed of fibrous materials, such as various papers, nonwoven fabrics, woven fabrics, or knitted fabrics. Examples of fibrous materials constituting these fiber structures include cellulosic fibers, modified cellulosic fibers, synthetic fibers, and mixtures of two or more thereof.

[0095]

In addition, porous structures obtained by dispersing air bubbles in a resin (for example, a sponge-like structure) can also be used as the substrate.

[0096]

Moreover, the method for cleaning hard surfaces in which a cleaning article impregnated with the liquid detergent composition for hard surfaces of the present invention is used to wipe-clean the hard surface is preferable for the light cleaning of a hard surface from the viewpoint of work efficiency of the cleaning work. The cleaning article impregnated with the liquid detergent composition for hard surfaces may either be an article in which the detergent composition is impregnated on a substrate in advance, or an article on which the liquid detergent composition for hard surfaces is impregnated on a dry substrate before use. Moreover, the cleaning article impregnated with the liquid detergent composition for hard surfaces may be used by being mounted on a mop-shaped cleaning tool, or may be directly held by hand and used for wipe-cleaning.

[0097]

When the liquid detergent composition for hard surfaces is impregnated in advance, the impregnation rate of the liquid detergent composition for hard surfaces is, from the viewpoint of cleanability, preferably 100 mass% or more, more preferably 150 mass% or more, and preferably 1000 mass% or less, more preferably 400 mass% or less, and further preferably 350 mass% or less, per substrate mass [that is, based on the mass of the substrate in an unimpregnated state (dry state)]. If the impregnation rate is 100 mass% or more, sufficient

cleaning performance against stains and dirt is obtained. If it is 1000 mass% or less, the amount of discharge of the liquid detergent composition for hard surfaces to the surface to be cleaned becomes appropriate, no stain or dirt remains on the surface to be cleaned, and it can be used without affecting cleaning surfaces made from various materials such as wood-based materials. When the substrate is a sheet in terms of further improving the cleanability, the basis weight before impregnation of the liquid detergent composition for hard surfaces is, from the viewpoint of the retention of the liquid detergent composition for hard surfaces necessary for cleaning a certain area and the sheet operability and cost, preferably 40 g/m² or more, more preferably 50 g/m² or more, and preferably 200 g/m² or less and more preferably 150 g/m² or less.

[0098]

When using the cleaning article impregnated with the liquid detergent composition for hard surfaces, the liquid detergent composition for hard surfaces of the present invention may be used separately while spraying the liquid detergent composition on the object to be cleaned or the cleaning article. A larger area is cleaned by this method of use.

[0099]

In relation to the above embodiments, the present invention further discloses the following liquid

detergent composition for hard surfaces, method for cleaning hard surfaces and method for removing water scale. In these aspects, the matters described in the liquid detergent composition for hard surfaces of the present invention, the method for cleaning hard surfaces and the method for removing water scale can be appropriately applied to each other.

[0100]

<1>

A liquid detergent composition for hard surfaces, containing:

(a) 0.2 mass% or more and 10 mass% or less of one or more chelating agents selected from phosphonic acid-based chelating agents and phosphoric acid-based chelating agents (hereinafter referred to as component (a)), (b) 0 mass% or more and 10 mass% or less of a chelating agent other than component (a) (hereinafter referred to as component (b)), (c) a surfactant (hereinafter referred to as component (c)) and water,

wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less and is used for cleaning where the composition is brought into contact with a hard surface and left for 1 minute or more.

[0101]

<2>

The liquid detergent composition for hard surfaces according to <1>, containing component (b) in an amount

of preferably 0.2 mass% or more, more preferably 0.5 mass% or more, further preferably 1 mass% or more, furthermore preferably 2 mass% or more, furthermore preferably 3 mass% or more, and preferably 8 mass% or less, more preferably 7 mass% or less and further preferably 6 mass% or less.

[0102]

<3>

The liquid detergent composition for hard surfaces according to <1> or <2>, wherein the mass ratio of the content of component (a) to the content of component (b), (a)/(b) is preferably 0.02 or more, more preferably 0.05 or more, further preferably 0.1 or more, furthermore preferably 0.15 or more, furthermore preferably 0.2 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 0.8 or less, furthermore preferably 0.6 or less and furthermore preferably 0.5 or less.

[0103]

<4>

The liquid detergent composition for hard surfaces according to any one of <1> to <3>, wherein the mass ratio of the content of an anionic surfactant to the total content of component (a) and component (b), [(anionic surfactant)/((a) + (b))] 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 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.01 or less, and preferably 0 or more.

[0104]

<5>

The liquid detergent composition for hard surfaces according to any one of <1> to <3>, wherein the mass ratio of the content of an anionic surfactant to the total content of component (a) and component (b), $[(\text{anionic surfactant})/((a) + (b))]$ is 0.

[0105]

<6>

A liquid detergent composition for hard surfaces, containing:

(a) 0.2 mass% or more and 10 mass% or less of one or more chelating agents selected from phosphonic acid-based chelating agents and phosphoric acid-based chelating agents (hereinafter referred to as component (a)), (b) 0.2 mass% or more and 10 mass% or less of a carboxylic acid-based chelating agent (b-1) (provided that component (a) is excluded) (hereinafter referred to as component (b-1)), (c) a surfactant (hereinafter referred to as component (c)) and water, wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less.

[0106]

<7>

The liquid detergent composition for hard surfaces according to <6>, wherein component (b-1) is one or more chelating agents selected from hydroxycarboxylic acids and salts thereof, and aminocarboxylic acids and salts thereof, preferably one or more selected from hydroxycarboxylic acids having 3 or more and 8 or less carbons and salts thereof, more preferably one or more selected from citric acid, malic acid, and salts thereof, and further preferably citric acid or a salt thereof.

[0107]

<8>

The liquid detergent composition for hard surfaces according to <6> or <7>, containing component (b-1) in an amount of preferably 0.5 mass% or more, more preferably 1 mass% or more, further preferably 2 mass% or more, furthermore preferably 3 mass% or more, and preferably 8 mass% or less, more preferably 7 mass% or less and further preferably 6 mass% or less.

[0108]

<9>

The liquid detergent composition for hard surfaces according to any one of <6> to <8>, wherein the mass ratio of the content of component (a) to the content of component (b-1), $(a)/(b-1)$ is preferably 0.02 or more, more preferably 0.05 or more, further preferably 0.1 or

more, furthermore preferably 0.15 or more, furthermore preferably 0.2 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 0.8 or less, furthermore preferably 0.6 or less and furthermore preferably 0.5 or less.

[0109]

<10>

The liquid detergent composition for hard surfaces according to any one of <6> to <9>, wherein the mass ratio of the content of an anionic surfactant to the total content of component (a) and component (b-1), $[(\text{anionic surfactant})/((a) + (b-1))]$ 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 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.01 or less, and preferably 0 or more.

[0110]

<11>

The liquid detergent composition for hard surfaces according to any one of <6> to <9>, wherein the mass ratio of the content of an anionic surfactant to the total content of component (a) and component (b-1), $[(\text{anionic surfactant})/((a) + (b-1))]$ is 0.

[0111]

<12>

The liquid detergent composition for hard surfaces according to any one of <1> to <11>, containing component (a) in an amount of preferably 0.3 mass% or more, more preferably 0.4 mass% or more, further preferably 0.5 mass% or more, furthermore preferably 1 mass% or more, furthermore preferably 1.5 mass% or more, and preferably 8 mass% or less, more preferably 6 mass% or less, further preferably 4 mass% or less and furthermore preferably 3 mass% or less.

[0112]

<13>

The liquid detergent composition for hard surfaces according to any one of <1> to <12>, containing component (c) in an amount of preferably 0.05 mass% or more, more preferably 0.1 mass% or more, further preferably 0.2 mass% or more, and preferably 2 mass% or less, more preferably 1.5 mass% or less, further preferably 1 mass% or less and furthermore preferably 0.5 mass% or less.

[0113]

<14>

The liquid detergent composition for hard surfaces according to any one of <1> to <13>, wherein the mass ratio of the content of an anionic surfactant to the content of all chelating agents including component (a) and component (b), (anionic surfactant)/(chelating agent) 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 0.1 or less, furthermore preferably 0.05 or less, furthermore preferably 0.02 or less, and preferably 0 or more.

[0114]

<15>

The liquid detergent composition for hard surfaces according to any one of <1> to <13>, wherein the mass ratio of the content of an anionic surfactant to the content of all chelating agents including component (a) and component (b), (anionic surfactant)/(chelating agent) is 0.

[0115]

<16>

The liquid detergent composition for hard surfaces according to any one of <1> to <15>, further containing (d) a thickener (hereinafter referred to as component (d)).

[0116]

<17>

The liquid detergent composition for hard surfaces according to <16>, wherein component (d) is a thickener selected from the following (1) to (3).

(1) Smectite clay minerals mainly composed of montmorillonite, hectorite, permiculite, attapulgite, sepiolite, and a mixture thereof.

(2) Natural polymers selected from nonionic polysaccharides selected from methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose, guar gum and locust bean gum, and anionic polysaccharides selected from xanthan gum, carrageenan, and gellan gum

(3) Synthetic polymers selected from polyvinyl alcohol, polyvinylpyrrolidone and polyethylene glycol.

[0117]

<18>

The liquid detergent composition for hard surfaces according to <16> or <17>, containing component (d) in an amount of preferably 0.01 mass% or more, more preferably 0.05 mass% or more, further preferably 0.1 mass% or more, furthermore preferably 0.2 mass% or more, and preferably 3 mass% or less, more preferably 2 mass% or less, further preferably 1 mass% or less, furthermore preferably 0.9 mass% or less, furthermore preferably 0.8 mass% or less and furthermore preferably 0.5 mass% or less.

[0118]

<19>

The liquid detergent composition for hard surfaces according to any one of <1> to <18>, further containing an aromatic alcohol (f) (hereinafter referred to as component (f)).

[0119]

<20>

The liquid detergent composition for hard surfaces according to <19>, wherein component (f) is one or more selected from benzyl alcohol, 2-phenoxyethanol, and 2-benzyloxyethanol.

[0120]

<21>

The liquid detergent composition for hard surfaces according to <19> or <20>, containing component (f) in an amount of preferably 0.3 mass% or more, more preferably 0.5 mass% or more, and preferably 10 mass% or less, more preferably 5 mass% or less, further preferably 3 mass% or less, furthermore preferably 2 mass% or less and further preferably 1.5 mass% or less.

[0121]

<22>

The liquid detergent composition for hard surfaces according to any one of <1> to <21>, containing water in an amount of preferably 60 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, furthermore preferably 85 mass% or more, and preferably 95 mass% or less and more preferably 93 mass% or less.

[0122]

<23>

The liquid detergent composition for hard surfaces according to any one of <1> to <22>, wherein the composition has a pH at 25°C of preferably more than 6, more preferably 6.3 or more, further preferably 6.5 or

more, furthermore preferably 6.8 or more, and preferably 9.5 or less, more preferably 9 or less and further preferably 8.5 or less.

[0123]

<24>

The liquid detergent composition for hard surfaces according to any one of <1> to <23>, wherein the viscosity at 25°C is preferably 10 mPa·s or more, more preferably 15 mPa·s or more, and preferably 800 mPa·s or less, more preferably 600 mPa·s or less, further preferably 400 mPa·s or less, furthermore preferably 200 mPa·s or less and furthermore preferably 100 mPa·s or less.

[0124]

<25>

The liquid detergent composition for hard surfaces according to any one of <1> to <24>, wherein the hard surface is tile, glass, stainless steel, plastic, or ceramic.

[0125]

<26>

A method for cleaning hard surfaces, using the liquid detergent composition for hard surfaces according to any one of <1> to <25>.

[0126]

<27>

A method for cleaning hard surfaces, including bringing a liquid detergent composition for hard surfaces

into contact with a hard surface, preferably coating the hard surface with the liquid detergent composition, and leaving the composition for 1 minute or more, the liquid detergent composition for hard surfaces containing:

(a) 0.2 mass% or more and 10 mass% or less of one or more chelating agents selected from phosphonic acid-based chelating agents and phosphoric acid-based chelating agents, (b) 0 mass% or more and 10 mass% or less of a chelating agent other than component (a), (c) a surfactant, and water, wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less.

[0127]

<28>

The method for cleaning hard surfaces according to <27>, wherein the standing time after bringing into contact with, preferably coating, the hard surface is preferably 2 minutes or more, more preferably 3 minutes or more, further preferably more than 3 minutes, furthermore preferably 4 minutes or more, furthermore preferably 5 minutes or more, and preferably 60 minutes or less, more preferably 30 minutes or less, further preferably 15 minutes or less and furthermore preferably 10 minutes or less.

[0128]

<29>

A method for removing water scale, including bringing a liquid detergent composition for hard surfaces into contact with a hard surface, preferably coating the hard surface with the liquid detergent composition, and leaving the composition for 1 minute or more, the liquid detergent composition for hard surfaces containing:

(a) 0.2 mass% or more and 10 mass% or less of one or more chelating agents selected from phosphonic acid-based chelating agents and phosphoric acid-based chelating agents, (b) 0 mass% or more and 10 mass% or less of a chelating agent other than component (a), (c) a surfactant, and water, wherein the composition has a viscosity at 25°C of more than 6 mPa·s and 1000 mPa·s or less.

[0129]

<30>

The method for removing water scale according to <29>, wherein the standing time after bringing into contact with, preferably coating, the hard surface is preferably 2 minutes or more, more preferably 3 minutes or more, further preferably more than 3 minutes, furthermore preferably 4 minutes or more, furthermore preferably 5 minutes or more, and preferably 60 minutes or less, more preferably 30 minutes or less, further preferably 15 minutes or less and furthermore preferably 10 minutes or less.

[0130]

Examples

Using the following formulated components, the liquid detergent composition for hard surfaces shown in Table 1 was prepared, and the following items were evaluated. The results are shown in Table 1. The liquid detergent composition for hard surfaces shown in Table 1 was prepared by a conventional method. That is, component (a) to component (f) were added to an appropriate amount of ion exchange water, dissolved at room temperature (25°C), then sodium hydroxide was added to adjust the pH (25°C) and perfume was added. All the mass% of the formulated components in Table 1 are a numerical value based on the active component. Moreover, for component (a) and component (b), the mass% based on the amount in terms of acid are shown. Moreover, for the sodium alkyl ether sulfate, component (c), the mass% based on the amount in terms of acid is shown. Moreover, Table 1 shows the viscosity of the liquid detergent composition for hard surfaces measured as a value after 1 minute using a B-type rotational viscometer at 60 rpm (25°C). For low viscosity, rotor No.1 was used and, if necessary, the rotor No.2 or 3 was used in order to fall within the viscosity measurement range.

[0131]

<Formulated components>

<Component (a)>

- Ethane-1-hydroxy-1,1-diphosphonic acid: phosphonic acid-based chelating agent, manufactured by Italmatch Japan Ltd., Dequest 2010CS, 60 mass% aqueous solution
- Aminotrimethylene phosphonic acid: phosphonic acid-based chelating agent, manufactured by Italmatch Japan Ltd., Dequest 2006, 39 mass% aqueous solution
- Tripolyphosphoric acid: Phosphoric acid-based chelating agent, manufactured by Aditya Birla Chemicals (Thailand), Limited

<Component (b)>

- Citric acid: carboxylic acid-based chelating agent (component (b-1)), manufactured by Wako Pure Chemical Industries, Ltd., Wako Special Grade

[0132]

<Component (c)>

- Lauramidopropyl betaine: amphoteric surfactant, compound in which in general formula (c1), R^{1c} is an alkyl group having 11 carbons and R^{2c} and R^{3c} are methyl groups, Amphitol 20AB, manufactured by Kao Corporation
- Polyoxyethylene (7) alkyl ether: nonionic surfactant, compound in which in general formula (c4), R^{8c} is an alkyl group having 12 carbons, l is 7 and j is 0, Softanol 70H, manufactured by Kao Corporation, () is the average number of added moles of the oxyethylene group
- Sodium alkyl ether sulfate: anionic surfactant, alkyl group having 12 to 16 carbons, average number of added

moles of the ethylene oxide: 4.0, ES-4K, manufactured by
Kao Corporation

[0133]

<Component (d)>

- Hydroxyethyl cellulose ether: natural polymer of nonionic polysaccharide, HEC Daicel SE850K, Daicel FineChem Ltd.
- Xanthan gum: natural polymer of anionic polysaccharide, KELZAN, manufactured by Sansho Co., Ltd.
- Polyvinylpyrrolidone: synthetic polymer, PVP K-90, manufactured by ISP TECHNOLOGIES, INC

<Component (e)>

- Diethylene glycol monobutyl ether: glycol solvent, BDG (butyl diglycol), manufactured by Nippon Nyukazai Co., Ltd.

<Component (f)>

- Benzyl alcohol: Wako Pure Chemical Industries, Ltd., benzyl alcohol, Wako Special Grade

[0134]

(1) Detergency evaluation

0.3 mL of 300 ppm SiO_2 /300 ppm CaCl_2 aqueous solution was applied as uniformly as possible to the lower 25 mm portion of a slide glass (76 mm $\times$ 26 mm), dried on a hot plate heated to 140°C, and then rinsed with ion exchange water. The operation of applying the solution on this slide glass and drying was repeated three times to produce a model stain of water scale. An absorbent

cotton (Curelet 4 × 4 cm², manufactured by Kawamoto Corporation) cut into the size of the model stain was placed on the slide glass to which the model stain was adhered, and 1 mL of each liquid detergent composition for hard surfaces was added dropwise and allowed to stand for a predetermined time as described in Table 1, then the entire surface of the slide glass was rubbed with a light force (about 200 g weight) 5 times back and forth. Thereafter, the slide glass was sufficiently rinsed with ion exchange water, and the detergency was determined according to the following criteria. As a specific method for the evaluation criteria, the slide glass with no stain applied, the slide glass after applying the stain and before cleaning, and the slide glass after cleaning were photographed with the same photographing conditions such as brightness, and the gray scale of each slide glass was measured from the obtained images. The cleaning rate of the plate after cleaning was calculated by setting the cleaning rate of the slide glass before cleaning to 0% and the cleaning rate of the slide glass with no stain applied to 100%. The image processing software Image J 1.47v was used for the gray scale measurement.

[0135]

(2) Evaluation of the rinsability after cleaning

24 mL of each cleaning solution was sprinkled on a 100 × 120 cm² bathroom floor, rubbed with a sponge 70

times, then rinsed with a tap water shower, and the time until the foam completely disappeared was evaluated according to the following criteria. The temperature of the tap water when rinsing was constant at 30°C and the flow rate at about 143 mL/second.

1: Foam disappears within 25 seconds and rinsing is complete.

2: Foam does not disappear even after 25 seconds.

3: It takes over 30 seconds for the foam to disappear.

[0136]

[Table 1]

		Example																				Comparative Example			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	1	2	3	4
Liquid detergent composition for hard surfaces	(a)	Ethane-1,1-hydroxy-1,1-diphosphonic acid	2	2	2	2	2	2	2	2	2	2	2						7	2	0.7	2	2		2
		Amino trimethylene phosphonic acid													2	2									
		Tripolyphosphoric acid																							
	(b)	(b-1) Citric acid		5	5	5	5	5	5	5	5		5		5		5	5	5	5	5	5	5	5	5
		Laurandipropyl betaine	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3			0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	(c)	Polyoxyethylene (7) alkyl ether																							
		Sodium alkyl ether sulfate							0.7	0.2	2.45														
	(d)	Hydroxyethyl cellulose ether	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.8	0.8						0.3	0.3	0.3	0.3			1
		Xanthan gum											0.5	0.5											
	(e)	Polyvinylpyrrolidone															0.3	0.3							
Diethylene glycol monobutyl ether		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
(f)	Benzyl alcohol																				1				
	Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
	Sodium hydroxide	1	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	1	4.3	1	4.3	1	4.3	1	4.5	3.5	4.3	4.3	4.3	3.5	1
		Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
	Ion exchange water																								
	Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
	Anionic surfactant/chelating agent (mass ratio)	-	-	-	-	-	-	0.1	0.03	0.35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
(a)/(b-1) (mass ratio)	-	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	-	0.4	-	0.4	-	0.4	-	0.4	0.14	0.14	0.4	0.4	0	-	
pH (25°C)	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	8	7	7	7	7	7	
Viscosity (25°C) (mPa)	35	25	25	25	25	25	25	20	30	25	740	720	325	425	55	80	30	25	25	25	2	1900	30	35	
Standing time (minutes)	10	10	5	3	2	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	30 seconds	
Evaluation	Detergency against water scale (%)		80	90	85	81	77	90	90	90	90	70	80	80	90	80	90	90	90	80	80	50	50	30	50
	Rinsability		1	1	1	1	1	1	2	1	3	1	1	1	1	1	1	1	1	1	1	1	3	1	

(3) On-site evaluation of detergency

A stainless steel plate was installed on a kitchen sink in a real home for one month, an absorbent cotton (Curelet 4 × 4 cm², manufactured by Kawamoto Corporation) cut into the size of 2 × 2 cm² was placed on the surface of the stainless steel plate to which water scale was adhered, and 1 mL of the liquid detergent composition for hard surfaces of Example 2 was added dropwise and allowed to stand for 20 minutes, then the entire surface of the faucet surface was rubbed with a light force (about 200 g weight) 5 times back and forth. Thereafter, the plate surface was sufficiently rinsed with ion exchange water. The hard surface of the stainless steel plate before and after cleaning was photographed under the same photographing conditions such as brightness. The photograph before cleaning is shown in Figure 1, and the photograph after cleaning is shown in Figure 2.

[0138]

Comparing Figure 1 and Figure 2 shows that after the scaly water scale that was adhering before cleaning was cleaned with the liquid detergent composition for hard surfaces of Example 2, almost all the scaly water scale was removed.

CLAIMS

1. A liquid detergent composition for hard surfaces, comprising:

(a) 0.3 mass% or more and 6 mass% or less of one or more chelating agents selected from phosphonic acid-based chelating agents and phosphoric acid-based chelating agents (hereinafter referred to as a component (a)), (b) 0.2 mass% or more and 10 mass% or less of a carboxylic acid-based chelating agent (b-1) (provided that the component (a) is excluded) (hereinafter referred to as a component (b-1)), (c) a surfactant (hereinafter referred to as a component (c)) and water,

wherein a mass ratio of the content of the component (a) to the content of the component (b-1), $(a)/(b-1)$, is 0.02 or more and 10 or less,

a mass ratio of the content of an anionic surfactant in the component (c) to the content of all chelating agents, $(\text{anionic surfactant})/(\text{chelating agent})$, is 0.2 or less, and

the composition has a viscosity of more than 6 mPa·s and 1000 mPa·s or less under the conditions of using a B-type viscometer at 60 rpm and at 25°C.

2. The liquid detergent composition for hard surfaces according to claim 1, wherein the composition has a pH at 25°C of more than 6.

3. The liquid detergent composition for hard surfaces according to claim 1 or 2, wherein the content of the component (c) is 2 mass% or less.

4. The liquid detergent composition for hard surfaces according to any one of claims 1 to 3, further comprising (d) a thickener.

5. The liquid detergent composition for hard surfaces according to any one of claims 1 to 4, wherein the hard surface is tile, glass, stainless steel, plastic, or ceramic.

6. A method for cleaning hard surfaces, using the liquid detergent composition for hard surfaces according to any one of claims 1 to 5.

7. A method for removing water scale, comprising bringing the liquid detergent composition for hard surfaces according to any one of claims 1 to 5 into contact with a hard surface and leaving the composition for 1 minute or more.