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(54) Hard-surface cleaning compositions containing biodegradable chelants

Reinigungsmittel für harte Oberflächen, biologisch abbaubare Chelatbildner enthaltend Compositions de nettoyage pour surfaces dures contenant des agents de chelation biodégradable

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Description

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FIELD OF THE INVENTION

The present invention relates to hard-surface cleaning compositions containing a binary mixture of an organic solvent and a biodegradable chelating agent.

BACKGROUND OF THE INVENTION

It is well known to formulate hard-surface cleaning compositions containing organic solvents and chelating agents. For example, European Patent Applications 0,040,882, 0,080,747 and 0,126,545 describe the use of solvents represented by mixtures of terpenes with benzyl alcohol or butyl carbitol, together with builders which are mainly polyphosphates, or nitrogen containing strong sequestrants such as nitrilotriacetic acid (NTA). European Patent 0,105,863 and U.S. Patent 3,591,510 describe the use of certain glycol ether derivatives as solvents in liquid cleaners, together with polyphosphate builders.

Such prior known solvent/builder combinations have proven very effective in hard-surface cleaning. However, in recent years, phosphates have come under scrutiny for environmental reasons. Other nonphosphate strong sequestering agents are also facing acceptability problems related to toxicity and environmental safety.

There exists therefore a need for hard-surface cleaning compositions which are effective and safe to overcome toxicity and environmental concerns.

Iminodisuccinic acid salts have been described as a detergency builder in U.S. Patent 3,697,453. Water soluble salts of N,N-di(carboxymethyl)-aspartic acid have also been disclosed as a builder in U.S. Patent 3,637,511. However, none of these references disclosed the use of these compounds in hard-surface cleaning compositions.

Accordingly, it is an object of the present invention to provide efficacious chelating agents for hard-surface cleaners which promote good soil removal, is ecologically safe, contains no phosphorus and is readily biodegradable.

It is a related objective of the invention to provide efficient hard-surface cleaning compositions containing the combination of a safe, biodegradable chelating agent and a suitable organic solvent.

Other important objects of this invention will become apparent from the ensuing description and appended claims.

30 SUMMARY OF THE INVENTION

The present invention relates to hard-surface cleaning compositions containing an organic solvent having a boiling point equal to or above 90°C, and a nonphosphorus-containing, biodegradable chelating agent.

DETAILED DESCRIPTION OF THE INVENTION

The chelants useful in the present invention have the following formula:

45 in which

m is -NR' or sulfur;

X is SO₃H or COOH;

Y is hydrogen, SO₃H or COOH;

R and R' are independently, hydrogen -CH(Z)CH₂(Z'), -CH(Z)CH(Z')(Z") or -CH₂COOH; and

Z, Z', and Z" are, independently, hydrogen, OH, SO₃H or COOH; and wherein any COOH or SO₃H radical may be present in the form of the sodium, potassium, ammonium or substituted ammonium salt.

The term "substituted ammonium" as used herein and in the appended claims refers to an ammonium radical substituted with one or more alkyl groups having up to about 6 carbon atoms, preferably from about 1 to 4 carbon atoms.

Preferred chelants of Formula I include those compounds in which X and Y are both COOH or a sodium, potassium, ammonium or substituted ammonium salt thereof; and Z, Z', and Z" are, independently, hydrogen or COOH or a sodium, potassium, ammonium or substituted ammonium salt thereof.

Specific examples of chelants in accordance with the invention include, for example, cysteic acid N,N-diacetic acid; cysteic acid N-monoacetic acid; alanine-N-monoacetic acid; N-(3-hydroxysuccinyl)aspartic acid; and N-[2-(3-hydroxysuccinyl)]-L-serine. Exemplary of the most preferred chelants are B-alanine-N,N-diacetic acid; aspartic acid N, N-diacetic acid; iminodisuccinic acid; aspartic acid N-monoacetic acid; and their potassium, sodium or ammonium salts.

The compounds of Formula I may be readily prepared by the use of steps generally described in the literature or by methods analogous or similar thereto and within the skill of the art.

The chelants of Formula I may be prepared by reacting an alkali metal salt of an appropriately substituted amino carboxylic acid with an alkali metal salt of an appropriately substituted carboxylic acid in an alkaline aqueous system in a manner as described in U.S. Patent No. 3,683,014 and U.S. Patent No. 3,637,511 to yield the corresponding appropriately substituted organic acid salt. Treatment of the organic salt with a mineral acid (e.g., HCI) or an acidic ion-exchange resin liberates the free acid to afford a compound of Formula I.

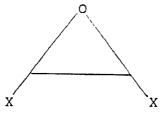
Compounds of Formula I may also be prepared in a manner as described in U.S. Patent No. 4,827,014. In accordance with this method, the chelants used according to the invention are prepared by reacting a compound of the formula

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Formula II

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where X is a substituent within the meaning of Formula I, with an appropriately substituted amine and, if as the case may be amide, ester or nitrile groups are present, hydrolyzing these groups in the presence of and acid or base, to yield a free acid or a salt conforming to Formula I.

Where m is sulfur, compounds of Formula I may be prepared by reacting the appropriate mercaptocarboxylic acid with maleic acid in an aqueous solution under neutral, acidic or basic conditions.

Chelants in accordance with the invention may also be prepared by method analogous to the procedure described in European Patent No. 89,115,896.3, Publication No. 0,356,972 A2 where an appropriately substituted imino carboxylic acid or its alkali metal or ammonium salt is reacted with acrylic acid in a non-basic or an alkaline or nitrogen basic aqueous medium to yield a compound of Formula I.

Chelants of Formula I may also be prepared in the manner as described in U.S. Patent No. 3,929,874, wherein an appropriately substituted amine is reacted with epoxysuccinic acid in a basic aqueous medium to yield a compound of Formula I.

Alkyliminodiacetic acids are available commercially but may be prepared cheaply and easily by the method for the preparation of methyliminodiacetic acid as described by G. J. Berchet in Organic Synthesis, Vol. 11, pages 397-398, which method is described in Example VI below.

Organic solvents suitable for use in combination with the above-described chelating agents must have a boiling point equal to or above 90° C, in order to give the unexpected soil-release benefits derivable from the solvent-chelating agent combination. For instance, C_1 - C_3 aliphatic alcohols such as isopropanol (B.P. 82°C) are not suitable for use in the present invention.

Representatives of organic solvents which are effective in the present context are: C_6 - C_9 alkyl aromatic solvents, especially the C_6 - C_9 alkyl benzenes, alpha-olefins, like 1-decene or 1-dodecene, benzyl alcohol, n-hexanol, phthalic acid esters.

A type of solvent especially suitable for the compositions herein comprises diols having from 6 to 16, preferably 8 to 12, carbon atoms in their molecular structure. Preferred diol solvents have a solubility in water of from about 0.1 to 20 g/100 g of water at 20°C. The most preferred diol solvents are 2,2,4-trimethyl-1,3-pentanediol, and 2-ethyl-1,3-hexanediol.

Glycol ethers are another class of particularly preferred solvents. In this category, are: water-soluble CARBITOL® solvents or water-soluble CELLOSOLVE® solvents. Water soluble CARBITOL® solvents are compounds of the 2-(2-alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl, butyl pentyl hexyl; a preferred water-soluble carbitol is 2-(2-butoxyethoxy)ethanol also known as butyl carbitol. Preferred are also hexyl carbitol and 2-methyl pentyl carbitol. Water-soluble CELLOSOLVE® solvents are compounds of the 2-alkoxyethoxy ethanol class, wherein the alkoxy group is preferably butyl or hexyl.

Still in the glycol ether category, certain propylene-glycol derivatives have been found to be particularly efficient

in the present context. These species include 1-n-butoxypropane-2-ol and 1(2-n-butoxy-1-methylethoxy)propane-2-ol (butoxypropanol), with the latter being especially preferred.

Mixtures of the above solvents can also be used, like butyl carbitol and/or benzyl alcohol together with diols and/or glycol ethers.

The organic solvent is present in an amount of from 1% to 20% by weight of the total composition, preferably from 1% to 10%.

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The benefits of the present compositions are derived from the combination of the specific chelating agents and organic solvents described hereinabove. They are particularly noticeable in terms of calcium soap-soil removal from surfaces such as bathtub surfaces. In order to obtain such an effect, the weight ratio or organic solvent to chelating agent is in the range from 2:3 to 2:1, preferably 1:1 to 2:1. The chelant is present in an amount of from 1% to 30% by weight of the total cleaning composition, preferably about 1% to 15% by weight of the total cleaning composition.

In addition to the essential chelating agent/solvent binary mixture described hereinabove, the compositions of the invention can contain additional ingredients, which are often highly desirable. For example, the compositions herein will usually contain a surface-active agent.

Water-soluble detersive surfactants useful herein include well-known synthetic anionic, nonionic, cationic, emphoteric and zwitterionic surfactants and mixtures thereof. Typical of these are the alkyl benzene sulfates and sulfonates, paraffin sulfonates, olefin sulfonates, alkoxylated (especially ethoxylated) alcohols and alkyl phenols, amine oxides, sulfonates of fatty acids and of fatty acids esters, and the like, which are well-known in the detergency art. In general, such detersive surfactants contain an alkyl group in the C₁₀-C₁₈ range; the anionic detersive surfactants are most commonly used in the form of their sodium, potassium or triethanolammonium salts. The nonionics generally contain from 3 to 17 ethylene oxide groups per mole of hydrophobic moiety. Cationic surfactants will generally be represented by quaternary ammonium compounds such as ditallow dimethyl ammonium chloride, and will be preferably used in combination with nonionic surfactants.

Especially preferred in the compositions of the present invention are: C_{12} - C_{16} alkyl benzene sulfonates, C_{12} - C_{18} paraffin-sulfonates and the ethoxylated alcohols of the formula $RO(CH_2CH_2O)_n$ with R being a C_{12} - C_{15} alkyl chain and n being a number from 6 to 10, and the ethoxylated alcohol sulfates of formula $RO-(CH_2CH_2O)_n$ - SO_3M , with R being a C_{12} - C_{18} alkyl chain on a number from 2 to 8, and M is H or an alkalimetal ion.

Anionic surfactants are frequently present at levels from 0.3% to 8% of the composition. Nonionic surfactants, are used at levels between 0.1% to 6% by weight of the composition. Mixtures of the like surfactants can also be used.

Other optional ingredients are represented by conventional detergency builders, which may be used in addition to the chelating agent herein; compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates (NTA), polycarboxylates, citrates, water-soluble phosphates such as tri-polyphosphate and sodium orthoand pyrophosphates, silicates, ethylene diamine tetraacetate (EDTA), amino-polyphosphonates (DEQUEST), phosphates and mixtures thereof.

Highly desirable ingredients for use herein are represented by conventional detergent hydrotropes. Examples of suitable hydrotropes are urea, monoethanolamine, diethanolamine, triethanolamine and the sodium potassium, ammonium and alkanol ammonium salts of xylene-, toluene-, ethylbenzene- and isopropyl-benzene sulfonates.

The hard-surface cleaning compositions of the invention may also contain an abrasive material. The abrasives suitable herein are selected from water-insoluble, non-gritty materials well-known in the literature for their relatively mild abrasive properties. It is highly preferred that the abrasives used herein not be undesirably "scratchy". Abrasive materials having a Mohs hardness in the range of about 7, or below, are typically used; abrasives having a Mohs hardness of 3, or below, can be used to avoid scratches on aluminum or stainless steel finishes. Suitable abrasives herein include inorganic materials, especially such materials as calcium carbonate and diatomaceous earth, as well as materials such as Fuller's earth, magnesium carbonate, China clay, actapulgite, calcium hydroxyapatite, calcium orthophosphate, dolomite and the like. The aforesaid inorganic materials can be qualified as "strong abrasives". Organic abrasives such as urea-formaldehyde, methyl methacrylate melamine-formaldehyde resins, polyethylene spheres and polyvinylchloride can be advantageously used in order to avoid scratching on certain surfaces, especially plastic surfaces.

Typically, abrasives have a particle size range of 10-1000 microns and are used at concentrations of 5% to 30% in the compositions. Thickeners are frequently added to suspend the abrasives.

Thickeners will preferably be included in the compositions of the inventions, mainly in order to suspend the abrasive; high levels of thickener are detrimental to the performance because they are difficult to rinse from the cleaned surfaces. Accordingly, the level will be kept under 2%, preferably from 0.2% to 1.5%. Common thickeners such as the polyacrylates, xanthan gums, carboxymethyl celluloses, swellable smectite clays, and the like, can be used herein.

Soaps can be included in the compositions herein, the soaps prepared from coconut oil fatty acids being preferred. Optional components are also represented by ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include perfumes, dyes, optical brighteners, soil suspending agents, detersive enzymes, gel-control agents, thickeners, freeze-thaw stabilizers, bactericides, preserv-

atives, and the like.

The hard-surface cleaning compositions herein will advantageously be prepared in the form of an aqueous liquid compositions, including concentrates, containing as essential ingredients a surface-active agent, and the solvent-chelating agent binary mixture according to the invention. Liquid formulations at normal dilution usually contain 2-6% surfactant and 8-12% solvent/chelating agent binary mixture. Concentrated liquid formulations usually contain 6-10% surfactant and 16-24% solvent/chelating agent binary mixture. Alternatively, the compositions herein will be in the form of a creamy scouring cleanser, containing an abrasive material, surface-active agent, and the solvent/chelating agent binary mixture of the invention. In both formulations, the pH of such compositions will be neutral or in the alkaline range, generally in the range of pH 5-11.

The following examples are given in order to further illustrate the invention detailed above, but are not intended to be limiting of the scope of the invention.

EXAMPLE I

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(Preparation of Aspartic acid-N,N-diacetic acid, tetrasodium salt)

A solution of 5.32 g (40 mmol) of aspartic acid and 3.2 g (80 mmol) of sodium hydroxide in 50 ml of water was heated to 60°C with stirring. A solution of 12.81 g (110 mmol) of sodium chloroacetate in 20 ml water was added dropwise over 12 hrs. During this addition, the pH of the reactor solution was maintained in the range 9 - 10 by addition of 10% sodium hydroxide solution until a total of 4.4 g (110 mmol) sodium hydroxide had been added. The reaction was heated at 60°C for an additional 12 hours. The solution was adjusted to a pH of 3 with concentrated hydrochloric acid and was cooled to 5°C. A threefold volume of methanol was added and the resulting precipitate was filtered off and washed with cold methanol.

25 EXAMPLE II

(Preparation of Aspartic acid-N-monoacetic acid)

A solution of 69.63 g (600 mmol) of maleic acid, 68 g (1700 mmol) of sodium hydroxide, and 37.53 g (500 mmol) of glycine in 200 ml water was heated at reflux for 17 hours. The resulting solution was cooled to room temperature and the pH was adjusted to 3 with concentrated hydrochloric acid. The precipitated mixture of maleic and fumeric acid was removed by filtration and the resulting solution was concentrated to dryness to yield the product as a white solid.

EXAMPLE III

(Preparation of N-(3-hydroxy succinyl) aspartic acid)

A solution a 5.72 g (43 mmol) of aspartic acid in 100 ml of water was neutralized with 3.44 g (86 mmol) of sodium hydroxide. To this was added 7.57 g (mmol) of epoxysuccinic acid. The resulting solution was refluxed overnight. The resulting solution was cooled and was concentrated under reduced pressure to get a crude product as a light yellow solid. Repeated crystallization from water (pH=10)/methanol yielded the pure product as a white solid.

EXAMPLE IV

45 (Preparation of Iminodisuccinic acid)

A mixture of 12.77 g (110 mmol) maleic acid, 19.2 g (300 mmol) of 28% aqueous ammonia, and 13.3 g (100 mmol) aspartic acid in 75 ml water was heated to 95°C with stirring. The solution was adjusted to a pH of 9 with 10% aqueous sodium hydroxide, then stored at 95°C for 20 hours. The resulting clear solution was cooled to room temperature and 11.95 g (300 mmol) concentrated hydrochloric acid was added. The resulting precipitate of maleic and fumeric acid was removed by filtration, and the supernatant was concentrated under pressure to yield the product as a white solid.

EXAMPLE V

55 (Preparation of Carboxymethylmercaptosuccinic acid)

A solution of 180 g (10 mol) of water and 98 g (1.0 mol) of maleic anhydride was heated to 400C. To this solution was added 92 g (1.0 mol) of thioglycolic acid and the reaction mixture was heated to 90°C with stirring. After three (3)

hours at 90°C, the water was evaporated off under reduced pressure. The resulting molten product was cast and ground prior to use.

EXAMPLE VI

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(Hard-Surface Cleaning in Solvent-based Formulations)

A major function of a chelant in a hard surface cleaner is to solubilized soap scum (Ca⁺² and Mg⁺² salts of soap) by chelating the calcium and magnesium ions. The ability of chelants in accordance with the invention to solubilize soap scum in the presence of solvent-based hard surface cleaner was tested by dipping a glass microscope slide coated with soap scum into the cleaner and visually observing whether the soil had been removed. The test was carried out using the following hard surface cleaning formulation:

| Dodecylbenzene sulfonic acid (sodium salt) | 4.0% |
|--|-------|
| 2-Ethyl-1,3-hexanediol | 6.0% |
| 1-Naphthalenesulfonic acid | 1.5% |
| Sodium Carbonate | 1.0% |
| Chelant | 4.0% |
| Water | 83.5% |

PROCEDURE

Soiling Of Microscope Slides. 100 ml of an aqueous solution containing 1% Ivory Soap and 400 ppm hardness (3: 1 Ca²⁺: Mg²⁺) was pipetted onto each slide. The slides were then allowed to air dry for 16 hours.

<u>Cleaning Procedure</u>. A soiled slide was dipped into a beaker containing hard surface cleaner for 5 seconds with gentle agitation. The slide was then removed, dipped into distilled water for 5 seconds, and air dried. Visual observation was used to determine soil removal. Three replicates were preformed with each chelant.

The results were compared to results obtained for hard-surface cleaning compositions containing either EDTA and water (blank sample). Results are recorded in Table I below.

TABLE I

| IADLLI | | |
|--------------------|---------------------|--|
| Chelant | Appearance of slide | |
| Blank ¹ | covered with a film | |
| EDTA ² | clean | |
| NTA ³ | clean | |
| BADA ⁴ | clean | |
| AspDA ⁵ | clean | |
| ISA ⁶ | clean | |
| AspMA ⁷ | clean | |
| MIDA ⁸ | clean | |
| CMMS ⁹ | clean | |

Blank = Water only

²EDTA = Ethylenediaminetetraacetic acid

³NTA = Nitrilotriacetic acid

 4 BADA = β -alanine-N,N-diacetic acid

⁵AspDA = Aspartic acid N,N-diacetic acid

 6 ISA = Iminodisuccinic acid

⁷AspMA = Aspartic acid N-monoacetic acid

⁸MIDA = Methyliminodiacetic acid

⁹CMMS = Carboxymethylmercaptosuccinic acid

EXAMPLE VII

(Determination of Biodegradability)

The biodegradability of chelating agents described hereinabove was determined using the Sturm ${\rm CO}_2$ Evolution

Test (J. Amer. Oil Chem. Soc., 50, 159(1973)). The Sturm Test measures the ultimate biodegradation of soluble organic materials. The term "ultimate biodegradation" is defined herein to indicate the complete mineralization of material to CO_2 generated from the degradation of the chelating agent was trapped using a series of three barium hydroxide traps. The barium hydroxide reacted with the CO_2 to form barium carbonate and the amount of CO_2 evolved was determined by titrating the unreacted barium hydroxide with hydrochloric acid.

Procedures

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The test was conducted in a two liter flask with the final volume of the test solution being one liter (Final volume equals the volume of the medium plus the volume of the test sample solution plus the volume of the inoculum). The test medium was a modified BOD (Biochemical Oxygen Demand) water which contains, per liter of distilled water, the following standard BOD reagent solutions:

| 1.0 ml | magnesium sulfate (2.25% W/V) | |
|-------------------------|-------------------------------|--|
| 1.0 ml | calcium chloride (2.75% W/V) | |
| 4.0 ml | ferric chloride (0.025% W/V) | |
| 1.0 ml | ammonium sulfate (4.99% W/V) | |
| 2.0 ml | phosphate buffer (pH 7.2) | |
| W/V = weight per volume | | |

A stock solution of the test compound was prepared at a concentration of 1000 mg/l and the pH adjusted to 7.0 if the initial pH was outside a 4.0-10.0 pH range.

The inoculum was prepared by taking unacclimated sludge and homogenizing it for two minutes, at room temperature, using a Waring Blender at medium speed. The homogenized sample was transferred to a beaker and left to settle for 15-30 minutes. The supernatant was carefully decanted and 10 ml of this solution was added to each test flask. Immediately prior to the beginning of the test, the viability of the test organisms was determined. There must be a least 1 x 10⁶ microorganisms per milliliter before this inoculum can be used. The inoculum was used the day it was prepared.

Each test flask was charged with 980 ml of test medium and then purged for twenty-four hours using $\rm CO_2$ free air. Following the removal of residual $\rm CO_2$, the test flasks were connected to a series of three barium hydroxide traps each containing 100 ml of 0.024 N barium hydroxide. The milliliters of the test sample stock suction was added to each flask followed by the addition of 10 ml of the inoculum prepared above.

The head space of each flask was aerated with $\rm CO_2$ free air at a flow rate of 50-100 cc/min for the duration of the test. Every 2-3 days the first barium hydroxide trap (nearest to the test flask) was titrated using 0.05N standardized HCL and the amount of $\rm CO_2$ evolved was determined. The remaining two barium hydroxide traps were moved forward to positions one and two and a new barium hydroxide trap was placed in position three. The length of the test was typically 26-30 days.

Included in each test were two blanks which were titrated along with the test samples. The amount of CO₂ found for each sample was determined using the following equation:

$$mg\ CO_{2(sample)} = [ml\ titrant_{(sample)} - ml\ titrant_{(blank\ ave.)}]\ x\ 1.1$$

Each test also included a sample of glucose which was used as a control to guarantee the activity of the microorganisms.

Each chelating agent tested was degraded as described hereinabove with the exception that AspDA was degraded using acclimated microorganisms. The microorganisms were acclimated in a bench scale semicontinuous activate sludge system. The initial activated sludge was adjusted to a suspended solids level of 2500-3000 mg/l. The activated sludge was exposed to increasing levels of test material over a five day period (4, 8, 12, 16, and 20 mg/l) and the maintained at 20 mg/l for an additional five days. The acclimated microorganisms were then treated as described above prior to the start of the Sturm test.

The results of each test are reported in Table II below. Results are recorded as a percentage of the theoretical CO_2 expected to evolve if there was 100% biodegradation. If the CO_2 production for the glucose flask did not plateau at 70% or more, the test results were discarded. The theoretical CO_2 for test samples was determined using a Total Organic Carbon Analyzer or other suitable analytical methods for determining total organic carbon.

| 17.022 11 | | |
|--------------------------|-------------------------------|--|
| Biodegradable Properties | | |
| Chelating agent | % of Theoret. CO ₂ | |
| CMMS ² | 85% | |
| AspDA ³ | 84% | |
| AspMA ⁴ | 78% | |
| ISA ⁵ | 76% | |
| BADA ⁶ | 73% | |
| citric acid | 82% | |
| NTA ⁷ | 73% | |
| glycine | 59% | |
| EDTA ⁸ | 0% | |

²CMMS = Carboxymethylmercaptosuccinic acid

Claims

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1. A hard-surface cleaning composition containing an organic solvent having a boiling point equal to or above 90°C and a chelating agent selected from a compound of the formula:

X-CH₂-CH-m-R

35 in which

m is NR' or sulfur;

X is SO₃H or COOH;

Y is hydrogen, SO₃H or COOH;

R and R' are, independently, hydrogen, -CH(Z)CH₂(Z'), -CH(Z)CH(Z') (Z") or -CH₂COOH; and

- Z, Z' and Z" are, independently, hydrogen, OH, SO₃H or COOH; or a sodium, potassium, ammonium or a substituted ammonium salt thereof, in an amount sufficient to clean a hard surface.
- 2. A composition of Claim 1 in which X and Y are both COOH or a sodium, potassium or ammonium or a substituted ammonium salt, thereof; and Z, Z', and Z" are, independently, hydrogen or COOH or a sodium, potassium, ammonium or substituted ammonium salt thereof.
 - 3. A composition in accordance with Claim 1 wherein the organic solvent is present in the amount of from 1% to 20% of the total composition and the chelating agent is present in the amount of from 1% to 30% of the total composition.
 - 4. A composition in accordance with Claim 3 wherein the weight ratio of organic solvent to chelating agent is from 2:
- 5. A composition in accordance with Claim 3 wherein the weight ratio of organic solvent to chelating agent is from 1: 1 to 2:1.
 - 6. A composition in accordance with Claim 1 wherein the organic solvent is selected from the group of benzyl alcohol,

³AspDA = Aspartic acid N,N-diacetic acid

⁴AspMA = Aspartic acid N-monoacetic acid

⁵ISA = Iminodisuccinic acid

⁶BADA = β-alanine-N.N-diacetic acid

⁷NTA = Nitrilotriacetic acid, comparative compound

⁸EDTA = Ethylenediaminetetraacetic acid, comparative compound

glycol ethers, and diols having 6 to 16 carbon atoms in their molecular structure.

- 7. A composition in accordance with Claim 5 wherein the organic solvent is selected from the group of butoxypropanol, butoxypropoxypropanol, 2-(2-butoxyethoxy-ethanol, benzyl alcohol, 2,2,4,-trimethyl-1,3-pentanediol.
- **8.** A composition in accordance with Claim 1 wherein the chelating agent is selected from aspartic acid N,N-diacetic acid; aspartic N-monoacetic acid; iminodisuccinic acid; carboxymethylmercaptosuccinic acid; β-alanine-N,N-diacetic acid; or cysteic acid N,N-diacetic acid.
- 9. A composition in accordance with Claim 1 which in addition contains an abrasive.

Patentansprüche

15 1. Zusammensetzung zur Reinigung harter Oberflächen enthaltend ein organisches Lösungsmittel mit einem Siedepunkt von 90°C oder mehr und einen Chelatbildner ausgewählt unter einer Verbindung mit der Formel:

25 in der

m NR' oder Schwefel ist; x SO₃H oder COOH ist;

Y Wasserstoff, SO₃H oder COOH ist;

 $\begin{tabular}{lll} 30 & R und R' & unabhängig von einander Wasserstoff, -CH(Z)CH_2(Z'), -CH(Z)CH(Z') (Z'') oder -CH_2COOH sind; \\ \end{tabular}$

und

Z, Z' und Z" unabhängig voneinander Wasserstoff, OH, SO₃H oder COOH sind; oder ein Natrium-, Kalium-,

Ammonium- oder substituiertes Ammoniumsalz davon, in einer zur Reinigung harter Oberflächen

ausreichenden Menge.

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- 2. Zusammensetzung nach Anspruch 1, in der X und Y beide COOH oder ein Natrium-, Kalium- oder Ammoniumoder ein substituiertes Ammoniumsalz davon sind; und Z, Z' und Z" unabhängig voneinander Wasserstoff oder COOH oder ein Natrium-, Kalium-, Ammonium- oder substituiertes Ammoniumsalz davon sind.
- 3. Zusammensetzung nach Anspruch 1, in der das organische Lösungsmittel in einer Menge von 1 bis 20 % der Gesamtzusammensetzung vorhanden ist und der Chelatbildner in einer Menge von 1 bis 30 % der Gesamtzusammensetzung vorhanden ist.
- **4.** Zusammensetzung nach Anspruch 3, in der das Gewichtsverhältnis von organischem Lösungsmittel zu Chelatbildner von 2:3 bis 2:1 beträgt.
 - **5.** Zusammensetzung nach Anspruch 3, in der das Gewichtsverhältnis von organischem Lösungsmittel zu Chelatbildner von 1:1 bis 2:1 beträgt.
- 50 **6.** Zusammensetzung nach Anspruch 1, in der das organische Lösungsmittel aus der Gruppe von Benzylalkohol, Glycolethern, und Diolen mit 6 bis 16 Kohlenstoffatomen in ihrer Molekülstruktur ausgewählt ist.
 - 7. Zusammensetzung nach Anspruch 5, in der das organische Lösungsmittel aus der Gruppe von Butoxypropanol, Butoxypropoxypropanol, 2-(2-Butoxyethoxy)ethanol, Benzylalkohol und 2,2,4,-Trimethyl-1,3-pentandiol ausgewählt ist.
 - **8.** Zusammensetzung nach Anspruch 1, in der der Chelatbildner unter Asparaginsäure-N,N-diessigsäure; Asparagin-N-monoessigsäure, Iminodibernsteinsäure, Carboxymethylmercaptobernsteinsäure, β-Alanin-N,N-diessigsäure

oder Cysteinsäure-N,N-diessigsäure ausgewählt ist.

9. Zusammensetzung nach Anspruch 1, welche zusätzlich ein Scheuermittel enthält.

Revendications

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1. Composition de nettoyage pour surfaces dures contenant un solvant organique ayant un point d'ébullition égal à ou au-dessus de 90°C et un agent de chélation sélectionné parmi un composé de la formule :

X-CH₂-CH-m-R

dans laquelle

m est NR' ou soufre;
 X est SO₃H ou COOH;
 Y est hydrogène, SO₃H ou COOH;
 R et R' sont, indépendamment, hydrogène,

-CH(Z)CH₂(Z'), -CH(Z)CH(Z') (Z") ou -CH₂COOH; et

Z, Z' et Z" sont indépendamment, hydrogène, OH, SO₃H ou COOH; ou bien un sel de sodium, de potassium, d'ammonium ou d'ammonium substitué de ceux-ci, en une quantité suffisante pour nettoyer une surface dure.

- 2. Composition de la revendication 1 dans laquelle X et Y sont tous deux COOH ou un sel de sodium, potassium, ammonium ou ammonium substitué de celui-ci ; et Z, Z', et Z" sont, indépendamment, hydrogène ou COOH ou un sel de sodium, potassium, ammonium ou ammonium substitué de ceux-ci.
- 3. Composition selon la revendication 1 où le solvant organique est présent à la quantité de 1% à 20% de la composition totale et l'agent de chélation est présent à la quantité de 1% à 30% de la composition totale.
 - **4.** Composition selon la revendication 3 où le rapport pondéral du solvant organique à l'agent de chélation est de 2 : 3 à 2 :1.
- 5. Composition selon la revendication 3 où le rapport pondéral du solvant organique à l'agent de chélation est de 1 : 1 à 2 :1.
 - **6.** Composition selon la revendication 1 où le solvant organique est sélectionné dans le groupe consistant en alcool benzylique, glycol éthers, et diols ayant 6 à 16 atomes de carbone dans leur structure moléculaire.
 - 7. Composition selon la revendication 5 où le solvant organique est sélectionné dans le groupe consistant en butoxypropanol, butoxypropanol, 2-(2-butoxyéthoxy-éthanol), alcool benzylique, 2,2,4,-triméthyl-1,3-pentanediol.
- **8.** Composition selon la revendication 1 où l'agent de chélation est sélectionné parmi acide aspartique acide N,N-diacétique; acide aspartique N-monoacétique; acide iminodisuccinique; acide carboxyméthylmercaptosuccinique; acide β-alanine-N,N-diacétique; ou acide cystéique acide N,N-diacétique.
 - 9. Composition selon la revendication 1 qui contient de plus un abrasif.

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