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(54) Titre : COMPOSITION DE NETTOYAGE LIQUIDE DESTINEE A UNE SURFACE DURE  
 (54) Title: LIQUID HARD SURFACE CLEANING COMPOSITION

(57) **Abrégé/Abstract:**

The present invention provides a method for removing soil or stains from a hard surface, the method comprising the steps in sequence of treating the surface with a malonic acid derivative, allowing the soil or stain to deposit and cleaning the surface to remove the soil or stains. The invention further provides compositions and uses for said method. In this connection, this method and composition provides an improved next time cleaning benefit.



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(54) Title: LIQUID HARD SURFACE CLEANING COMPOSITION

(57) Abstract: The present invention provides a method for removing soil or stains from a hard surface, the method comprising the steps in sequence of treating the surface with a malonic acid derivative, allowing the soil or stain to deposit and cleaning the surface to remove the soil or stains. The invention further provides compositions and uses for said method. In this connection, this method and composition provides an improved next time cleaning benefit.

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## LIQUID HARD SURFACE CLEANING COMPOSITION

**Field of the invention**

The present invention relates to methods for cleaning hard  
5 surfaces, and to compositions suitable for that purpose,  
involving the application of malonic acid to such surfaces.

**Background of the invention**

Household surfaces are normally cleaned using compositions  
10 which contain one or more ingredients which assist in  
removal of fatty/oily/greasy soil and/or any visible  
staining such as from associated solid debris. Such  
compositions may be applied as diluted or concentrated  
aqueous solutions e.g. with a cloth, wipe or other  
15 implement or as a spray, such as a trigger spray dispenser  
or other aerosol applicator, optionally followed by  
rinsing.

Such compositions may be either acidic or alkaline. Acidic  
20 compositions often contain carboxylic acids which may be  
mono-, di- or polycarboxylic acids, such as citric acid,  
sorbic acid, acetic acid, formic acid, maleic acid, adipic  
acid, lactic acid, malic acid and glycolic acid. Unless the  
type of soil specifically requires the presence of a strong  
25 mineral acid, such acids are generally not recommended  
because of the damage they may cause on delicate and acid-  
sensitive surfaces. Acidic cleaners are generally used for  
removing acid sensitive soil, such as limescale. For  
removal of fatty soil alkaline compositions are generally  
30 preferred.

The use of malonic acid in acidic hard surface cleaners is known in the art. In UK 2,392,167 a composition is described comprising malonic acid. The composition as described is formulated as an acidic composition and intended for lavatory cleaning.

In US 5,294,364 and US 5,039,441 another type of acidic hard surface cleaner is described, for the cleaning of surface items that are acid resistant or are of zirconium white enamel. The compositions exclude malonic acid as it may be too strong for delicate hard surfaces.

In WO00/32737 and WO00/27983 a cleaning process is described, using acids with  $pK_a > 3.5$ , to prevent damage to enamel surfaces. Malonic acid is an optional ingredient in the composition and is described as chelating agent. Although the  $pK_a$  of malonic acid is 2.8, no reference is made to that fact.

In WO94/016045 machine dish washing compositions are disclosed comprising bicarboxylic acids, such as malonic acid, for corrosion inhibition.

Whether for acidic or alkaline cleaning conditions it would be advantageous to have a material applied to the surface to be cleaned which would assist removal of soil and/or staining during subsequent cleaning.

#### Summary of the invention

It has been found that after a surface has been treated with malonic acid, certain malonic acid derivatives or their salts, soils or stains subsequently deposited on that

surface are more easily removed than without the previous treatment. This effect is generally referred to as "next time cleaning benefit".

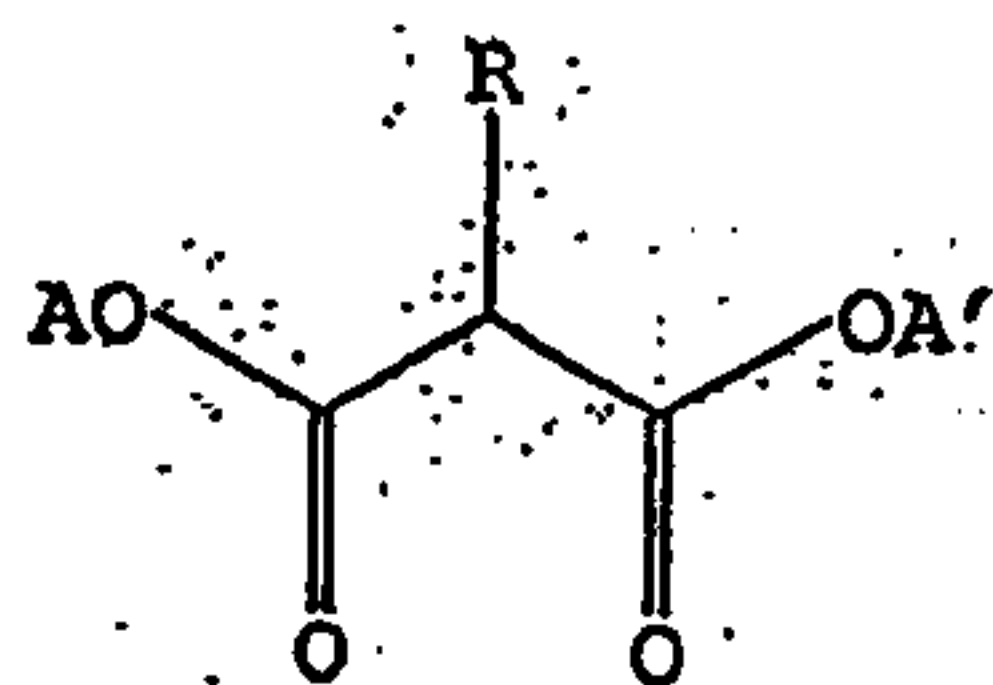
5 Thus, it is an object of the present invention to provide a method for removing soil or stains from hard surfaces involving treating the surface with malonic acid, certain malonic acid derivatives or their salts.

10 It is a further object of the invention to provide hard surface cleaning compositions comprising malonic acid, certain malonic acid derivatives or their salts.

15 All percentages mentioned herein are by weight calculated on the total composition unless specified otherwise.

Accordingly, the present invention provides a method for removing soil or stains from a hard surface, the method  
20 comprising the steps in sequence of:

- (a) treating the surface with a compound according to the general formula 1:



Formula 1

25

wherein A and A' are independently selected from -H, alkali and alkaline earth metal ions, quaternary ammonium ions, trivalent metal ions, and organic

cations, and wherein R is selected from -H or C<sub>1</sub>-C<sub>4</sub> alkyl or a combination of such compounds;

- (b) allowing the soil or stain to deposit on the surface; and
- 5 (c) cleaning the surface to remove the soil or stains.

The present invention further provides a liquid hard surface cleaning composition comprising:

- 10 (a) 0.01 to 10% by weight of a compound according to the general formula 1 above; and
- (b) 0.01 to 50% by weight of the total composition of surfactant material, wherein the surfactant comprises anionic and nonionic surfactant in a
- 15 ratio between 20:1 and 1:10.

The expressions "soil" and "stain" as used herein generally comprise all kinds of soils and stains generally encountered in the household, either of organic or

20 inorganic origin, whether visible or invisible to the naked eye, including soiling solid debris and/or with bacteria or other pathogens. Specifically the method and compositions according to the invention may be used to treat fatty or greasy soil and stains, more specifically those caused by

25 natural fat or oil.

Whilst not being bound by any particular theory or explanation, we believe that malonic acid exerts its effect by depositing on the surface and exerting an influence on

30 soil or stains subsequently depositing on the surface such that such soil or stains are prevented from getting strongly attached to that surface.

Therefore in a preferred embodiment of the invention a compound according to formula 1 (hereinafter briefly referred to as "malonic acid") is applied to the surface as  
5 a solution, preferably an aqueous solution, which is thereafter left to dry on the surface.

Step (c) of the method is advantageously effected using a hard surface cleaning composition comprising malonic acid  
10 again so that soil or stain is removed and new malonic acid is applied, effectively constituting step (a) of a subsequent process according to the first aspect of the invention. Step (c) is optionally followed by a rinsing step, preferably with water.

15

Malonic acid proper may be derived from sugar beet and can therefore be classified as a natural material, something that is increasingly important to present day consumers.

20 As used herein the term "malonic acid" is meant to include malonic acid derivatives and salts or mixtures of these compounds as defined above by formula 1. Preferably R is selected from -H or -CH<sub>3</sub> or -CH<sub>2</sub>CH<sub>3</sub>.

25 The present invention may also deliver other benefits such as improved surface feel (e.g. smoothness) during and/or after cleaning, olfactory benefits (e.g. reduction in rancid odour) before cleaning, less surface corrosion and less noise during cleaning. Further aspects of the present  
30 invention comprise use of malonic acid or compositions containing malonic acid, for obtaining one or more of these other benefits in a hard surface cleaning operation and/or

use of malonic acid in the manufacture of products for delivering one or more such other benefits. Furthermore, malonic acid does not discolour, which is a particular advantage for a cleaning method according to the invention.

5

Methods, uses, compositions and articles according to the present invention are useful for treating any household surface such as found in kitchens and bathrooms, including cooker tops, extractor fans, tiles, floors, baths, toilets, wash basins, showers, dishwashers, taps, sinks, work surfaces. These surfaces may, for example, be made of plastics, glass, enamel, ceramic, wood (painted, lacquered or otherwise) or metal (eg. stainless steel or chrome).

#### 15 Form of utilisation

Malonic acid is preferably applied to the surface in the form of a composition containing malonic acid or by means of a wipe impregnated with malonic acid or with a composition containing malonic acid.

20

#### Hard Surface Treatment Compositions

Malonic acid can be employed according to the present invention in any suitable composition.

25 The composition must be suitable for depositing malonic acid material onto a hard surface. Malonic acid may be present in the composition in any suitable form, for example in the form of a solution or dispersion. Except where expressed or implied to the contrary, the component  
30 may also be in solid form, to be wetted upon use. However, in preferred embodiments they are liquids. The term "liquid" includes solutions, dispersions, emulsions, gels,

pastes and the like. In liquid form, they preferably have a pH above 6.

Suitable liquid compositions include solutions, dispersions  
5 or emulsions in a liquid carrier, which may be an organic solvent or water or a combination thereof. Preferably the solvent is predominantly (i.e. 50% or more) water. The compositions may be used only to deposit malonic acid, or they may have additional functions such as cleaning. The  
10 total malonic acid compound of any such composition, is preferably at least 0.01%, more preferably at least 0.1%, and not more than 10%, preferably not more than 5%, more preferably not more than 2% of that composition and suitably not more than 1% of that composition.

15

The composition may be applied by any suitable means in diluted or concentrated form. For example, it can be poured or sprayed onto the surface from a container or from an aerosol can or from a spray gun applicator. Alternatively  
20 it may be applied using a cloth, wipe or other implement which has been wetted with the composition.

Compositions for use in the present invention may include ingredients well known for use in hard surface cleaning  
25 compositions.

The hard surface cleaning compositions of the invention comprise at least one surfactant and optional other hard surface cleaning components.

30

It is especially preferred that the composition is a "liquid" having a viscosity of at least 100 mPa's as

measured at a shear rate of  $21\text{s}^{-1}$  at room temperature, but preferably no more than 5,000 mPa's. This viscous liquid composition may be in the form of a viscous liquid per se, or a gel, foam, mousse or paste. The viscosity may be due to one or more other components in the system, for example an "external polymeric thickener", which may be a synthetic polymer, e.g. of the polycarboxylate type such as Carbopol™, or a natural polysaccharide gum such as xanthan gum or guar gum. Alternatively, an "internal structuring" system may be used, employing one or more surfactants and optionally electrolyte, to create an ordered or liquid crystalline phase within the composition. These various techniques for increasing viscosity are all very well known to those skilled in the art.

15

Foams and mousses are normally supplied from a dispenser which gassifies or aerates the product dispensed therefrom.

#### pH

20 In the liquid hard surface treatment compositions according to the invention the pH of the composition is preferably above 6, more preferably at least 6.5, and not more than 14, preferably not more than 13, more preferably not more than 12. In alkaline compositions, the pH is preferably at least 7.

The pH of the solution may be adjusted with organic or inorganic acids or bases. Preferred inorganic bases are preferably alkali or alkaline earth hydroxides, ammonia, carbonates or bicarbonates. The alkali metal preferably being Sodium ( $\text{Na}^+$ ) or Potassium ( $\text{K}^+$ ) or the alkaline earth metal preferably being Calcium ( $\text{Ca}^{2+}$ ) or Magnesium ( $\text{Mg}^{2+}$ ).

30

The organic bases are preferably amine oxides. Inorganic acids may include hydrochloric acid, sulphuric acid or phosphoric acid, and organic acids may include acetic acid, citric acid or formic acid as well as dicarboxylic acid mixtures such as Radimix (trade mark, Radici Group) and Sokalan DCS (trade mark, BASF).

### Surfactants

The compositions according to, or for use in, the invention comprise surfactants (detergent actives) which are generally chosen from both anionic and nonionic detergent actives. The composition may further comprise cationic, amphoteric and zwitterionic surfactants. In surfactant-containing compositions of the present invention, the total amount of surfactant to be employed will generally be from 0.01 to 50%. Preferably, the amount is at least 0.1%, more preferably at least 0.5%, still more preferably at least 1%. The maximum amount is usually 30% or less, preferably not more than 20%, or even at or below 10%.

20

Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid mono-esters and sulphonic acids which have in the molecular structure a branched or straight chain alkyl group containing from 6 to 22 carbon atoms in the alkyl part.

Examples of such anionic surfactants are water soluble salts of:

- (primary) long chain (e.g. 6-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols

30

produced by reducing the glycerides of tallow or coconut oil;

- alkyl benzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
  - 5 - secondary alkanesulphonates;
- and mixtures thereof.

Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the  
10 ethers of fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- sulphates of ethoxylated aliphatic alcohols containing 1-12 ethyleneoxy groups;
- 15 - alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali,  
20 and mixtures thereof.

The preferred water-soluble synthetic anionic surfactants are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts  
25 of alkyl-benzenesulphonates and mixtures with olefinsulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates.

The most preferred anionic surfactants are alkyl-aromatic  
30 sulphonates such as alkylbenzenesulphonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium

salts of alkylbenzenesulphonates or of alkyl-toluene-,  
-xylene- or -phenolsulphonates, alkyl-naphthalene-  
sulphonates, ammonium diamyl-naphthalene-sulphonate, and  
sodium dinonyl-naphthalene- sulphonate.

5

If synthetic anionic surfactant is to be employed the amount  
present in the compositions of the invention will generally  
be at least 0.1%, preferably at least 0.5%, more preferably  
at least 1.0%, but not more than 20%, preferably at most  
10 10%, more preferably at most 8%.

A suitable class of nonionic surfactants can be broadly  
described as compounds produced by the condensation of  
simple alkylene oxides, which are hydrophilic in nature,  
15 with an aliphatic or alkyl-aromatic hydrophobic compound  
having a reactive hydrogen atom. The length of the  
hydrophilic or polyoxyalkylene chain which is attached to  
any particular hydrophobic group can be readily adjusted to  
yield a compound having the desired balance between  
20 hydrophilic and hydrophobic elements. This enables the  
choice of nonionic surfactants with the right HLB.

Particular examples include:

- the condensation products of aliphatic alcohols having  
from 8 to 22 carbon atoms in either straight or  
25 branched chain configuration with ethylene oxide, such  
as a coconut alcohol/ethylene oxide condensates having  
from 2 to 15 moles of ethylene oxide per mole of  
coconut alcohol;
- condensates of alkylphenols having C6-C15 alkyl groups  
30 with 5 to 25 moles of ethylene oxide per mole of  
alkylphenol;

- condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from  
5 5,000 to 11,000.

Other classes of nonionic surfactants are:

- alkyl polyglycosides, which are condensation products of long chain aliphatic alcohols and saccharides;
- 10 - tertiary amine oxides of structure  $RRRN_0$ , where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure  $RRRP_0$ , where  
15 one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulphoxides of structure  $RRS_0$  where one R is  
20 an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- fatty acid alkylolamides, such as the ethanol amides;
- alkylene oxide condensates of fatty acid  
25 alkylolamides;
- alkyl mercaptans.

The amount of nonionic surfactant to be employed in the cleaning composition of the invention will preferably be at  
30 least 0.1%, more preferably at least 0.5%, most preferably at least 1%. The amount is suitably at most 15%, preferably not more than 10% and most preferably not more than 7%.

The compositions may contain amounts of both anionic and nonionic surfactants which are chosen, bearing in mind the level of electrolyte if present, so as to provide a structured liquid detergent composition, i.e. one which is 'self-thickened'. Thus, in spite of the presence of organic solvent, thickened liquid cleaning compositions can be made without the need to employ any additional thickening agent and which nevertheless have a long shelf life over a wide temperature range.

The weight ratio of anionic surfactant to nonionic surfactant may vary, taking the above considerations in mind, and will depend on their nature, but is in the range of from 20:1 to 1:10, preferably from 15:1 to 1:5, and ideally above 10:1 to 1:2.

According to an embodiment illustrating any aspect of the invention, the compositions may comprise from 0.1% to 7% by weight of malonic acid, from 0 to 20%, preferably from 0.5% to 10% by weight of water-soluble, synthetic anionic sulphate or sulphonate surfactant salt containing an alkyl radical having from 8 to 22 carbon atoms in the molecule, and from 0.5 to 7% by weight of ethoxylated nonionic surfactant derived from the condensation of an aliphatic alcohol having from 8 to 22 carbon atoms in the molecule with ethylene oxide, such that the condensate has from 2 to 15 moles of ethylene oxide per mole of aliphatic alcohol, the balance being other optional ingredients and water.

It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in the compositions according to the invention.

5 Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-  
10 sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate.

Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small  
15 aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium bromide.

A specific group of surfactants are the tertiary amines obtained by condensation of ethylene and/or propylene oxide  
20 with long chain aliphatic amines. The compounds behave like nonionic surfactants in alkaline medium and like cationic surfactants in acid medium.

Examples of suitable zwitterionic surfactants can be found  
25 among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance betaine and betaine derivatives such as alkyl  
30 betaine, in particular C<sub>12</sub>-C<sub>16</sub> alkyl betaine, 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine,

3- (cetylmethyl-phosphonium) -propane-1-sulphonate betaine and N,N-dimethyl-N-dodecyl-glycine. Other well known betaines are the alkylamidopropyl betaines e.g. those wherein the alkylamido group is derived from coconut oil fatty acids.

5

Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks: "Surface Active Agents" Vol.1, by Schwartz & Perry, Interscience 1949; "Surface Active Agents" Vol.2 by Schwartz, Perry & Berch, Interscience 1958; the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company; "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

15

The compositions according to the present invention may include abrasives. However, these are generally not preferred as abrasives tend to damage or remove the thin layer of malonic acid being deposited on the surface. The compositions may contain other ingredients which aid in their cleaning performance. For example, they may contain detergent builders such as nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates (especially ortho-, pyro- or polyphosphates or mixtures thereof), zeolites and mixtures thereof in an amount of up to 25%. Some of these builders can additionally function as abrasives if present in an amount in excess of their solubility in water. If present, the builder preferably will form at least 0.1% of the composition.

30

Metal ion sequestrants such as ethylenediaminetetraacetate or diethylenetriaminepentaacetate, amino-polyphosphonates (DEQUEST<sup>[TM]</sup>) and phosphates and a wide variety of poly-functional organic acids and salts, can also optionally be  
5 employed provided they are compatible with malonic acid.

A further optional ingredient for compositions according to the invention is a suds regulating material, which can be employed in compositions which have a tendency to produce  
10 excessive suds in use. Examples thereof are fatty acids or their salts (soap), isoparafins, silicone oils and combinations thereof.

Soaps are salts of fatty acids and include alkali metal  
15 soaps such as the sodium, potassium and ammonium salts of fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 10 to about 20 carbon atoms. Particularly useful are the sodium and potassium and mono-, di- and triethanolamine salts of the mixtures of  
20 fatty acids derived from palm oil, coconut oil and ground nut oil. When employed, the amount of fatty acid or soap can form at least 0.005%, preferably 0.1% to 2% by weight of the composition. Commercially available fatty acid mixtures such as Prifac 7901<sup>[TM]</sup> have been found to be suitable for this  
25 purpose.

Where a hydrocarbon co-solvent is present at a sufficiently high level this may itself provide some or all of the required antifoaming activity.

30

Compositions according to the invention may also contain, in addition to the ingredients already mentioned, various other

optional ingredients such as colourants, whiteners, optical brighteners, soil suspending agents, deterative enzymes, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), gel-control  
5 agents, further freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), hydrotropes and perfumes.

#### Polymers

10 The composition of the inventions may optionally comprise polymers, in particular polymers that aid the binding of Malonic acid to the surface and thus providing additional rinse resistance. Preferred polymers are nonionic and anionic polymers.

15

#### Polymer to malonic acid ratio

For optimal benefits, the polymer/malonic acid ratio (by weight) should be in the range 1:1 to 20:1, preferably in the range 2:1 to 15:1, most preferably in the range 3:1 to  
20 10:1.

Preferred polymers are those polymers having an average molecular weight above 4,000 Dalton. More preferably the molecular weight is at least 10,000 D, even more preferably  
25 above 100,000 D or even above 1,000,000 D. The polymers normally have a molecular weight below 5,000,000 Dalton, preferably below 4,000,000 D.

Suitable polymers are either water-soluble or water-  
30 dispersible, preferably water-soluble.

Non-ionic polymer

The non-ionic polymer may be chosen from cellulose-based nonionic polymers such as celluloses, alkylcelluloses, hydroxyalkylcelluloses, cellulose ethers, cellulose esters  
5 and cellulose amides, such as methylcellulose, ethylcellulose, hydroxymethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose. Other polysaccharide polymers, such as starches and modified starches, and dextrans, such as maltodextrin, are  
10 also suitable.

Furthermore, the polymer may be chosen from fully synthetic polymers such as polyvinyl alcohols, polyvinylpyrrolidones, polyalkylene glycols such as polyethylene glycol,  
15 polyalkylene oxides, polyamides, polyacrylamides, polyvinylethers such as polymethylvinylether, polyvinyl acetates, and copolymers thereof.

Polyacrylic acids, polymethacrylic acids and their  
20 homologues, and other polycarboxylic acids may also be used in compositions where the polymers behave as nonionic polymers. Such compositions are typically acidic compositions with pH values below about 4.

25 Most preferably the non-ionic polymer is selected from polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and combinations thereof.

The compositions preferably comprise at least 0.1%, more  
30 preferably at least 0.5% by weight non-ionic polymer and at most 20%, preferably at most 10%, more preferably at most 5%.

The PVP includes substituted and unsubstituted vinyl pyrrolidone polymerization products

Anionic polymer

5 Preferred anionic polymers are water soluble anionic polymers. Suitable polymers are mainly synthetic, but natural or nature-derived polymers may also be used. Suitable polymers include polyacrylic acids and polymethacrylic acids and their homologues, other  
10 polycarboxylic acids, polyaminoacids or peptides, polyanhydrides, polystyrene sulphonic acids, polyvinylsulfonic acids, and their copolymers and their copolymers with nonionic monomers and polymers. Natural gums, such as xanthan, locust bean and carrageenans, and  
15 cellulose derivatives, such as carboxymethylcellulose, may also be suitable.

If anionic polymers are present, the compositions preferably comprise at least 0.1%, more preferably at least  
20 0.5% by weight anionic polymer and at most 20%, preferably at most 10%, more preferably at most 5%.

Liquid Dispensers

25 Liquid compositions may be stored in and dispensed by any suitable means, but spray applicators are particularly preferred. Pump dispensers (whether spray or non-spray pumps) and pouring applicators (bottles etc) are also possible. Thus, the present invention provides a container  
30 for a liquid hard surface cleaner, the container comprising a reservoir containing malonic acid solution or a liquid composition having a pH above 6 and comprising malonic

acid, and spray dispenser for dispensing the composition in the form of a spray. The spray dispenser is preferably a trigger spray but may be any mechanical means for ejecting the liquid in spray or aerosol form.

5

#### Wipes

Wipes can be impregnated with neat malonic acid or with a composition containing malonic acid. The material may be impregnated dry, or more preferably in wet form (i.e. as a  
10 thin or a viscous liquid). Suitable wipes include woven or nonwoven cloths, natural or synthetic sponges or spongy sheets, "squeegee" materials and the like.

The present invention provides a wipe impregnated with malonic acid or a composition containing malonic acid, such  
15 as any composition as defined or described elsewhere in this specification.

#### **Examples**

In the examples all parts and percentages are by weight  
20 unless otherwise indicated.

As test surface, a 5 by 5 cm area of standard stainless steel tiles are used. The tiles are degreased prior to soiling using powdered calcite applied with a damp cloth.

25

Pretreatment is done by applying an evenly spread layer of 0.08 ml of the pretreatment composition to the target area of the tile.

30 The soil material used in the examples is Castor oil (ex John L. Seaton, Ref 9725). The castor oil is used as received.

Castor oil is applied to the target area as an even film. The tiles are then baked in an oven at 100°C for one hour. The tile is then weighed to ensure that the target amount of 0.04 +/- 0.004g) of oil is on the tile.

The cleaning is carried out using a Martindale (trade mark, SDL International) abrasion instrument. The tile to be cleaned is placed in the "holder" for the Martindale machine, and submerged under 20g of cleaning fluid. A Ballerina cloth is fastened to the cleaning head of the Martindale machine, and this is rubbed across the surface of the tile using a pre-set pattern covering the whole tile. In the examples below the pattern is repeated three times for each application.

After the Martindale has cleaned the tiles for 3 cycles, the tiles are rinsed under running water to remove excess cleaning product. The tiles are then left to dry in air

The castor oil stain removal is measured by re-weighing the dried tiles and calculating the percentage castor oil removed as:

$$\text{castor oil removed} = \frac{\text{castor oil applied} - \text{castor oil after cleaning}}{\text{castor oil applied}} \cdot 100\%$$

**Example 1 and comparative example A.**

As cleaning solution the compositions of Table 1 are used.

In example 1 tiles are first treated with "Composition 1", then a castor oil stain is applied according to the method above and finally the tiles are cleaned with "Composition A".

In comparative example A, tiles are first treated with "Composition A", then a castor oil stain is applied according to the method above and finally the tiles are cleaned with "Composition A".

Table 1: Compositions

Composition 1	Composition A
4% Neodol 91,8 <sup>1)</sup>	4% Neodol 91,8
0.5% Malonic acid	-
Balance water	Balance water
pH=10, adjusted with NaOH	pH=10, adjusted with NaOH

1) Neodol is a trademark of Shell Chemicals.

10 By first treating the tiles with a malonic acid comprising composition in example 1 and the same composition without malonic acid in comparative example A, thereafter applying the stain and finally cleaning both sets of tiles with a composition without malonic acid, the example gives a fair  
15 comparison between stains on a surface treated with malonic acid and a surface that is not treated with malonic acid.

Table 2: Results at pH=10

Example	Castor oil removed (%)
1	76.4
A	10.5

20 The results of this cleaning clearly show that the treatment of a surface with a composition comprising malonic acid prior to the stain deposition has a significant effect on the cleaning of the surface.

**Examples 2 and 3 and comparative example B.**

As cleaning solution the compositions of Table 3 are used.

In example 2 tiles are first treated with "Composition 2",  
5 then a castor oil stain is applied according to the method  
above and finally the tiles are cleaned with  
"Composition B".

In example 3 tiles are first treated with "Composition 3",  
10 then a castor oil stain is applied according to the method  
above and finally the tiles are cleaned with  
"Composition B".

In comparative example B, tiles are first treated with  
15 "Composition B", then a castor oil stain is applied  
according to the method above and finally the tiles are  
cleaned with "Composition B".

Table 3: Compositions

Composition 2	Composition 3	Composition B
4% Neodol 91,8 <sup>1)</sup>	4% Neodol 91,8	4% Neodol 91,8
0.5% Malonic acid	0.5% Ethylmalonic acid	-
Balance water	Balance water	Balance water
pH=4, adjusted with citric acid	pH=4, adjusted with citric acid	pH=4, adjusted with citric acid

20 1) Neodol is a trademark of Shell Chemicals.

By first treating the tiles with a malonic acid (as defined  
herein) comprising composition in example 2 and 3 and the  
same composition without malonic acid in comparative  
25 example B, thereafter applying the stain and finally

cleaning both sets of tiles with a composition without malonic acid, the example gives a fair comparison between stains on a surface treated with malonic acid and a surface that is not treated with malonic acid.

5

Table 4: Results at pH=4

Example	Castor oil removed (%)
2	98.5%
3	55.3%
B	15.3%

The results of this cleaning clearly show that the treatment of a surface with a composition comprising malonic acid prior to the stain deposition has a significant effect on the cleaning of the surface.

#### Examples 4, 5 and 6.

These examples show the effect of an intermediate rinse of the pretreated tile, for compositions with and without polymer. Methods for preparing the tiles and pretreatment are as indicated above. Compositions used are shown in Table 4.

20 Table 4: Compositions

	Composition 4	Composition 5	Composition 6
Neodol 91,8 <sup>1)</sup>	4%w	4%w	4%w
Malonic acid	0.5%w	0.5%w	0.5%w
Glascol E15 <sup>2)</sup>		0.5%w	1.0%w

1) Neodol is a trademark of Shell Chemicals.

2) Glascol E15 is 2.5MD MW polyacrylic acid ex Ciba.

The pH in all compositions is adjusted with citric acid to pH=4. And water is added up to 100%.

In the examples clean, degreased tiles are first pretreated with the one of the compositions of Table 4. The tiles are left to dry for 15 minutes and rinsed with 300 ml of water, poured gently from a beaker. In example 4, 5 and 6, compositions 4, 5 and 6 are used respectively.

10 After pretreating the tiles and rinsing them, Castor oil is applied and the tiles are cleaned according to the methods above. The results of the cleaning (i.e. the Castor oil removal) is given in Table 5

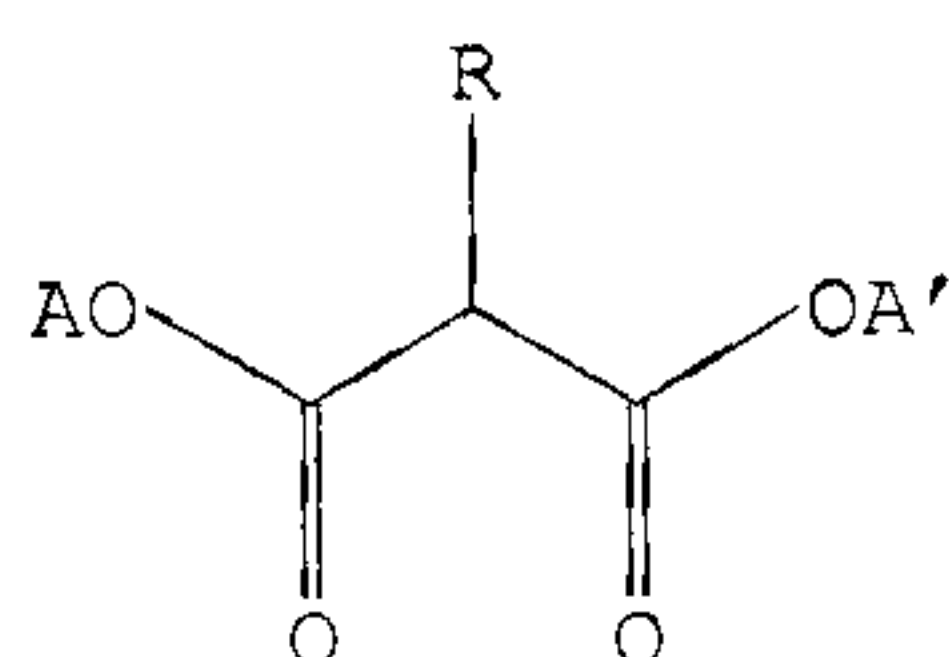
15 Table 5: Results

Example	% Castor oil removed
4	4.18%
5	12.85%
6	16.28%

As can be seen, although the general cleaning of the surface pretreated with Malonic acid is not nearly as good as without rinsing, improved results are obtained by the  
20 addition of a polymer.

**Claims**

- 1 A liquid hard surface cleaner composition comprising:  
(a) 0.01 to 10% by weight of malonic acid, malonic acid derivatives and their salts is of the formula:



- wherein A and A' are independently selected from -H, alkali and alkaline earth metal ions, quaternary ammonium ions, trivalent metal ions, and organic cations, and wherein R is selected from -H or C<sub>1</sub>-C<sub>4</sub> alkyl or a combination of these compounds;
- (b) 0.01 to 50% by weight of the total composition of surfactant material, wherein the surfactant comprises anionic and nonionic surfactant in a ratio between 20:1 and 1:10 by weight; and wherein the composition further comprises a polymer, wherein the polymer/malonic acid ratio is in the range of 1:1 to 20:1 by weight.
- 2 A liquid hard surface cleaner composition according to claim 1 having a pH of above 6.
- 3 A liquid hard surface cleaner composition according to claims 1 or 2, wherein the nonionic surfactant is present in a concentration of less than 7% by weight.

- 4 A liquid hard surface cleaner composition according to any one of claims 1 to 3, wherein R is -H , -CH<sub>3</sub> or -CH<sub>2</sub>CH<sub>3</sub>.
- 5 A liquid hard surface cleaner composition according to any one of claims 1 to 4, wherein A and A' are independently selected from -H, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> or Mg<sup>2+</sup>.
- 6 A method for removing soil or stains from a hard surface, the method comprising the steps in sequence of:
- (a) treating the surface with the composition of any one of claims 1-5;
  - (a) allowing the soil or stain to deposit; and
  - (b) cleaning the surface to remove the soil or stains.
- 7 A method according to claim 6 wherein the soil or stain is a fatty soil or stain.
- 8 A container for a liquid hard surface cleaner, the container comprising a reservoir containing the cleaning composition according to any one of claims 1 to 5, and a spray dispenser for dispensing said composition in the form of a spray.
- 9 A container according to claim 8, wherein the spray dispenser is a trigger spray.
- 10 A wipe impregnated with the liquid hard surface cleaner of any one of claims 1 to 5.