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(54) HARD SURFACE CLEANING COMPOSITION

REINIGUNGSZUSAMMENSETZUNG FÜR HARTE OBERFLÄCHEN

COMPOSITION DE NETTOYAGE DE SURFACES DURES

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Description

Field of the invention

[0001] The present invention relates to a cleaning composition for hard surfaces, comprising at least a specific polymer and a surfactant that is useful against soil, especially greasy soil. The invention also relates to a method for cleaning a hard surface wherein said cleaning composition is used and wherein a next time cleaning benefit is obtained.

Background of the invention

[0002] Hard surfaces in the home or office are usually cleaned using liquid compositions which comprise one or more surfactants and, possibly, also pH adjusters like citric acid or sodium salts of citrate. Such compositions may further comprise additional components for targeting specific stains or soils.

[0003] The cleaning compositions can be applied in diluted (in water) or undiluted form, in a spray, or rubbed using a cloth and any other convenient way. Optionally the cleaning composition may be rinsed from the surface after the cleaning. It would be advantageous if the hard surface to be cleaned could be treated with a material which would assist in easier removal of soil and/or stains during subsequent cleaning. This is referred to as the next time cleaning benefit.

[0004] Soils on hard surfaces can become more difficult to remove when not cleaned soon after deposition. When not cleaned promptly, soils can become more adherent to surfaces, more viscous and generally tougher, and require more effort to clean. While not being bound by theory, this more difficult removal of soils can arise from the effects of drying out of soils, from chemical changes in soils, from reactions of soils with environmental agents such as oxygen, etc. Some soils are more susceptible than others to toughening reactions and processes. Soils comprising or containing chemically unsaturated oils and fats can become very tough and difficult to clean over time, especially when exposed to elevated temperatures. Even light can cause such fatty soils to toughen over time. As well as environmental factors, the processes of toughening of soils can be affected by the nature and composition of the surface on which the soil is located. Hard-surface cleaning compositions may be either acidic or alkaline. Acidic compositions often contain citric acid, sorbic acid, acetic acid, formic acid, maleic acid, adipic acid, lactic acid, malic acid and glycolic acid. Acidic cleaners are generally used for removing acid sensitive soil, such as limescale. For removal of fatty soil alkaline compositions are generally preferred.

[0005] EP-A 0859046 describes a liquid hard-surface cleaning composition having a pH above 9 and comprising a copolymer of N-vinylpyrrolidone and alkylenically unsaturated monomer or mixtures thereof. The examples describe compositions comprising surfactants and polymers (Polyquat™ 11; Luviskol™ 73W; PEG DME-2000).

[0006] EP-A 1927651 describes a liquid composition having, a pH between 3 and 7, comprising: non ionic surfactant; amine oxide; a glycol ether solvent; a chelant; and a cationic polymer.

[0007] WO-00/58228 discloses a composition for rust and/or corrosion removal that contains a reducing agent, a chelating agent and a surfactant. Said composition which may also contain a polymer dispersant, is said to form stable protective coating after cleaning.

[0008] US 2008/233061 discloses structured surfactant compositions which may optionally contain polyglyceryl methacrylate.

[0009] WO-2005/030282 discloses the use of a coating composition comprising polymeric micelles, wherein the polymer has an ionic block and a neutral hydrophobic block, for surface modification or surface treatment. More particularly, this document discloses the use of said composition for preventing bacteria proliferation, disinfecting, suppressing odors or for providing easy-cleaning or soil-release properties.

[0010] In view of this prior art, there remains a need for a polymer-containing cleaning composition which is suitable for removing mobile soil from hard surfaces preferably a cleaning composition that does not require the formation of complex polymeric micelles at the interface. In particular, there is a need for such a cleaning composition which provides a secondary cleaning benefit with regard to mobile soil.

[0011] WO-2010/003783 describes a laundry detergent composition comprising:

a) a detersive surfactant at a concentration between 3 and 85% by weight of the total composition;
b) a copolymer at a concentration between 0.5 and 25% by weight of the total composition, said copolymer comprising the monomers glycerol (meth) acrylate and poly (alkylene oxide) alkyl ether (meth) acrylate, and having a number average molecular weight between 2,000 and 100,000 Dalton;
c) optionally other detergent ingredients up to 100% by weight of the total composition.

[0012] Accordingly, it is an object of the invention to provide a cleaning composition with which a next time cleaning benefit is achieved with regard to the removal from hard surfaces of mobile soil, in particular greasy soil. A further objective is that said benefit can be obtained across the pH-spectrum, with both acid and alkaline cleaning compositions.

It is yet another object to achieve a next time cleaning benefit without leaving residues of compounds that may be considered to be harmful to the consumer.

[0013] The inventors have now surprisingly found that one or more of these objects can be achieved using the cleaning composition of the invention which comprises a surfactant and a specific type of polymer.

Definition of the invention

[0014] Accordingly in a first aspect the present invention provides an aqueous hard surface cleaning composition according to claim 1.

[0015] Furthermore, in a second aspect the present invention provides method for cleaning a hard surface and obtaining a next time cleaning benefit for said surface according to claim 5.

[0016] In a third aspect the present invention provides the use of the aqueous hard surface cleaning composition for cleaning a hard surface and obtaining a next time cleaning benefit for said surface.

Detailed description of the invention

[0017] In the context of the present invention, 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 inorganic origin, whether visible or invisible to the naked eye, including soiling solid debris and/or with bacteria or other pathogens.

[0018] Furthermore, the phrase "next time cleaning benefit" as used herein refers to an improved ease of removal of soil after re-soiling of a hard surface cleaned using the method of the present invention. This improved ease may be indicated by an increased amount of soil being removed from a hard surface using a certain fixed cleaning effort (e.g. the same no. of wiping actions using the same force per wiping action). Evidence of this type of improved ease of the removal of soil is shown in the examples. Alternatively, the improved ease of the removal of soil may also be indicated by the lower effort (e.g. less wiping actions, less force per wiping action or a combination thereof) necessary to reach a similar level of soil removal. In this case, less effort would be required to remove a certain amount of soil from a hard surface that is treated using the method of the present invention prior to deposition of the soil, as compared to the effort required to remove an equal amount of soil from a similar hard surface that is pre-treated using a general cleaning method of the prior art.

[0019] Clearly, the improved ease of removal may also be indicated by a combination of the above-mentioned effects (i.e. increased amount of soil removed with less effort).

[0020] It is further noted that the method of the invention includes the step of removing soils and stains, preferably mobile soils. In this connection, the term "mobile soils" as used herein is intended to mean soils that are not significantly cross-linked or dried-out, and thus are able to be moved on the surface with a dry cloth. Such mobile soils are e.g. greasy soils.

The polymer

[0021] The polymer of the present invention has a molecular weight of more than 100,000 Daltons, and most preferably more than 500,000 Daltons.

[0022] The polymer present in the cleaning composition of the invention is a polyglycerol methacrylate (PGMA) homopolymer. And the molecular weight of said homopolymer is more than 100,000 Daltons, and most preferably more than 500,000 Daltons.

[0023] The concentration of said polymer is 0.01 - 1 wt%, preferably 0.01 - 0.5 wt% of the cleaning composition of the invention.

Surfactants

[0024] The cleaning composition of the invention comprises additionally a surfactant selected from anionic surfactants, nonionic surfactants and mixtures thereof, at a concentration of 1 - 50 wt%, preferably 20 wt%, more preferably 1 - 10 wt%.

[0025] 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.

[0026] Examples of such anionic surfactants are water soluble salts of:

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

- secondary alkanesulphonates;

and mixtures thereof.

[0027] Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- sulphates of ethoxylated aliphatic alcohols containing 1-12 ethyleneoxy groups;
- alkylphenol ethylenoxy-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,

and mixtures thereof.

[0028] 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 of alkyl-benzenesulphonates and mixtures with olefin-sulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates.

[0029] The most preferred anionic surfactants are alkyl-aromatic 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, alkylnaphthalene-sulphonates, ammonium diamylnaphthalene-sulphonate, and sodium dinonyl-naphthalene-sulphonate.

[0030] If synthetic anionic surfactant is to be employed the amount present in the cleaning compositions of the invention will generally be at least 0.1%, preferably at least 0.5%, more preferably at least 1.0%, but preferably at most 15%, more preferably at most 10%.

[0031] 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, 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 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 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 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 5,000 to 11,000.

[0032] Other classes of nonionic surfactants are:

- tertiary amine oxides of structure $R^1R^2R^3N$-O, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure $R^1R^2R^3P$-O, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulphoxides of structure $R^1R^2S{=}O$, where R^1 is an alkyl group of from 10 to 18 carbon atoms and R^2 is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- fatty acid alkylolamides, such as the ethanol amides;
- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans;
- alkyl polyglucosides.

[0033] The concentration of the nonionic surfactant to be employed in said cleaning composition of the invention will preferably be at least 0.1%, more preferably at least 0.5%, most preferably at least 1%. The amount is preferably not more than 15% and most preferably not more than 10%.

[0034] It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in said compositions.

[0035] 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-sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate.

[0036] 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 aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium chloride.

[0037] A specific group of surfactants are the tertiary amines obtained by condensation of ethylene and/or propylene oxide with long chain aliphatic amines. The compounds behave like nonionic surfactants in alkaline medium and like cationic surfactants in acid medium.

[0038] Examples of suitable zwitterionic surfactants can be found 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 betaine, in particular C_{12}-C_{16} 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.

[0039] 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.

pH

[0040] In a preferred embodiment the method of the invention is carried out at a pH of from 2 to 13, more preferably at least 3, and not more than 12.

[0041] Cleaning methods of the invention intended for cleaning kitchen hard surfaces may advantageously be carried out at a pH in the alkaline range. When used for this purpose, said method is preferably carried out at a pH between roughly 6.0 and 12, more preferred between 7.0 and 12.

[0042] Alternatively, when the cleaning method of the invention is intended for cleaning bath room hard surfaces, said method is preferably carried out at a pH between 3.0 and 7.0, more preferably between 3.0 and 6.0.

[0043] The pH of the cleaning composition used in the method of the invention 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 or potassium or the alkaline earth metal preferably being calcium or magnesium. The organic bases are preferably amines, alkanolamines and other suitable amino compounds. 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).

Other optional ingredients

[0044] The cleaning composition used according to the present invention may include abrasives. However, these are generally not preferred as abrasives tend to damage or remove the thin layer being deposited on the surface when carrying out the method of the invention. In a preferred embodiment the composition used according to the present invention does not contain an abrasive.

[0045] The compositions may contain other ingredients which aid in their cleaning performance. For example, they may contain detergent builders and mixtures of builders in an amount of up to 25%, in particular when the composition contains one or more anionic surfactants. If present, the builder preferably will form at least 0.1% of the cleaning composition. Suitable inorganic and organic builders are well known to those skilled in the art.

[0046] A further optional ingredient for compositions used according to the invention is a suds regulating material, which can be employed in compositions which have a tendency to produce excessive suds in use. Examples thereof are fatty acids or their salts (soap), isoparaffins, silicone oils and combinations thereof.

[0047] Soaps are salts of fatty acids and include alkali metal 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 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.

[0048] The cleaning composition of the invention preferably comprises perfume in a concentration of from 0.001 to 5 %wt, more preferably 0.1 to 2 %wt.

[0049] Compositions may also contain, in addition to the ingredients already mentioned, various other optional ingredients such as colourants, whiteners, optical brighteners, soil suspending agents, detersive enzymes, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), solvents, co-solvents, gel-control agents, further freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), and hydrotropes.

[0050] In a preferred embodiment the composition of the present invention does not comprise tannic acid or related compounds such as gallic acid and/or propyl gallate. It was found that when tannic acid is formulated into alkaline liquid cleaning compositions it produces aesthetically less-pleasing yellow-brown coloured solutions, and it may lead to browning of cement in joints between tiles.

[0051] In another preferred embodiment the composition of the present invention does not comprise malonic acid. An antioxidant like malonic acid needs relatively high concentrations to achieve a next time cleaning benefit. Moreover consumers may regard residues of malonic acid on the hard surfaces in e.g. kitchen and bathroom to be harmful and undesired.

[0052] In yet another preferred embodiment the composition of the present invention does not comprise formic acid. Formic acid has a pungent odour, and residues on hard surfaces are aesthetically undesirable.

Liquid Dispensers

[0053] The aqueous cleaning composition according to the invention 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, in a preferred embodiment the second aspect of the invention provides the use of an aqueous cleaning composition according to the invention, wherein said composition is comprised in a container, and wherein the container further comprises a spray dispenser for dispensing said 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.

Appearance

[0054] In general, the aqueous cleaning composition of the invention may have any appearance, ranging from opaque to fully transparent. However, said composition is preferably at least partially transparent or translucent, more preferably transparent.

[0055] By at least partially transparent or translucent is meant that a 1 cm thick sample of the composition transmits at least 20%, preferably at least 50%, of visible light. By transparent is meant that a 1 cm thick sample of the composition transmits at least 70%, preferably at least 90%, of visible light.

Method of the invention

[0056] In a preferred embodiment of the first aspect, the present invention provides a method for cleaning a hard surface, and obtaining a next time cleaning benefit, the method comprising the following sequential steps:

(a) applying to the surface an aqueous cleaning composition according to the invention;
(b) rinsing the surface with water;
(c) allowing new soil or stains to deposit; and
(d) cleaning the surface to remove said soil or stains.

[0057] Preferably the soil or stain is a soil or stain containing fatty material, which has not undergone a significant toughening reaction and is, therefore, still mobile (see the above definition of "mobile soil").

Examples

[0058] The following non-limiting examples further illustrate the present invention.

[0059] The next time cleaning benefit on mobile soil was assessed for a variety of test formulations, both at alkaline as well as acid pH, using a laboratory methodology to simulate the practical cleaning situation.

Method for assessing the contribution of test formulations to easier cleaning of mobile soil.

[0060] The basic steps in the methodology are:

- Pre-cleaning of worktop laminate test piece surface;
- Treatment of the surface with test solution;
- Application of a film of mobile soil onto the surface;

- Leave overnight to age;
- Cleaning of the soiled surface by a trained operator;
- Recording of the effort to clean (lower effort = better).

Pre-cleaning of test piece surface

[0061] Treatments are evaluated on large pieces of worktop laminate (Fundamentals matt white ex Formica). Said test pieces are pre-cleaned by wiping them with ethanol.

Treatment of Surfaces

[0062] Each large piece of worktop laminate can fit 4x A4 treatment patches, which are evenly spaced across the laminate and do not touch each other. 2 ml of the test solution is applied to the surface of each A4 patch and distributed uniformly over the area thereof using a dry perforated viscose cloth (e.g. J-cloth). The treatment is allowed to dry naturally for 5 minutes. Subsequently the surface is rinsed with water for 30 seconds using a shower head with flow rate fixed at about 5-6L/minute.

Soiling of the Surface

[0063] Mobile soil is applied to the treated test surface using a compressed air spray gun. The composition of this soil is as follows:

Component	%wt
Glycerol Tripalmitate	2
Glycerol Trioleate (Triolein)	1
Liquid paraffin	0.4
Palmitic Acid	0.2
Carbon Black	0.02
Absolute Ethanol	To 100%

[0064] The soil is prepared by first making a large batch (ca. 2kg) without carbon black. This is sheared using a Silverson mixer for 60 minutes or until ca. 45°C. The soil is left to cool overnight. Then, before use a smaller batch of the soil is taken, carbon black added, and sheared again for 30 minutes or until ca. 45°C using a Silverson mixer at a lower shear rate.

[0065] The resulting soil is a dispersion of triglycerides, mineral oil and fatty acid plus carbon black in a dispersant (ethanol) that allows the soil to be sprayed using a compressed air spray gun.

[0066] The soil is sprayed evenly onto each A4 patch to a level of 6.80g per A4 patch based on weight of soil in the spray gun.

Cleaning

[0067] Cleaning of the thus-soiled test surface is carried out by a trained operator using up to 6 ml of a simple liquid detergent, i.e. an aqueous cleaning solution of a mixture of alcohol ethoxylates at a ratio such that an un-pretreated soiled A4 patch requires an average effort of greater than 1000 Ns to completely clean said patch to a visibly clean end point. Typically, this ratio is such that the cleaning solution contains 4% Neodol 91-5 and 1% Neodol 91-8 in water. The cleaning is carried out on an ergonomics rig and continued until the trained operative designates the patch completely clean (which means that all visible and tactile evidence of the soil has been removed), or for at most 2 minutes. Subsequently, the effort to clean is recorded. If not all of the soil is removed during the maximum time of 2 minutes, then the patch is declared "not clean".

Reference Examples 1-6

[0068] Various test formulations were prepared by stirring together all of the ingredients apart from the pH adjuster and a small amount of the water (5%). After all the ingredients had dispersed, the pH was adjusted using the relevant pH adjuster and the balance of the formulation made up with water.

[0069] These test formulations which were used to pre-treat worktop laminate test surfaces as described above, have following compositions.

Component	%wt of Component					
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Neodol 91-8 ex Shell	5	5	5	5	5	5
Glascol E11 Poly(AA), MW~250 000)ex Ciba				0.5	0.5	0.5
PGMA MW ~ medium, ex Unilever	0.5	0.5	0.5			
Sodium Carbonate			0.35			0.35
pH adjuster (HCl/ NaOH)	to pH 4	to pH 7	to pH 11.4	to pH 4	to pH 7	to pH 11.4
Water	To 100%	To 100%	To 100%	To 100%	To 100%	To 100%
wherein: * Glascol E11 poly (AA): Polyacrylic Acid ex Ciba. * Medium MW PGMA: PGMA having a molecular weight in the range of 50k-500k Daltons.						

[0070] The cleaning formulation used for cleaning the re-soiled surface on the ergonomics rig was an aqueous solution containing 4% Neodol 91-5 (ex Shell), 1% Neodol 91-8 (ex Shell) and water.

[0071] The test results were expressed as the amount of effort (in Ns) for completely removing the soil from the test surface, as measured on the ergonomics rig. The lower the effort required the more effective the test formulation used for the pre-treatment of the test surface.

[0072] The following results were obtained for the various test formulations

Example Number	Effort to Remove Soil (Ns)			
	Replicate 1	Replicate 2	Replicate 3	Replicate 4
1	109	69	265	162
2	79	192	164	216
3	105	104	118	142
4	814	688	875	577
5	1956	987	791	811
6	1664	910	1105	1034
No pre-treatment step	1294	894	1442	1128

[0073] As can be seen, the above table also shows the cleaning results for cleaning soiled surfaces which have not been pre-treated with a test formulation in order to determine the benefit offered by pretreatment over no pretreatment.

[0074] It can further be noticed that the pretreatment with the PGMA containing test formulations of examples 1-3 results in much lower effort than the pretreatment with the PAA containing test formulations of examples 4-6. It can also be noticed that the benefit (in terms of lower cleaning effort) for the PGMA containing test formulations extends for a range of pH-values between pH4 to pH 11.4, whereas for the PAA containing test formulations of examples 3-6 the effort increases as the pH value increases. This clearly shows that the polyglycerol methacrylate (PGMA) containing formulation of the invention is more effective at reducing cleaning effort than the polyacrylic acid (PAA) containing formulation of the prior art.

Reference Examples 7-10

[0075] Similarly as in examples 1-6, test formulations were prepared by stirring together all of the ingredients apart from the pH adjuster and a small amount of the water (5%). After all the ingredients had dispersed, the pH was adjusted using the relevant pH adjuster and the balance of the formulation made up with water. These test formulations which were used to pre-treat worktop laminate test surfaces described above, have following compositions.

Component	**%wt of Component**			
	Example 7	**Example 8**	**Example 9**	**Example 10**
Neodol 91-8 ex Shell	5	5	5	5
Poly(AA), MW ≈ low ex Unilever			0.5	0.5
PGMA MW ≈ low ex Unilever	0.5	0.5		
Sodium Carbonate		0.35		0.35
pH-adjuster (HCl/NaOH)	to pH 4	to pH 11.4	to pH 4	to pH 11.4
Water	To 100%	To 100%	To 100%	To 100%
wherein: *MW ≈ low: (which refers to both PGMA and poly(AA))a molecular weight of less than 50k Daltons.				

[0076] The cleaning formulation used for cleaning the re-soiled surface on the ergonomics rig was an aqueous solution containing 4% Neodol 91-5 (ex Shell), 1% Neodol 91-8 (ex Shell) and water.

[0077] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

Example Number	**Effort to Remove Soil (Ns)**			
	Replicate 1	**Replicate 2**	**Replicate 3**	**Replicate 4**
7	391	433	331	599
8	751	580	632	517
9	721	669	569	1049
10	863	995	985	1131
No-pretreatment for pH 4 data	1362	1222	1121	1193
No pre-treatment for pH 11.4 data	988	1068	1147	921

[0078] When comparing the results obtained in examples 7 and 9, it can be noticed that the results obtained after pretreatment with PGMA containing test formulation having a pH value of 4 (example 7) are considerably better than those obtained with a PAA containing test formulation having a pH value of 4. The same observation can be made when comparing examples 8 and 10 in which test formulations having a pH value of 11.4 were applied for pretreatment of the test surfaces.

Reference Examples 11-14

[0079] Similarly as in the previous examples, test formulations were prepared by stirring together all of the ingredients apart from the pH adjuster and a small amount of the water (5%). After all the ingredients had dispersed, the pH was adjusted using the relevant pH adjuster and the balance of the formulation made up with water.

[0080] These test formulations which were used to pre-treat worktop laminate test surfaces described above, have following compositions.

Component	**%wt of Component**			
	Comp. Example 11	**Example 12**	**Comp. Example 13**	**Example 14**
Neodol 91-8 ex Shell	5	5	5	5
50/50 Poly(DMAEMA/AA) MW ~ medium ex Unilever	0.5			

(continued)

Component	%wt of Component			
	Comp. Example 11	Example 12	Comp. Example 13	Example 14
Poly(DMAEMA/AA/GMA) MW ~ medium ex Unilever		0.5		
Poly(AA) MW ~ medium ex Unilever			0.5	
50/50 Poly(GMA/AA) MW ~ medium ex Unilever				0.5
Sodium Carbonate	0.35	0.35	0.35	0.35
pH adjuster (HCl/NaOH)	to pH 11.4	to pH 11.4	to pH 11.4	to pH 11.4
Water	To 100%	To 100%	To 100%	To 100%
wherein: *DMAEMA = dimethylaminoethyl methacrylate; *AA = acrylic acid *GMA = glycerol methacrylate. *Medium MW = molecular weight in the range of 50k-500k Dalton.				

[0081] The cleaning formulation used for cleaning the re-soiled surface on the ergonomics rig was an aqueous solution containing 4% Neodol 91-5 (ex Shell), 1% Neodol 91-8 (ex Shell) and water.

[0082] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

Example Number	Effort to Remove Soil (Ns)			
	Replicate 1	Replicate 2	Replicate 3	Replicate 4
11	761	846	947	979
12	154	366	326	78
13	771	955	714	878
14	151	92	86	109
No pre-treatment	988	1068	1147	921

[0083] When comparing the results obtained in examples 11 and 12, and also when comparing the results of examples 13 and 14, it can be noticed that even when combined with other monomers in a co- or ter-polymer the benefits of the PGMA are still observed, even though the other monomers are demonstrated to be ineffective.

Examples 15-20

[0084] PGMA was prepared by a RAFT technique to generate polymers of various specific molecular weights (MW). RAFT (Reversible Addition-Fragmentation chain Transfer) polymerization is a type of radical polymerization. It makes use of a chain transfer agent to afford control of the generated molecular weight (MW) and polydispersity during polymerization. The resulting polymers were then used for formulating the following test formulations.

Component	%wt of Component					
	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
Neodol 91-8 ex Shell	5	5	5	5	5	5
PGMA (MW 10k ex Unilever	0.5					
PGMA (MW 25k ex Unilever		0.5				
PGMA (MW 50k ex Unilever			0.5			

(continued)

Component	**%wt of Component**					
	Example 15	**Example 16**	**Example 17**	**Example 18**	**Example 19**	**Example 20**
PGMA (MW 100k ex Unilever				0.5		
PGMA (MW 250k ex Unilever					0.5	
PGMA (MW 500k ex Unilever						0.5
Sodium Carbonate	0.35	0.35	0.35	0.35	0.35	0.35
pH adjuster (HCl/NaOH)	to pH 11.4	to pH 11.4	to pH 11.4	to pH 11.4	to pH 11.4	to pH 11.4
Water	To 100%	To 100%	To 100%	To 100%	To 100%	To 100%

[0085] Examples 15-18 are comparative.

[0086] The cleaning formulation used for cleaning the re-soiled surface on the ergonomics rig was an aqueous solution containing 4% Neodol 91-5 (ex Shell), 1% Neodol 91-8 (ex Shell) and water.

[0087] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

Example Number	**Effort to Remove Soil (Ns)**			
	Replicate 1	**Replicate 2**	**Replicate 3**	**Replicate 4**
15	801	1243	1205	1039
16	669	783	827	811
17	607	580	585	790
18	464	518	469	612
19	172	91	261	236
20	219	246	183	106
No pre-treatment	1126	1175	1173	1363

[0088] It can be noticed, that statistically all of the examples in which PGMA-containing test formulations were used for pre-treatment excluding example 15 show significantly better results at removal of the soil than when no pre-treatment is carried out. It is also noticeable that the efficacy of the polymer improves as the molecular weight of the polymer increases.

Examples 21-26

[0089] PGMA was prepared by the RAFT technique (as defined here above) to generate polymers of specific molecular weight (MW). The resulting polymers were then used for formulating the following test formulations.

Component	**% wt of Component**					
	Example 21	**Example 22**	**Example 23**	**Example 24**	**Example 25**	**Example 26**
Neodol 91-5 ex Shell	5	5	5	5	5	5
PGMA (MW 10k ex Unilever	0.5					
PGMA (MW 25k ex Unilever		0.5				
PGMA (MW 50k ex Unilever			0.5			

(continued)

Component	% wt of Component					
	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26
PGMA (MW 100k ex Unilever				0.5		
PGMA (MW 250k ex Unilever					0.5	
PGMA (MW 500k ex Unilever						0.5
pH adjuster (HCl/NaOH)	to pH 4	to pH 4	to pH 4	to pH 4	to pH 4	to pH 4
Water	To 100%	To 100%	To 100%	To 100%	To 100%	To 100%

[0090] Examples 21-24 are comparative.

[0091] The cleaning formulation used for cleaning the re-soiled surface on the ergonomics rig was an aqueous solution containing 4% Neodol 91-5 (ex Shell), 1% Neodol 91-8 (ex Shell) and water.

[0092] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

Example Number	Effort to Remove Soil (Ns)			
	Replicate 1	Replicate 2	Replicate 3	Replicate 4
21	777	1075	1030	1195
22	795	1441	1305	783
23	893	970	967	781
24	736	827	872	680
25	710	239	559	632
26	353	474	646	168
No pre-treatment	1126	1175	1173	1363

[0093] It can be noticed, that statistically all of the examples in which PGMA-containing test formulations were used for pre-treatment show significantly better results at removal of the soil than when no pre-treatment is carried out. It is also noticeable that the efficacy of the polymer improves as the molecular weight of the polymer increases.

Examples 27-30

[0094] The contribution of test formulations to easier cleaning of mobile soil was assessed using the procedure described earlier with the following adaptations:
The composition of the soil was as follows:

NAME	WT (%)
"Tripalmitin" [1]	2.56
Glyceryl Trioleate	1.28
Liquid Paraffin (Nujol)	0.51
Palmitic Acid	0.26

(continued)

NAME	WT (%)
Ethanol	95.39
0.02% Carbon black is added for visualisation. [1] Blend of Tripalmitin and Glyceryl Trioleate (60:40). Required amounts are melted in an oven at 70°C. The molten mixture is manually stirred and then placed into a freezer to solidify (-10 minutes). The solidified material is then transferred into a polythene bag and broken into small pieces by hand. This material is then ready to use.	

Making the Soil

[0095] The soil ingredients were weighed into a suitably sized beaker and placed under a Silverson high shear mixer and mixed at setting 3.5 until the soil mixture reaches 34°C. When the soil has reached this temperature any evaporated ethanol is replaced, cooled back to room temperature and is ready for spraying. The resulting soil is a dispersion of triglycerides, mineral oil and fatty acid plus carbon black in a dispersant (ethanol) that allows the soil to be sprayed using a compressed air spray gun.

Spraying of Soil

[0096] The large Formica sheet is masked so that 4 A4 patches are exposed. The soil is sprayed evenly onto each A4 patch to a level of 6.80g per A4 patch based on weight of soil in the spray gun.

[0097] The following samples were made up and tested for secondary cleaning.

	%wt of components			
	Example 27	Comp. Example 28	Comp. Example 29	Comp. Example 30
Neodol 91-8	5	5	5	5
Sodium carbonate	0.35	0.35	0.35	0.35
PGMA 500k	0.5			
Luviskol VA 73W [1]		0.5		
Polyquat 11 AT 1 [2]			0.5	
pH (HCl/NaOH)	To 11.4	To 11.4	To 11.4	To 11.4
Water	To 100%	To 100%	To 100%	To 100%
[1] Luviskol VA 73W: 70/30 Vinylpyrrolidone(VP)/vinyl acetate(VA) copolymer ex BASF [2] Luviquat PQ 11 AT 1: quaternised copolymer of vinyl pyrrolidone (VP) and dimethylaminoethyl methacrylate (DMAE-MA) in aqueous solution ex BASF				

[0098] Formulations were prepared by mixing together the surfactant, sodium carbonate and polymer with most of the water. The pH was then adjusted to the desired value using either HCl or NaOH as appropriate, and then water added to make the sample up to 100%.

[0099] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

	Effort to Remove Soil (Ns)			
Example Number	Replicate 1	Replicate 2	Replicate 3	Replicate 4
27	197	480	383	286
28	1077	868	1631	2218
29	611	1174	595	1105
30	1295	1645	1455	1451
No pre-treatment	1393	1729	661	2369

[0100] Statistical analysis of the data using Dunnett's Method, choosing the formulation of Example 30 as control (base formulation with no polymer) shows that only the sample containing PGMA results in significantly lower effort than the base formulation.

Examples 31-34

[0101] The contribution of test formulations was assessed using the procedure described in Examples 27-30. The following samples were made up and tested for secondary cleaning.

	%wt of components			
	Example 31	**Comp. Example 32**	**Comp. Example 33**	**Comp. Example 34**
Neodol 91-5	5	5	5	5
PGMA 500k	0.5			
Luviskol VA 73W [1]		0.5		
Polyquat 11 AT 1 [2]			0.5	
pH (HCl/NaOH)	To 4	To 4	To 4	To 4
Water	To 100%	To 100%	To 100%	To 100%

[1] Luviskol VA 73W: 70/30 Vinylpyrrolidone(VP)/vinyl acetate(VA) copolymer ex BASF

[2] Luviquat PQ 11 AT 1: quaternised copolymer of vinyl pyrrolidone (VP) and dimethylaminoethyl methacrylate (DMAEMA) in aqueous solution ex BASF

[0102] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

	Effort to Remove Soil (Ns)			
Example Number	**Replicate 1**	**Replicate 2**	**Replicate 3**	**Replicate 4**
31	110	208	308	740
32	639	1669	939	1505
33	618	778	1717	476
34	1176	1755	1290	991
No pre-treatment	1575	1140	938	1252

[0103] Statistical analysis of the data using Dunnett's Method, choosing the formulation of Example 34 as control (base formulation with no polymer) shows that only the sample containing PGMA results in significantly lower effort than the base formulation.

Examples 35-37

[0104] The contribution of test formulations was assessed using the procedure described in Examples 27-30. The following samples were made up and tested for secondary cleaning.

	%wt of components		
	Example 35	**Comp. Example 36**	**Comp. Example 37**
Neodol 91-8	5	5	5
Sodium carbonate	0.35	0.35	0.35
PGMA 500k	0.5		
Rhodia polymer [1]		0.5	

(continued)

	%wt of components		
	Example 35	Comp. Example 36	Comp. Example 37
pH (HCl/NaOH)	To 11.4	To 11.4	To 11.4
Water	To 100%	To 100%	To 100%
[1] Rhodia Polymer = polymer synthesised in house following procedure described in US 6569261 and US0234432 to yield a random copolymer of acrylic acid and diquat monomer as described in EP 1927651			

[0105] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

	Effort to Remove Soil (Ns)			
Example Number	Replicate 1	Replicate 2	Replicate 3	Replicate 4
35	228	455	244	131
36	1742	1393	985	1928
37	2460	1582	1212	2143
No pre-treatment	2079	1165	1374	2122

[0106] Statistical analysis of the data using Dunnett's Method, choosing the formulation of Example 37 as control (base formulation with no polymer) shows that only the sample containing PGMA results in significantly lower effort than the base formulation.

Examples 38-40

[0107] The contribution of test formulations was assessed using the procedure described in Examples 27-30. The following samples were made up and tested for secondary cleaning.

	%wt of components		
	Example 38	Comp. Example 39	Comp. Example 40
Neodol 91-5	5	5	5
PGMA 500k	0.5		
Rhodia polymer [1]		0.5	
pH (HCl/NaOH)	To 4	To 4	To 4
Water	To 100%	To 100%	To 100%
[1] Rhodia Polymer = polymer synthesised in house following procedure described in US 6569261 and US0234432 to yield a random copolymer of acrylic acid and diquat monomer as described in EP 1927651.			

[0108] For these test formulations, the following results expressed as the amount of effort (in Ns) for completely removing the soil from the test surface were obtained.

	Effort to Remove Soil (Ns)			
Example Number	Replicate 1	Replicate 2	Replicate 3	Replicate 4
38	727	299	224	1016
39	1478	1688	1162	1260
40	1405	1495	1945	1396

(continued)

Example Number	Effort to Remove Soil (Ns)			
	Replicate 1	Replicate 2	Replicate 3	Replicate 4
No pre-treatment	2079	1165	1374	2122

[0109] Statistical analysis of the data using Dunnett's Method, choosing the formulation of Example 40 as control (base formulation with no polymer) shows that only the sample containing PGMA results in significantly lower effort than the base formulation.

Claims

1. Aqueous hard surface cleaning composition comprising:

   (a) 0.01 -1% by weight of a polymer selected from the group of a polyglycerol methacrylate (PGMA) homopolymer, a statistical copolymer containing glycerol methacrylate monomer and mixtures thereof wherein the polymer is PGMA homo-polymer with a molecular weight of more than 100,000 Daltons;
   (b) 1- 50% by weight, preferably 1-20% by weight of a surfactant selected from anionic surfactants, nonionic surfactants and mixtures thereof.

2. Cleaning composition according to claim 1, wherein the composition is at least partially transparent or translucent, wherein by at least partially transparent or translucent is meant that a 1 cm thick sample of the composition transmits at least 20%, preferably at least 50%, of visible light.

3. Cleaning composition according to claim 1 or claim 2, wherein the composition further contains 0.001 - 5% by weight of perfume.

4. Cleaning composition according to any one of claims 1 to 3, wherein the homopolymer has a molecular weight of more than 500,000 Daltons.

5. Method for cleaning a hard surface and obtaining a next time cleaning benefit for said surface, wherein said method includes the steps of:

   (i) Applying to the surface an aqueous cleaning composition according to any of claims 1 to 4, and
   (ii) Removing soil and stains, preferably mobile soils, from said surface;

   wherein next time cleaning benefit refers to an improved ease of removal of soil after re-soiling of a hard surface cleaned.

6. Method according to claim 5, wherein the method comprises the following sequential steps:

   (a) Applying an aqueous cleaning composition according to any of claims 1 to 4 to the surface;
   (b) Rinsing the surface;
   (c) Allowing new soil or stains to deposit on the surface; and
   (d) Cleaning the surface to remove said soil or stains.

7. Use of an aqueous hard surface cleaning composition according to any one of claims 1 to 4 for cleaning a hard surface and obtaining a next time cleaning benefit for said surface.

Patentansprüche

1. Wässrige Reinigungszusammensetzung für harte Oberflächen, umfassend:

   (a) 0,01-1 Gewichts-% eines Polymers, ausgewählt aus der Gruppe eines Polyglycerinmethacrylat (PGMA)-ho-

mopolymers, eines statistischen Copolymers, das Glycerinmethacrylat-monomer enthält, und Mischungen davon, wobei das Polymer PGMA-homopolymer ein Molekulargewicht von mehr als 100.000 Dalton aufweist;
(b) 1-50 Gewichts-%, vorzugsweise 1-20 Gewichts-% eines Tensids, das aus anionischen Tensiden, nichtionischen Tensiden und Mischungen davon ausgewählt ist.

2. Reinigungszusammensetzung nach Anspruch 1, wobei die Zusammensetzung mindestens partiell transparent oder durchscheinend ist, wobei mindestens partiell transparent oder durchscheinend bedeutet, dass eine 1 cm dicke Probe der Zusammensetzung mindestens 20%, vorzugsweise mindestens 50% sichtbares Licht durchlässt.

3. Reinigungszusammensetzung nach Anspruch 1 oder Anspruch 2, wobei die Zusammensetzung ferner 0,001 - 5 Gewichts-% Parfüm enthält.

4. Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 3, wobei das Homopolymer ein Molekulargewicht von mehr als 500.000 Dalton aufweist.

5. Verfahren zum Reinigen einer harten Oberfläche und Erzielen eines Vorteils für die Oberfläche beim nächstmaligen Reinigen, wobei das Verfahren die Schritte einschließt:

(i) Auftragen einer wässrigen Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 4 auf die Oberfläche und
(ii) Entfernen von Schmutz und Flecken, vorzugsweise mobilem Schmutz, von der Oberfläche,

wobei sich der Vorteil des nächstmaligen Reinigens auf eine verbesserte Leichtigkeit des Entfernens von Schmutz nach erneutem Verschmutzen einer gereinigten harten Oberfläche bezieht.

6. Verfahren nach Anspruch 5, wobei das Verfahren die folgenden sequenziellen Schritte umfasst:

(a) Auftragen einer wässrigen Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 4 auf die Oberfläche;
(b) Abspülen der Oberfläche;
(c) Abscheidenlassen von neuem Schmutz oder Flecken auf der Oberfläche und
(d) Reinigen der Oberfläche, um den Schmutz oder die Flecken zu entfernen.

7. Verwendung einer wässrigen Reinigungszusammensetzung für harte Oberflächen nach irgendeinem der Ansprüche 1 bis 4 zum Reinigen einer harten Oberfläche und zum Erzielen eines Vorteils für die Oberfläche beim nächstmaligen Reinigen.

Revendications

1. Composition aqueuse de nettoyage de surfaces dures comprenant :

(a) 0,01 à 1 % en poids d'un polymère choisi dans le groupe comprenant un homopolymère de poly(méthacrylate de glycérol) (PGMA), un copolymère statistique contenant un monomère de méthacrylate de glycérol et leurs mélanges, lequel polymère est un homopolymère de PGMA ayant une masse moléculaire supérieure à 100 000 Daltons ;
(b) 1 à 50 % en poids, de préférence 1 à 20 % en poids, d'un tensioactif choisi parmi les tensioactifs anioniques, les tensioactifs non-ioniques et leurs mélanges.

2. Composition de nettoyage selon la revendication 1, laquelle composition est au moins partiellement transparente ou translucide, dans laquelle, par au moins partiellement transparente ou translucide, on entend qu'un échantillon de la composition ayant une épaisseur de 1 cm transmet au moins 20 %, de préférence au moins 50 %, de la lumière visible.

3. Composition de nettoyage selon la revendication 1 ou la revendication 2, laquelle composition contient en outre 0,001 à 5 % en poids de parfum.

4. Composition de nettoyage selon l'une quelconque des revendications 1 à 3, dans laquelle l'homopolymère a une masse moléculaire supérieure à 500 000 Daltons.

5. Procédé pour nettoyer une surface dure et obtenir un bénéfice de nettoyage pour la fois suivante de ladite surface, lequel procédé comprend les étapes consistant à :

(i) appliquer sur la surface une composition aqueuse de nettoyage selon l'une quelconque des revendications 1 à 4, et
(ii) éliminer les taches et salissures, de préférence les salissures mobiles, sur ladite surface ;

dans lequel le bénéfice de nettoyage pour la fois suivante se réfère à une plus grande facilité d'élimination des salissures après qu'une surface dure nettoyée a été de nouveau salie.

6. Procédé selon la revendication 5, lequel procédé comprend les étapes successives suivantes consistant à :

(a) appliquer sur la surface une composition aqueuse de nettoyage selon l'une quelconque des revendications 1 à 4 ;
(b) rincer la surface ;
(c) laisser de nouvelles taches ou salissures se déposer sur la surface ; et
(d) nettoyer la surface pour éliminer lesdites taches ou salissures.

7. Utilisation d'une composition aqueuse de nettoyage de surfaces dures selon l'une quelconque des revendications 1 à 4 pour nettoyer une surface dure et obtenir un bénéfice de nettoyage pour la fois suivante de ladite surface.

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