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(54) **Title**: HARD SURFACE TREATMENT COMPOSITION

(57) **Abstract**: The present invention is in the field of hard surface treatment compositions; and in particular relates to hard surface treatment compositions to render a substrate hydrophobic and also repellent to aqueous stains and soils, as well as giving good cleaning on tough soils and stains. It is therefore an object of the present invention to provide easier cleaning upon the subsequent wash; also knows as a next time cleaning benefit. It has been found that a composition comprising a solvent, a carboxylic polymer, a metal ion and a cationic surfactant and having a pH of between 2 and 6, provides both stain repellence as well as good primary and secondary cleaning.



WO 2014/040869 A1

HARD SURFACE TREATMENT COMPOSITION

Field of the invention

The present invention is in the field of hard surface treatment compositions; and in particular relates to hard surface treatment compositions to render a substrate
5 hydrophobic and also repellent to aqueous stains and soils, as well as giving good cleaning on tough soils and stains.

Background of the invention

10 Water droplets have a tendency to stick to surfaces. These water droplets are usually a mixture of water and fine particulate matter in the form of dust or dirt. The particulate matter is either present on the surface before being wetted or is already in a mixture with water when the droplets come in contact with the surface. When the water droplets settle on a surface and eventually dry up, they leave spots or streaks on the surface
15 giving a stain-like appearance. Such an appearance on surfaces is not appreciated by present day consumers.

Without wishing to be bound by a theory, it is believed that the behaviour of a liquid droplet on a surface depends on the adhesive forces between the surface and the
20 liquid. If the adhesive forces are attractive, the liquid droplet is pulled towards the surface and remains on the surface. It is therefore thought that by making said surfaces hydrophobic, water droplets can be repelled by the surface, minimizing the contact of the water droplets with the surface and causing water droplets to bead and cover less of the surface when the surface is horizontal and even roll off inclined and vertical
25 surfaces, and thus preventing surfaces from water damage and deposition of stains and soils.

Metal soap based compositions have been proposed in the past for imparting hydrophobicity to surfaces. Our co-pending application IN-2963/MUM/2011 describes
30 hard surface cleaning compositions. It particularly relates to a method and composition for cleaning of a surface and imparting repellence of soils. It relates to the object of providing a stable surface cleaning composition which can make the surface hydrophobic and oleophobic as well as provide superior cleaning; and proposes a composition comprising fluoro silane with a solvent and a polyvalent metal salt was
35 found to render both hydrophobicity and oleophobicity making the surface less

susceptible to soiling, by both aqueous and oily stains and also provides better cleaning. However, the composition described therein is an opaque composition due to the presence of metal complexes, and the use of which is also less preferred as it not perceived as being eco-friendly. Thus, there is an unfulfilled need for a hydrophobic
5 composition which is transparent and devoid of metals.

US 2004/0077517 and US 2004/0171515 disclose laundry (wash, rinse or care) composition comprising a cationically modified polymer and metal ions and cationic surfactants. They further disclose that the formulation may be applied onto both soft
10 and hard surfaces. They further disclose the use of solvents including low molecular weight alcohols and glycols. What remains to be desired is a composition that imparts improved hydrophobicity to a surface. US 2004/0077517 and US 2004/0171515 do not disclose the use of glycol ethers in the compositions. The present inventors have shown that inclusion of glycol ethers enhance the repellence to water in addition to
15 cleaning. This is thought to be caused by orientation of surfactants and polymers in such a way that after water evaporation, the hydrophilic components form a core and the hydrophobic parts get exposed to the environment to give the desired water and aqueous soil repellence property.

20 IN-1293/MUM/2011 describes a hard surface cleaning composition comprising poly-aluminium-chloride (PAC), soap of C8-C18 fatty acid, a surfactant selected from non-ionic surfactants or quaternary ammonium cationic surfactants, poly vinyl alcohol(PVA) and a quaternary silicon oil. However, metal soaps formed therein contribute to the opaqueness of the composition, thereby leaving a need for transparent hydrophobic
25 compositions.

Hard surface cleaning compositions comprising carboxylic polymers are disclosed in WO97/24425 (The Procter & Gamble Company). These compositions provide improved cleaning and especially improved gloss on a surface, thought to be caused
30 by the combination of a carboxylic polymer, surfactant and a divalent ion. However, improved results on the subsequent cleaning remain to be desired.

Currently known compositions providing a next time cleaning benefit are not performing well on cleaning; they do not provide good stain removal, and leave water streaks
35 and/or spots after wetting a treated surface upon drying.

It is therefore an object of the present invention to provide easier cleaning upon the subsequent wash; also known as a next time cleaning benefit.

It is a further object of the invention to provide a composition for tough stain removal.

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It is a further object of the invention to provide a composition that provides both good primary and good secondary cleaning.

Surprisingly it has been found that a composition comprising a solvent, a carboxylic
10 polymer, a metal ion and a cationic surfactant and having a pH of between 2 and 6, provides both stain repellence as well as good primary and secondary cleaning.

Summary of the invention

Accordingly, the present invention provides a hard surface cleaning composition
15 comprising 0.2-6% by weight of a block or alternate copolymer having moieties A and B, wherein A= polystyrene, polyethylene, polypropylene, polyisobutylene, and B= Water soluble alkali metal salt (sodium/ potassium) of the following acids: acrylic acid, C2-7 dicarboxylic acids; 0.2-8% by weight of a water miscible glycol ether solvent of the formula: $R1 - O - R2OH$; wherein, R1 is a substituted or unsubstituted C2 - C4
20 alkyl group or a substituted or unsubstituted aryl group, preferably phenyl; and R2 is a substituted or unsubstituted C2-C4 alkylene group; 0.01-0.5% by weight of a water soluble metal ion selected from: trivalent and tetravalent metal; and/or bivalent transition metal; and 0.002-0.08% by weight of a cationic surfactant; wherein the pH is from 2 to 6.

25

In a second aspect, the invention further provides for a method for cleaning a hard surface comprising the steps in sequence of: (a) treating a surface with the composition according to anyone of the preceding claims; (b) leaving the surface for soils or stains to deposit; and (c) cleaning the surface with the compositions according to any one of
30 the preceding claims.

For the avoidance of doubt, by primary cleaning is meant that the composition itself, upon first use on a surface provides cleaning efficacy. By secondary cleaning is meant that after first applying the composition to a surface, then leaving it to dry and leaving it

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for dirt to deposit, cleaning efficacy is obtained while applying the composition for a second or subsequent time.

These and other aspects, features and advantages will become apparent to those of
5 ordinary skill in the art from a reading of the following detailed description and the
appended claims. For the avoidance of doubt, any feature of one aspect of the present
invention may be utilised in any other aspect of the invention. The word "comprising" is
intended to mean "including" but not necessarily "consisting of" or "composed of." In
other words, the listed steps or options need not be exhaustive. It is noted that the
10 examples given in the description below are intended to clarify the invention and are
not intended to limit the invention to those examples per se. Similarly, all percentages
are weight/weight percentages unless otherwise indicated. Except in the operating and
comparative examples, or where otherwise explicitly indicated, all numbers in this
description indicating amounts of material or conditions of reaction, physical properties
15 of materials and/or use are to be understood as modified by the word "about".
Numerical ranges expressed in the format "from x to y" are understood to include x and
y. When for a specific feature multiple preferred ranges are described in the format
"from x to y", it is understood that all ranges combining the different endpoints are also
contemplated.

20

Detailed description of the invention

Thus, the invention provides a hard surface treatment composition comprising a block
or alternate copolymer having moieties A and B, wherein A= polystyrene, polyethylene,
polypropylene, polyisobutylene, and B= Water soluble alkali metal salt
25 (sodium/potassium) of the following acids: acrylic acid, C2-7 dicarboxylic acids; a water
miscible glycol ether; a siloxane; a metal salt and a cationic surfactant, wherein the pH
is from 2 to 6, preferably from 3 to 5.

Without wishing to be bound by a theory, it is thought that the composition leaves a
30 deposition of a complex on the hard surface that is treated with the composition.

It is further thought that the polymer-metal complex that forms in the current
composition provides a more hydrophobic layer that is better and more homogeneously
deposited onto the surface than the hydrophobic layers that have been disclosed in the
35 art. The deposition is only achieved in the pH range of the invention.

This imparts hydrophobicity to the surface and makes it water repellent. Hydrophobicity is measured by the contact angle of a water droplet on a treated surface. A contact angle above 90° is acceptable, above 100° is preferred.

5 Polymer

It is thought that a small amount of the, when deposited onto a hard surface, reduces the surface energy of the surface and provides a hydrophobic layer on said surface, thereby preventing the water spilt on a surface to spread and result in stains.

- 10 The polymer is typically a block or alternate copolymer having moieties A and B, wherein:

A = polystyrene, polyethylene, polypropylene, polyisobutylene, and

B = Water soluble alkali metal salt (sodium/ potassium) of the following acids: acrylic acid, C2-7 dicarboxylic acids;

15

In a preferred embodiment, the copolymer may be a styrene/maleic copolymers, selected from block or alternate copolymer having, wherein A is selected from polystyrene; and B is maleic acid, forming the preferred polymers including poly(styrene-alt-maleic acid)sodium salt, poly(styrene-co-maleic acid) sodium salt, and
20 poly (styrene-alt-maleic anhydride).Block copolymers consist of two or more block sequences, at least one of which is not a homopolymer or uniformly random copolymer sequence. In case of random copolymers the composition changes continuously along the polymer chain and with conversion, without giving rise to a detectable block structure (JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 1581-1591

25 (1967))

Other preferred polymers of this type include poly(styrene-co-acrylic acid) sodium salt and polystyrene-block-poly (acrylic acid)sodium salt.

- 30 The most preferred copolymers of the present invention are poly(styrene-alt-maleic acid) and poly (styrene-alt-maleic anhydride).

The polymer is present in the composition a concentration of from 0.2 to 6% by weight of the composition, preferably at least 0.3%, more preferably at least 0.5% by weight, but typically not more than 5%, more preferably not more than 3%, still more preferably
35 not more than 2% by weight.

The polymer composition concentrations beyond the scope of the invention deteriorate hydrophobicity.

Glycol ether

5 The composition comprises a water miscible glycol ether to improve the hydrophobicity or water repellency imparted by the composition, and to also enhance the cleaning properties of the composition. It is thought that these properties are imparted to the composition due to the HLB of the glycol ether.

10 Water miscible glycol ethers used in the present invention are of the formula
 $R_1 - O - R_2OH$

wherein, R_1 is a substituted or unsubstituted $C_2 - C_4$ alkyl group, aryl group (preferably phenyl), or alkylaryl group; and R_2 is a substituted or unsubstituted $C_2 - C_4$ alkylene
15 group.

Non-limiting examples of the water miscible glycol ethers include ethylene glycol monophenyl ether (2- phenoxyethanol), ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethylene glycol monobenzyl
20 ether, propylene glycol propyl ether. The most preferred water miscible glycol ethers are ethylene glycol monophenyl ether (2- phenoxyethanol) and propylene glycol propyl ether, especially propylene glycol n-propyl ether.

When added to the composition, water miscible glycol ether may be present in the
25 composition in a concentration of 0.003 – 5%, preferably between 0.005% - 4%, more preferably at least 0.2 %, but preferably not more than 2% by weight of the total composition. The best cleaning results are obtained at a concentration of between 0.2 and 5% by weight.

30 By water miscible, it is meant that at least 5% of the glycol ether is soluble in or miscible with water.

Metal ion

The composition further comprises a metal ion. It is thought that the metal ion of the
35 salt aids in the deposition of a complex on the surface and imparts additional

hydrophobicity. This is thought to be due to the metal polymer complex formation, which deposits on the surface of the substrate. It also aids the deposition of the optional siloxane onto the surface. It is further thought that a higher positive charge on the metal ion also helps in deposition on negatively charged surfaces like glass or
5 ceramics.

The metal ion is selected from water soluble trivalent and tetravalent metal ions; and/or bi valent transition metal ions. Any combination of two or more of the metal or transition metal ions is also included in the purview of the present invention. The metal ions
10 include: bivalent Zn(II), trivalent Al(III), Ti(III), Fe(III), Tetravalent Ti(IV). The commercially most viable are Zn(II), Al(III) and Fe(III).

The most preferred metal ions are aluminium (Al^{3+}) and Zinc (Zn^{2+}), of which aluminium (Al^{3+}) is the most preferred.
15

The metal ion is typically added to the composition in the form of a salt; preferred salts are halides, nitrate, sulphate and acetate for the metal ions indicated. The preferred salts are Aluminum chloride, polyaluminum chloride, aluminium nitrate, zinc nitrate, zinc chloride, zinc sulphate and zinc acetate.
20

The metal ion is present in the composition in a concentration of between 0.01 and 0.5% by weight. The metal ion is preferably present in a concentration of at least 0.02% or even at least 0.05% by weight of the composition, but typically not more than 0.45% or even not more than 0.4% by weight of the composition. The best hydrophobicity
25 results are obtained at a concentration of between 0.05 and 0.25% by weight.

Cationic surfactants

The composition comprises a cationic surfactant. The most preferred cationic surfactants are quaternary ammonium cationic surfactants.
30

The quaternary ammonium surfactants are preferably halides of Benzalkonium, Cetyl-trimethyl-ammonium, Tetradecyl-trimethyl-ammonium, Dodecyl-trimethyl-ammonium, Stearyl-trimethyl-ammonium, Octadecyl-trimethyl-ammonium, Dodecylpyridinium, Cetylpyridinium, Tetraethyl-ammonium, Tetraheptyl-ammonium, 1,3-Decyl-2-methyl-imidazolium, 1-Hexadecyl-3-methyl-imidazolium, Didecyl-dimethyl-ammonium, Didecyl-
35

dimethyl-ammonium. The most preferred cationic surfactant are Cetyl-trimethyl-ammonium halides.

From a safety perspective, chlorides and iodides are the most preferred, bromide and
5 fluorides are equally contemplated in the context of the invention.

The cationic surfactant is present in the composition in a concentration of between 0.002 and 0.07% by weight. The cationic surfactant is preferably present in a concentration of at least 0.01% or even at least 0.02% by weight of the composition,
10 but typically not more than 0.06% by weight of the composition. The best hydrophobicity results are obtained at a concentration of between 0.02 and 0.06% by weight

Siloxane

15 The composition according to the invention may further comprise a siloxane of the formula $-\text{[SiHX-O]}_n-$, wherein $X = \text{H}$ or CH_3 and $n \geq 5$.

When the siloxane is present in the composition a further increase in hydrophobicity or water repellency is achieved.
20

Siloxanes that are preferred in the present invention are preferably of the following classes: a) siloxanes with reactive hydrogen b) non reactive siloxanes of high molecular weight and c) non reactive siloxanes of low molecular weight.

25 a) Siloxanes with reactive hydrogen

Non-limiting examples of siloxanes with reactive hydrogen preferably include poly(methylhydrosiloxane), poly(ethylhydrosiloxane), poly(propylhydrosiloxane) or hexyldihydrosiloxane. These siloxanes preferably have a molecular mass of between 1700 and 3200 u. The most preferred siloxane in this class is
30 poly(methylhydrosiloxane) (PMHS)

b) Non reactive siloxanes of high molecular weight

Non-limiting examples of non reactive siloxanes of high molecular weight preferably include polydimethyl siloxane having a molecular mass of between 800 and 14000 u.
35 Above 14000 u, the kinematic viscosity becomes too high (typically more than 4000 cSt

(centistokes; Stokes (St) being cm^2/s), while it becomes too low below 800 u, typically less than 50 cSt. The most preferred siloxane in this class is polydimethyl siloxane, preferably having an approximate molecular weight of between 6000 u and 13650 u.

5 c) Non reactive siloxanes of low molecular weight

Non-limiting examples of non reactive siloxanes of low molecular weight preferably include low viscosity cyclomethicones, including hexamethylcyclotrisiloxanes, octamethylcyclotetrasiloxanes or decamethylcyclopentasiloxanes. The most preferred siloxane in this class is cyclopentasiloxane.

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The most preferred siloxanes are polymethylhydrosiloxane (PMHS), polydimethylsiloxane (PDMS) and cyclopentasiloxane; and mixtures thereof.

When siloxane is present in the composition, it may be present in the composition in a concentration of between 0.1 and 10% by weight, preferably not less than 0.5% by weight, but preferably not more than 8% or even not more than 5% by weight of the total composition. The best hydrophobicity results are obtained at a concentration of between 0.5 and 5% by weight.

20 **Optional ingredients**

In a preferred embodiment, the composition according to the invention further comprises an acid stable abrasive material; both natural acid stable abrasives and synthetic materials are considered in the purview of the present invention.

25 Common cleaner and aesthetic additives such as perfumes, fluorescers and optical brighteners, antimicrobial agents (antibacterial agents such as essential oils, eugenol, cationic amino surfactants), fluoropolymers and/or fluorosurfactants, viscosity modifiers such as gum resins, polysaccharides, fatty alcohols, polyols (such as polyvinyl alcohol, glycerol) essential oils etc may also be included.

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Method

The invention further provides for a method for cleaning a hard surface comprising the steps in sequence of: (a) treating a surface with the composition according to anyone of the preceding claims; (b) leaving the surface for soils or stains to deposit; and (c)

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cleaning the surface with the compositions according to any one of the preceding claims.

Ideally surface is not rinsed between steps (a) and (b).

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Product format

The composition may be packaged in the form of any commercially available bottle for storing the liquid or in the form of a kit comprising the concentrated liquid along with instructions for its use.

10

The bottle containing the liquid can be of different sizes and shapes to accommodate different volumes of the liquid; preferably between 0.25 and 2 L, more preferably between 0.25 and 1.5 L or even between 0.25 and 1 L. The bottle is preferably provided with a dispenser, which enables the consumer an easier mode of dispersion of the liquid. Spray or pump-dispensers may be used. However, a trigger spray dispenser is the most preferred.

15

Examples

The invention will now be illustrated by means of the following non-limiting examples.

20

Ingredients used:

1. Block copolymer:

25

- a. Poly (styrene-*alt*-maleic acid) sodium salt solution 13 wt. % in H₂O (ex Sigma Aldrich, Product number 662631);
- b. polyethylene -co-acrylic acid sodium salt (ex Sigma Aldrich).

2. Glycol ether solvent:

- a. Propylene Glycol n-Propyl Ether (Dowanol PnP, Sigma Aldrich);
- b. 2 -phenoxyethanol (Sigma Aldrich)

30

3. Siloxane (OPTIONAL INGREDIENT)

- a. PMHS : Poly(methylhydrosiloxane)-average M_n 1,700-3,200 (ex Sigma Aldrich)
- b. PDMS-cyclopentasiloxane : Polydimethyl siloxane - cyclopentasiloxane (ex Dow Corning, DC 245 fluid)
- c. PDMS-350 cSt : Polydimethyl siloxane polymer fluid with viscosity 350 cSt (ex Dow Corning, DC 200)

35

4. Metal salt: Polyaluminum chloride (Arya PAC ex Grasim)
5. Cationic Surfactant:
 - a. Cetyltrimethylammonium bromide (ex Sigma Aldrich);
6. Other surfactants:
 - 5 a. Anionic: Sodium dodecyl sulphate (ex Sigma Aldrich)
 - b. Non-ionic: C₁₂EO_{<7>} (ex BASF)

Treatment procedure:

0.25 ml of the treatment solution was spread uniformly on a 2.5 cm X 12 cm clean
10 glass microscopic slide. The solution was left on the glass substrate for 1 minute and
wiped with a tissue paper till completely dry. The dried treated slide was used for
checking water repellency.

Primary cleaning of glass substrate:

15 Farrell (extra virgin olive oil, commercially available ex: Jindal; Batch No. L11370263)
was used to stain the glass surface. 0.1 ml of olive oil was smeared uniformly on a 2.5
cm x 12 cm clean glass microscopic slide. The stained glass slide was heated in an air
oven at 95°C for 48 hours. The aged glass surface was treated with treatment
formulation (treatment procedure discussed above). The gloss was measured on the
20 glass substrate using a gloss meter (Sheen Instruments Ltd UK, cat No. 4174) at a
detector angle set at 60° against a black background (R=0, G=0, B=0). Higher gloss
measurement value is an indication of higher cleaning. A good glossy surface typically
has a gloss value of 110 or above by this measurement protocol.

25 Secondary cleaning of glass substrate:

To measure the secondary cleaning benefit imparted by the treatment formulation on
the treated substrate, 0.1 ml of olive oil was smeared uniformly on a 2.5 cm X 12 cm
clean glass microscopic slide. The glass surface was treated with treatment formulation
(treatment procedure discussed above). The gloss was measured on the glass
30 substrate using a gloss meter (Sheen Instruments Ltd UK, cat No. 4174) at a detector
angle set at 60° against a black background (R=0, G=0, B=0). Higher gloss
measurement value is an indication of higher cleaning. A good glossy surface typically
has a gloss value of 110 or above by this measurement protocol.

Test for water repellence:

The contact angle of the sessile droplet was measured using a Kruss goniometer by placing a 10 microlitre of distilled water droplet on the glass slide. The angle was analyzed by the image J software using the Drop snake plug-in. Higher contact angle is an indication of higher hydrophobicity imparted by a treatment formulation on a substrate. A contact angle of 93° and above is considered hydrophobic by this measurement protocol.

The present invention gives the benefit of rendering a hard surface (like glass) to provide both superior primary and secondary cleaning (as reflected by gloss values of 110 and above at 60° angle) and is also hydrophobic (water contact angle of 93° and above) when treated with the composition mentioned in the claim.

Example 1a: Effect of ingredients:

The hydrophobicity of compositions with all individual components of the invention (Example compositions 1 and 2), is compared with compositions lacking one or more of the essential components (Comparative example compositions A-I).

The following compositions were compared. In all examples the pH is 4.

	Polymer (%w/w)	PMHS (optional) (%w/w)	Dowanol PnP¹⁾ (%w/w)	Metal ion (%w/w)	Metal ion	Surfactant (%w/w)	type
A	1.5	2	2	0.1	Al	0	
B	1.5	0	0	0.1	Al	0	
C	1.5	0	2	0.1	Al	0	
1	1.5	2	2	0.1	Al	0.02	CTAB
2	1.5	0	2	0.1	Al	0.02	CTAB
D	1.5	0	0	0.1	Al	0.02	CTAB
E	0	0	2	0		0	
F	0	2	0	0		0	
G	1.5	0	0	0		0	
H	0	0	0	0.1	Al	0	
I	0	0	0	0		0.02	CTAB

The results on hydrophobicity (contact angle, CA) and primary as well as secondary cleaning are given in the table below.

	Contact angle (°)	Gloss at 60° primary cleaning	Gloss at 60° secondary cleaning
A	94	129	96
B	84	106	115
C	89	112	97
1	101	131	118
2	97	127	119
D	89	121	93
E	45	90	97
F	78	109	82
G	48	128	132
H	37	103	119
I	32	126	100

- 5 The table above shows that good hydrophobicity (> 90° contact angle) is obtained with a formulation according to the invention. Incorporation of siloxane (PMHS) as an optional ingredient further boosts the contact angle. Removal of any of the ingredients affects hydrophobicity. Comparative example A, without the cationic surfactant, also shows good hydrophobicity, but the secondary cleaning performance is inadequate.

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Example 1b: Effect of ingredients:

The hydrophobicity of compositions with all individual components of the invention in a higher concentration (Example compositions 1A and 2A), is compared with compositions lacking one or more of the essential components (Comparative example compositions AA-II).

15

The following compositions were compared. In all examples the pH is 4.

	Polymer (%w/w)	PMHS (optional) (%w/w)	Dowanol PnP¹ (%w/w)	Metal ion (%w/w)	Metal ion	Surfactant (%w/w)	type
AA	6	8	8	0.5	Al	0	

BB	6	0	0	0.5	Al	0	
CC	6	8	8	0.5	Al	0	
1A	6	8	8	0.5	Al	0.10	CTAB
2A	6	0	8	0.5	Al	0.10	CTAB
DD	6	0	0	0.5	Al	0.10	CTAB
EE	0	0	8	0		0	
FF	0	8	0	0		0	
GG	6	0	0	0		0	
HH	0	0	0	0.5	Al	0	
II	0	0	0	0		0.10	CTAB

1) Dowanol PnP is propylene glycol n-propyl ether

The results on hydrophobicity (contact angle, CA) and primary as well as secondary cleaning are given in the table below.

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	Contact angle (°)	Gloss at 60° primary cleaning	Gloss at 60° secondary cleaning
AA	100	134	96
BB	96	104	115
CC	97	116	97
1A	104	139	127
2A	98	131	129
DD	86	124	84
EE	38	92	96
FF	66	111	89
GG	54	125	136
HH	29	109	115
II	30	129	112

The table above shows that good hydrophobicity (> 90° contact angle) is obtained with a formulation according to the invention. Incorporation of siloxane (PMHS) as an

optional ingredient further boosts the contact angle. Removal of any of the ingredients affects hydrophobicity. Comparative example AA, without the cationic surfactant, also shows good hydrophobicity, but the secondary cleaning performance is inadequate.

5 Example 2: Effect of different types of surfactants

In this example the effect of different types of surfactants are compared. Example 3 comprises cationic surfactant, while comparative examples J and K comprise anionic surfactant and nonionic surfactant respectively.

10 All compositions had a pH of 4.

	Polymer (%w/w)	PMHS (%w/w)	dowanol PnP (%w/w)	Al³⁺ ion (%w/w)	surfactant (%w/w)	type of surf	CA (°)
J	1.5	2	2	0.1	0.02	SDS	65
K	1.5	2	2	0.1	0.02	EO	69
3	1.5	2	2	0.1	0.02	CTAB	102

From the table above it can be concluded that hydrophobicity is provided when the formulation includes cationic surfactants, whereas anionic and non ionic surfactants do not provide adequate hydrophobicity.

15

Example 3: Effect of different metal ions.

In this example different metal ions are compared; Aluminium and zinc (example compositions 4, 5 and 6) according to the invention and are compared with comparative example compositions L and M, with calcium and magnesium respectively. The pH in all compositions was 4 and the surfactant was CTAB.

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	Polymer (%w/w)	PMHS (%w/w)	dowanol PnP (%w/w)	metal ion ¹⁾ (%w/w)	Metal ion	surfactant (%w/w)	CA (°)
4	1.5	2	2	0.1	Al	0.02	110
5	1.5	0	2	0.1	Al	0.02	105
6	1.5	2	2	0.25	Zn	0.02	98
L	1.5	2	2	0.15	Ca	0.02	68
M	1.5	2	2	0.1	Mg	0.02	71

1) Weight% adjusted to equal molar concentration.

Trivalent metal ions (Al) and bivalent transition metal ion (Zn)-containing formulations provide hydrophobic effect on substrate while those containing non transitional bivalent metal ions do not provide hydrophobicity.

Example 4: Effect of surfactants concentration

In this example the effect of the surfactant concentration is demonstrated.

Examples 7-10 are within the claimed range, while examples N and O are outside. All compositions had a pH of 4, and the metal ion was Al^{3+} and the surfactant was CTAB.

	polymer (%w/w)	PMHS (%w/w)	dowanol PnP (%w/w)	metal ion (%w/w)	surfactant (%w/w)	CA (°)
7	0.3	1	0.4	0.02	0.004	92
8	0.3	1	0.4	0.02	0.02	95
9	0.3	1	0.4	0.02	0.04	99
10	0.3	1	0.4	0.02	0.06	95
N	0.3	1	0.4	0.02	0.08	89
O	0.3	1	0.4	0.02	0.1	87

From the table we can conclude that examples 7-10, according to the invention perform better than the examples outside the claimed range (N and O).

Example 5: Effect of siloxanes

In this example the effect of the different siloxanes is shown.

Examples 7-10 are within the claimed range, while examples N and O are outside. All compositions had a pH of 4, and the metal ion was Al^{3+} and the surfactant was CTAB at a concentration of 0.02%w.

	polymer (%w/w)	siloxane (%w/w)	dowanol PnP (%w/w)	metal ion (%w/w)	Siloxane type	CA (°)
11	1.5	5	2	0.1	PMHS	112
12	1.5	4	2	0.1	PMHS	111

13	1.5	2	2	0.1	PMHS	109
14	1.5	1	2	0.1	PMHS	108
15	1.5	0.5	2	0.1	PMHS	105
16	1.5	5	2	0.1	Dc200-350cst	105
17	1.5	4	2	0.1	Dc200-350cst	101
18	1.5	2	2	0.1	Dc200-350cst	102
19	1.5	1	2	0.1	Dc200-350cst	101
20	1.5	0.5	2	0.1	Dc200-350cst	101
21	1.5	5	2	0.1	DC245	99
22	1.5	4	2	0.1	DC245	99
23	1.5	2	2	0.1	DC245	98
24	1.5	1	2	0.1	DC245	97
25	1.5	0.5	2	0.1	DC245	100

It can be concluded that different siloxanes from all preferred classes can further improve the contact angle when added to the formulation. Of the different siloxanes tried in the experiment, PMHS (reactive siloxanes) performs best.

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Example 6: Effect of the solvent concentration.

Different solvents were compared. Propylene glycol n-propyl ether (dowanol PnP) and 2-phenoxy ethanol (both according to the invention) are compared with comparative solvents (ethanol and iso-propanol (IPA))

10

In all examples the base composition was as given in the table below. All compositions had a pH of 4, and the metal ion was Al^{3+} at a concentration of 0.1%w, the polymer was present in a concentration of 1.5%w and the surfactant was CTAB at a concentration of 0.02%w. The solvent percentage is varied.

15

	Solvent (%w/w)	Dowanol PnP CA (°)	phenoxy ethanol CA (°)	Ethanol CA (°)	Iso-propanol CA (°)
26	5	108	104	87	86
27	4	106	105	88	85
28	3	106	105	86	86
29	2	105	105	87	84
30	1	100	100	85	85

31	0.5	101	99	86	86
32	0.25	99	99	86	88
33	0.2	96	95	-	-
34	0.15	89	88	-	-
35	0.1	85	85	85	83
36	0.05	88	85	88	81
37	0	87	86	84	82

From the above table it can be concluded that from 0.2 % by weight of 2 phenoxy ethanol and propylene glycol n-propyl ether (dowanol PnP) show good hydrophobicity, whilst alcohols (ethanol and IPA) do not show that effect.

5

Example 7: Effect of the solvent concentration on the primary and secondary cleaning efficacy

In this example the solvent concentration was varied.

- 10 In all compositions the metal ion was Al^{3+} at a concentration of 0.1% by weight and the surfactant was CTAB at a concentration of 0.02% by weight, and the pH was 4.

	polymer (%w/w)	dowanol PnP (%w/w)	CA (°)	Gloss @ 60° primary cleaning	Gloss @ 60° secondary cleaning
PP	1.5	10	72	146	121
38A	1.5	8	93	133	122
38B	1.5	6	104	135	124
38	1.5	5	108	139	122
39	1.5	3	106	134	121
40	1.5	1	100	132	121
41	1.5	0.25	99	127	119
P	1.5	0.15	89	122	112
Q	1.5	0.05	88	119	105
R	1.5	0	87	121	93

- 15 The primary and secondary cleaning along with high contact angle is best achieved for solvent concentration above 0.2 wt %but less than 10 wt %.

Example 8: Effect of the metal ion concentration.

In this example the metal ion concentration was varied.

All compositions had a pH of 4, and the metal ion was Al^{3+} and the surfactant was

5 CTAB at a concentration of 0.02%w.

	polymer (%w/w)	PMHS (%w/w)	dowanol PnP (%w/w)	metal ion (%w/w)	CA (°)
S	1.5	2	2	0.003	84
T	1.5	2	2	0.006	89
42	1.5	2	2	0.01	95
43	1.5	2	2	0.02	103
44	1.5	2	2	0.05	105
45	1.5	2	2	0.1	108
46	1.5	2	2	0.15	109
47	1.5	2	2	0.2	108

From the above table it can be concluded that for metal ion concentration above 0.01% by weight the hydrophobicity reaches an acceptable level.

10

Example 9: Effect of the pH.

In this example the pH was varied.

In all compositions the metal ion was Al^{3+} at a concentration of 0.1% by weight and the

15 surfactant was CTAB at a concentration of 0.02% by weight.

	polymer (%w/w)	PMHS (%w/w)	dowanol PnP (%w/w)	pH	CA (°)
48	1.5	2	2	2	102
49	1.5	2	2	4	108
50	1.5	2	2	5	103
51	1.5	2	2	6	100
U	1.5	2	2	7	81
V	1.5	2	2	8	77

The table above shows that the formulation according to the invention imparts hydrophobicity onto a surface in a pH range of 2-6.

Claims

- 1 A hard surface cleaning composition comprising:
 - a 0.2-6% by weight of a block or alternate copolymer having moieties A and B, wherein
 - i A= polystyrene, polyethylene, polypropylene, polyisobutylene, and
 - ii B= Water soluble alkali metal salt (sodium/ potassium) of the following acids: acrylic acid, C2-7 dicarboxylic acids;
 - b 0.2-8% by weight of a water miscible glycol ether solvent of the formula:
$$R1 - O - R2OH$$
; wherein,
R1 is a substituted or unsubstituted C2 – C4 alkyl group or a substituted or unsubstituted aryl group, preferably phenyl; and
R2 is a substituted or unsubstituted C2- C4 alkylene group;
 - c 0.01-0.5% by weight of a water soluble metal ion selected from:
 - i trivalent and tetravalent metal; and/or
 - ii bivalent transition metal; and
 - d 0.002-0.08% by weight of a cationic surfactant;wherein the pH is from 2 to 6.
- 2 A composition according to claim 1, further comprising 0.1-10% by weight of a siloxane of the formula $-[SiHX-O]_n-$, wherein X = H or CH₃; And n >=5
- 3 A composition according to claim 2, wherein the siloxane is selected from polymethylhydrosiloxane (PMHS), polydimethylsiloxane (PDMS) or cyclopentasiloxane; and mixtures thereof.
- 4 A composition according to anyone of claims 2 or 3, wherein the siloxane is present in a concentration of 0.5 to 5% by weight of the composition.
- 5 A composition according to any one of the preceding claims, further comprising 1-10% by weight of an acid stable abrasive.

- 6 A composition according to any one of the preceding claims, wherein the water miscible glycol ethers is selected from ethylene glycol monophenyl ether (2-phenoxyethanol) and propylene glycol propyl ether.
- 7 A composition according to any one of the preceding claims, wherein the metal ion is selected from aluminium (Al^{3+}) and Zinc (Zn^{2+}).
- 8 A composition according to any one of the preceding claims, wherein the metal salt is present in a concentration of between 0.1 and 1% by weight of the composition.
- 9 A composition according to any one of the preceding claims, wherein the copolymer is selected from poly(styrene-alt-maleic acid) and poly (styrene-alt-maleic anhydride).
- 10 A composition according to any one of the preceding claims, wherein the glycol ether solvent is present in a concentration of between 0.2 and 5% by weight of the composition.
- 11 A composition according to any one of the preceding claims, wherein the copolymer is present in a concentration of between 0.2 and 2% by weight of the composition.
- 12 A composition according to any one of the preceding claims, wherein the cationic surfactant is present in a concentration of between 0.02 and 0.06% by weight of the composition.
- 13 A method for cleaning a hard surface comprising the steps in sequence of:
 - a Treating a surface with the composition according to anyone of the preceding claims;
 - b Leaving the surface for soils or stains to deposit; and
 - c Cleaning the surface with the compositions according to any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/068047

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D3/00 C11D3/37 C11D3/04 C11D3/20 C11D1/62 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 19 December 2013		Date of mailing of the international search report 07/01/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Loiselet-Taisne, S

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