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(54) **USE OF POLYMERIC MATERIAL IN THE TREATMENT OF HARD SURFACES**

VERWENDUNG VON POLYMEREM MATERIAL ZUR BEHANDLUNG HARTER OBERFLÄCHEN

UTILISATION DE MATIERE POLYMERE DANS LE TRAITEMENT DE SURFACES DURES

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DescriptionIntroduction

[0001] The present invention relates to the use of polymeric material in the treatment of hard surfaces to deal with scale forming calcium salts. Scale is an important soil in bathrooms and kitchens and one which is not easy to remove. Household water supplies contain varying levels of calcium and magnesium salts. Residual water left after, e.g. bathing, showering, dishwashing, rinsing, etc. will eventually evaporate leading to the deposition of calcium salts on surfaces as scale.

[0002] The scale deposits formed can become unsightly, hard and very difficult to remove. This can happen particularly quickly in hard water areas where the level of calcium in domestic water is high.

[0003] Conventional hard surface cleaners may comprise acid or abrasive in order to assist with the removal of scale. However, enamel and marble surfaces are susceptible to acid damage and all surfaces may become scratched and unsightly due to the excessive use of abrasive.

[0004] Polymeric materials have been used in the water treatment art to prevent precipitation of scale forming salts from standing water. However, these require a body of water in which the scale forming salts remain suspended. In domestic hard surfaces, droplets of water containing calcium or magnesium salts will eventually evaporate to dryness and the calcium salts will inevitably be deposited.

[0005] Attempts have been made in the art to deposit polymeric material onto hard surfaces to allow subsequently deposited soil such as grease to be easily removed.

[0006] It has not however been generally believed in the art that it is possible to provide a release polymer for limescale.

[0007] WO 99/60086 discloses acidic compositions comprising polyvinylpyrrolidone and a polysaccharide such as xanthan. The compositions provide a next-time cleaning benefit and are said to reduce or prevent the formation of limescale. However, no data are given to support this claim.

[0008] EP 0 875 555 discloses acidic compositions comprising a polysaccharide such as xanthan. Again the compositions provide a next-time cleaning benefit and are said to reduce or prevent the formation of limescale, but again, no data are given to support this claim.

[0009] The present inventors have realised that, whereas it may not be possible to prevent deposition of calcium salts, it will be possible to control the mechanism of calcium salt deposition and thereby affect the strength of bond between calcium salts and the hard surface.

[0010] Scale can deposit onto household surfaces in two main ways:

(a) crystallisation in the bulk solution; here, scale can form by homogeneous nucleation or by heterogeneous nucleation onto e.g. dust particles which can act as seeds for nucleation. Bulk heterogeneous nucleation and homogeneous nucleation require high supersaturation of scale forming salts and can be rapid. Scales formed under these conditions are likely to be amorphous and adhere only weakly to the substrate. Scales which nucleate via bulk heterogeneous nucleation on dust particles can form at lower supersaturations and tend to form more slowly; they are therefore likely to be more crystalline but will still adhere only weakly to the household surface.

(b) crystallisation at the hard surface; here, crystals can form by heterogeneous nucleation in which the household surface acts as the site for nucleation.

In this case, scale is formed at low supersaturation; the process is comparatively slow and results in crystalline deposits which are compact and intimately bound to the surface.

[0011] The present inventors have realised that a polymeric material can be deposited onto a hard surface to inhibit heterogeneous nucleation at that surface. The majority of the nucleation will then occur in the bulk solution leading to the deposition of scale forming salts that are easy to remove. The polymer also reduces further aggregation and toughening of new scale on already existing scale deposits.

[0012] Furthermore it has been found that such polymers provide an anticorrosion benefit when applied to metal surfaces.

[0013] Preventing scale from forming or adhering to household surfaces will retain the smoothness of the surface and prevent it from dulling. This is particularly important for surfaces which are likely to come in extensive contact with water such as can be found in bathrooms, toilets, kitchens and the like. Such surfaces are often made of metal, vitreous materials or hard plastics.

Summary of the invention

[0014] The present invention accordingly provides the use of a polymeric material to reduce heterogeneous nucleation

of calcium and magnesium salts at hard surfaces comprising depositing onto the hard surface, a polymeric material which is a natural polymer modified with nitrogen containing species and wherein furthermore the polymeric material has a weight average molecular weight greater than 10,000 and has cationic groups or groups which become cationic at the pH of use.

[0015] The invention also provides a process for preventing scale from forming or adhering to metal, vitreous or hard plastic surfaces comprising applying to the surface a cleaning composition comprising a detergent surfactant and a polymeric material as described above

Detailed description of the invention

Polymeric Material

[0016] Many types of polymeric material are suitable for use in the present invention. It is required that the polymer is one which, when deposited onto a hard surface at a suitable level, will reduce heterogeneous nucleation of scale forming salts at that surface. Preferably, polymeric material achieves a reduction in the nucleation rate (number of nuclei per unit area per unit time) of scale forming salts at the surface. The following test has been derived to determine whether a polymeric material achieves a reduction in nucleation density (number of nuclei per unit area), which can easily be converted into a nucleation rate if the duration of the experiment is also recorded.

[0017] The test comprises applying a solution of polymer of known concentration to a first area sample of a hard surface, providing a second area sample of the hard surface having no polymer thereon and flowing a supersaturated solution of a scale forming salt over each area sample of the hard surface for a known period of time and comparing the number of nuclei formed per unit area per unit time for the area sample treated with the polymeric material with the number of scale nuclei formed per unit area per unit time for the untreated area sample to obtain an estimate of the reduction of the rate of heterogeneous nucleation at the hard surface.

The apparatus for measuring reduction of nucleation density

[0018] The apparatus for use in the test for determining whether a polymeric material is suitable for reducing nucleation density at a surface is described below:

The apparatus 1 comprises means for delivering two solutions which, when mixed, will produce a supersaturated solution of scale forming salt. The apparatus for delivering the two solutions comprises a pair of syringes 2 and 3. The syringes 2 and 3 contain solutions A and B respectively. In order to ensure that the flow rates of the solutions A and B are the same, a common driving mechanism 4 for both syringes is provided. The mechanism 4 is configured to deliver a constant flow of solutions A and B. The mechanism 4 may comprise a dual drive syringe-type pump which can be obtained from CP Instruments, Model 200. A mixing cell 5, which will be described further below is provided to mix the solutions A and B. The mixed solutions A and B are then directed onto a surface to be tested in a manner which will be described further below. Spent solution is discharged.

[0019] All tubing used in the apparatus comprises PTFE tubing for example OD 3.2 mm, ID 1.5 mm obtainable from Omnifit (Trade Mark). The apparatus is jacketed in nitrogen to ensure that carbon dioxide is not reabsorbed.

[0020] The mixing cell 5 comprises a block of PTFE which has a hollow spherical space 7 formed in its interior. The spherical space 7 is of volume 1 mm³. Projecting through the block and into the space 7 are two capillary tubes, 8 and 9 along which solutions A and B are delivered respectively. The capillary tubes 8 and 9 terminate in nozzles close to the centre of the hollow space 7. The solutions A and B are directed towards one another and mixed in the centre of the hollow space 7. As the block is formed of PTFE, even though a supersaturated solution is formed in the space 7, substantially no adhesion or precipitation of crystalline material onto the surface of the space 7 occurs. The resulting mixed solution leaves the hollow space 7 through a duct 10, whence it is delivered to the experimental surface to be tested. The capillaries 8 and 9 have end openings of 100 micrometres diameter.

[0021] The mixture of solutions is directed onto a surface to be tested. The surface 11 to be tested is mounted beneath a nozzle 12, through which the mixed solution from the mixing cell 5 is delivered to the surface 11. The resulting flow pattern is a wall-jet flow pattern, which is well understood by the person skilled in the art. The flow is radially outwards from the centre of the surface 11 to be tested, and is uniform.

[0022] The nozzle 12 is a 0.8 mm internal diameter PTFE nozzle placed 3 mm above the surface 11. The mixed solution is delivered at a flow rate of 4 cm³/min. The wall jet apparatus 6 is jacketed in nitrogen to prevent CO₂ absorption.

[0023] All experiments were carried out in an air-conditioned laboratory. The temperature is measured at the start of each run. Temperatures are typically 23°C.

[0024] The apparatus allows continual refreshment of the surface with solution of known composition allowing crystal

growth to occur under conditions of constant supersaturation.

Method

[0025] The apparatus is used to test a surface by the following method.

[0026] A supersaturated solution is created in a manner known to the person skilled in the art by mixing together two stable, undersaturated solutions. The solutions are degassed before use using N_2 to remove dissolved CO_2 .

[0027] Solution is flowed over the surface to be treated for a fixed time. A suitable time is 45 minutes.

[0028] As a result of the flow of solution over the surface 11 to be tested, scale forming salt is deposited onto the surface. At the end of each experiment, any crystals at the air/water interface are suctioned away using a small piece of tubing attached to a water pump. The surface is then removed from the apparatus 6, rinsed briefly with a saturated solution of the scale forming salt, dried with nitrogen and inspected under a microscope.

[0029] Characterisation of the degree of crystal growth on a surface to be tested can be achieved using a digitised map of the surface produced by micrographics. This map may then be processed using image analysis software (for example Aequitas, Dynamic Data Links Ltd) which allows automated measurements of crystal size, number and distribution over a choice of area. This allows the nucleation density to be measured.

[0030] The surfaces to be tested can be prepared and treated in any way as long as the surface remains reasonably flat. Sample surfaces are preferably polished to a finish of 1/20 micrometres using 0.05 gamma alumina obtainable from Buehler.

[0031] In order to study the effect of polymer deposited onto the surface 11 to be tested, half of the surface is masked and half is treated with a solution or dispersion of the polymeric material. A 50 microlitre drop of the polymer solution is placed onto the unmasked half of the sample surface and allowed to wet that part of the surface. The drop is left until dry and washed with 10 sprays of deionised water from a trigger spray gun. Drying time may be from 5 minutes to 20 hours, as appropriate.

[0032] Preferably, the surface 11 to be tested is in the form of a disc.

[0033] Preferably, a set of discs of the same size is used, consisting of a stainless steel disc, a ceramic disc, an enamel coated disc, a glass disc and a perspex disc.

[0034] The nucleation density on the untreated half can then be compared to the nucleation density on the treated half.

[0035] The experiment may be repeated with different types of calcium salt, for example, calcium carbonate or calcium sulphate or with magnesium salts such as magnesium carbonate or magnesium sulphate.

[0036] Polymers which are particularly suitable for use in the present invention reduce the nucleation density at the surface by at least 10% on at least one of the test surfaces (glass, steel, ceramic, enamel or perspex) with at least one of the salts (calcium carbonate, calcium sulphate, magnesium sulphate, magnesium carbonate). More preferably the polymer will reduce the nucleation rate by at least 20%, even more preferably by at least 30% and most preferably by at least 50%.

[0037] It is further preferred that the polymer should achieve a reduction in nucleation density of at least 10%, more preferably at least 20% with both calcium carbonate and calcium sulphate, on any one of the surfaces, more preferably on both of steel and glass and most preferably on all of steel, glass, ceramic and enamel.

[0038] It has also been found that there is a correlation between the contact angle made by a drop of water on a polymer treated steel surface on the one hand and the ease of cleaning the steel surface from scale deposits (measured as set out below) and reduction in nucleation density on the other hand. Thus it has been found that polymers which cause the contact angle to be $< 30^\circ$ or $> 60^\circ$ cause a significant increase in cleaning score compared with polymers which cause a contact angle within these limits. Preferred are those polymers which cause the contact angle to be $< 20^\circ$, even more preferred are those which cause it to be $> 60^\circ$ or even $\geq 65^\circ$.

[0039] Without being bound by theory it is believed that the contact angle is a manifestation of the surface energy at the interface between water and the polymer-treated surface which in turn determines the degree to which developing scale crystal nuclei are bonded to the surface. It appears this bonding is strongest for surfaces causing the contact angle to be between 30° and 60° .

[0040] The contact angle made by a drop of water on the treated steel surface can be measured by any of the commonly known methods. For the purposes of this invention the measurements can be made using a travelling microscope with a simple goniometer head, in which the eyepiece is fitted with crosshairs. A $20\mu l$ drop of water is pipetted onto the horizontal treated steel surface. The crosshairs in the microscope eyepiece are aligned such that the horizontal mark is aligned with the steel surface (i.e., along the steel/water interface). The centre of the cross is aligned with the three phase contact point (i.e., the water/steel/air interface). The crosshairs are then rotated to align with the edge of the water drop (i.e., along the air/water interface) and the resulting angle is read off on the goniometer scale.

Deposition of Polymer Material

[0041] Polymers for use in the present invention preferably deposit well onto hard surfaces. They may be applied in any way known in the art. Preferably they are applied in the form of a liquid composition containing the polymer in solution or dispersion. More preferably such compositions are aqueous liquids.

[0042] Compositions containing the polymers for use in the present invention may be applied in a number of ways, as will be discussed below. For example, they may be applied to a surface and left in contact to evaporate to dryness. In this case, it is simply required that the polymer should be capable of forming a thin and smooth layer, suitably of the order of a few molecular layers of submicron thickness. Other compositions may be applied to the surface with the intention of the surface being subsequently wiped dry. In such cases, it is preferable that the polymer should also have an increased tendency to adsorb to the hard surface.

[0043] Examples of compositions containing the polymers are cleaning compositions which have the additional effect of depositing a polymer for inhibiting nucleation at the surface to be treated. Such compositions will normally contain one or more detergent surfactants in addition to the polymer.

[0044] It is preferred that the polymer has activity at the solid/liquid interface. It is particularly preferred that the polymer should adhere sufficiently strongly to the surface to be resistant to removal by rinsing. However, the polymer should not adhere too strongly to the surface, otherwise there may be a tendency for the polymer to build up on the surface which might lead to negative effects, e.g. poor appearance.

[0045] Some surfaces which are particularly prone to scale deposits, such as those made of steel, ceramic, glass and enamel, are known to be negatively charged. The polymer should have cationic groups or groups which become cationic at the pH of use. It is preferred that the polymer should comprise amine groups, particularly quaternary ammonium or tertiary amine groups.

[0046] Deposition of the polymer may also be assisted if it has a relatively high molecular weight. The weight average molecular weight is greater than 10,000, preferably greater than 50,000.

[0047] Deposition of the polymer may also be assisted if the polymer or a complex of the polymer with a surfactant is rigid or semi-rigid. The polymeric material may have an inflexible backbone e.g. due to unsaturation or the presence of rings. Alternatively, it may have a positive charge, either permanently or temporarily at the pH of the composition, restricting conformation of the backbone due to repulsion between charges, or it may have a backbone which is flexible in principle but restricted in molecular conformation derived from polymer architecture, e.g. branching, unsaturation, rings or bulky side groups.

[0048] If the polymer itself is not net positively charged (for example, if it is negatively charged or neutral), deposition of the polymer may also be encouraged by the use of a deposition aid such as a cationically charged polymer or surfactant.

Nucleation Inhibiting Effect

[0049] In order to provide a polymer that inhibits nucleation at a surface on which it is deposited, it is preferred that the polymeric material has at least one of the following properties:

1. Hydrophobicity. The polymeric material may have hydrophobic parts. As noted above, in order to enhance deposition of the polymer onto surfaces such as steel, glass, etc., it is preferred that the polymer will also have hydrophilic parts. Accordingly, it is particularly preferred in this case that the polymer is surface active, having hydrophilic and hydrophobic parts on different parts of the molecule, for example on different sides of the polymer backbone.

Ways of providing hydrophobicity will be discussed below.

2. Steric Factors. The inhibition of nucleation may be obtained by steric factors. Preferably, the polymer will comprise large, bulky substituents (for example, incorporating a tertiary carbon atom and/or more than 5 non-hydrogen atoms). Preferably, these are spaced along the polymer backbone at distances which are less than the critical stable microcrystal size. In this way if a microcrystal forms on the surface of the polymer, it will be prevented by steric factors from growing to a size at which it becomes thermodynamically stable. Preferably, the substituents are unevenly spaced to further inhibit nucleation.

Solubility

[0050] Polymeric materials for use in the present invention are preferably soluble or dispersible in surfactant solution but difficultly soluble or dispersible in water. However, the polymeric material may also be partially water-soluble and soluble in aqueous surfactant solution of the type used in hard surface cleaning compositions. The solubility of the polymeric material in an aqueous surfactant solution is suitably in the range of 0.01-50% by weight, more preferably in the range 0.05-10%, most preferably around 0.1-1.0%, particularly 0.4-1.0% by weight. The surfactant concentration is suitably in the range 0.1-20% by weight, preferably 1.0-10% or 6% by weight.

Polymer Types:

[0051] The present application may be carried out with many types of polymer of suitable structure to achieve the properties described above. The following non-limiting examples may be given.

[0052] Polymers suitable for use in the present invention may be produced by any suitable polymerisation method, for example emulsion or solution polymerisation. Copolymers may for example be produced by graft, block or bulk copolymerisation.

[0053] Hydrophobicity may be introduced into polymers for example by including hydrophobic side chains, such as C₈-C₂₂ alkyl, alkenyl or alkylaryl chains. These can be introduced for example as esters of C₈-C₂₂ alcohols or the like.

[0054] Polymers which are used in the present invention comprise natural polymers, such as starches and gums, modified with nitrogen containing species. For example, the polymer may comprise guar gum, cellulose, locust bean gum, starch, starch amylose or similar natural polymers. The natural polymer may be modified by reaction of the hydroxyl groups with other groups, to provide side groups to modify the substantivity of the polymer surface or to provide nucleation inhibiting effects.

[0055] For example, the natural polymer may be modified with nitrogen containing species such as hydroxypropyltrimethylammonium groups. For example, the polymers may comprise cationic guar gums such as hydroxypropyltrimethylammonium guar gum with a degree of substitution in the range 0.11 to 0.22, available commercially under the trade marks JAGUAR C13S, JAGUAR C14S, JAGUAR C17 and JAGUAR C-162.

[0056] Another class of polymers which may be used in the present invention comprises polyquaternary polymers such as Polyquat 10 which is commercially available under the trademarks Polymer JR30M, JR125 and JR400.

[0057] Hydrophobicity may be provided by modifying the natural polymer with, for example, hydrophobic substituents such as C₈-C₂₂ alkyl chains, tertiary alkyl groups etc.

Other Suitable Properties

[0058] Preferably, the polymeric material is not highly coloured across the pH range of interest (3-12).

[0059] Polymers which have been found to significantly reduce the nucleation are given in the table below:

Product name/type (* = Tradename)	Chemical class
Ucare Polymer JR-30M*	Polyquaternium-10-Cationic Hydroxyethyl Cellulose
Jaguar C162*	Hydroxypropyl Guar Hydroxypropyltrimonium Chloride
Croten C*	Collagen Derivative
Celquat L200*	Grafted cationic polymer onto a cellulose backbone
Polymer JR 125*	Polyquaternium-10 - Cationic Hydroxyethyl Cellulose
Polymer JR-400*	Polyquaternium-10 - Cationic Hydroxyethyl Cellulose
Chitosonium betaine	
Jaguar C-13S*	Guar Hydroxypropyltrimonium Chloride
Crodacel*	Quaternised Cellulose derivatives
Croten O*	Collagen Derivative
Celquat H-100*	Grafted cationic polymer onto a cellulose backbone
Celquat SC240C*	Cationic derivative of hydroxyethyl cellulose
Chitosan acetic acid salt	Chitosan
Chitosan 4-hydroxy-L-proline	Chitosan
Chitosan lactobionic acid	Chitosan
Chitosan 2-hydroxycaprylate	Chitosan

[0060] Other polymers which are chemically equivalent to the polymers mentioned above may be used instead. Such polymers are known to the person skilled in the art.

Hard Surface Treatment Compositions

[0061] The polymeric material can be used according to the present invention in any suitable formulation.

[0062] The formulation must be suitable for depositing the polymeric material onto a hard surface. The polymeric material may be present in the formulation in any suitable form, for example in the form of a solution or dispersion.

[0063] Suitable formulations include solutions, dispersions or emulsions of the polymeric material in a carrier, for example a substantially non-aqueous material such as ethanol, but preferably water. The compositions may be used only to deposit polymeric material, or they may have additional functions such as cleaning.

[0064] The composition may be applied by any suitable means. 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.

[0065] Compositions for use in the present invention may include any normal ingredients for hard surface cleaning compositions.

[0066] Preferably, a hard surface cleaning composition comprises at least one detergent surfactant and optional other hard surface cleaning components.

Surfactants:

[0067] The composition according to the invention will comprise detergent actives (surfactants) which are generally chosen from both anionic and nonionic detergent actives.

[0068] Suitable anionic surfactants are water-soluble salts of organic sulphuric acid esters and sulphonic acids which have in the molecular structure an alkyl group containing from 8 to 22 carbon atoms.

[0069] Examples of such anionic surfactants are water soluble salts of:

- long chain (i.e. 8-22 C-atom) 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.

[0070] Also suitable are salts of:

- alkyl glyceryl ether sulphates, especially those ethers of the fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- sulphates of the reaction product of one mole of a fatty alcohol and from 1 to 6 moles of ethylene oxide;
- salts of 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;

and mixtures thereof.

[0071] 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 alkylbenzenesulphonates and mixtures with olefin-sulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates. The most preferred anionic surfactants are alkylaromatic 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 diaminonaphthalene-sulphonate, and sodium dinonylnaphthalene-sulphonate.

[0072] If synthetic anionic surfactant is to be employed the amount present in the compositions of the invention will generally be at least 0.5%, preferably at least 1.0%, more preferably at least 2.0%, but not more than 20%, preferably at most 10%, more preferably at most 8%

[0073] Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is attached to any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB, taking into account the presence of the organic solvent and possible hydrocarbon cosolvent in the composition.

[0074] Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the

reaction product of ethylenediamine 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.

[0075] Other examples are: Alkylglycosides which are condensation products of long chain aliphatic alcohols and saccharides; tertiary amine oxides of structure RRRN₀, where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure RRRP₀, where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide; and dialkyl sulfoxides of structure RRS₀ where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulfoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans. Ethoxylated aliphatic alcohols are particularly preferred.

[0076] The amount of nonionic surfactant to be employed in the cleaning composition of the invention will preferably be at least 0.2%, more preferably at least 0.5%, most preferably at least 1%. The maximum amount is suitably 15%, preferably 10% and most preferably 70.

[0077] The compositions may contain amounts of both anionic and nonionic surfactants which are chosen, bearing in mind the level of electrolyte 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.

[0078] 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 preferably in the range of from 1:9 to 9:1, more preferably from 1:4 to 4:1, and ideally above 1:1.

[0079] According to an embodiment, illustrating this aspect of the invention, the cleaning compositions will comprise from 0 to 10% by weight of a water-soluble, synthetic anionic sulphate or sulphonate surfactant salt containing a C₈-C₂₂ alkyl group, and from 0.5 to 7% by weight of an ethoxylated alcohol nonionic surfactant having a C₈-C₂₂ alkyl group and 2 to 15 ethyleneoxy groups.

[0080] It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in the compositions according to the invention.

[0081] Suitable amphoteric surfactants that optionally can be employed are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 18 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-hydroxydodecyl-N-methyl taurate.

[0082] Suitable cationic surfactants are quaternary ammonium salts having one or two aliphatic groups of from 8 to 18 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethyl ammonium bromide.

[0083] Suitable zwitterionic surfactants that optionally can be employed are 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 3-(N,N-dimethyl-N-hexadecylammonium) propane-1-sulphonate betaine, 3-(dodecyl methyl sulphonium) propane-1-sulphonate betaine and 3-(cetylmethyl phosphonium) ethane sulphonate betaine.

[0084] Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume II by Schwartz, Perry and Berch.

[0085] If surfactants are to be present in the compositions of the present invention, the total amount of surfactant compound to be employed will generally be from 0.5 to 20%. Preferably the amount is at least 1%, more preferably at least 3%. The maximum amount is usually 15% or less, preferably not more than 10%. Preferably the kind of surfactant and its amount is chosen such that it does not form a complex with the polymer which cannot be maintained dissolved or dispersed in the composition.

[0086] The compositions according to the present invention may contain other ingredients which aid in their cleaning performance. For example, the compositions may contain insoluble abrasives such as calcites, silica and other abrasive materials known in the art, or they may contain detergency 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.

[0087] Metal ion sequestrants such as ethylenediaminetetraacetates, amino-polyphosphonates (DEQUEST[™]) and phosphates and a wide variety of poly-functional organic acids and salts, can also optionally be employed provided they are compatible with polymer and optional abrasive material.

[0088] 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 excessive suds in use. One example of a suds regulating material is soap. Soaps are salts of fatty acids and include alkali metal 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 tri-ethanolamine salts of the mixtures of fatty acids derived from coconut oil and groundnut oil. When employed, the amount of soap can form at least 0.005%, preferably 0.1% to 2% by weight of the composition. A further example of a suds regulating material is silicone oil.

[0089] A further optional ingredient which may be used in compositions according to the invention is an acidic material which helps in removing scale deposits. Examples thereof are well known in the art and include phosphoric acid and many di- and polycarboxylic acids.

[0090] Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as colourants, whiteners, optical brighteners, soil suspending agents, detergent enzymes, compatible bleaching agents such as active chlorine compounds or hydrogen peroxide, gel-control agents, freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), perfumes and hydrotropes.

[0091] The hard surface treatment composition can have any suitable pH. However, it is preferred that compositions are either mildly alkaline (particularly if they are formulated as surface cleaning compositions, in order to enhance the effect of surfactants), neutral or slightly acidic (particularly if they include cationic species or amine groups which become protonated and cationic in an acid environment, in order to assist deposition). However, it is preferred that the compositions should not be too acidic, in order to avoid damage to acid sensitive surfaces. In particular, it is important to minimise or avoid the presence of sequestering organic acids which are prone to attack surfaces such as enamel. Preferably the pH is in the region 3-12, with the ranges 3.5-6.0 and 10-12 being particularly preferred. In any event, the pH is suitably above 3.0 and more preferably above 3.5.

[0092] Use of polymeric material according to the present invention can, in addition to scale inhibiting effects, give a longer lasting shine, better surface appearance, a smooth feel to treated surfaces.

[0093] Compositions according to the present invention are useful for treating household surfaces in for example kitchens and bathrooms, including walls, floors, toilets, dishwashers, and work surfaces. They are particularly suitable for treating surfaces which are prone to remain in prolonged contact with water such as: shower walls and floors, bath tubs and rims, taps, shower heads, wash basins, sinks and the like.

[0094] The present invention will be described further by way of reference to the following non-limiting examples.

Examples

[0095] All percentages mentioned herein are by weight based on the total composition unless specifically mentioned otherwise.

[0096] Surface treatment compositions were prepared according to the following formulations (* indicate the nucleation inhibiting polymers):

Example 1- Bathroom cleaning formulation

[0097]

Alcohol Ethoxylate 8EO	6.00
Dicarboxylic Acids	4.00
2-butoxy ethoxy ethanol	2.00
Phosphoric Acid	0.50
Coconut Fatty Acid	0.25
Magnesium Sulphate 7H ₂ O	1.00
Sodium Hydroxide	0.34
1,2 Benzisothiazolin -3-one	0.016
Perfume	0.50
*Polymer JR-30M	0.50
Water	to 100

Example 2 - Bathroom cleaning formulation

[0098]

Alcohol Ethoxylate 8EO	6.00
Dicarboxylic Acids	4.00

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(continued)

2-butoxy ethoxy ethanol	2.00
Magnesium Sulphate 7H ₂ O	1.00
*Polymer Jag C162	0.50
Water	to 100

Tests for Ease of Removal of Scale from Treated Surfaces

[0099] Steel tiles formed of certain surfaces are obtained from Mersey Metals. The tiles were 0.9 mm thickness, 100 x 100 mm square in size, finished to 304 specification with a mirror finish and plastic backed on one side. The tiles are thoroughly cleaned and rinsed using demineralised water. The tiles are then left to dry.

[0100] A 0.5% by weight aqueous solution of polymer is applied in an even layer to each tile using a K-bar applicator, K-bar number 0010. 0.5 ml of solution is pipetted across the top edge of the tile next to the K-bar. The driving speed of the K-bar is set to 16.5 cm/s.

[0101] The tiles are left to dry for up to 24 hours.

[0102] Dried tiles are then mounted at 10° to the horizontal.

Each tile is then rinsed with 200 ml of demineralised water pumped across the tile by a peristaltic pump at a rate of 812 ml/min. The tile is then laid horizontally to dry.

[0103] Plastic templates in the form of square sheets of acetate film having a square hole in the centre are adhered to each tile. 0.5 ml of Prenton water (27°FH) is added to each tile within the square defined by the plastic template.

The drop is left to dry. The step is repeated for 6 x 0.5 ml additions of Prenton water, each of which is left to dry. The treated tiles are then subjected to a cleaning test using a WIRA (Wool Institute Research Association) machine. This apparatus measures the number of cycles required to clean a defined area. The area to be cleaned corresponds to the exposed area defined by the plastic template. The tiles are cleaned using a damp J-cloth™ on a WIRA machine which is operated for 4 cycles (16 x 4 = 64 strokes under the maximum load). Once cleaned, the tiles are left to dry and assessed for scale, and tarnish. Scale and tarnish are assessed subjectively and rated on a scale of 1 to 4, 1 corresponding to no or very little removal and 4 corresponding to a completely clean surface.

Results

[0104] The method of Example 2 is conducted with the polymeric materials listed in the table below. The tarnish results were assessed and the scores are set out below.

Treatment	Average score
	(uncertainty at 95% confidence limit in brackets)
Jif (trade mark) cleaned	1.93(7)
Surfactant cleaned only	1.7(2)
Celquat L200 (trade mark)	2.9(3)
JR-30-M (trade mark)	3.6(2)
Jaguar C162 (trade mark)	3.4(4)
Crotein C (trade mark)	3.6(4)

Measurement of nucleation density

[0105] The apparatus described above for measuring nucleation density can be used to test the effect of polymer on nucleation density at a surface, as follows.

[0106] A 10 mm diameter stainless steel sample (steel type 304) polished to a 0.05 micrometre finish was masked on one half. The other half was treated with a 0.5%wt aqueous solution of polymer.

[0107] Solution A comprises calcium chloride (obtained from Aldrich 99.99% plus pure) in 0.1 M NaCl (obtained from Fisons, 99.9% plus pure) and solution B comprise NaHCO₃ (obtained from BDH, 99.5% plus pure) in 0.1 M NaCl. The concentrations of calcium chloride and sodium bicarbonate are altered to achieve supersaturation of calcium carbonate in a manner known to the person skilled in the art.

[0108] The pH is regulated to 8.5 using NaOH (obtainable from Fisons, 86% plus pure) or HCl (obtainable from Aldrich, 0.5098 N, ACS grade).

[0109] The experiment was repeated with a number of different types of polymer. The results are shown in the following

table:

	Polymer (all indicated by trademark)	Number of crystals per m ² treated half	Number of crystals per m ² untreated half	Ratio of % nucleation density	reduction in nucleation density
5	Celquat L200	5.280e7	2.139e8	1:4.1	75%
	JR-30M	2.934e7	1.630e8	1:5.6	82%
	Ucare LK	5.128e8	1.439e9	1:2.8	64%
10	Alcogum L520	3.876e8	6.431e8	1:1.7	40%
	Narlex ST15	1.852e9	8.718e8	1:0.5	-112%

[0110] Narlex ST15 is not a polymer according to the invention and is included in the table as a comparative example.

Claims

1. The use of a polymeric material to reduce heterogeneous nucleation of calcium and magnesium salts at a hard surface comprising depositing onto the hard surface a polymeric material which is a natural polymer modified with nitrogen containing species and wherein furthermore the polymeric material has a weight average molecular weight greater than 10, 000 and has cationic groups or groups which become cationic at the pH of use.
2. The use according to claim 1, wherein a reduction of nucleation density at the hard surface of at least 10% is achieved with at least one salt selected from the group consisting of calcium carbonate, calcium sulphate, magnesium sulphate, magnesium carbonate and mixtures thereof, in the method described herein using the apparatus for measuring reduction of nucleation density as described herein and using a test disc chosen from stainless steel, ceramic, enamel, glass or Perspex.
3. The use according to claim 1, wherein a polymeric material is used which achieves a reduction in nucleation density of at least 10% with both calcium carbonate and calcium sulphate on all surfaces of the group consisting of steel, glass, ceramic and enamel.
4. The use according to claims 1 and 2, wherein the polymeric material has hydrophobic parts.
5. The use according to claims 1 and 2 wherein the polymeric material comprises bulky substituents.
6. The use according to any preceding claim, wherein the polymeric material comprises quaternary ammonium or tertiary amine groups.
7. The use according to any preceding claim wherein the natural polymer is chosen from guar gum, cellulose, locust bean gum, starch or amylose.
8. the use according to claim 6 wherein the polymeric material is a cationic guar gum or a polyquaternary polymer.
9. The use according to any preceding claim, wherein the polymeric material is deposited from a hard surface cleaning composition comprising at least one surfactant and other optional hard surface cleaning components.
10. A process for preventing scale from forming or adhering to metal, vitreous or hard plastic surfaces comprising applying to the surface a cleaning composition comprising a detergent surfactant and a polymeric material as described in any of the preceding claims.

Patentansprüche

1. Verwendung eines polymeren Materials zum Verringern der heterogenen Keimbildung von Calcium- und Magnesiumsalzen auf einer harten Oberfläche, umfassend das Abscheiden eines polymeren Materials, welches ein natürliches Polymer ist, das durch Stickstoff-enthaltende Spezies modifiziert wurde, und wobei das polymere Material

ferner ein gewichtsmittleres Molekulargewicht von mehr als 10.000 aufweist und kationische Gruppen oder Gruppen, die bei dem Verwendungs-pH kationisch werden, besitzt, auf der harten Oberfläche.

2. Verwendung nach Anspruch 1, wobei eine Verringerung der Keimbildungsdichte auf der harten Oberfläche von mindestens 10 % mit mindestens einem Salz, ausgewählt aus der Gruppe, bestehend aus Calciumcarbonat, Calciumsulfat, Magnesiumsulfat, Magnesiumcarbonat und Gemischen davon, in dem hierin beschriebenen Verfahren unter Verwendung der Vorrichtung zum Messen der Verringerung der Keimbildungsdichte, wie hierin beschrieben, und unter Verwendung einer Testscheibe, ausgewählt aus Edelstahl, Keramik, Emaille, Glas oder Plexiglas, erreicht wird.
3. Verwendung nach Anspruch 1, wobei ein polymeres Material verwendet wird, welches eine Verringerung in bezug auf die Keimbildungsdichte von mindestens 10 % mit sowohl Calciumcarbonat als auch Calciumsulfat auf allen Oberflächen der Gruppe, bestehend aus Stahl, Glas, Keramik und Emaille, erreicht.
4. Verwendung nach den Ansprüchen 1 und 2, wobei das polymere Material hydrophobe Teile ausweist.
5. Verwendung nach den Ansprüchen 1 und 2, wobei das polymere Material voluminöse Substituenten umfaßt.
6. Verwendung nach einem vorhergehenden Anspruch, wobei das polymere Material quartäre Ammonium- oder tertiäre Amingruppen umfaßt.
7. Verwendung nach einem vorhergehenden Anspruch, wobei das natürliche Polymer aus Guargummi, Cellulose, Johannisbrotgummi, Stärke oder Amylose ausgewählt ist.
8. Verwendung nach Anspruch 6, wobei das polymere Material ein kationischer Guargummi oder ein polyquartäres Polymer ist.
9. Verwendung nach einem vorhergehenden Anspruch, wobei das polymere Material aus einer Reinigungszusammensetzung für harte Oberflächen, umfassend mindestens ein oberflächenaktives Mittel und andere optionale Reinigungskomponenten für harte Oberflächen, abgeschieden wird.
10. Verfahren zum Verhindern, daß sich Kesselstein bildet oder an Metall-, gläserne oder harte Kunststoffoberflächen haftet, umfassend das Aufbringen einer Reinigungszusammensetzung, die eine reinigungsaktive Substanz und ein polymeres Material, wie in einem der vorhergehenden Ansprüche beschrieben, umfaßt, auf die Oberfläche.

Revendications

1. Utilisation d'une substance polymère pour réduire la nucléation hétérogène de sels de calcium et de magnésium au niveau d'une surface dure comprenant le dépôt sur la surface dure d'une substance polymère qui est un polymère naturel modifié avec des espèces contenant de l'azote et dans laquelle la substance polymère possède en outre un poids moléculaire moyen en poids supérieur à 10 000 et des groupes cationiques ou des groupes qui deviennent cationiques au pH d'utilisation.
2. Utilisation selon la revendication 1, dans laquelle une réduction de la densité de nucléation au niveau de la surface dure d'au moins 10 % est obtenue avec au moins un sel choisi dans le groupe constitué par le carbonate de calcium, le sulfate de calcium, le sulfate de magnésium, le carbonate de magnésium et leurs mélanges, dans la méthode décrite dans ce document en utilisant l'appareil permettant de mesurer la réduction de la densité de nucléation décrit dans ce document et en utilisant un disque de test choisi parmi l'acier inoxydable, la céramique, l'émail, le verre et le Perspex.
3. Utilisation selon la revendication 1, dans laquelle il est utilisé une substance polymère qui permet de réduire la densité de nucléation d'au moins 10 % à la fois avec le carbonate de calcium et le sulfate de calcium sur toutes les surfaces du groupe constitué de l'acier, du verre, de la céramique et de l'émail.
4. Utilisation selon les revendications 1 et 2, dans laquelle la substance polymère possède des parties hydrophobes.
5. Utilisation selon les revendications 1 et 2, dans laquelle la substance polymère comprend des substituants volumi-

neux.

6. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle la substance polymère comprend des groupes de type ammonium quaternaire ou amine tertiaire.

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7. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le polymère naturel est choisi parmi la gomme de guar, la cellulose, la gomme de caroube, l'amidon ou l'amylose.

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8. Utilisation selon la revendication 6, dans laquelle la substance polymère est une gomme de guar cationique ou un polymère polyquaternaire.

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9. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle la substance polymère est déposée à partir d'une composition de nettoyage de surface dure comprenant au moins un tensioactif et d'autres composants de nettoyage de surface dure facultatifs.

10. Procédé pour empêcher la formation ou l'adhérence du tartre sur des surfaces en métal, en verre ou en plastique dur comprenant l'application sur la surface d'une composition de nettoyage comprenant un tensioactif détersif et une substance polymère selon l'une quelconque des revendications précédentes.

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REFERENCES CITED IN THE DESCRIPTION

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