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(54) Title: ABRASIVE HARD SURFACE CLEANING COMPOSITIONS

(57) Abstract: The present invention relates to synergistic cleaning compositions and a process for cleaning hard surfaces comprising 0.1-40% of detergent active and 0.1-40% of shape selective particulate abrasive particulates having a roundness factor of 0.6-1.



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Abrasive hard surface cleaning compositions

5 **Technical field**

The present invention relates to synergistic cleaning compositions for cleaning hard surfaces, comprising shape selective abrasive particulates and in particular abrasive
10 particulates of a defined roundness factor. The cleaning compositions of the present invention involving such shape selective abrasives provide excellent cleaning while reducing significantly the damage caused on the hard surface.

15

Background

Cleaning compositions in the form of liquids, gels, pastes, powders and bars are commonly used for cleaning hard surfaces.
20 Abrasive cleaning compositions usually comprise a detergent active or surfactant, an abrasive material, and liquid or solid carrier materials. They are used for cleaning hard surfaces typically constituted of ceramic, metal (e.g. stainless steel), stone, wood, vitreous enamel and chrome plated surfaces.

25

Abrasives conventionally used in such cleaning compositions are both organic and inorganic in nature. Common inorganic abrasives include calcite, chalk, quartz, feldspar, marble, dolomite and aluminium oxide. Inorganic abrasives are usually
30 irregularly shaped, powdered or mined materials of average particle diameter of about 1 to 500 microns. The abrasive in the composition helps in removal and dislodgment of the soil, especially those that fix onto the substrate, such as tough

soils. While abrasives should not damage or scratch the surface from which the soil is to be removed, usually the abrasive needs to be so selected as to be harder than the soil to be removed and softer than the surface to be cleaned. Thus, 5 the required hardness of abrasives for removal of tough soils cause scratching of the hard surface being cleaned. Further, on repeated use of the cleaning composition, there is a loss of lustre and gloss over time giving a dull look to the hard surface.

10

JPO2080497 (Asahi Chem Ind Co Ltd) discloses detergent compositions comprising 5-50% of a nonionic surfactant and 5-30% of organic abrasives such as powdered polyethylene, powdered wood or cellulosic materials. The detergent

15 compositions remove soils such as carbon without scratching the surface. The abrasives have a particle size of 10-500 microns and a specific gravity of 0.7 to 2.0.

US4992476 (Warner-Lambert Company) discloses skin cleansing and 20 moisturizing compositions that comprise an oil phase comprising a non-ionic surfactant, an aqueous phase comprising a thickening agent and an abrasive. The shape of the abrasive particle can be irregular, fiber, spherical, semi-spherical or spheroidal with a preferred particle size of about 3 to 10 25 micron.

GB2351502 (Mahmoud Salem) discloses liquid abrasive cleaning and polishing materials that contain pulverized fly ash. To achieve a creamy product which can be effectively applied to 30 any part of the body use of spherical and non-angular pulverized fly ash particles is proposed. The principal application is as a suitable abrasive material for face/body wash. The compositions are directed to have a runny to viscous

consistency and the teachings are principally directed towards replacing corrosive and hazardous chemicals in cleaning compositions.

5 US5213588 (The Procter & Gamble Company) discloses abrasive wiping articles for cleaning hard surfaces comprising 30 to 70% by weight of carboxylated, ionically charged polymeric abrasive particles and scrubbing bead mixture. Commercially available polymeric beads are generally substantially spherical. However,
10 according to the patent it is preferred that the spherical particles be milled or ground to fracture the particle into smaller particles having the desired angular edges to improve their abrasive properties.

15 WO9826040 (Kao Corporation) relates to a detergent impregnated wiping article useful for cleaning hard surfaces such as glass. The article essentially comprises a surfactant along with the solid abrasive particles and a protective layer forming polymeric component, an organic solvent, a drying accelerator,
20 and thickening polysaccharide. To achieve desired spreadability and ease of wiping away the solid abrasive particles are spherical in nature and have an average particle size of 0.01 to 15 micron. The wiping article is not intended to remove stubborn soil

25 It would be apparent from the above that abrasives, given their purpose for cleaning, are preferably particulates with rough/irregular and angular particles of varied shapes and sizes. Selective spherically shaped abrasives are proposed
30 only for use with a cleaning article or in liquid compositions for skin cleansing to achieve spreadability or maintain a smooth contact of the abrasives with the body/skin so as to avoid rough edges which can damage the skin during

application/use. Moreover, even as regards the use of spherical abrasive particulate in cleaning compositions to achieve spreadability and easy wiping away of the dried composition it is preferred in the prior art to limit the particle size to 15
5 micron.

It is important to note that cleaning compositions for cleaning hard surfaces have distinct purpose and formulation requirements vis-à-vis the cleaning articles or the liquid
10 skin/body cleaning formulations. In particular, detergent formulations for hard surface cleaning are generally considered to require particulate abrasives with rough /irregular edges of varied shapes and sizes suitable to remove tough soil by their abrasive action. However repeated use of such abrasive based
15 cleaning compositions for cleaning can cause damage to the surface or loss of lustre in case of polished surfaces.

Objects and summary of the Invention

20

It is the basic object of the present invention to provide a synergistic cleaning composition for hard surfaces which on one hand enables incorporation of particulate abrasives of varying particle size ranges from 1-600 micron so as to obtain superior
25 tough soil cleaning and on the other hand ensure that the cleaning achieved does not affect the desired lustre and surface character of the substrate being cleaned.

It is a further object of the invention to provide a process
30 for cleaning hard surfaces comprising the step of applying to the surface a cleaning composition incorporating particulate abrasive which will enable to obtain superior tough soil cleaning and on the other hand ensure that the cleaning

achieved does not affect the desired lustre and surface character of the substrate being cleaned.

These objects are achieved by the use in a hard surface
5 cleaning composition of shape selective abrasive particles
which also meet the desired characteristics of being harder
than the soil to be removed, but softer than the surface to be
cleaned. Thus, the invention provides hard surface cleaning
compositions comprising detergent active (surfactant) and a
10 shape selective particulate abrasive having specified roundness
factor as hereinbelow defined.

Detailed description of the Invention

15 Thus, according to one aspect of the present invention there is
provided a synergistic cleaning composition for hard surface
cleaning comprising:

- 0.1 to 40% by weight of detergent active;
- 20 - 0.1 to 40% by weight of shape selective particulate
abrasive, said shape selective particulate of the abrasive
having 0.6 to 1.0 Roundness Factor such as herein defined;
- optionally other abrasives such that the total amount of
abrasives is from 0.1 to 98% by weight of the total
25 composition.

It was found that incorporation of the shape selective abrasive
particles having a Roundness Factor of from 0.6 to 1.0 in
cleaning composition improves tough soil cleaning, apart from
30 significantly reducing scratch on the hard surface being
cleaned. This is a surprising finding given the prevailing
opinion in the art that only irregular/rough edged abrasives
favour the cleaning of tough soils. The problem of scratching

is well recognized while cleaning polished surfaces and it is now possible by way of the composition of the invention to not only effectively clean such polished surfaces but also avoid damage to the surface/loss of surface finish of the substrate
5 surface being cleaned.

In accordance with a preferred aspect of the present invention there is provided a cleaning composition for hard surface cleaning as defined above wherein the abrasives have a weight
10 average particle size ranging from 1 to 600 microns, preferably 1 to 200 microns, most preferably 10 to 50 microns.

It is thus possibly by way of the above shape selective abrasive to provide cleaning compositions with abrasive of wide
15 ranging particulate size which apart from achieving superior cleaning would not affect the surface lustre of the substrate being cleaned.

In accordance with another preferred aspect of the present
20 invention there is provided a cleaning composition for hard surface cleaning as defined above, wherein the abrasives have a hardness of 10-5000 Kg/mm² preferably 50-5000 Kg/mm², more preferably 100-3000 kg/mm².

25 According to a further preferred aspect of the invention, there is provided a cleaning composition as defined above wherein the roundness factor of the shape selective particulate abrasive is between 0.7 and 1.

30 According to further preferred aspects of the invention, the cleaning compositions as defined above may comprise as optional, but preferred ingredients any or all of:

- up to 25% weight of alkanolamine and/or salt thereof, preferably at least 0.1%;
- up to 30% by weight of organic solvent;
- an alkaline material.

5

Detergent actives

The compositions according to the invention comprise detergent
10 actives (surfactants), which are generally chosen from anionic, non-ionic, cationic, amphoteric or zwitterionic detergent actives. The detergent active is preferably non-soap

A suitable class of anionic surfactants are water-soluble salts
15 of organic sulphuric acid mono-esters and sulphonic acids having in the molecular structure a branched or straight chain alkyl group containing 8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part.

20 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 from tallow or coconut oil or the synthetic alcohols derived from
25 petroleum;
- alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates.

Also suitable are the salts of:

- 30 - 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 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 neutralized with alkali.

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.

Other classes of nonionic surfactants are:

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

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.

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.

30

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 bromide.

Examples of suitable zwitterionic surfactants can be found among
5 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-
10 (dodecylmethyl-sulphonium)-propane-1-sulphonate betaine and 3-
(cetylmethyl-phosphonium)-ethanesulphonate betaine. Other well
known betaines are the alkylamidopropyl betaines e.g. those
wherein the alkylamido group is derived from coconut oil fatty
acids.

15

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"
20 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.

25 It is preferred that the compositions according to the
invention comprise an anionic detergent active such as
the alkali metal (e.g. sodium or potassium) and alkaline earth
metal (such as calcium and magnesium) salts of alkyl benzene
sulphonates, olefin sulphonates, alkyl sulphates, and the fatty
30 acid monoglyceride sulphates and mixtures thereof.

Soap may also optionally and additionally be added to the cleaning composition of the invention. The term "soap" is used to denote the metal, ammonium or alkylammonium salt of a fatty acid of natural or synthetic origin. The usual metal counterions are sodium and potassium, but other metal ions such as zinc, aluminium or magnesium may be used as desired.

Shape selective abrasive particles

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A shape selective particulate abrasive is an essential component of compositions according to the present invention. The particulate can be organic or inorganic in nature and is present in an amount of 0.1-40% wt of the total composition, preferably in an amount of at least 1%, more preferably at least 2%.

The shape selective abrasive particles of the invention have a Roundness Factor of from 0.6 to 1, preferably 0.7 to 1, more preferably 0.9 to 1.

Shape measures are physical dimensional measures that characterize the appearance of an object. Measures that determine the departure or approach of an object towards a circular/spherical shape include convexity, roundness, sphericity etc. For the purposes of this invention, the Roundness Factor is used to determine the circular/spherical nature of the abrasive particles.

The Roundness Factor is a measure that excludes local irregularities and is obtained as the ratio of the projected area of an object to the area of a circle with the same convex perimeter. It is usually based on measurement of the two

dimensional projection of a particle. Optical microscopy is one method of measuring the Roundness Factor. The Roundness Factor can be calculated as follows:

RF = $4\pi A/P^2$ wherein P is the perimeter and A is the surface area of the two-dimensional projection.

For a perfect circle/spherical particle, $A=\pi r^2$ and $P=2\pi r$ and RF equals 1. RF is less than 1 for an object that departs from circularity.

- 10 Suitable abrasives are selected from inorganic or organic, synthetic or natural sources. These abrasives can be solid, porous or hollow. Examples of natural inorganic abrasives include apatite, feldspar, quartz, topaz, calcite, alumina, limonite, kimenite, ceramic, leucite, glass, taconite, silica
- 15 sand, flint, vermiculite, fire clay, diaspore, bauxite, limestone, iron pyrite, magnetite and hematite. Examples of synthetic inorganic abrasives include various silicates & silica, glass, alumina, ferrite, pearlite, austenite, martensite, cemetite, carbides of chromium, tungsten, silicon,
- 20 titanium and vanadium. Suitable organic abrasives are selected from polystyrene, polyacrylate, polymethylmethacrylate, polycarbonate, polyethylene etc, and can be with varying degrees of cross polymerisation.
- 25 Examples of such abrasives are ZeeospheresTM & ScotchliteTM available from 3M. Examples of glass beads are DurasphereTM and AccusphereTM available from MO-SCI Corporation, Rolla, US; glass bead BL, glass bead AF, glass bead AQ available from Bharat Glass Beads, Mumbai, INDIA. A range of spherical glass
- 30 materials is also available from Potters Industries Inc. US. The spherical glass materials can be solid or hollow and hence have varying bulk density ranging from 0.1 to 3.0 g/ml. They

are available in varying colours, while the preferred colour is colourless. The refractive index typically ranges from 1.46 to around 1.9. In certain formulations it may be desirable to use shape selective particles of a refractive index that matches that of the formulation so as to make the particles invisible. Polymeric spherical beads can be of varying softening or melting point. The preferred melting point is above 100°C. Example is various polymeric beads available from Reliance Co, INDIA, Phenoset microsphere from Eastech, Philadelphia, US.

10

The hardness of the abrasives may range from 10 to 5000 Kg/mm² and the preferred abrasives for use in general purpose compositions have a hardness 50 to 5000 Kg/mm², more preferably 100-3000 Kg/mm². The bulk density of the abrasives may range from 0.1 to 3.5 g/ml and the preferred bulk density is from 0.3 to 2.8 g/ml.

The average particle size of the shape selective abrasives may range from 1-600 microns and the preferred average particle size is at least 10µm and more preferably above 15µm. The preferred maximum average particle size is 300µm, more preferably 200µm, even more preferably 100µm or even 50µm. Particles sizes as mentioned herein are obtained using a Malvern Particle Sizer Hydro 200S.

25

Optional other abrasives

Optionally, other abrasives may be present in the compositions of the invention, such that the total amount of abrasive in the composition is between 0.1 to 98%. Depending upon the product form, the amount of detergent active and abrasive can be

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suitably varied to ensure optimum properties as to formulation and consumer benefits. The optional abrasives can be irregularly shaped, can be organic or inorganic in nature, can have an average particle size from 1 to 500 μm and a hardness from 70-5000 Kg/mm^2 .

The optional abrasive can be a water insoluble particulate or the abrasive may be soluble and present in such excess to its solubility in any water present in the composition that solid abrasive exists in the composition. A particulate abrasive with a liquid absorptive capacity of 100 to 300% may optionally be incorporated and can be selected from precipitated or spray dried silica.

The cleaning compositions of the present invention preferably contain from 10% to 95%, more preferably from 20% or even 40% to 90%, even more preferably from 60% to 85%, of total abrasive material (inclusive of the shape selective abrasive). Preferred other abrasive materials for use herein are silica, various forms of calcium carbonate, feldspar, and mixtures thereof. Other abrasives such as plastic, polymeric beads, kaolin, anthracite, gypsum, mica, bauxite, calcite, dolomite, siderite, fluorite can be used. The abrasive particles should have a average particle size of from 300 μm to about 1 μm , preferably 200-10 μm . Suitable abrasive materials are disclosed for example in US Patent Nos. 3,583,922; 3,829,385; 3,715,314; and 4,287,080.

(Alkanol)amines and salts thereof

5 Amines and/or their salts can optionally be used in the cleaning compositions according to the invention. The amine may be a mono- or di-amine or a substituted amine such as an alkanolamine. It is preferable that the molecular weight of the
10 amine is less than 300 and the pKa is greater than 8.0. It is also preferable that the amine is a primary amine.

The alkanolamine for the present invention can be mono- or poly-functional as regards the amine and hydroxy moieties.
15 Preferred alkanolamines are generally of the formula H_2N-R_1-OH where R_1 is a linear or branched alkyl chain having 2-6 carbons. Preferred alkanolamines include 2-amino-2-methyl-1-propanol, aminomethyl propane-diol, mono- di- and tri-ethanolamine, mono- di- and tri-isopropanolamine, dimethyl-, diethyl- or dibutyl-
20 ethanolamine, and mixtures thereof. It is envisaged that cyclic alkanolamines such as morpholine can also be employed. Particularly preferred alkanolamines, especially to help cleaning tough or aged soil are 2-amino-2-methyl-1-propanol (AMP) and monoethanolamine (MEA).

25 The acid part of the amine salts may be inorganic or organic. Suitable inorganic acid are phosphoric, hydrochloric, sulphuric acid, and organic acids are oxalic, acetic, malonic, etc.

30 It is particularly preferred to use phosphoric acid salt of monoethanolamine (MEA) or 2-amino-2-methyl-1-propanol (AMP) as the amine salt.

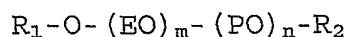
Alkaline material

An alkaline material can optionally be used in the composition of the invention. The alkaline material is preferably chosen
5 from alkali and alkaline earth metal hydroxides like Na, K or Ca hydroxide, or alkali metal salts such as sodium carbonate, sodium bicarbonate, sodium tripolyphosphate (STPP), tetrasodium pyrophosphate (TSPP), alkaline silicate, alkaline meta
silicate, sodium aluminate, and combinations of these. These
10 builder/buffer salts are suitably used in an amount ranging from 0.5 to 25% by wt, preferably from 5 to 15% by wt. When an amine salt is employed in the composition of the invention, it is preferred to use an alkaline material.

15

Solvents

Solvents can optionally be used in the cleaning compositions of the invention. Suitable solvents include saturated and
20 unsaturated, linear or branched hydrocarbons, and/or materials of the general formula:



wherein R_1 and R_2 are independently C1-7 alkyl or H, but not
25 both hydrogen, m and n are independently 0-5.

Preferred solvents are selected from the group comprising terpenes, C₁₀-C₁₆ straight chain paraffins, and the glycol ethers. Suitable glycol ethers include di-ethylene glycol mono
30 n-butyl ether, mono-ethylene glycol mono n-butyl ether, propylene glycol n-butyl ether and mixtures thereof.

Suitable terpenes include d-limonene. Preferred paraffins include the materials such as those available in the marketplace as Shellsol-T™.

5 Typical levels of solvent range from 1-15% wt. It is particularly preferred to use terpenes at levels 1-3% wt. Some of these terpene materials, such as limonene, have the further advantage that they exhibit insect-repellency. The straight chain paraffins can be used at higher levels than the
10 terpenes, as these materials are less aggressive to plastics.

The glycol ethers are preferred over the other solvents, at typical levels of 3-10% wt. on product with di-ethylene glycol mono n-butyl ether being particularly preferred.

15 Advantageously, a portion of the solvent can be introduced as a perfume component, although the levels of solvent required would generally require the addition of higher levels of this component that would normally be present as a perfume
20 ingredient in cleaning compositions. Preferably the terpenes are used in this manner as selected terpenes, such as limonene, have a pleasant citrus smell, whereas paraffins and glycol ethers are generally odourless or have a low odour.

25

Other optional ingredients

The composition according to the invention can contain other ingredients that aid in their cleaning performance. For
30 example, the composition can contain detergent builders other than the alkaline salts mentioned above, such as nitrilo-triacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates especially polyphosphates, mixtures of

ortho- and pyrophosphates, zeolites and mixtures thereof. Such builders can additionally function as abrasives if present in an amount in excess of their solubility in water and having the required particle size and hardness. In general, the builder
5 other than the alkaline salts when employed, preferably will form from 0.1 to 25% by weight of the composition.

Composition according to the invention can also contain, in addition to the ingredients already mentioned, various other
10 optional ingredients such as structurants, polymers, viscosity modifiers, colourants, hydrotropes, whiteners, optical brighteners, soil suspending agents, deterative enzymes, compatible bleaching agents (particularly hypohalites), and preservatives.

15

The composition of the invention can be in the form of a liquid, gel, paste, mousse, aerosol, powder or a bar. Preferred forms are a solid composition and aqueous liquids. The pH of the compositions may range from 0.5-13, depending on the
20 cleaning purpose for which they are intended. Solid compositions preferably have pH 6-11. They are particularly suitable for removing fatty and other food-derived soils. Acidic compositions are particularly suited for cleaning hard surfaces where lime scale and hard soap deposition and/or rust
25 is a problem e.g. bathrooms. Such compositions will be capable of providing superior cleaning without scratching the surface.

It is also possible to provide the cleaning compositions of the invention in the form of a cleaning kit, for example providing
30 the composition with a cleaning implement like a sponge, pouf or scrubber along with an instruction manual describing the appropriate procedure to be followed for the effective use of the cleaning system.

The cleaning compositions of the invention can be made by any conventional process known in the art. Preferred forms are liquid abrasive cleaners, pastes, gels, powders and bars.

5

Although the cleaning compositions of the invention could in principle be converted into a ready to use wet wipe by absorbing the composition onto a flexible base body, this is not a preferred embodiment of the invention. Also, the
10 compositions of the invention do preferably not have a protective layer-forming component such as defined in WO98/26040, as they have no role to play in the cleaning processes for which the compositions according to the invention are intended. Finally, the invention does not comprise
15 compositions in which the shape selective abrasive particles are affixed to a flexible base body.

According to a further aspect of the present invention there is provided a process for cleaning hard surfaces comprising the
20 step of applying to the surface a cleaning composition as defined above. In this process the composition may be applied directly to the surface, or it may first be applied to a cleaning tool such as a brush, cloth, scrubber or similar implement whereafter the surface is cleaned with the cleaning
25 tool. Usually the cleaning composition is thereafter removed from the surface, together with the soil, by rinsing with water, and further wiping if desired.

EXAMPLES**Effect of shape selective abrasives on tough soil cleaning:****5 Comparative Example A:**

1.8 kg of sodium carbonate was mixed with 2.5 kg of linear alkyl benzene sulphonate in a sigma mixer. This was followed by addition of 8.0 kg of dolomite, 0.54 Kg of calcined alumina, with a roundness factor of 0.45 and the other ingredients
10 mentioned in table 1. All ingredients were mixed, followed by extrusion, billeting and stamping of the whole mass into bars.

Example 1:

The procedure of Comparative Example A was followed except that
15 0.54 Kg of synthetically prepared calcium carbonate with a roundness factor of 0.9 and a hardness of 100 Kg/mm² was added instead of calcined alumina.

Example 2:

20 The procedure of Comparative Example A was followed except that 0.9 Kg of spherical glass beads with a hardness of 300 Kg/mm² was added instead of calcined alumina.

The detergent bars of Comparative Examples A and Examples 1-2
25 were processed as a batch of 18 kg. The composition details and results on tough soil cleaning are presented in Table 1.

The Roundness Factor of the abrasive particles of Comparative Example A and Examples 1-2 were obtained from the SEM pictures
30 of representative samples of the selected abrasives.

Evaluation of tough soil cleaning:

A mixture of sunflower oil and wheat flour was used as the 'soil' whose removal was evaluated. The soil was placed evenly on a square SS-304 stainless steel plate of 1mm thickness. A
5 sponge was used to spread the soil mixture on the plate. The soiled plate was placed on a hot plate of >300°C. The soil mixture turned into a black carbonized soil. The carbonized soil plate was aged for 2 h at room temperature and then taken for cleaning.

10

The soiled stainless steel plates were cleaned with the formulations of Comparative Example A and Examples 1-2. 10% product concentration is used for the cleaning and the plates are cleaned by providing a constant cleaning effort for 90
15 seconds. The cleaning efficacy is reported as percentage tough soil cleaned.

Cleaning is measured by placing a grid consisting of criss-cross lines spaced 1 cm apart. Cleaning is measured by
20 counting the number of 1cm² grid area of steel surface exposed.

A calibration curve was plotted for percentage tough soil cleaned. A scale was constructed using 10 plates that had been cleaned to various levels. A completely soiled plate (totally covered) was taken as 0% cleaned and a completely clean plate
25 (where the steel is completely exposed) was taken as 100% cleaned. The percentage tough soil cleaned is calculated using the ratio: % tough soil cleaned in 90 seconds = (Area exposed/original soiled area) x 100

Table 1

Composition (%. Wt)	A	1	2
Linear alkylbenzene sulphate, sodium salt (Na LAS)	14	14	14
Sodium Carbonate	10	10	10
China clay	15	15	15
Dolomite	45	45	45
Alkaline Silicate	3	3	3
Magnesium sulphate	1	1	1
Perfume, colour	0.2	0.2	0.2
Water	To 100	To 100	To 100
Abrasive Alumina (irregular)	3	-	-
Abrasive calcite (spherical)	-	3	-
Abrasive glass beads (spherical)	-	-	5
Roundness Factor of Abrasive	0.45	0.9	0.9
Hardness of abrasive (Kg/mm ²)	2000	100	300
Tough soil cleaning (% cleaned in 90 seconds)	39	44	56

The data in Table 1 shows that the cleaning compositions 1 and 2 according to the invention demonstrates superior tough soil cleaning.

Effect of Shape selective Abrasives on shine loss

10 Example 3:

The procedure of Comparative Example A was followed except that 0.54 Kg of spherical alumina (GMU from Indal Ltd., India) that had a hardness of 200 Kg/mm² was added in place of calcined alumina.

15

Example 4:

The procedure of Comparative Example A was followed except that 0.54 Kg of spherical ceramic abrasive (G850TM ex 3M Minnesota Mining and Manufacturing Company, U.S) that had a hardness of 20 900 Kg/mm² was added in place of calcined alumina.

The detergent bars of Examples 3-4 were processed as a batch of 18 kg. The Roundness Factor of the abrasive particles of Comparative Examples 3-4 were determined as described for Comparative Example A and Example 1-2.

5

The shine loss for Comparative Example A and Example 3-4 was determined as described below. The composition details and results on tough soil cleaning and shine loss for Comparative Example A and Examples 3-4 are presented in Table 2.

10

Evaluation of loss of shine:

New stainless steel plates with an initial gloss of about 1100 gloss units as measured in TriMicroglossmeter (Sheen Instruments Ltd. Kingston, England) were used in the study.

15 The plates were cleaned with the compositions of Comparative Examples A and Examples 3-4 using a trained in-house panel of 20 members. The cleaning of plates was carried out in a manner conventionally practiced in Indian homes. The gloss was recorded after intervals of every 90 wash cycles. The shine
20 loss was calculated as follows:

$$\text{Shine Loss} = (\text{Gloss})_{\text{initial}} - (\text{Gloss})_{\text{final}}$$

Table 2

Composition (%. Wt)	A	3	4
Na LAS	14	14	14
Sodium Carbonate	10	10	10
China clay	15	15	15
Dolomite	45	45	45
Alkaline Silicate	3	3	3
Magnesium sulphate	1	1	1
Perfume, colour	0.2	0.2	0.2
Water	To 100	To 100	To 100
Abrasive Alumina (irregular)	3	-	-
Abrasive alumina (spherical)	-	3	-
Abrasive Ceramic (spherical)	-	-	3
Roundness Factor of Abrasive	0.45	0.84	0.93
Hardness of abrasive (Kg/mm ²)	2000	2000	900
Tough soil cleaning	39	53	55
Shine loss	388	115	256

The data in Table 2 shows that the cleaning compositions according to the invention demonstrates superior tough soil
5 cleaning and better maintenance of shine.

Effect of addition of alkanolamine:

10 Comparative Example-B

2.5 kg of linear alkyl benzene sulphonate was taken in a sigma mixer. This was followed by addition of dolomite, 0.68 Kg of monoethanolamine (MEA) salt of phosphoric acid, calcium hydroxide, and other minor ingredients and the mass was mixed.

15 The mass was then extruded, billeted and stamped.

Comparative Example-C

The procedure of Comparative Example B was followed except that 0.54 kg of calcined alumina (irregular shape) was added.

In Example 5, the spherical abrasive, 0.54 Kg of G850TM ex 3M was added instead of the calcined alumina of Comparative Example C.

5 The detergent bars were processed as a batch of 18 kg. The tough soil cleaning for the formulations of Comparative Example B, C and Example 5 was evaluated as per the procedure given for Comparative Example A and Example 1-4. The shine loss was determined as per the procedure for Examples A and 3-4. The
10 composition details and the results of evaluation of the detergent formulations are presented in Table 3.

Table 3

Composition (%. Wt)	B	4	C	5
Na LAS	14	14	14	14
Sodium Carbonate	10	10	10	10
China clay	15	15	15	15
MEA salt of phosphoric acid	4	-	4	4
Calcium hydroxide	2	-	2	2
Alkaline Silicate	3	3	3	3
Magnesium sulphate	1	1	1	1
Dolomite	37	45	37	37
Perfume, colour	0.2	0.2	0.2	0.2
Water	To 100	To 100	To 100	To 100
Abrasive Alumina	-	-	3	-
Abrasive G850 TM	-	3	-	3
Roundness Factor	-	0.93	0.45	0.93
Hardness (Kg/mm ²)	-	900	2000	900
Tough soil cleaning	40	55	53	68

15 The data presented in Table 3 shows that when MEA salt of phosphoric acid and spherical abrasive is used in the detergent formulation (Example 5), there is a further synergistic improvement in tough soil cleaning. The detergent formulation according to the invention (Example 5) also helps in improved
20 maintenance of shine.

Effect of shape selective abrasives on cleaning of accumulated calcium soap through cream formulation:

5 Comparative Example D

The composition was formulated in the form of a cream. The ingredients described in Table 4 were added in a sequential manner in a 2 l glass beaker and mixed using an overhead stirrer. A gap of 5-10 minutes mixing was given prior to
10 addition of a fresh ingredient. Perfume was added after the final temperature of the mixture was below 25 C.

Examples 6 and 7:

The composition is described in Table 4 and part (5% by wt.) of
15 calcite was replaced with glass beads, which is an abrasive with a roundness factor of 0.96 which is according to the invention.

Evaluation of calcium soap cleaning:

20 One of the tough soils encountered in household is the bathroom soil that is formed due to the accumulation of calcium soaps on basins, tiles and tubs. The efficacy of formulations containing substantially spherical abrasives was tested on soils generated under lab conditions.

25

Soils of calcium soap were prepared by coating a uniform layer of the solution on enamel plates. These soils were dried in an oven for fixed period of time and were then cooled to room temperature. Samples were tested by placing 5 g of product
30 (Examples D, 6 and 7, on the soil area of 25 sq. cm and cleaned with a load of 1 kg using a cloth tool. Cleaning efficacy was evaluated by calculation the area cleaned using a grid.

Evaluation of loss of shine:

Damage tests were carried for products (Examples D, 6 and 7) . A model black surface of Perspex (with an initial gloss of 87 units as measured on a TriMicroglossmeter at 85 degrees) was chosen for this study. The loss in gloss of this substrate using 5 g of product using a cloth tool under 1 Kg load for 100 revolutions on a to and fro jig was measured. The higher the loss in gloss, the higher is the damage potential of the product. The cleaning performance of the cream formulations is presented in Table 5.

Table 4

Composition (%. Wt)	Example D	Example 6	Example 7
Na LAS	0.6	0.6	0.6
Calcite	30	25	25
Sodium carbonate	0.2	0.2	0.2
Solvent	0.5	0.5	0.5
Spherical abrasive	0	5 ^a	5 ^b
Polymer	0.6	0.6	0.6
Colour	0.004	0.004	0.004 .
Perfume	0.35	0.35	0.35
Preservative	0.02	0.02	0.02
Water	To 100	To 100	To 100

a: glass bead with D50 of 250 micron

15 b: glass bead with D50 of 500 micron

Table 5

Performance Parameter	Example D	Example 6	Example 7
Cleaning of Ca soap soil (%clean)	10	30	40
Loss of shine on Perspex substrate	3	6	11

20 The data presented show that even when a part of the abrasive is replaced with the shape selective abrasive having a roundness factor according to the invention the formulation

gives superior cleaning benefits while maintaining the surface shine of the substrate.

5 **Effect of pH and shape selective abrasives on cleaning of accumulated calcium soap through cream formulation:**

Comparative Examples E, F, G

The compositions were formulated in the form of a cream. The
10 ingredients described in Table 6 were added in a sequential manner in a 2 l glass beaker and mixed using an overhead stirrer. A gap of 5-10 minutes mixing was given prior to addition of a fresh ingredient. Perfume was added after the final temperature of the mixture was below 25° C. The
15 composition was formulated at different pH ranges 2, 7 and 11. Calcite was used as the abrasive when the pH of the formulation was 7 or 11 and feldspar was used as the abrasive when the pH of the formulation was 2.

20 Examples 8 - 10:

The compositions described in Table 6 were prepared and part (5% by wt.) of calcite or Feldspar was replaced with glass beads, which is an abrasive with a roundness factor of 0.96 according to the invention. The composition was formulated at
25 different pH ranges 2, 7 and 11. The evaluation of the cleaning of accumulated calcium soap was done by the procedure described above.

Table 6

Composition (%. Wt)	Ex. E	Ex. 8	Ex. F	Ex. 9	Ex. G	Ex. 10
Na LAS	0.6	0.6	0.6	0.6	0.6	0.6
Calcite	25	20	25	20	0	0
Feldspar	0	0	0	0	25	20
Sodium carbonate	0.2	0.2	0.2	0.2	0.2	0.2
Solvent	0.5	0.5	0.5	0.5	0.5	0.5
Spherical abrasive *)	0	5	0	5	0	5
Polymer	0.6	0.6	0.6	0.6	0.6	0.6
Colour	0.004	0.004	0.004	0.004	0.004	0.004
Perfume	0.35	0.35	0.35	0.35	0.35	0.35
Preservative	0.02	0.02	0.02	0.02	0.02	0.02
Water	To 100	To 100	To 100	To 100	To 100	To 100
pH	11	11	7	7	2	2
Performance Parameter						
% cleaning of Ca soap	16	54	20	54	57	66

*) Glass beads with D50 of 500 micron)

The data presented show that the superior cleaning benefit
 5 obtained by replacing the abrasive with shape selective
 abrasive having a roundness factor according to the invention
 is not influenced even when the pH of the composition is varied
 over a wide range from 2 to 11. Thus the cleaning compositions
 of the present invention surprisingly achieved superior tough
 10 soil cleaning in use of the shape selective particulate
 abrasives and also avoided shine loss with reduced scratching
 on the hard surface.

CLAIMS

1. A synergistic cleaning composition for hard surface cleaning, comprising:
 - 0.1 to 40% by weight of detergent active;
 - 0.1 to 40% by weight of shape selective particulate abrasive, said shape selective particulate of the abrasive having 0.6 to 1.0 Roundness Factor such as herein defined;
 - optionally other abrasives such that the total amount of abrasives is from 0.1 to 98% by weight of the total composition.
2. A synergistic cleaning composition for hard surface cleaning according to claim 1 wherein the abrasives have an average particle size ranging from 1 to 600 microns.
3. A synergistic cleaning composition for hard surface cleaning according to claims 1 and 2 wherein the shape selective abrasives have a hardness of 10-5000 Kg/mm², preferably 100-3000 Kg/mm².
4. A synergistic cleaning composition as claimed in anyone of claims 1 to 3 wherein the shape selective abrasive has a Roundness Factor of 0.7 to 1.0.
5. A synergistic cleaning composition as claimed in anyone of claims 1 to 4 comprising of 0.1 to 25% weight of an alkanolamine and/or a salt thereof.
6. A synergistic cleaning composition as claimed in anyone of claims 1 to 4 wherein the said detergent actives are

selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent actives.

6. A synergistic cleaning composition as claimed in anyone of claims 1 to 5 wherein the said detergent active is anionic with at least one of an alkali, alkaline earth metal, ammonium and alkanolamine counter ion or a mixture thereof.
7. A synergistic cleaning composition as claimed in anyone of claims 1 to 6 wherein the shape selective abrasive has a specific gravity of 0.1 to 2.8.
8. A synergistic cleaning composition as claimed in anyone of claims 1 to 7 wherein the shape selective abrasive is a mineral abrasive selected from apatite, feldspar, quartz, topaz, calcite, alumina, limonite, kimenite, ceramic, leucite, glass, taconite, silica sand, flint, vermiculite, fire clay, diaspore, bauxite, limestone, iron pyrite, magnetite and hematite.
9. A synergistic cleaning composition as claimed in anyone of claims 1 to 8 wherein the shape selective abrasive is a synthetic abrasive selected from ferrite, pearlite, austenite, martensite, cemetite, carbides of chromium, tungsten, silicon, titanium and vanadium, suitable organic polymeric abrasives such as selected from polystyrene, polyacrylate, polymethylmethacrylate, polycarbonate and polyethylene.
11. A synergistic cleaning composition as claimed in anyone of claims 1 to 14 comprising other abrasives irregularly

shaped, selected from organic or inorganic having a particle size from 1 to 500 microns and a hardness from 70 to 5000 Kg/mm².

11. A synergistic cleaning composition as claimed in anyone of claims 1 to 15 wherein the pH is between 0.5 and 13.
12. A process for cleaning hard surfaces comprising the step of applying to the surface a cleaning composition according to any one of claims 1-11.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/07229

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/14

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)

IPC 7 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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02 38720 A (UNILEVER) 16 May 2002 (2002-05-16) page 5, line 25 -page 8, line 11; claims ---	1-12
A	WO 00 20544 A (UNILEVER) 13 April 2000 (2000-04-13) page 1, line 26 -page 10, line 18; claims ---	1-12
A	GB 2 351 502 A (SALEM MAHMOUD) 3 January 2001 (2001-01-03) cited in the application claims; examples --- -/--	1,2,6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International Application No

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