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(54) **LIQUID ABRASIVE CLEANING COMPOSITIONS**

FLÜSSIGES REINIGUNGSZUSAMMENSETZUNGEN ENTHALTEND SCHLEIFMITTEL

COMPOSITIONS LIQUIDES DE NETTOYAGE ABRASIF

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Description

Field of the invention

[0001] The invention relates to aqueous liquid compositions which include an abrasive and a polymeric thickening agent to keep the abrasive suspended in the liquid.

Background of the invention

[0002] Liquid abrasive cleaning compositions are well known in the art and often comprise a combination of anionic and nonionic surfactants, which together form a lamellar micelle aqueous phase which acts as a suspending system to keep the solid abrasive in a stable suspension. Often a polymeric thickening agent is added to further improve the stability of the suspension.

[0003] Thus, in WO 91/08283 liquid abrasive cleaning compositions are disclosed comprising 0.02-20% of detergent, 1-70% of particulate abrasive and 0.01-10% of a thickening mixture consisting of a linear non-starch type polymer and a branched starch type polymer (amylopectin).

[0004] In WO 95/08619 liquid abrasive cleaning compositions are disclosed comprising a cross-linked polyacrylate, at least one non-ionic surfactant, a pH adjusting agent and a calcium carbonate abrasive. The compositions contain 0.1-2% of polyacrylate, 0.1-10% of nonionic, up to 10% anionic and 5-60% abrasive. Similar compositions are disclosed in EP 649898 with the extra proviso that they contain hypochlorite and that the surfactant is bleach-stable.

[0005] In WO 96/35771 liquid abrasive cleaning compositions are disclosed comprising 10-30% of inorganic abrasive and a thickening system which consists of a cross-linked polyacrylate polymer and a smectite-type clay whereby the latter forms 50-80% of the thickening system. The thickening system comprises 1-2.5% of the composition.

[0006] EP 0 301 885 discloses liquid abrasive cleaning compositions comprising up to 70% of abrasive, an aqueous suspending medium made of a combination of anionic surfactants and electrolyte and also comprising a polyacrylate material having a molecular weight of between 500 and 3000.

[0007] EP 0 570 226 discloses liquid abrasive cleaning compositions comprising a water-soluble abrasive in an amount exceeding the solubility in the composition, but at least 20%. Na tripolyphosphate is mentioned as one of the possible abrasives. The composition furthermore contains at least 0.5% of an anionic surfactant and 1% or more of a low molecular weight (<10,000) polyacrylate thickener.

[0008] A similar kind of product is disclosed in EP 0 193 375 comprising at least 6% of the water soluble salt used as the abrasive and at least 1.5% of a surfactant mixture having structuring and suspending properties. The composition may optionally contain up to 10% of insoluble abrasive and a polymeric structuring aid such as Carbopol™ .

[0009] WO 98/49261 discloses liquid abrasive cleaning compositions comprising a combination of anionic and nonionic surfactants forming a suspending system. That combination generally comprises at least 1.0% of anionic surfactant and at least 0.5% of nonionic surfactant. The composition may optionally contain a polymeric structuring aid such as Carbopol™. The composition may also optionally contain a detergent builder such as a water-soluble phosphate.

[0010] Liquid abrasive cleaning compositions are normally sold in a ready to use form that contains 10-50%, generally 20-45% solid abrasive. Such compositions cannot be diluted to e.g. 10-20% solid abrasive content without losing their stability leading to sedimentation. Although in the patent literature abrasive contents of up to 70% are quoted, such contents are not normally found in commercial products.

[0011] In WO 01/05931 liquid abrasive cleaning compositions are disclosed comprising 10-95% of abrasive and 0.05-0.70% of an anionic thickening polymer. The preferred abrasive is calcite. Compositions comprising up to 50% abrasive are primarily intended as ready-to-use products. Compositions containing 45% abrasive or more can also be diluted with water to form a stable ready-to-use abrasive cleaner.

[0012] While anionic polymers are generally efficient thickening agents for liquid abrasive cleaning compositions (LAC), it was found that such polymers which are hydrophobically modified and/or have a relatively low charge density do not give a totally satisfactory rheology for liquid ready-to-use products and may be lead to instability of the suspension at high temperatures. On the other hand, anionic polymers with a high content of carboxylate groups do give the right reology and high temperature stability, but in LAC's comprising calcite or dolomite as the abrasive, they are the cause of instability if the compositions are subjected to repeated freeze/thaw cycles, as may occur during storage in winter. This instability results in flocculation or even sedimentation of the solids in the composition.

Brief description of the invention

[0013] It is an object of the present invention to provide aqueous liquid abrasive cleaning compositions comprising calcite or dolomite abrasive and a polycarboxylate thickener wherein the carboxylate group content of the polymer is at least 50%, which can be frozen and thawed without loosing stability.

[0014] Accordingly, the invention provides liquid aqueous abrasive cleaning compositions comprising an insoluble abrasive, an anionic thickening polymer with a high carboxylate group content and a phosphate or phosphonate salt capable of sequestering Ca^{2+} ions.

Detailed description of the invention

[0015] All percentages given herein are by weight and based on the total composition unless specified otherwise.

[0016] The term "liquid" as used herein refers to products which are easily pourable, as well as to products which are thick, almost paste-like, but because of their flow properties can physically still be classified as liquids.

[0017] The aqueous liquid abrasive cleaning compositions according to the invention comprise 10-80% of a calcite and/or dolomite abrasive, 0.05-1.5% of a polycarboxylate thickening polymer with a high carboxylate group content and a stabilising amount of a phosphate or phosphonate capable of sequestering Ca^{2+} ions.

Abrasive

[0018] A dispersed, suspended solid particulate abrasive is an essential ingredient of the liquid abrasive compositions according to the present invention. Preferably the amount of abrasive is at least 20% and for practical purposes generally not more than 75%, more preferably at most 70

[0019] The products may be formulated and packaged as ready-to-use compositions having an abrasive content as specified above. Such compositions may have the form of thick, viscous, almost paste-like products, or they may have the form of easily pourable liquids, which can easily be dispensed from a bottle with a relatively narrow opening and are similar in appearance to the products presently well known in the trade as "liquid abrasive cleaners" (LAC). The thick-viscous type of ready-to-use products preferably have a high abrasives content of at least 45%, more preferably more than 50%, even more preferably at least 55%, most preferably at least 60%. The pourable liquid type of ready-to-use compositions, on the other hand, preferably have a low abrasives content i.e. below 55%, more preferably 50% or less, even more preferably at most 45%.

[0020] Alternatively the compositions of the invention may be formulated and packaged as concentrates that are diluted before use by the addition of a suitable amount of water. Such compositions have the advantage that they require smaller packaging for the same ultimate amount of ready-to-use product and thus provide an advantage in storage and transport. They may be prepared and transported in bulk as intermediates to a production facility close to the consumers where they are diluted with water and then packaged and sold as ready-to-use products. On the other hand, they may also be packaged directly and sold as concentrates, to be diluted with water by the consumer at home. These products have a high abrasives content of preferably at least 45%, more preferably more than 50%, even more preferably at least 55%, most preferably at least 60%.

[0021] Calcite and dolomite are the abrasives that are most widely used in the art and the invention specifically pertains to the use of these abrasives.

[0022] Preferred weight average particle sizes for the abrasives fall in the range 0.5-500 microns, preferably 5-250 microns, with values of 10-100 microns being particularly preferred. In this range an acceptable compromise between good cleaning behaviour and low substrate damage is achieved.

[0023] The polycarboxylate thickening polymers with a high carboxylate group content are used for obtaining a stable suspension of the abrasive particles in the aqueous medium.

Polymer

[0024] For the purposes of this invention polycarboxylate thickening polymer with a high carboxylate group content (high carboxylate polymers) are defined as polymers in which at least 50% of the monomeric units in the polymer carry a carboxylic acid or carboxylate ion group, herein collectively referred to as carboxylate group. Preferably the amount of monomers carrying a carboxylate group in the polymer (hereinafter referred to as "carboxylate group content") is at least 70%, more preferably at least 80% or even 90%. The polymers are preferably cross-linked. These polymers are available in various forms and from many suppliers, e.g. as aqueous suspensions or in solid powdered form.

[0025] A suitable way of determining the carboxylate group content is to determine the acid value of the polymer by titrating with NaOH. It was found that polymers which on the one hand give satifactory rheology, and on the other hand benefit from the addition of phosphate or phosphonate to increase freeze/thaw stability generally have an acid value of 250 or higher (measured as mg NaOH to titrate 1g of polymer to pH 10), preferably $\geq$ 350, more preferably $\geq$ 425 or even $\geq$ 475.

[0026] The polymers preferably have a molecular weight of at least 100,000. Suitable polymers are to be found among the various acrylic, methacrylic and maleic acid homopolymers and copolymers with each other or with other ethylenic monomers (such as acrylate esters). Such polymers generally have a molecular weight of at least 200,000 or even

500,000 or more, often well over 1000,000. Very suitable are synthetic polycarboxylate polymers e.g. carbomers (solid powdered polyacrylic acids).

[0027] Polymers for use according to the invention include:
POLYGEL/NEUTRAGEL series DA, DS, DR and DB;
CARBOPOL series ETD 2690, ETD 2691, ETD 2623, EZ-1, EZ-2, CARBOPOL 600 series (e.g. 663, 644, 674, 676).

[0028] Well-known thickening polymers that are not according to the invention are e.g.:
ACUSOL HASE and ASE series such as 820, 823 and 842;

[0029] ACUSOL is a trademark of Rohm & Haas;
CARBOPOL is a trademark of Noveon Inc.
POLYGEL and NEUTRAGEL are trademarks of Sigma 3V.

[0030] The amount of polymer is preferably between 0.07 and 1.0% For "high abrasives content" products, i.e. products in which the amount of abrasive is at least 45%, more preferably more than 50%, even more preferably at least 55%, most preferably at least 60%, the polymers are preferably used in an amount of at least 0.10, more preferably 0.15% or more. For those products the maximum level of polymers generally does not need to exceed 0.70% and is preferably at or below 0.65, more preferably at most 0.60, most preferably at most 0.55% or even 0.50%.

[0031] For the easy flowing ready-to-use products, on the other hand, the amount of polymer is preferably at least 0.10%, but the maximum level is preferably less than 0.50%, more preferably at most 0.40% or even 0.35%, most preferably at or below 0.30 or even 0.25%.

[0032] Other thickening agents, such as thickening clays or thickening silica are not necessary to achieve the required suspension stability and preferred embodiments of the invention do not contain such thickeners.

Phosphate or phosphonate

[0033] The phosphate and/or phosphonate capable of sequestering Ca^{2+} ions may be an inorganic phosphate such as an alkali metal orthophosphate, polyphosphate or pyrophosphate, particularly sodium or potassium tripolyphosphate, or an organic phosphonate such as are marketed by Monsanto in the Dequest™ range. The inorganic phosphates are preferred.

[0034] The phosphate/phosphonate is used in the LAC in an amount effective to provide sufficient stability to the composition, but not exceeding the solubility in the aqueous phase. Thus, the amount is dependent on the type and amount of carboxylate polymer, on the kind of phosphate or phosphonate used and on the stability requirements, i.e. the freezing temperature and the number of freeze/thaw cycles the product should be able to withstand. These conditions are all easily determinable in standard laboratory freeze/thaw test procedures. An amount of at least 0.005% in the composition is preferred, more preferably at least 0.01%, whereas an amount of more than 5% is not normally advantageous. Preferably the amount is at most 1%, more preferably 0.5% or less. In general satisfactory results are obtained with a polymer:phosphate (or phosphonate) ratio between 20:1 and 1:1, preferably at most 10:1 and at least 1.5:1 or even 2:1.

[0035] The use of inorganic phosphates further improves easy dilution and dispersion of concentrates intended to be diluted to obtain ready-to-use products.

Optional components

[0036] As outlined above, no surfactant is needed in the compositions according to the invention for stability reasons. Nevertheless, it may be useful to add a limited amount of detergent surfactant to improve the cleaning properties of the products on certain types of soils and/or to give foaming during use which is desired by many consumers. Nonionic, anionic, zwitterionic and amphoteric surfactants may be used. Nonionic surfactants are preferred, but they may be combined with other classes of surfactants, particularly anionic surfactants. Generally, the presence of zwitterionic or cationic surfactants, although possible, does not serve any useful purpose and compositions without such surfactants are a preferred embodiment of the invention.

[0037] Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxides that are hydrophilic with an organic hydrophobic compound that may be aliphatic or alkylaromatic. The length of the hydrophilic polyalkyleneoxy group that is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements:

[0038] 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 condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols, whose alkyl groups contain 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 condensate containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000; tertiary amine oxides

of structure R_3NO, where one group R is an alkyl group of 8 to 18 carbon atoms and the others are each methyl, ethyl or hydroxyethyl groups, for instance dimethyl-dodecylamine oxide; tertiary phosphine oxides of structure R_3PO, where one group R is an alkyl group of from 10 to 18 carbon atoms, and the others are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide; and dialkyl sulphoxides of structure R_2SO where the group 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; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans. The nonionic can also be selected from a range of alkyl polyglycosides.

[0039] Particularly suitable are the ethoxylated aliphatic alcohol surfactants, such as C9-C11 5EO, C12-C13 6.5EO and C13-C15 7EO (EO numbers are averages), and the tertiary amine oxides such as dimethyl-decyl-, dimethyl dodecyl- and dimethyl tetradecylamine oxide and amine oxide mixtures containing a large proportion of one or more of these.

[0040] Suitable anionic surfactants are water-soluble salts of organic sulphuric acid esters and of sulphonic acids which have in the molecular structure an alkyl group containing 6-22 C-atoms. They are usefully added to provide the compositions with good foaming properties, which are often considered desirable by the consumer.

[0041] Examples of such anionic surfactants are water-soluble salts of:

- long chain (i.e. 8-22 C-atom) alcohol sulphates (also referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
- alkylbenzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms (also referred to as LAS);
- secondary alkane sulphonates (also referred to as SAS).

[0042] 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 (also referred to as LES);
- 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;

and mixtures thereof.

[0043] The preferred water-soluble synthetic anionic surfactants are the sodium, potassium, magnesium and ammonium salts of alkylbenzene sulphonates, olefin sulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates.

[0044] 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.

[0045] Further examples of suitable surfactants are compounds commonly used as surface-active agents mentioned in the well-known textbooks: "Surface Active Agents" Vol.1, by Schwartz &.Perry, Interscience 1949; "Surface Active Agents" Vol.2 by Schwartz, Perry & Berch, Interscience 1958; the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company; "Tenside-Taschenbuch", H. Stache, 2nd Edn. Carl Hauser Verlag, 1981.

[0046] The compositions according to the invention may contain a total amount of 0-2% of surfactant, preferably at most 1.0%. More preferably the total level of surfactant does not exceed 0.6%. For a useful increase in cleaning and/or foaming properties a minimum level of 0.01% of total surfactant is advisable, preferably at least 0.02%, more preferably at least 0.05%, or even 0.1%. However, surfactant is generally not present in a sufficient amount to provide a structuring system capable of suspending the abrasive.

[0047] The level of nonionic surfactant should preferably be below 2.0%, more preferably be at or below 1.0% and most preferably at or below 0.60% or even at or below 0.50%. To improve the cleaning properties of the composition the level of nonionic is preferably at least 0.01%, more preferably at least 0.02%.

[0048] The compositions according to the invention are alkaline, more particularly they have pH above 8, preferably 9 or higher. Thus the compositions can be made alkaline with use of a suitable base such as an alkali metal hydroxide or carbonate, ammonia or an organic base with pKa above 9 such as triethylamine, amino-methylpropanol (AMP), aminobutanol, mono-, di- or tri-ethanolamine, monoisopropylamine or aminomethylpropanediol. AMP is particularly useful, and preferably if added in an amount of up to 1.0%, more preferably 0.2-0.7% in the absence of another base or 0.1-0.5% in the presence of another base.

[0049] The compositions according to the invention generally do not need any extra electrolyte other than the phos-

phate/phosphonate, the base for setting the pH and the optional anionic surfactant. Preferably the level of additional electrolyte is below 0.3%, more preferably below 0.2%.

[0050] The abrasive compositions according to the invention may contain further optional components which improve their cleaning properties such as organic solvents known in the art for use in abrasive cleaning compositions, particularly solvents of which the molecules bear a polar group, such as C1-C6 alkanols (e.g. hexanol), (di)ethylene- and (di)propylene glycol C1-C6 alkyl ethers, etc. Preferably the compositions do not contain hydrocarbon solvents apart from those which may be present in a perfume.

[0051] The compositions may also contain bleaching agents, particularly halogen bleaching agents such as hypochlorite, chlorocyanurates or chlorohydantoins, more particularly hypochlorite, provided that chlorine-stable polymers and surfactants are used.

[0052] Furthermore they may contain additional components such as:

- components to further increase their appeal to the consumer, such as colorants, optical brighteners and perfumes;
- preservatives to prevent microbial contamination.

Liquid properties

[0053] Satisfactory "low abrasives content" ready-to-use LAC's according to the invention have such liquid flow characteristics that they are stable suspensions when not in use, but thin enough to pour the liquid from the packaging container and spread it on the soiled surface without appearing thin and watery. Thus, the liquid product preferably has the following liquid flow properties:

- η_0 is at least 2000Pa.s;
- σ_c is 2.5-25;
- η_{21} is at least 0.1Pa.s;

wherein: η_0 is the viscosity at zero shear rate (determined by extrapolation); σ_c is the shear stress at which the viscosity is $0.1.\eta_0$; and η_{21} is the viscosity at a shear rate of 21 s^{-1}. Preferably η_0 is at least 5000Pa.s, more preferably at least 20,000Pa.s. Also, preferably η_{21} is 0.3-5.0, more preferably 0.6-1.8, most preferably 1.0-1.5Pa.s.

[0054] Measurements made on:

- CSL 100 (TA Instruments) with vane and basket measuring system (basket internal diameter 48mm, vane diameter 38mm and height 24.5mm) to measure viscosity from a stress (σ) of 0.01 Pa to the stress required to give a shear rate of 1 s^{-1};
- Haake RV20 with M5 measuring head and SV2p measuring geometry to measure viscosity between shear rates of 0.1 and 389 s^{-1}.

All measurements made at 20°C.

[0055] Satisfactory "high abrasives content" concentrated liquid abrasive cleaning compositions are liquids or pastes which are suitable for dilution with water to 1.2-4 times, preferably 1.5-3 times, more preferably 2-3 times the original volume, thereby producing a stable ready-to-use liquid abrasive cleaning composition, preferably a cleaning composition with the liquid flow properties specified above.

[0056] Satisfactory "high abrasives content" ready-to-use liquid abrasive cleaning compositions are generally viscous, or almost paste-like liquids. Although they do not generally spread easily when put on a surface, they do obtain a smooth and "undisturbed" surface again when left alone for a few minutes to a few hours in the container. Such products are preferably not packaged in a container from which they have to be dispensed by pouring, however, containers such as a tub or tin, from which suitable amounts can be taken out on a suitable applicator such as a wet cloth or sponge, or containers from which they can be dispensed by squeezing, such as a tube, are very useful.

Preparation

[0057] The compositions according to the invention may simply be prepared by mixing the various components. One preferred way is to first make a dilute (e.g. 1-2%) aqueous solution or dispersion of the polymer and then mix in the other components subsequently. The other components may be first made into a slurry with the remaining amount of water after which the solution (dispersion) and the slurry are mixed. Sometimes it is advantageous to neutralise the aqueous polymer solution with part of the base before mixing it with the other components.

[0058] The products according to the invention may also be prepared by adding a pre-prepared dry mix of all the ingredients to the required amount of water, followed by shaking or stirring. The mix may be in powder, granule, prill or

any other form suitable for easy dispersion in water. Powders, granules or prills should preferably be free flowing. Spray-drying, fluid bed drying, granulation and similar processes known in the art are very suitable to obtain products, which are free flowing and easily dispersible without lumping. Layering agents may be added to prevent lumping of the dry composition (examples: Alusil ET, a porous aluminium silicate marketed by J. Crosfield, and Socal P2V, marketed by Solvay). For granulation the addition of a granulating aid such as a polyethylene glycol with mol. weight of 1500-4000 may be useful.

Examples 1-3

[0059] Liquid abrasive cleaning compositions according to the Examples 1-3 in the table below were prepared.

Ingredients	**Percentage levels**		
	1	2	3
Dodecyl-dimethyl amine oxide	0.20	0.20	0.20
Calcite (Omyacarb™ 30)	45.00	45.00	45.00
Polygel DR	0.17	0.17	0.17
NaOH	0.048	0.048	0.048
2-Amino-2-methylpropanol	0.18	0.18	0.18
Na tripolyphosphate	0.00	0.02	0.05
Perfume	0.40	0.40	0.40
Water	to 100	to 100	to 100

[0060] The compositions were prepared by first preparing a solution of the polymer and neutralising it with NaOH solution. Preferably the tripolyphosphate is added to the polymer solution although it could be post-dosed. The polymer solution is stirred at room temperature until it appears homogeneous, while taking care that the solution is not aerated. The remaining components and the remainder of the water of the formula are made into an aqueous slurry and the polymer solution is carefully added while stirring. Stirring is continued until a homogeneous suspension is obtained, again taking care that aeration is avoided.

[0061] All three examples were tested for stability by subjecting eight samples of each of them to repeated freeze/thaw cycles at -5°, -10° and -24°C. The -5°C cycle consisted of 18 hours freezing and 6 hours at room temperature; the -10° and -24°C cycles consisted of 16 hours freezing and 8 hours at room temperature. For example 1 six samples were unstable after one -5° cycle and all of them were unstable and sedimented after one -10° or after one -24° cycle. For example 2 two samples showed some signs of separation after eight -5° cycles, which disappeared again after storage at room temperature. All of the samples survived eighteen -5° cycles or seven -10° or -24° cycles. For example 3 all samples survived eighteen -5° cycles or seven -10° or -24° cycles without any sign of instability.

Example 4

[0062] A high calcite content liquid abrasive cleaning composition suitable for use as such or for dilution to a 30-35% calcite LAC was prepared according to the table below:

Polygel DB	0.42%
NaOH	0.103%
Amino-2-methyl-2-propanol	0.381%
Calcite (Omyacarb 65)	63.91%
Dodecyl-dimethyl amine oxide	0.32%
Na tripolyphosphate	0.21%
Perfume	0.48%
Proxel GXL (preservative)	0.026%

(continued)

water	To 100%

[0063] The product was prepared by making a dry premix of calcite and dry polymer. This premix was dispersed in a solution of the tripolyphosphate in the water taking care that aeration is avoided. Subsequently, the NaOH, the AMP, the perfume, the amine oxide and the preservative were added.

[0064] For cleaning the resulting paste-like product could be used as such, taken from a tub with a wet cloth or it could first be diluted to a creamy pourable liquid. In both forms it was stable through repeated freeze/thaw cycles.

Claims

1. Aqueous liquid abrasive cleaning compositions comprising 10-80% of calcite or dolomite abrasive and an anionic thickening polymer **characterised in that** it contains 0.05-1.5% of a polycarboxylate thickening polymer wherein the carboxylate group content of the polymer is at least 50%, and that the composition comprises a stabilising amount of a phosphate or phosphonate salt capable of sequestering Ca^{2+} ions, which amount does not exceed the limit of solubility in the aqueous phase.

2. Compositions according claim 1 **characterised in that** the amount of abrasive is 20-70%.

3. Compositions according to any one of claims 1-2 **characterised in that** the amount of anionic polymer is 0.07-1.0%.

4. Composition according to any one of claims 1 to 3 **characterised in that** the polymer has an acid value of at least 250.

5. Compositions according to any one of claims 1 to 4 **characterised in that** the anionic polymer is a polycarboxylate polymer chosen from acrylate, methacrylate and maleic acid homopolymers and copolymers with each other or with other ethylenic monomers, having a molecular weight of at least 200,000.

6. Compositions according to any one of claims 1 to 5 **characterised in that** the phosphate is an inorganic phosphate, preferably an alkali metal orthophosphate, pyrophosphate or polyphosphate.

7. Compositions according to claim 6 **characterised in that** the phosphate is sodium or potassium tripolyphosphate.

8. Compositions according to any one of claims 1-8 to 7 **characterised in that** the phosphate or phosphonate is present in an amount such that the polymer to phosphate/phosphonate ratio is between 20:1 and 1:1.

9. Composition according to claim 8 **characterised in that** the ratio is between 10:1 and 1.5:1 and at least 0.01% of phosphate or phosphonate is present.

Patentansprüche

1. Wässrige flüssige abrasive Reinigungszusammensetzungen, umfassend 10 bis 80 % Calcit- oder Dolomitschleifmittel und ein anionisches Verdickungspolymer, **dadurch gekennzeichnet, dass** es 0,05 bis 1,5 % eines Polycarboxylatverdickungspolymers enthält, wobei der Carboxylatgruppengehalt des Polymers mindestens 50 % ist, und dass die Zusammensetzung eine stabilisierende Menge eines Phosphat- oder Phosphonatsalzes umfasst, das Ca^{2+}-Ionen maskieren kann, wobei die Menge die Löslichkeitsgrenze in der wässrigen Phase nicht überschreitet.

2. Zusammensetzungen nach Anspruch 1, **dadurch gekennzeichnet, dass** die Menge an Schleifmittel 20 bis 70 % ist.

3. Zusammensetzungen nach einem der Ansprüche 1 bis 2, **dadurch gekennzeichnet, dass** die Menge an anionischem Polymer 0,07 bis 1,0 % ist.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** das Polymer eine Säurezahl von mindestens 250 aufweist.

5. Zusammensetzungen nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** das anionische Polymer ein Polycarboxylatpolymer, ausgewählt aus Acrylat-, Methacrylat- und Maleinsäurehomopolymeren und -copolymeren miteinander oder mit anderen ethylenischen Monomeren, mit einem Molekulargewicht von mindestens 200000 darstellt.

6. Zusammensetzungen nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** das Phosphat ein anorganisches Phosphat, vorzugsweise ein Alkalimetallorthophosphat, -pyrophosphat oder -polyphosphat darstellt.

7. Zusammensetzungen nach Anspruch 6, **dadurch gekennzeichnet, dass** das Phosphat Natrium- oder Kaliumtripolyphosphat darstellt.

8. Zusammensetzungen nach einem der Ansprüche 1 1 bis 7, **dadurch gekennzeichnet, dass** das Phosphat oder Phosphonat in einer derartigen Menge vorliegt, dass das Polymer-zu-Phosphat/Phosphonat-Verhältnis zwischen 20:1 und 1:1 liegt.

9. Zusammensetzung nach Anspruch 8, **dadurch gekennzeichnet, dass** das Verhältnis zwischen 10:1 und 1,5:1 ist und mindestens 0,01 % Phosphat oder Phosphonat vorliegt.

Revendications

1. Compositions liquides aqueuses de nettoyage abrasif comprenant de 10 % à 80 % d'abrasif calcite ou dolomite et un polymère épaississant anionique **caractérisées en ce qu'**elles contiennent de 0,05 % à 1,5 % de polymère épaississant polycarboxylate, dans lesquelles la teneur en groupes carboxylates du polymère est d'au moins 50 %, et **en ce que** la composition comprend une quantité stabilisante d'un sel de phosphate ou de phosphonate capable de piéger des ions Ca^{2+}, dont la quantité ne dépasse pas la limite de solubilité dans la phase aqueuse.

2. Compositions selon la revendication 1, **caractérisées en ce que** la quantité d'abrasif est de 20 % à 70 %.

3. Compositions selon l'une quelconque des revendications 1-2, **caractérisées en ce que** la quantité de polymère anionique est de 0,07 % à 1,0 %.

4. Composition selon l'une quelconque des revendications 1 à 3, **caractérisée en ce que** le polymère possède un degré d'acidité d'au moins 250.

5. Compositions selon l'une quelconque des revendications 1 à 4, **caractérisées en ce que** le polymère anionique est un polymère polycarboxylate choisi parmi des homopolymères et des copolymères d'acrylate, de méthacrylate et d'acide maléique les uns avec les autres ou avec d'autres monomères éthyléniques, ayant une masse moléculaire d'au moins 200 000.

6. Compositions selon l'une quelconque des revendications 1 à 5, **caractérisées en ce que** le phosphate est un phosphate inorganique, de préférence un orthophosphate, un pyrophosphate ou un polyphosphate de métal alcalin.

7. Compositions selon la revendication 6, **caractérisées en ce que** le phosphate est un tripolyphosphate de sodium ou de potassium.

8. Compositions selon l'une quelconque des revendications 1 à 7, **caractérisées en ce que** le phosphate ou le phosphonate est présent dans une quantité telle que le rapport du polymère sur le phosphate/phosphonate est compris entre 20:1 et 1:1.

9. Composition selon la revendication 8, **caractérisée en ce que** le rapport est compris entre 10:1 et 1,5:1 et qu'au moins 0,01 % de phosphate ou de phosphonate est présent.