Abstract:

The invention relates to a composition for cleaning and/or protecting acid sensitive surfaces and a liquid concentrate composition or a ready-to-use solution. The composition for cleaning and/or protecting acid sensitive surfaces comprises at one phosphorous acid compound and a nanoparticulate degreasing agent, wherein the composition has a pH in the range from equal or more than about 1 to equal or less than about 7.
Acid marble cleaner

Field of the Invention
The invention relates to a composition for cleaning and/or protecting acid sensitive surfaces, especially marble.

Background of the Invention
Usual commercial and domestic articles for cleaning of surfaces in sanitary areas are acidic to assure effective cleaning. Such acidic compositions are not suitable for cleaning acid sensitive surfaces especially carbonate-containing surfaces like marble without damage. Already weak acids react with the carbonate and damage the carbonate-containing surface like marble visually.

However, marble is a preferred material in high-quality sanitary furniture. Especially in the hospitality market like hotels the material compatibility of cleaning products with marble is a very important criterion. Therefore, for marble cleaning mainly neutral or mild alkaline cleaners are used. However, neutral or mild alkaline cleaners have disadvantages in not preventing lime built-up.

It is still a need to provide a composition for effectively cleaning acid sensitive surfaces from lime scale without negatively affecting the surface.

Summary of the Invention
It is provided a composition for cleaning and/or protecting acid sensitive surfaces, comprising at least one phosphorous acid compound and a nanoparticulate degreasing agent, wherein the composition has a pH in the range from equal or more than about 1 to equal or less than about 7.

It has been surprisingly found that the composition according to the invention is remarkably gentle to acid sensitive surfaces. Specifically, it has been found that an acidic composition according to the invention can be used for the cleaning of acid sensitive surfaces.
without apparent damage to the acid sensitive surface. Advantageously, the surface retains its
bright or satin finish without changes due to the use of the composition according to the
invention. The present invention moreover has the advantage of providing care and protection
for acid sensitive surfaces. Surprisingly, it was found that the composition according to the
invention provides a protecting effect that can render acid sensitive surfaces less susceptible
to acids.

Definitions

The term "acid sensitive surfaces" identifies those surfaces that exhibit damage when
exposed to an acidic solution. An acidic solution is an aqueous solution having a pH that is
lower than 7. Exemplary acid sensitive surfaces include carbonate-containing surfaces like
marble.

The term "liquid concentrate composition" refers to a composition that is diluted to
form a ready-to-use solution which is used for cleaning and/or protecting acid sensitive
surfaces. The concentrate is preferably a liquid. The "ready-to-use solution" refers to a
composition that is applied to a surface to clean and/or protect an acid sensitive surface.

The term "alkyl" according to the invention is to be understood as meaning straight-
chain or branched alkyl groups. The term "Cl-C18-alkyl" as used herein refers to straight-
chain or branched alkyl groups having 1 to 18 carbon atoms. Preferred Cl-C18-alkyl groups
are selected from the group comprising methyl, ethyl and the isomers of propyl, butyl, pentyl,
such as for example isopropyl, isobutyl, tert.-butyl, sec.-butyl and isopentyl, hexyl, octyl,
decyl, dodecyl, hexadecyl, and octadecyl.

The term "organosilicons" identifies organic compounds containing carbon silicon
bonds.

A solvent, preferably water, can be added add. 100 wt.-% to the composition of the
invention. The solvent content, such as the water content, of the composition according to the
invention is simply determined by subtracting the amounts of all the usual ingredients from
100 wt.-

Weight percent, weight-% or wt.-% are synonyms that refer to the concentration of a substance as the weight of the substance divided by the weight of the composition and multiplied by 100. The weight-% (wt.-%) of the components are calculated based on the total weight amount of the composition, if not otherwise stated.

The total amount of all components of the composition does not exceed 100 wt.-%.

All numeric values are herein assumed to be modified by the term "about", whether or not explicitly indicated. As used herein, the term "about" refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods; and the like. The term "about" also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

It should be noted that, as used in this specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

**Phosphorous Acid Compound**

The composition for cleaning and/or protecting acid sensitive surfaces comprises at least one phosphorous acid compound. The phosphorous acid compound can be selected from the group of phosphoric acid, phosphonic acid, polyphosphoric acid $\text{HO(P}_2\text{O}_x\text{OH})_y\text{H}$ wherein $x$ is in the range from 2 to 9, phosphoric acid ester, phosphonic acid ester, polyphosphoric acid ester $\text{HO(P}_2\text{OR}_x\text{H}$ wherein $x$ is in the range from 2 to 9 and $R$ is a straight-chain or branched C1-C18 alkyl group, and mixtures thereof.

The phosphoric acid ester can be selected from the group of phosphoric acid mono and dialkyl esters, wherein the alkyl group is a straight-chain or branched C1-C18 group.
Preferably the phosphoric acid mono and dialkyl ester is selected from the group of phosphoric acid mono and di-methyl ester, ethyl ester, propyl ester, isopropyl ester, butyl ester, isobutyl ester, pentyl ester, isopentyl ester, hexyl ester, decyl ester, dodecyl ester, hexadecyl ester, octadecyl ester, and mixtures thereof. Especially suitable phosphoric acid esters are mono- and/or diesters of phosphoric acid with aliphatic alcohols of chain length CI to CI8. Particularly preferred are phosphoric acid esters selected from the group of phosphoric acid dimethyl ester, phosphoric acid diisopropyl ester and phosphoric acid methyl isopropyl ester. Particular preference is given to a diester of phosphoric acid with methyl on one side and isopropyl on the other.

A phosphoric acid ester that can be used is marketed by Clariant under the tradename Hordaphos® CC MIS.

Indeed, the presence of a phosphoric acid compound provides strong cleaning benefits which are particularly noticeable in marble cleaning.

The phosphonic acid ester can be selected from the group of phosphonic acid alkyl esters, wherein the alkyl group is a straight-chain or branched CI-CI8 group. Preferably the phosphonic acid mono and dialkyl ester is selected from the group of phosphonic acid methyl ester, ethyl ester, propyl ester, isopropyl ester, butyl ester, isobutyl ester, pentyl ester, isopentyl ester, hexyl ester, decyl ester, dodecyl ester, hexadecyl ester, octadecyl ester, and mixtures thereof. Particularly preferred are phosphonic acid esters selected from the group of phosphonic acid methyl ester and phosphonic acid isopropyl ester.

The polyphosphoric acid can be selected from HO(P0₂OH)ₓH wherein x is in the range from 2 to 9. The term "x" relates to the number of phosphoric units in the molecule. Particularly preferred are diprophosphoric acid and triphosphoric acid. Diphosphoric acid is also known under the name pyrophosphoric acid.

The polyphosphoric acid ester can be selected from the group of polyphosphoric acid esters HO(P0₂OR)ₓH wherein x is in the range from 2 to 9 and R is a straight-chain or branched CI-CI8 alkyl group. Particularly preferred the polyphosphoric acid ester is selected from the group of methyl ester, ethyl ester, propyl ester, isopropyl ester, butyl ester, isobutyl
ester, pentyl ester, isopentyl ester, hexyl ester, decyl ester, dodecyl ester, hexadecyl ester, octadecyl ester, and mixtures thereof. Particularly preferred are polyphosphoric acid esters selected from the group of polyphosphoric acid methyl ester and polyphosphoric acid isopropyl ester.

The phosphorous acid compound can be used in quantities of equal or more than about 0.01 wt.-% to equal or less than about 20 wt.-%, preferably equal or more than about 0.01 wt.-% to equal or less than about 10 wt.-%, further preferred equal or more than about 0.01 wt.-% to equal or less than about 5 wt.-%, and more preferred equal or more than about 0.01 wt.-% to equal or less than about 2.5 wt.-%, based on the total weight of the composition.

**Degreasing Agent**

The composition for cleaning and/or protecting acid sensitive surfaces comprises at least one nanoparticulate degreasing agent. The nanoparticulate degreasing agent can be selected from the group of metal oxides, carbonates, hydroxides, and inorganic silicon compounds preferably selected from the group comprising silicon dioxide, preferably amorphous silicon dioxide, silicates, alumosilicates, silica sols, fumed silica, organo silicon, or mixtures thereof.

The term "nanoparticles" as used herein means particles with an average particulate diameter of about 500 nm or less. Suitable nanoparticles which may be used in the present invention are inorganic metal oxides for example silica- or alumina-based nanoparticles.

Examples for suitable metal oxides representing suitable compounds for the formation of nanoparticles are aluminum oxide, zirconium oxide, titanium oxide, cerium oxide, zinc oxide and mixtures thereof. A preferred metal oxide is titanium oxide.

However, it is preferred to select the one or more types of nanoparticles from the group comprising silicon dioxide, preferably amorphous silicon dioxide, silicates, alumosilicates, silica sols, fumed silica, organo silicon, or mixtures thereof.

Silica- or alumina-based nanoparticles can either be naturally occurring or synthetic. Fumed silica may also be used, preferably in powdered form, which is also commercially available in the form of its nanoparticles.
In a preferred embodiment colloidal, nanoparticulate silica sols can be used. A colloidal nanoparticulate silica sol in the sense of the present invention represents a stable mainly aqueous dispersion of amorphous, particulate silicon dioxide SiO$_2$ preferably plus a nonionic surfactant. Corresponding silica sol nanoparticles are commercially available.

In some compositions it might be helpful to use a silica sol in which the surface of the colloidal silica nanoparticles is modified. Suitable modifications of the surface of the silica nanoparticles represent silanizing, an alumina-modification and a coating with aluminium oxide. Further suitable silica sols having a silica surface modification represent a silica sol in which the surface of the silica particles is silanized.

A silicon dioxide nanoparticulate degreasing agent that preferred can be used is for example marketed by AkzoNobel under the tradename Berosol®EC.

Suitable organosilicon compounds are selected from the group of organosilanes, siloxides and silyl halides. Preferred organosilicon compounds are organosilanes, especially tetraorganosilanes.

Preferably, the nanoparticulate degreasing agent is selected from the group of silicon dioxide, titanium dioxide and organosilicons. A particularly preferred nanoparticulate degreasing agent is silicon dioxide.

The nanoparticles can have an average particle size of equal or more than about 1 to equal or less than about 50 nm, preferably of equal or more than about 2 to equal or less than about 40 nm and more preferred of equal or more than about 4 to equal or less than about 20 nm.

Advantageously, the particles are small enough that gravity does not cause them to settle, but large enough not to pass through a membrane. Preferably, a stabilization can be achieved by nonionics which prevent sedimentation.

The presence of a nanoparticulate degreasing agent provides strong benefits in the care and protection of the surface which are particularly noticeable in the cleaning of marble surfaces.
The nanoparticulate degreasing agent can be used in quantities of equal or more than about 0.1 wt.-% to equal or less than about 40 wt.-%, preferably equal or more than about 0.1 wt.-% to equal or less than about 30 wt.-%, further preferred equal or more than about 0.1 wt.-% to equal or less than about 20 wt.-%, and more preferred equal or more than about 0.1 wt.-% to equal or less than about 10 wt.-%, based on the total weight of the composition.

**Acidity**

The pH of the composition according to the present invention can be in the range from equal or more than about 1 to equal or less than about 7, preferably in the range from equal or more than about 2 to equal or less than about 6, more preferably in the range from equal or more than about 2.5 to equal or less than about 5. Alternatively, the pH of the composition can be adjusted to equal or more than about 3 to equal or less than about 7, preferably to equal or more than about 3.5 to equal or less than about 6. Preferred is an aqueous composition having a light acidic pH. Preferably the pH of the composition can be in the range from equal or more than about 3.8 to equal or less than about 5, further preferred in the range from equal or more than about 4 to equal or less than about 4.5. Advantageously, a pH in such ranges can provide good cleaning benefits combined with a protective effect of the compositions according to the invention which is particularly noticeable in marble cleaning.

The pH of the composition can be adjusted by using inorganic acids or an alkaline source, preferably an alkaline source. The alkaline source can be any source of alkalinity that is compatible with the other components of the composition and that will provide a use solution, i.e. a liquid concentrate composition as well as a ready-to-use solution with the desired pH. Exemplary sources of alkalinity include alkali metal hydroxides, alkali metal salts, phosphates, and mixtures thereof. Exemplary alkali metal hydroxides include sodium hydroxide, potassium hydroxide, and lithium hydroxide. Exemplary alkali metal salts include sodium carbonate, trisodium phosphate, potassium carbonate, and mixtures thereof. Exemplary phosphates include sodium pyrophosphate, potassium pyrophosphate, and mixtures thereof. The composition can comprise preferably at least one alkaline source...
selected from the group of sodium hydroxide, sodium carbonate, potassium hydroxide, and lithium hydroxide.

The source of alkalinity, preferably an alkali metal hydroxide, may be added to the composition in a variety of forms, including for example in the form of solid beads, dissolved in an aqueous solution or a combination thereof. Preferably, an alkali metal hydroxides like sodium hydroxide can be added to the composition in the form of an aqueous solution, as for example as a 45 wt.-%, 50 wt.-% or a 73 wt.-% solution.

The amount of a 50 wt.-% solution of sodium hydroxide can be from equal or more than about 0.005 wt.-% to equal or less than about 5 wt.-%, preferably equal or more than about 0.005 wt.-% to equal or less than about 2 wt.-%, further preferred equal or more than about 0.005 wt.-% to equal or less than about 1 wt.-%, and more preferred equal or more than about 0.005 wt.-% to equal or less than about 0.1 wt.-%, based on the total weight of the composition.

**Surfactants**

The composition for cleaning and/or protecting acid sensitive surfaces can comprise at least one surfactant. Preferably, the at least one non-ionic surfactant is selected from the group of fatty alcohol ethoxylates, alkylphenol ethoxilates, and alkylpolyglycosides. The fatty alcohol ethoxylate preferably is selected from the group of isotridecanol ethoxylate, tridecanol ethoxylate, isodecanol ethoxylate, decanol ethoxylate, dodecanol ethoxylate, hexadecanol ethoxylate, octadecenyl ethoxylate, octadecanol ethoxylate, tetradeanol ethoxylate, undecanol ethoxylate, and mixtures of fatty alcohol ethoxylates selected from the group of coco oil alcohol ethoxylate, and tallow alcohol ethoxylate.

A preferred non-ionic surfactant is isotridecanol ethoxylate. A preferred non-ionic surfactant is for example marketed by BASF under the tradename Lutensol® TO 8.

The amount of the at least one non-ionic surfactant can be from equal or more than about 0.01 wt.-% to equal or less than about 10 wt.-%, preferably equal or more than about 0.01 wt.-% to equal or less than about 5 wt.-%, further preferred equal or more than about 0.01 wt.-% to equal or less than about 2.5 wt.-%, more preferred equal or more than about
0.01 wt.-% to equal or less than about 1 wt.-%, and even more preferred equal or more than about 0.05 wt.-% to equal or less than about 1 wt.-%, wherein the weight-% are based on the total weight of the composition.

**Corrosion Inhibitors**

The composition for cleaning and/or protecting acid sensitive surfaces can comprise at least one corrosion inhibitor. The corrosion inhibitor can be selected from the group comprising silicate, sodium silicate, calcium acetate, calcium chloride, calcium gluconate, calcium phosphate, calcium borate, calcium carbonate, calcium citrate, calcium lactate, calcium sulfate, calcium tartrate, benzotriazole, 1,2,3-benzotriazole and mixtures thereof.

**Sequestering Agents**

The composition for cleaning and/or protecting acid sensitive surfaces can comprise at least one sequestering agent. The sequestering agent can be selected from the group comprising sodium gluconate, pentasodium salt of diethylenetriamine pentaacetic acid, sodium glucoheptonate, salts of ethylene diamine tetraacetic acid, salts of ethylene diamine tetraacetic acid, salts of hydroxyethyl ethylene diamine triacetic acid, salts of hydroxyethyl ethylene diamine triacetic acid, salts of nitrilotriacetic acid, salts of nitrilotriacetic acid, diethanolglycine sodium salt, ethanoldiglycine disodium salt, salts of hydroxymonocarboxylic acid compounds, salts of hydroxydicarboxylic acid compounds, salts of amine containing carboxylic acids, terasodium N,N-bis(carboxylatomethyl)-L-glutamate (GDLA) and mixtures thereof.

It should be understood that the sequestering agent can include mixtures of different sequestering agents.

**Hydrophilizing agent**

The composition for cleaning and/or protecting acid sensitive surfaces can comprise at least one hydrophilizing agent. The hydrophilizing agent can be selected from the group of amphoteric organic polynitrogen compounds, ethanol and mixtures thereof. It should be understood that the hydrophilizing agent can include mixtures of different hydrophilizing
agents. In preferred embodiments, the composition for cleaning and/or protecting acid sensitive surfaces comprises an amphoteric organic polynitrogen compound and ethanol.

The term "hydrophilization" of a surface in the sense of the present invention means the affinity between water and the surface is increased. This can result in an improved wetting of the surface and in a reduced amount of water spots.

The term "organic polynitrogen compound" in the sense of the present invention means an organic compound comprising at least 3 nitrogen atoms which are contained in the molecule in the form of an amine, like a primary, a secondary or a tertiary amine, and/or in the form of an amide. By the term "amphoteric" is meant that the same compound may function as acceptor as well as donator for protons.

Suitable functional groups imparting proton donator properties represent carboxy residues or derivatives thereof, like amides, anhydrides or esters, as well as salts thereof, like alkali salts, for example sodium or potassium salts, or ammonium salts, which may be converted into the carboxy group. Depending on the size of the polynitrogen moiety there may be one or more proton donating functionalities in the molecule. It is preferred that more than one proton donating functionalities are present in the amphoteric polynitrogen compound.

In a preferred embodiment the amphoteric organic polynitrogen compound is a polymeric amphoteric organic polynitrogen-compound. This means it preferably has an average molecular weight of at least 300. A preferred amphoteric organic polynitrogen compound is an amphoteric polyamine. One particularly preferred compound of the amphoteric organic polynitrogen compounds which may be used in the composition of the present invention is commercially available under the trade name Sokalan® HP70, supplied by BASF.

In embodiments, the composition for cleaning and/or protecting acid sensitive surfaces can comprise equal or more than about 0.001 wt.% to equal or less than about 10 wt.%, preferably from equal or more than about 0.002 wt.% to equal or less than about 8 wt.%, more
preferred from equal or more than about 0.01 wt.% to equal or less than about 5 wt.% of an amphoteric organic polynitrogen compound, based on the total weight of the composition.

Those amounts refer to the amount of the active substance. In case commercially available products are employed which are diluted for example with water this has to be taken into account.

The composition for cleaning and/or protecting acid sensitive surfaces can comprise ethanol. In embodiments, the composition for cleaning and/or protecting acid sensitive surfaces can comprise equal or more than about 0.01 wt.% to equal or less than about 10 wt.%, preferably from equal or more than about 0.02 wt.% to equal or less than about 8 wt.%, more preferred from equal or more than about 0.05 wt.% to equal or less than about 5 wt.% of ethanol, based on the total weight of the composition.

**Additives**

The composition for cleaning and/or protecting acid sensitive surfaces can comprise at least one additive. The additive can be selected from the group comprising detergents, builders, defoamers, thickening agents, gelling agents, complexing agents, antimicrobial agents, clear rinsing agents, dyes, perfumes and mixtures thereof.

Builders and complexing agents help boost the cleaning performance of surfactant systems and are typically associated with materials that are capable of complexing with polyvalent cations, such as calcium and magnesium. Thickening agents such as alkyl cellulososes, alkoxy celluloses, xanthan gum, guar gum, and polyacrylamide derivatives, such as the polymer of 2-acrylamido-2-methylpropane sulfonic acid, hectorite, synthetic hectorite, magnesium aluminum silicate, bentonite, montmorillonite, and amorphous silicon dioxide can affect retention, flow and lubricity.

The composition further can comprises defoamers. Such an anti-foam component preferredly is a silicone-based anti-foam component.

Additives can be comprised in an amount in the range of equal or more than about 0.001 wt.-% to equal or less than about 5 wt.-%, preferably in the range of equal or more than about 0.01 wt.-% to equal or less than about 3 wt.-%, more preferably in the range of equal or
more than about 0.01 wt.-% to equal or less than about 2 wt.-%, even more preferably in the range of equal or more than about 0.01 wt.-% to equal or less than about 1.5 wt.-%, based on the total weight of the composition.

As already mentioned before, it should be understood that surfactants, corrosion inhibitors, sequestering agents, hydrophilizing agents and additive are optional components and can be omitted.

**Solvents**

The composition for cleaning and/or protecting acid sensitive surfaces can comprise at least one solvent. Suitable solvents include, but are not limited to, water, alcohols, glycols, glycol ethers, esters, and the like, or combinations thereof. Suitable alcohols include, but are not limited to, ethanol, isopropanol (propan-2-ol), 2-butoxy ethanol (butyl glycol), 1-decanol, benzyl alcohol, glycerin, monoethanolamine (MEA) and combinations thereof. The solvent can be selected from the group comprising water, alcohols, ethanol, isopropanol, 2-butoxy ethanol, 1-decanol, benzyl alcohol, glycerin, monoethanolamine, glycols, ethylene glycol, diethylene glycol, propylene glycol, butoxy diglycol, triethylene glycol, tetraethylene glycol, glycerin, propylene glycol, dipropylene glycol, hexylene glycol, glycol ethers, esters, or combinations thereof. Preferably, the composition comprises one or two solvents. More preferred, the composition comprises at least water. Preferably, the water is deionized.

**Composition**

According to one embodiment of the invention, the composition for cleaning and/or protecting acid sensitive surfaces can comprise:

- equal or more than about 0.001 wt.-% to equal or less than about 20 wt.-%, preferably equal or more than about 0.002 wt.-% to equal or less than about 10 wt.-%, further preferred equal or more than about 0.005 wt.-% to equal or less than about 5 wt.-%, and more preferred equal or more than about 0.01 wt.-% to equal or less than about 3 wt.-%, of at least one phosphorous acid compound;
- equal or more than about 0.01 wt.-% to equal or less than about 40 wt.-%, preferably equal or more than about 0.02 wt.-% to equal or less than about 20 wt.-%, further
preferred equal or more than about 0.05 wt.-% to equal or less than about 10 wt.-%, and
more preferred equal or more than about 0.07 wt.-% to equal or less than about 8 wt.-%,
of at least one nanoparticulate degreasing agent;
- a solvent, preferably water, added add. 100 wt.-%; wherein the weight-% of the
components are based on the total weight of the composition.

The amounts of phosphoric acid compound and nanoparticulate degreasing agent can
provide especially good cleaning and protecting effects.

A preferred optional compound is at least one surfactant. According to another
embodiment of the invention, the composition for cleaning and/or protecting acid sensitive
surfaces can comprise equal or more than about 0.001 wt.-% to equal or less than about 10
wt.-%, preferably equal or more than about 0.005 wt.-% to equal or less than about 5 wt.-%,
further preferred equal or more than about 0.01 wt.-% to equal or less than about 3 wt.-%,
and more preferred equal or more than about 0.02 wt.-% to equal or less than about 2.5 wt.-%,
of at least one surfactant, preferably a non-ionic surfactant, wherein the weight-% are based on
the total weight of the composition.

According to another embodiment of the invention, the composition for cleaning
and/or protecting acid sensitive surfaces can comprise:
- equal or more than about 0.001 wt.-% to equal or less than about 20 wt.-%, preferably
equal or more than about 0.002 wt.-% to equal or less than about 10 wt.-%, further
preferred equal or more than about 0.005 wt.-% to equal or less than about 5 wt.-%,
and more preferred equal or more than about 0.01 wt.-% to equal or less than about 3
wt.-%, of at least one phosphoric acid alkyl ester, preferably phosphoric acid methyl
isopropyl ester;
- equal or more than about 0.01 wt.-% to equal or less than about 40 wt.-%, preferably
equal or more than about 0.02 wt.-% to equal or less than about 20 wt.-%, further
preferred equal or more than about 0.05 wt.-% to equal or less than about 10 wt.-%,
and more preferred equal or more than about 0.07 wt.-% to equal or less than about 8
wt.-%, of silicon dioxide nano particles;
- equal or more than about 0.001 wt.-% to equal or less than about 10 wt.-%, preferably
  equal or more than about 0.005 wt.-% to equal or less than about 5 wt.-%, further
  preferred equal or more than about 0.01 wt.-% to equal or less than about 3 wt.-%, and
  more preferred equal or more than about 0.02 wt.-% to equal or less than about 2.5
  wt.-%, of fatty alcohol ethoxylates, preferably isotridecanol ethoxylate;

- equal or more than about 0.0001 wt.-% to equal or less than about 2 wt.-%, preferably
  equal or more than about 0.0005 wt.-% to equal or less than about 1.5 wt.-%, further
  preferred equal or more than about 0.001 wt.-% to equal or less than about 1 wt.-%, and
  more preferred equal or more than about 0.005 wt.-% to equal or less than about 1
  wt.-%, of at least one alkali metal hydroxide, preferably sodium hydroxide; and

- a solvent, preferably water, added at 100 wt.-%; wherein the weight-% of the
  components are based on the total weight of the composition.

Various optional ingredients may also be present in the composition. Preferred
optional compounds are selected of corrosion inhibitors, sequestering agents, hydrophilizing
agents and additives. In other embodiments, the composition for cleaning and/or protecting
acid sensitive surfaces can comprise:

- equal or more than about 0.001 wt.-% to equal or less than about 5 wt.-%, preferably
  equal or more than about 0.002 wt.-% to equal or less than about 3 wt.-%, further
  preferred equal or more than about 0.005 wt.-% to equal or less than about 2 wt.-%,
  and more preferred equal or more than about 0.01 wt.-% to equal or less than about 1.5
  wt.-% of at least one corrosion inhibitor; and/or

- equal or more than about 0.0001 wt.-% to equal or less than about 10 wt.-%,
  preferably equal or more than about 0.0002 wt.-% to equal or less than about 8 wt.-%,
  further preferred equal or more than about 0.005 wt.-% to equal or less than about 5
  wt.-%, and more preferred equal or more than about 0.01 wt.-% to equal or less than
  about 3 wt.-% of at least one sequestering agent; and/or

- equal or more than about 0.001 wt.-% to equal or less than about 6 wt.-%, preferably
  equal or more than about 0.002 wt.-% to equal or less than about 5 wt.-%, further
preferred equal or more than about 0.005 wt.-% to equal or less than about 3 wt.-%,
and more preferred equal or more than about 0.01 wt.-% to equal or less than about 2
wt.-% of at least one additive; wherein the weight-% of the components are based on
the total weight of the composition.

In other embodiments, the composition for cleaning and/or protecting acid sensitive
surfaces can further comprise equal or more than about 0.01 wt.% to equal or less than about
3 wt.%, preferably from equal or more than about 0.1 wt.% to equal or less than about 1.5
wt.%, more preferred from equal or more than about 0.2 wt.% to equal or less than about 0.5
wt.% of an amphoteric organic polynitrogen compound, based on the total weight of the
composition.

In further embodiments, the composition for cleaning and/or protecting acid sensitive
surfaces can further comprise equal or more than about 0.001 wt.% to equal or less than about
10 wt.%, preferably from equal or more than about 0.002 wt.% to equal or less than about 8
wt.%, more preferred from equal or more than about 0.005 wt.% to equal or less than about 5
wt.% of ethanol, based on the total weight of the composition.

**Liquid concentrate composition**

The composition for cleaning and/or protecting acid sensitive surfaces according to the
invention can be a liquid concentrate composition. The compositions according to the
invention can take the form of a single concentrate or multiple concentrates that can be diluted
and combined to provide a ready-to-use solution.

The composition can be in the form of a concentrate that can be diluted with a solvent,
such as water, to provide a ready-to-use solution that can be used for cleaning and/or
protecting acid sensitive surfaces.

It is advantageous to provide a concentrate and then to dilute the concentrate at the
situs of use in order to decrease transportation costs associated with transporting large
amounts of solvent, such as water. Specifically, a concentrate is often easier and less
expensive to ship than a use composition. Further, a low amount of water contributes to the
stabilization of the concentrate composition during storage.
The source of alkalinity and the addition of the solvent, preferably water, can be adjusted so that the liquid concentrate composition, preferably aqueous liquid concentrate composition, according to the present invention may have a pH in the range from equal or more than about 1 to equal or less than about 7, preferably in the range from equal or more than about 2 to equal or less than about 6, more preferably in the range from equal or more than about 2.5 to equal or less than about 5.

According to one embodiment of the invention, the liquid concentrate composition can comprise:

- equal or more than about 0.01 wt.-% to equal or less than about 20 wt.-%, preferably equal or more than about 0.015 wt.-% to equal or less than about 10 wt.-%, further preferred equal or more than about 0.02 wt.-% to equal or less than about 5 wt.-%, and more preferred equal or more than about 0.05 wt.-% to equal or less than about 3 wt.-%, of at least one phosphorous acid compound;

- equal or more than about 0.1 wt.-% to equal or less than about 40 wt.-%, preferably equal or more than about 0.2 wt.-% to equal or less than about 20 wt.-%, further preferred equal or more than about 0.5 wt.-% to equal or less than about 10 wt.-%, and more preferred equal or more than about 0.7 wt.-% to equal or less than about 8 wt.-%, of at least one nanoparticulate degreasing agent;

- a solvent, preferably water, added add. 100 wt.-%; wherein the weight-% of the components are based on the total weight of the composition.

According to another embodiment of the invention, the liquid concentrate composition can comprise equal or more than about 0.01 wt.-% to equal or less than about 10 wt.-%, preferably equal or more than about 0.05 wt.-% to equal or less than about 5 wt.-%, further preferred equal or more than about 0.1 wt.-% to equal or less than about 3 wt.-%, and more preferred equal or more than about 0.2 wt.-% to equal or less than about 2.5 wt.-%, of at least one surfactant, preferably a non-ionic surfactant, wherein the weight-% are based on the total weight of the composition.
According to another embodiment of the invention, the liquid concentrate composition can comprise:

- equal or more than about 0.01 wt.-% to equal or less than about 20 wt.-%, preferably equal or more than about 0.015 wt.-% to equal or less than about 10 wt.-%, further preferred equal or more than about 0.02 wt.-% to equal or less than about 5 wt.-%, and more preferred equal or more than about 0.05 wt.-% to equal or less than about 3 wt.-% of at least one phosphoric acid alkyl ester, preferably phosphoric acid methyl isopropyl ester;

- equal or more than about 0.1 wt.-% to equal or less than about 40 wt.-%, preferably equal or more than about 0.2 wt.-% to equal or less than about 20 wt.-%, further preferred equal or more than about 0.5 wt.-% to equal or less than about 10 wt.-%, and more preferred equal or more than about 0.7 wt.-% to equal or less than about 8 wt.-%, of silicon dioxide nano particles;

- equal or more than about 0.01 wt.-% to equal or less than about 10 wt.-%, preferably equal or more than about 0.05 wt.-% to equal or less than about 5 wt.-%, further preferred equal or more than about 0.1 wt.-% to equal or less than about 3 wt.-%, and more preferred equal or more than about 0.2 wt.-% to equal or less than about 2.5 wt.-%, of fatty alcohol ethoxylates, preferably isotridecanol ethoxylate;

- equal or more than about 0.001 wt.-% to equal or less than about 2 wt.-%, preferably equal or more than about 0.005 wt.-% to equal or less than about 1.5 wt.-%, further preferred equal or more than about 0.01 wt.-% to equal or less than about 1 wt.-%, and more preferred equal or more than about 0.05 wt.-% to equal or less than about 1 wt.-%, of at least one alkali metal hydroxide, preferably sodium hydroxide; and

- a solvent, preferably water, added add. 100 wt.-%; wherein the weight-% of the components are based on the total weight of the composition.

In other embodiments, the liquid concentrate composition can comprise:

- equal or more than about 0.01 wt.-% to equal or less than about 5 wt.-%, preferably equal or more than about 0.02 wt.-% to equal or less than about 3 wt.-%, further preferred equal
or more than about 0.05 wt.-% to equal or less than about 2 wt.-%, and more preferred equal or more than about 0.01 wt.-% to equal or less than about 1.5 wt.-% of at least one corrosion inhibitor; and/or

- equal or more than about 0.01 wt.-% to equal or less than about 10 wt.-%, preferably
equal or more than about 0.02 wt.-% to equal or less than about 8 wt.-%, further preferred
equal or more than about 0.05 wt.-% to equal or less than about 5 wt.-%, and more preferred equal or more than about 0.1 wt.-% to equal or less than about 3 wt.-% of at least one additive; wherein the weight-% of the components are based on the total weight of the composition.

In other embodiments, the liquid concentrate composition can comprise equal or more than about 0.001 wt.% to equal or less than about 10 wt.% of an amphoteric organic polynitrogen compound based on the total weight of the composition.

In further embodiments, the liquid concentrate composition can comprise equal or more than about 0.01 wt.% to equal or less than about 10 wt.% of ethanol, based on the total weight of the composition.

The ratio of the solvent, preferably water, to liquid concentrate composition to yield a ready-to-use solution can be in the range of from about 1 : 1 to about 1000 : 1, preferably in the range of from about 10 : 1 to about 100 : 1.
The liquid concentrate composition can be used for cleaning, removing lime and/or protecting acid sensitive surfaces, preferably carbonate-containing surfaces, more preferably marble.

**Ready-to-use Solution**

The composition for cleaning and/or protecting acid sensitive surfaces according to the invention can be a ready-to-use solution.

In addition, the composition can be provided as a relatively dilute solution that can be, without the addition of water, provided in form of an organic ready-to-use solution, for example an alcohol based ready-to-use solution, that can be applied for cleaning and/or protecting acid sensitive surfaces.

The ready-to-use solution can be obtainable by diluting the liquid concentrate composition with a solvent, preferably water, to form the ready-to-use solution. Preferably, the ready-to-use solution comprises the liquid concentrate composition in the range of equal or more than about 0.001 wt.-% to equal or less than about 2 wt.-%, preferably in the range of equal or more than about 0.0015 wt.-% to equal or less than about 1 wt.-%, more preferably in the range of equal or more than about 0.002 wt.-% to equal or less than about 0.5 wt.-%, based on the total weight of the ready-to-use solution.

If the amount of phosphorous acid compound in the ready-to-use solution of the present invention is selected too high, the composition will have a very low pH and the ready-to-use solution can be corrosive and damaging to acid sensitive surfaces like marble. However, if the amount of phosphorous acid compound is selected too low, the cleaning action is insufficient. In order to minimize the potential to damage to the acid sensitive surface and maximize the cleaning effect, the pH of the ready-to-use solution can be adjusted to be in the range from equal or more than about 3 to equal or less than about 7, preferably in the range from equal or more than about 3.5 to equal or less than about 6, more preferably in the range from equal or more than about 3.8 to equal or less than about 5, further preferred in the range from equal or more than about 4 to equal or less than about 4.5.
According to one embodiment of the invention, the ready-to-use solution can comprise:

- equal or more than about 0.001 wt.-% to equal or less than about 2 wt.-%, preferably equal or more than about 0.002 wt.-% to equal or less than about 1 wt.-%, further preferred equal or more than about 0.005 wt.-% to equal or less than about 0.5 wt.-%, and more preferred equal or more than about 0.01 wt.-% to equal or less than about 0.5 wt.-%, of at least one phosphorous acid compound;

- equal or more than about 0.01 wt.-% to equal or less than about 4 wt.-%, preferably equal or more than about 0.02 wt.-% to equal or less than about 2 wt.-%, further preferred equal or more than about 0.05 wt.-% to equal or less than about 1 wt.-%, and more preferred equal or more than about 0.07 wt.-% to equal or less than about 8 wt.-%, of at least one nanoparticulate degreasing agent;

- a solvent, preferably water, added add. 100 wt.-%; wherein the weight-% of the components are based on the total weight of the composition.

According to another embodiment of the invention, the ready-to-use solution can comprise equal or more than about 0.001 wt.-% to equal or less than about 1 wt.-%, preferably equal or more than about 0.005 wt.-% to equal or less than about 0.5 wt.-%, further preferred equal or more than about 0.01 wt.-% to equal or less than about 0.3 wt.-%, and more preferred equal or more than about 0.02 wt.-% to equal or less than about 0.25 wt.-%, of at least one surfactant, preferably a non-ionic surfactant, wherein the weight-% are based on the total weight of the composition.

According to another embodiment of the invention, the ready-to-use solution can comprise:

- equal or more than about 0.001 wt.-% to equal or less than about 2 wt.-%, preferably equal or more than about 0.002 wt.-% to equal or less than about 1 wt.-%, further preferred equal or more than about 0.005 wt.-% to equal or less than about 0.5 wt.-%, and more preferred equal or more than about 0.01 wt.-% to equal or less than about 0.5 wt.-%,
of at least one phosphoric acid alkyl ester, preferably phosphoric acid methyl isopropyl ester;
- equal or more than about 0.01 wt.-% to equal or less than about 4 wt.-%, preferably equal or more than about 0.02 wt.-% to equal or less than about 2 wt.-%, further preferred equal or more than about 0.05 wt.-% to equal or less than about 1 wt.-%, and more preferred equal or more than about 0.07 wt.-% to equal or less than about 0.8 wt.-%, of silicon dioxide nano particles; and
- equal or more than about 0.001 wt.-% to equal or less than about 1 wt.-%, preferably equal or more than about 0.005 wt.-% to equal or less than about 0.5 wt.-%, further preferred equal or more than about 0.01 wt.-% to equal or less than about 0.3 wt.-%, and more preferred equal or more than about 0.02 wt.-% to equal or less than about 0.25 wt.-%, of fatty alcohol ethoxylates, preferably isotridecanol ethoxylate;
- equal or more than about 0.0001 wt.-% to equal or less than about 2 wt.-%, preferably equal or more than about 0.0005 wt.-% to equal or less than about 1.5 wt.-%, further preferred equal or more than about 0.001 wt.-% to equal or less than about 1 wt.-%, and more preferred equal or more than about 0.005 wt.-% to equal or less than about 0.5 wt.-%, of at least one alkali metal hydroxide, preferably sodium hydroxide; and
- a solvent, preferably water, added add. 100 wt.-%; wherein the weight-% of the components are based on the total weight of the composition.

In other embodiments, the liquid concentrate composition can comprise:
- equal or more than about 0.001 wt.-% to equal or less than about 5 wt.-%, preferably equal or more than about 0.002 wt.-% to equal or less than about 3 wt.-%, further preferred equal or more than about 0.005 wt.-% to equal or less than about 2 wt.-%, and more preferred equal or more than about 0.001 wt.-% to equal or less than about 1.5 wt.-% of at least one corrosion inhibitor; and/or
- equal or more than about 0.0001 wt.-% to equal or less than about 10 wt.-%, preferably equal or more than about 0.0002 wt.-% to equal or less than about 8 wt.-%, further preferred equal or more than about 0.005 wt.-% to equal or less than about 5 wt.-%, and
more preferred equal or more than about 0.01 wt.-% to equal or less than about 3 wt.-% of
at least one sequestering agent; and/or
- equal or more than about 0.001 wt.-% to equal or less than about 6 wt.-%, preferably
equal or more than about 0.002 wt.-% to equal or less than about 5 wt.-%, further
preferred equal or more than about 0.005 wt.-% to equal or less than about 3 wt.-%, and
more preferred equal or more than about 0.01 wt.-% to equal or less than about 2 wt.-% of
at least one additive; wherein the weight-% of the components are based on the total
weight of the composition.

In other embodiments, the ready-to-use solution can comprise equal or more than
about 0.01 wt.% to equal or less than about 3 wt.%, preferably from equal or more than about
0.1 wt.% to equal or less than about 1.5 wt.%, more preferred from equal or more than about
0.2 wt.% to equal or less than about 0.5 wt.% of an amphoteric organic polynitrogen
compound based on the total weight of the composition.

In further embodiments, the ready-to-use solution can comprise equal or more than
about 0.001 wt.% to equal or less than about 5 wt.%, preferably from equal or more than
about 0.002 wt.% to equal or less than about 3 wt.%, more preferred from equal or more than
about 0.005 wt.% to equal or less than about 1 wt.% of ethanol, based on the total weight of
the composition.

The ready-to-use solution can be used for cleaning, removing lime and/or protecting
acid sensitive surfaces, preferably carbonate-containing surfaces, more preferably marble.

**Cleaning Method**

The compositions of the invention, especially the liquid concentrate composition
and/or the ready-to-use solution are suitable to treat any surface contaminated with a wide
variety of contaminants. Specifically, the compositions especially the liquid concentrate
composition and/or the ready-to-use solution are suitable to treat acid sensitive surfaces,
preferably carbonate-containing surfaces such as marble. Exemplary soilings include lime
scale or scum and water hardness soiling, soap residues, and grease for example left by
touching the surface.
A further aspect of the present invention relates to the use of the compositions especially the liquid concentrate composition and/or the ready-to-use solution according to the invention for cleaning, removing lime scale and/or protecting acid sensitive surfaces, preferably carbonate-containing surfaces, more preferably marble.

Further, the present invention provides a method of cleaning, removing lime scale and/or protecting acid sensitive surfaces, preferably carbonate-containing surfaces, more preferably marble, wherein the surface is treated with a composition especially the liquid concentrate composition and/or a ready-to-use solution according to the invention.

Advantageously, the compositions especially the liquid concentrate composition and the ready-to-use solution are employable for acid sensitive surfaces. The compositions according to the present invention can be used as a household cleaner in the bathroom or in the kitchen. Especially in bathrooms and kitchens, marble surfaces often are used for example as shelf space and quickly soil with lime scale or scum and water hardness soiling.

Advantageously, the compositions especially the liquid concentrate composition and the ready-to-use solution is particularly useful for the cleaning of such acid sensitive surfaces without apparently damaging such sensitive surface. Advantageously, the surface retains its brilliant or satin finish without changes due to the use of the liquid concentrate composition or the ready-to-use solution according to the invention.

Moreover, the compositions especially the liquid concentrate composition and the ready-to-use solution have an advantage of providing care and protection for acid sensitive surfaces. Surprisingly, it was found that a use of the compositions especially the liquid
concentrate composition and/or the ready-to-use solution provides a protecting effect that can render acid sensitive surfaces less susceptible to acids.

Preferably, the compositions especially the liquid concentrate composition or the ready-to-use solution is used daily and/or for all cleaning actions. A daily use provides strong protection benefits of acid sensitive surfaces which are particularly noticeable in marble cleaning. Especially beneficial protection can be provided if the compositions especially the liquid concentrate composition or the ready-to-use solution are used from the beginning. This may not only provide a protecting effect, but also may prevent damage to the surface.

The compositions especially the liquid concentrate composition and/or the ready-to-use solution may be applied to a surface in a variety of ways including wiping, immersing, flooding, spraying or foaming.

Preferably, the compositions especially the liquid concentrate composition and/or the ready-to-use solution can be prepared and/or applied to the surface by spraying or as a foam.

The compositions especially the liquid concentrate composition and/or the ready-to-use solution can be in any form including liquid, gel, paste and slurry. The compositions especially the liquid concentrate composition and/or the ready-to-use solution may be a liquid or may be formulated in the form of a thickened or gelled solution, or a foam. Thickened or gelled solutions and foams can provide a longer contact time.

Cleaning may preferably be carried out manually. The composition is particularly useful for manual cleaning of delicate acid sensitive surfaces, for example by wiping, spraying or foaming methods. However, cleaning of acid sensitive surfaces may also be carried out as automated application for example in washers or scrubber dryer cleaners.

Generally, cleaning may be performed by contacting the surface with the compositions for example the liquid concentrate composition and preferably the ready-to-use solution according to the present invention as described above, and then removing the cleaning composition from said surfaces.
The aqueous cleaning solutions of this invention, especially the liquid concentrate composition and/or the ready-to-use solution may be used at any temperature, preferably at ambient temperature.

All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains. The invention has been described to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

For a more complete understanding of the invention, the following examples are given to illustrate some embodiments. These examples and experiments are to be understood as illustrative and not limiting.

**Example**

The following examples were carried out to illustrate the effects of cleaning and care of the composition according to the invention.
Table 1
Compositions of the invention

<table>
<thead>
<tr>
<th>Components</th>
<th>12A</th>
<th>13A</th>
<th>14A</th>
<th>15A</th>
<th>17A</th>
<th>18A</th>
</tr>
</thead>
<tbody>
<tr>
<td>phosphoric acid methyl isopropyl ester, [wt-%]</td>
<td>0.014</td>
<td>0.014</td>
<td>0.014</td>
<td>0.014</td>
<td>0.014</td>
<td>0.028</td>
</tr>
<tr>
<td>isooctyl ethoxylate [wt-%]</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>nano-particulate silicon dioxide [wt-%]</td>
<td>0.125</td>
<td>0.125</td>
<td>0.25</td>
<td>0.25</td>
<td>0.125</td>
<td>0.125</td>
</tr>
<tr>
<td>Sokalan® HP70 [wt-%]</td>
<td>0.25</td>
<td>0.25</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ethanol [wt-%]</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>methanesulfonic acid, [wt-%]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaOH 5 % [wt-%]</td>
<td>0.094</td>
<td>0.094</td>
<td>0.09</td>
<td>0.09</td>
<td>0.1</td>
<td>0.21</td>
</tr>
<tr>
<td>water, deionized [wt-%]</td>
<td>Add. 100</td>
<td>Add. 100</td>
<td>Add. 100</td>
<td>Add. 100</td>
<td>Add. 100</td>
<td>Add. 100</td>
</tr>
<tr>
<td>pH</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 2
Compositions for comparison

<table>
<thead>
<tr>
<th>Components</th>
<th>16A</th>
<th>19A</th>
<th>25A</th>
<th>28A</th>
</tr>
</thead>
<tbody>
<tr>
<td>phosphoric acid methyl isopropyl ester, [wt.-%]</td>
<td>-</td>
<td>-</td>
<td>0.014</td>
<td>0.014</td>
</tr>
<tr>
<td>isododecanol ethoxylate [wt.-%]</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>nano-particulate silicon dioxide [wt.-%]</td>
<td>0.125</td>
<td>0.125</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sokalan® HP70 [wt.-%]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ethanol [wt.-%]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>methanesulfonic acid, [wt.-%]</td>
<td>0.007</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaOH 5 % [wt.-%]</td>
<td>0.04</td>
<td>0.103</td>
<td>0.131</td>
<td>0.04</td>
</tr>
<tr>
<td>water, deionized [wt.-%]</td>
<td>Add. 100</td>
<td>Add. 100</td>
<td>Add. 100</td>
<td>Add. 100</td>
</tr>
<tr>
<td>pH</td>
<td>3.9</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

**Lime-removal capacity**

This test method provides a basis to assess the lime-removal capacity of the composition of the invention.

**Test method**

The lime-removal capacity was tested using the marble-block method which is a standard method to assess the lime-removal capacity of cleaning compositions. According to this method marble blocks (Carrara Bianco) of 30x30x20 mm dimension were brushed under deionized water, dipped in 96 % (v/v) ethanol and dried for 24 hours in a drying chamber at 125°C. For cooling and storage the marble blocks were transferred to a desiccator.

For the examination of the lime-removing capacity the marble-block was placed in 200 ml of the compositions for 24 hours at room temperature. Room temperature, as used
herein refers to temperatures in the range of 20°C to 30°C. The lime-removing capacity is the amount of marble in milligrams that dissolves within 24 hours. After the exposure time of 24 hours the marble blocks were rinsed with deionized water and dried for 24 hours in a drying chamber at 125°C. For cooling and storage the marble blocks were transferred to a desiccator. The samples were run in triplicate.

The difference in weight of the marble block at the beginning and in the end of the dissolving procedure is equal to the lime-removing capacity.

The compositions of the invention 12A to 15A, and 17A, as shown above in Table 1 and the compositions for comparison 16A and 19A as shown above in Table 2 were tested for lime-removal capacity. An average lost the range from about 0.006 wt-% to about 0.01 wt-% was observed for all tested compositions according to the invention which is considered a good lime-removal capacity. The results for the compositions of the invention 12A, 13A, 14A, 15A, and 17A were 0.006 wt-%, 0.007 wt-%, 0.01 wt-%, 0.01 wt-%, and 0.007 wt-%, respectively. For the compositions for comparison 16A and 19A an average lost the range from about 0.005 wt-%> and about 0.003 wt-%>, respectively, was observed which is considered an insufficient lime-removal capacity.

**Wiping test**

This test method provides a basis to assess the changes of gloss resulting from the use of the composition of the invention on marble.

**Test method**

White limestone plates (Carrara Bianco) were provided. Each plate was wiped half-page with a polifix® microclin wiping cloth (Ecolab Inc.).

The wiping microfiber cloths were submerged into the test solution, removed from the test solution and allowed to drain. The cloths were compressed for 5 seconds manually. The limestone plates were wiped 30 times with those damp clothes containing the cleaning solution. In between each wiping lay enough time so that the limestone surface was
completely dry. After every fifth wiping the gloss of the dry plates was measured with a Byk Gardner Micro Tri-gloss device. For control, treatment with damp clothes with tap water under identical conditions was used. The samples were run in duplicate.

The compositions of the invention 12A to 15A, 17A, and 18A as shown above in Table 1 and the composition for comparison 16A as shown above in Table 2 were tested. The gloss of the untreated plates was set to zero. The test results after 30 wiping cycles are shown in Table 3 below.

<table>
<thead>
<tr>
<th>Example</th>
<th>change in gloss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12A</td>
<td>1.25</td>
</tr>
<tr>
<td>13A</td>
<td>1</td>
</tr>
<tr>
<td>14A</td>
<td>0.3</td>
</tr>
<tr>
<td>15A</td>
<td>-2.1</td>
</tr>
<tr>
<td>17A</td>
<td>0.35</td>
</tr>
<tr>
<td>18A</td>
<td>1.2</td>
</tr>
<tr>
<td>16A</td>
<td>5.25</td>
</tr>
<tr>
<td>water</td>
<td>0.45</td>
</tr>
</tbody>
</table>

As can be seen from the results in Table 3, the change in gloss of the compositions prepared according to the invention performed much better than composition 16A that contained methanesulfonic acid instead of phosphoric acid methyl isopropyl ester. Preferably as little gloss change as possible is observed, as was case for compositions 14A and 17A. Especially, compositions 14A and 17A caused changes in gloss that were comparable to the treatment with tap water.

**Drop test**
The formulation according to Example 17A as provided in Table 1 was compared against commercially available cleaners for marble in regard of the damage to marble and limestone.

Test method

Polished limestone plates "Crema Marfil" purchased from Dartmann & Gaiatto GmbH, Dusseldorf, Germany, and marble plates "Carrara Bianco" of 30x30x20 mm dimension were provided. The plates were cleaned with deionized water to remove soils.

Microfiber cloths (polifix® microcline, Ecolab Inc) of 4 cm² were soaked with the compositions and positioned for 48 hours at room temperature on the plates. Every 1.5 hours, except for the night times, 1 ml of the compositions was poured evenly distributed onto the cloths to prevent that the cloths dried and that the surface was wet during the 48 hours of testing. After 48 hours of exposure to the microfiber cloths soaked with the compositions the damage to the limestone and marble plates was visually assessed.

The samples were run in triplicate. The compositions of the invention 17A as shown above in Table 1 was used and compared against the commercially available neutral sanitary cleaners Lavidol, Dr. Schnell Chemie GmbH, Germany in 1:5 dilution and SP40 Drizzle red 7, Buzil-Werk Wagner GmbH & Co. KG, Germany used without dilution which are recommended for usage on marble.

The compositions of the invention 17A performed well against the comparative examples and showed barely visible changes to the surface while Lavidol caused a raw and matted surface and the pH neutral SP40 Drizzle red 7 caused a raw, matt, and slightly white surface.

Cleaning capacity

To test the cleaning capacity of the composition of the invention black tiles were soiled with a mixture of soap and water and cleaned with different compositions.

Test method
Lime soap was simulated by preparing a mixture of soap and hard water. For this purpose, 100 g of a Original Hollanderin buttermilk soap (Ecolab Inc.) was mixed under heating and stirring with portions of altogether 550 ml water of a hardness of 64 dH (dH = German water hardness). The dissolved mixture of soap in 550 ml water was cooled overnight to room temperature.

A tiled wall with polished and matted black tiles (Vitra, Eczacibasi, Turkey) of 15 cm x 15 cm were coated with the lime soap soiling paste using Microfiber cloths (Phazer application mop, Ecolab Inc., cut into (10 x 5)cm² pieces) of about 50 cm². Lime soap soiling paste was applied with a self-made manual application device apparatus of stainless steel plane plate of (10 x 5)cm² to which a Velcro tape was plastered, with a 25 cm handle welded to the back of the plate in 45° angle. The weight of the application device was ca. 425 g. The lime soap soiling paste was applied with vertical strokes 4 times in each direction. The paste was allowed to dry for two hours.

For the evaluation of the cleaning capacity the following test was undertaken for the composition of the invention 17A as provided in Table 1 and compared to the formulation 16A as shown above in Table 2.

Tiles were sprayed with one or three strokes, respectively, each of 1.1 ml of the compositions from a spray bottle (Oasis Pro Refill bottle, Ecolab Inc.) and the effect of the composition to the lime soap was evaluated visually. Each composition was tested on 4 tiles.

It could be observed that the composition of the invention 17A visibly dissolved the lime soap after one stroke while the formulation 16A dissolved the lime soap after three strokes. This shows that the compositions of the invention 17A performed better than the comparative example 16A.

In summary, the above evaluations show that the cleaning compositions according to the invention have a good lime-removing capacity and good cleaning properties and cause much less damage to marble surface compared to cleaning compositions of the state of the art.
What is claimed is:

1. A composition for cleaning and/or protecting acid sensitive surfaces, comprising at least one phosphorous acid compound and a nanoparticulate degreasing agent, wherein the composition has a pH in the range from equal or more than about 1 to equal or less than about 7.

2. The composition according to claim 1, wherein the phosphorous acid compound is selected from the group of phosphoric acid, phosphonic acid, polyphosphoric acid

\[ \text{HO(P0}_\text{2} \text{OH)}_x \text{H} \text{ wherein } x \text{ is in the range from 2 to 9, phosphoric acid ester, phosphonic acid ester, polyphosphoric acid ester } \text{HO(P0}_\text{2} \text{OR)}_x \text{H} \text{ wherein } x \text{ is in the range from 2 to 9 and } R \text{ is a straight-chain or branched C1-C18 alkyl group, and mixtures thereof.} \]

3. The composition according to claims 1 or 2, wherein:

- the phosphoric acid ester is selected from the group of phosphoric acid mono and dialkyl esters, wherein the alkyl group is a straight-chain or branched C1-C18 group, preferably the phosphoric acid mono and dialkyl ester is selected from the group of phosphoric acid mono and di- methyl ester, ethyl ester, propyl ester, isopropyl ester, butyl ester, isobutyl ester, pentyl ester, isopentyl ester, hexyl ester, decyl ester, dodecyl ester, hexadecyl ester, octadecyl ester, and mixtures thereof, further preferred selected from the group of phosphoric acid dimethyl ester, phosphoric acid diisopropyl ester and phosphoric acid methyl isopropyl ester; and/or

- the phosphonic acid ester is selected from the group of phosphonic acid alkyl esters, wherein the alkyl group is a straight-chain or branched C1-C18 group, preferably selected from the group of phosphonic acid methyl ester, ethyl ester, propyl ester, isopropyl ester, butyl ester, isobutyl ester, pentyl ester, isopentyl ester, hexyl ester, decyl ester, dodecyl ester, hexadecyl ester, octadecyl ester, and mixtures thereof,
further preferred selected from the group of phosphonic acid methyl ester and phosphonic acid isopropyl ester; and/or
- the polyphosphoric acid is selected from \( \text{HO(P}_2\text{O})_x\text{H} \) wherein \( x \) is in the range from 2 to 9, further preferred selected from the group of diphosphoric acid and triphosphoric acid; and/or
- the polyphosphoric acid ester is selected from the group of polyphosphoric acid esters \( \text{HO(P}_2\text{O}_2\text{OR})_x\text{H} \) wherein \( x \) is in the range from 2 to 9 and \( R \) is a straight-chain or branched C1-C18 alkyl group.

4. The composition according to claims 1 to 3, wherein the nanoparticulate degreasing agent is selected from the group of metal oxides, carbonates, hydroxides, and inorganic silicon compounds preferably selected from the group comprising silicon dioxide, preferably amorphous silicon dioxide, silicates, alumosilicates, silica sols, fumed silica, organosilicon, and mixtures thereof.

5. The composition according to claims 1 to 4, wherein the nano particles have an average particle size of equal or more than about 1 to equal or less than about 50 nm, preferably of equal or more than about 2 to equal or less than about 40 nm and more preferred of equal or more than about 4 to equal or less than about 20 nm.

6. The composition according to claims 1 to 5, wherein the composition comprises a pH in the range from equal or more than about 2 to equal or less than about 6, preferably in the range from equal or more than about 2.5 to equal or less than about 5.

7. The composition according to claims 1 to 6, wherein the composition comprises at least one alkaline source selected from the group of sodium hydroxide, sodium carbonate, potassium hydroxide, and lithium hydroxide.
8. The composition according to claims 1 to 7, wherein the composition comprises at least one surfactant, preferably at least one non-ionic surfactant, further preferred the non-ionic surfactant is selected from the group of fatty alcohol ethoxylates, and alkylpolyglycosides, wherein the fatty alcohol ethoxylates preferably is selected from the group of isotridecanol ethoxylate, tridecanol ethoxylate, isodecanol ethoxylate, decanol ethoxylate, dodecanol ethoxylate, hexadecanol ethoxylate, octadecenyl ethoxylate, octadecanol ethoxylate, tetradecanol ethoxylate, undecanol ethoxylate, and mixtures of fatty alcohol ethoxylates selected from the group of coco oil alcohol ethoxylate, and tallow alcohol ethoxylate.

9. The composition according to claims 1 to 8, wherein the composition comprises at least one solvent selected from the group comprising water, alcohols, ethanol, isopropanol, 2-butoxy ethanol, 1-decanol, benzyl alcohol, glycerin, monoethanolamine, glycols, ethylene glycol, diethylene glycol, propylene glycol, butoxy diglycol, triethylene glycol, tetraethylene glycol, glycerin, propylene glycol, dipropylene glycol, hexylene glycol, glycol ethers, esters, or combinations thereof.

10. The composition according to claims 1 to 9, comprising:
    - equal or more than about 0.001 wt.-% to equal or less than about 20 wt.-%, preferably equal or more than about 0.002 wt.-% to equal or less than about 10 wt.-%, further preferred equal or more than about 0.005 wt.-% to equal or less than about 5 wt.-%, and more preferred equal or more than about 0.01 wt.-% to equal or less than about 3 wt.-%, of at least one phosphorous acid compound, preferably of at least one phosphoric acid alkyl ester, preferably of phosphoric acid methyl isopropyl ester;
    - equal or more than about 0.01 wt.-% to equal or less than about 40 wt.-%, preferably equal or more than about 0.02 wt.-% to equal or less than about 20 wt.-%, further preferred equal or more than about 0.05 wt.-% to equal or less than about 10 wt.-%, and more preferred equal or more than about 0.07 wt.-% to equal or less than about 8
wt.-%, of at least one nanoparticulate degreasing agent, preferably of silicon dioxide nanoparticles; and
- a solvent, preferably water, added add. 100 wt.-%; wherein the weight-% of the components are based on the total weight of the composition.

11. The composition according to claims 1 to 10, wherein the composition is a liquid concentrate composition or a ready-to-use solution.

12. The composition according to claim 11, wherein the ready-to-use solution is obtainable by diluting the liquid concentrate composition with a solvent to form the ready-to-use solution, preferably the ready-to-use solution comprising the liquid concentrate composition in the range of equal or more than about 0.001 wt.-% to equal or less than about 2 wt.-%, preferably in the range of equal or more than about 0.0015 wt.-% to equal or less than about 1 wt.-%, more preferably in the range of equal or more than about 0.002 wt.-% to equal or less than about 0.5 wt.-%, based on the total weight of the ready-to-use solution.

13. Use of the composition according to claims 1 to 12, preferably the liquid concentrate composition and/or the ready-to-use solution of claims 11 or 12, for cleaning, removing lime scale and/or protecting acid sensitive surfaces, preferably carbonate-containing surfaces, more preferably marble.

14. Use of a composition for cleaning and/or protecting acid sensitive surfaces, comprising at least one phosphorous acid compound and a nanoparticulate degreasing agent, wherein the composition has a pH in the range from equal or more than about 3 to equal or less than about 7 when diluted in an aqueous solution in ready-to-use form, for cleaning, removing lime scale and/or protecting acid sensitive surfaces, preferably carbonate-containing surfaces, more preferably marble.
15. A method of cleaning, removing lime scale and/or protecting acid sensitive surfaces, preferably carbonate-containing surfaces, more preferably marble, wherein the surface is treated with a composition according to claims 1 to 12, preferably a liquid concentrate composition and/or a ready-to-use solution of claims 11 or 12.
**INTERNATIONAL SEARCH REPORT**

**International application No**

PCT/EP2011/061340

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According to International Patent Classification (IPC) or to both national classification and IPC

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal , WPI Data

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Name and mailing address of the ISA/

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Bertran Nadal, Josep

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<td>wo 02/061028 Al (S C JOHNSON COMM MARKETS INC [US]) 8 August 2002 (2002-08-08) page 1, line 27 - page 2, line 20 page 10, lines 7-9</td>
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<td>US 1 574 406 A (NELSON GUSTAF A [US]) 23 February 1926 (1926-02-23) page 1, lines 40-45; claim 2</td>
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<td>wo 2005/017083 Al (HENKEL KGAA [DE]) 24 February 2005 (2005-02-24) page 3, paragraph 3-6 page 16, paragraph 3 page 19, last paragraph - page 20, paragraph 1 examples</td>
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