(54) Title: SILANE/SILOXANE EMULSIONS FOR MASONRY SURFACES

(57) Abstract

An aqueous silane/siloxane emulsion comprising (a) 4 % to 50 % by weight of an alkylalkoxy silane of the formula R<sub>n</sub>-Si-R<sup>1</sup><sub>(4-a)</sub> wherein, R is a hydrocarbyl group containing from 1 to 20 carbon atoms; R<sup>1</sup> is an alkoxy group containing from 1 to 6 carbon atoms; and n is 1 or 2; (b) 15 % to 95 % by weight of water; (c) 0 % to 5 % by weight of an emulsifier which is an amine soap; and (d) 1 % to 30 % by weight of a siloxane which is either a polyalkylsiloxane produced from a monomer of the general formula R-Si-(OIR)<sub>2</sub> where R is defined above and R<sup>2</sup> is a hydrocarbyl group having 1 or 2 carbon atoms; or a silicon fluid of the formula (R<sup>2</sup>ySiO<sub>x+2y</sub>) where R<sup>2</sup> is a hydrocarbyl group containing from 1 to 6 carbons atoms, x is 1 or 2 and y is 2 or more; with provisos that: when the siloxane is a polyalkylsiloxane and no emulsifier is present, a polymerisation catalyst which is a mixture of a benzenesulfonic acid and an alkali metal salt of a benzenesulfonic acid is employed to produce the polyalkylsiloxane; and when the siloxane is a silicone fluid at least 0.5 % by weight of emulsifier is present in the emulsion. A process for rendering permeable masonry water repellent by applying the emulsion to its surface and curing the composition.
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Code</th>
<th>Name</th>
<th>Code</th>
<th>Name</th>
<th>Code</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>GB</td>
<td>United Kingdom</td>
<td>MR</td>
<td>Mauritania</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GE</td>
<td>Georgia</td>
<td>MW</td>
<td>Malawi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GN</td>
<td>Guinea</td>
<td>NE</td>
<td>Niger</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GR</td>
<td>Greece</td>
<td>NL</td>
<td>Netherlands</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>HU</td>
<td>Hungary</td>
<td>NO</td>
<td>Norway</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IE</td>
<td>Ireland</td>
<td>NZ</td>
<td>New Zealand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>IT</td>
<td>Italy</td>
<td>PL</td>
<td>Poland</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>JP</td>
<td>Japan</td>
<td>PT</td>
<td>Portugal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>KE</td>
<td>Kenya</td>
<td>RO</td>
<td>Romania</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>RU</td>
<td>Russian Federation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KP</td>
<td>Democratic People’s Republic</td>
<td>SD</td>
<td>Sudan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>SE</td>
<td>Sweden</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>SI</td>
<td>Slovenia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI</td>
<td>Côte d’Ivoire</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SK</td>
<td>Slovakia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CM</td>
<td>Cameroun</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>SN</td>
<td>Senegal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LU</td>
<td>Luxembourg</td>
<td>TD</td>
<td>Chad</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LV</td>
<td>Latvia</td>
<td>TG</td>
<td>Togo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>MC</td>
<td>Monaco</td>
<td>TJ</td>
<td>Tajikistan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MG</td>
<td>Madagascar</td>
<td>UA</td>
<td>Ukraine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>ML</td>
<td>Mali</td>
<td>US</td>
<td>United States of America</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>MN</td>
<td>Mongolia</td>
<td>UZ</td>
<td>Uzbekistan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td></td>
<td></td>
<td>VN</td>
<td>Viet Nam</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SILANE/SILOXANE EMULSIONS FOR MASONRY SURFACES

The present invention relates to the treatment of materials to impart water repellency thereto. More particularly this invention relates to water repellent compositions containing aqueous emulsions of silanes, siloxanes and silane/siloxanes for use on materials used in building to make them water repellant.

There are two distinct means of making building materials water repellant. Hydrophobic additives may be added to the building materials before they are formed, or the building material may be impregnated or coated after they are formed. The present invention relates to a method of treating the building material after it has been formed, whereby to make it water repellent.

Organosilicone products dissolved in organic solvents have been used for rendering masonry and other substrates water repellent for many years. The products in use are silanes, siloxanes or mixtures of silanes and siloxanes. These have been used in varying concentrations with or without catalysts. Although very expensive, pure silanes without the use of solvent carrier have been used. In general, with the correct choice of active material, these products have been technically successful in terms of good penetration depth, low water absorption of the treated substrate and alkali stability of the final polymer.

Alkylalkoxysilanes have been used widely to impregnate permeable mineral building materials to render them water repellent. The action of alkylalkoxysilanes in rendering a surface hydrophobic is known to be based on the fact that when an alkylalkoxysilane is applied onto the surface, the atmospheric moisture, and in some cases the water that is on the surface, causes the silane to be hydrolysed and alkyl silanols are formed as intermediates. The hydroxyl groups of the silanol react with the hydroxyl groups of the material, and with other hydroxyl groups of silanols forming siloxanes. A bond between alkyl siloxanes and the mineral boundary surface is produced in which the alkyl group of
the siloxane is exposed on the surface. This boundary surface bond greatly increases the surface tension of the mineral materials with respect to water, and the surface becomes water repellent. The degree of water repellency on the surface of the substrate depends on the nature of the alkyl group of the alkylalkoxysilane. The bond between the alkyl group and the silicon atom of the silane can be destroyed by light and ultraviolet rays. For long term hydrophobicity, the silane should penetrate deep into the surface to be protected from the destructive action of light and ultraviolet rays.

Solutions of silanes in various solvents such as alcohols, or hydrocarbons, have been employed for treating masonry surfaces for many years. However, the solvents used to carry the active material to the substrate are generally flammable and have become increasingly expensive. In addition, the odour, environmental effects and the physiological effects of organic solvents are important factors against the use of organic solvent-based products. In various countries there is now legislation in place limiting the use of organic solvents. Therefore, there is an increasing demand for water repellent materials which may be delivered to the substrate in water and where the penetration into the substrate and performance of the treated substrate is similar to that achieved with organic solvent-based materials.

Water-based materials in the form of the alkali metal organosilicones have been used for many years. These solutions are highly alkaline and are therefore difficult to handle and are corrosive. In addition, the alkali metal methylsiliconates are not suitable for the treatment of alkaline substrates containing free lime and having a pH of 8 or more.

Various aqueous emulsion-type and solution-type silane compositions have been developed in an attempt to overcome the
problems of organic solvent-based products and the alkalinity of organosiliconates.

U.S Patent No. 3,294,725 to Findlay et al. disclosed a method of preparing stable organopolysiloxane latex emulsions by polymerising siloxanes and silcarbanes, using a surface active sulfonic acid catalyst. The emulsions produced by this method are very stable and have very fine particle sizes.

U.S. Patent 4,175,159 to Raleigh discloses a silicone emulsion for treating silicate particulate matter such as perlite and vermiculite. This emulsion of a silicone polymer is produced with an emulsifier of the ammonium salt of a long chain aliphatic carboxylic acid. Following treatment of the silicate particulate matter, the silicate particles are heated and the silicone fluid forms a coating on the silicate surface and the ammonia evaporates to leave the oily aliphatic carboxylic acid on the surface.

U.S Patent No. 4,648,904 to De Pasquale et al. discloses an aqueous silane emulsion as a masonry water repellent which comprises an alkoxyssilane, an emulsifier and water. The emulsions prepared in this manner show acceptable penetration depths and acceptable water absorption values. However, the surface does not exhibit a good beading effect, possibly due to the adsorbed non-ionic surfactant at the surface undergoing rewetting on exposure to water. This effect causes a wetting of the very surface of the substrate and therefore would not be acceptable in freezing climatic conditions. In addition pollutive, substances could be carried into the substrate in this wetted layer. These silane emulsions could be buffered at pH 6-8 by the use of a buffering agent as disclosed in U.S. Patent No. 4,877,654 to Wilson. The buffering agent enables the addition of a biocide to the emulsion without a change in the pH of the emulsion. U.S. Patent No. 4,889,747 to Wilson describes the use of these buffered aqueous silane emulsions to treat expanded perlite compositions.
In U.S. Patent No. 4,937,104 to Pühringer, an emulsion of a silane including a deactivatable surfactant is prepared and applied to masonry. Following application of the emulsion, the surfactant is deactivated with water containing an alkaline or acid substance. The drawbacks of the one treatment silane emulsions such as the wetting effect of the residual surfactant left on the surface of the substrate is discussed in U.S. Patent No. 5,037,873 to Heaton. This patent discloses the addition of a neutralised copolymer of an acrylic acid and a long chain alkylmethacrylate as a water thickening agent to ease emulsion formation and to increase emulsion stability. The properties of the copolymer are claimed to enable the inclusion of water beading additives as solid particulates to give the effect of visual water repellency to partially overcome the wetting effect of the non-ionic surfactants. According to this patent, the aqueous silane emulsions containing a copolymer of acrylic acid and a long chain alkylmethacrylate are stable under conditions of widely fluctuating temperatures such as freeze/thaw cycles and elevated temperatures.

An emulsion of a polysiloxanediol, an aminosilane, a higher alkysilane and a mixture of non-ionic surfactants is disclosed in E.P. 0 476 452 A2 to Seyffert et al. U.S. Patent No. 5,091,002 to Schamberg et al. discloses a composition which comprises an emulsion of an alkylalkoxysilane, an emulsion of a polysiloxane, a non-ionic or anionic surfactant and a filler.

However, the performance of these compositions and emulsions in a comparison with solvent-based product is not as good in terms of stability, penetration depth, and the beading effect of the treated substrate. Therefore, it is continually desirable to provide alternative aqueous water repellent silane emulsions which are stable, capable of effectively impregnating alkaline substrates and achieving a good water repellent effect.
In accordance with the invention there is provided an aqueous silane/siloxane emulsion comprising

(a) 4% to 50% by weight of an alkylalkoxysilane of the formula R\textsubscript{n}Si-R\textsubscript{1(4-n)} wherein,

R is a hydrocarbyl group containing from 1 to 20 carbon atoms;
R\textsubscript{1} is an alkoxy group containing from 1 to 6 carbon atoms; and
n is 1 or 2

(b) 15% to 95% by weight of water;
(c) 0% to 5% by weight of an emulsifier which is an amine soap; and
(d) 1% to 30% by weight of a siloxane which is either a polyalkylsiloxane produced from a monomer of the general formula R-Si-(OR\textsubscript{2})\textsubscript{3} where R is as defined above and R\textsubscript{2} is a hydrocarbyl group having 1 or 2 carbon atoms; or a silicone fluid of the formula \((R^3\text{SiO}_{\frac{4-x}{2}})_y\)

where R\textsuperscript{3} is a hydrocarbyl group containing from 1 to 6 carbon atoms, x is 1 or 2 and y is 2 or more; with the provisos that;

when the siloxane is a polyalkylsiloxane and no emulsifier is present, a polymerisation catalyst which is a mixture of a benzenesulfonic acid and an alkali metal salt of a benzenesulfonic acid is employed to produce the polyalkylsiloxane; and
when the siloxane is a silicone fluid at least 0.5% by weight of emulsifier is present in the emulsion.

The present invention also provides a process for rendering permeable masonry water repellent by applying to the surface of the permeable substrate a composition containing the emulsion as
above defined and allowing the composition to cure. The invention also extends to such treated products.

When used herein, the term "masonry" means any permeable inorganic substrate that consists of or contains constituents capable of reacting with silanes. Masonry materials containing hydroxy groups or metal oxides can react with silanes so that a siloxane film can be formed in the surface capillaries. The building materials best fulfilling these requirements are concrete, light clinker and light ballast concrete, lightweight concrete, mortars, plaster of Paris and products prepared from gypsum, fiber cement, materials and products prepared from fired or sintered clay, ballast and fibre containing silica or glass.

Generally, the emulsions prepared by the method of this invention are useful for rendering any permeable substrates that possess latent alkalinity or latent catalytic activity, water repellent. It is believed that the latent alkalinity of such substrates promotes the hydrolysis and condensation of the alkylalkoxysilane into a resinous silicone matrix which is permanently formed and deposited within the interior capillaries of the substrates. The masonry to be treated with the water repellent compositions in this invention is preferably dry, although it may be somewhat wet.

The emulsions prepared by the method of this invention are stable for a long period of time. These emulsions are effectively neutral and maintain high effective levels of original active ingredients content, on long term storage.

One of the advantages of using a silicone fluid in this invention is that it can function as a co-surfactant due to its surface activity property.

The use of a silicone fluid or a polyalkylsiloxane prepared as in this invention also makes the determination of the optimum HLB value at which alkylalkoxysilanes can be emulsified unnecessary.
A silicone fluid or a polyalkylsiloxane also improve the beading effect of the emulsions prepared by this invention.

It has been found that the penetration depth of the emulsions prepared by the method of this invention is comparable to that obtained from the solvent-based products.

Another advantage of the emulsions prepared by this invention is that as the emulsions contain no solvent they can be considered as environmentally friendly products which comply with the volatile organic content regulations.

The alkylalkoxysilanes useful in the method of this invention generally have a molecular weight in excess of 135 and preferably greater than 190 up to about 600 for the monomers. It should be noted that mixtures of various silanes may be used, if desired.

The hydrocarbyl group R may be aliphatic, or cycloaliphatic, or aralkyl, or aryl. These hydrocarbyl radicals may also contain one or more halogen substituents, and/or nitrogen, oxygen or sulfur hetero atoms. R is preferably propyl, butyl, pentyl, hexyl, octyl, nonyl or decyl. To obtain good alkali stability of the final treated substrate, R will contain more than three carbon atoms. R\(^1\) is preferably a methoxy or ethoxy group.

Alkylalkoxysilanes that are useful in accordance with the present invention include, but are not limited to:

- methyltrimethoxysilane;
- isobutyltriethoxysilane;
- octyltriisopropoxysilane; methyltrithioxysilane;

- n-hexyltrimethoxysilane; 2-ethylhexyltrimethoxysilane; methyltri-n-propoxysilane; 6-chlorohexyltrimethoxysilane;
- ethyltrimethoxysilane; 4-chlorobenzyltrimethoxysilane;
- ethyltriethoxysilane; 6,6,6-trifluorohexyltrimethoxysilane;

- dimethyldimethoxysilane; dimethyldiethoxysilane;
- cyclohexyltrimethoxysilane; decyltrimethoxysilane; ethyltri-n-propoxysilane; 4-bromobenzyltri-n-propoxysilane;
- dodecyltrimethoxysilane; propyltrithoxysilane;
dodecyltribromosilane; propyltri-n-propoxysilane;
phenyltrimethoxysilane; tetradecyltriethoxysilane;
butyltrimethoxysilane; phenyltriethoxysilane;
hexadecyltriethoxysilane; isobutyltrimethoxysilane;
octyltrimethoxysilane; octadecyltriethoxysilane; di-
isobutyldimethoxysilane; octyltriethoxysilane;
eicosyltrimethoxysilane
and the like, mixtures of any of them alone, and in admixture with
dimers, trimers and other oligomers thereof.

The emulsions prepared by the method of this invention
consist of four to about fifty percent by weight of the
alkylalkoxysilane or mixtures of silanes, and preferably the
emulsions include twenty to fifty percent by weight of the
alkylalkoxysilane or mixtures thereof.

The polyalkylsiloxane which may be used in the present
invention is the polymerisation product of an alkylalkoxysilane of
the general formula: R-Si-(OR²)₃, wherein R is a hydrocarbyl group
containing from 1 to 20 carbon atoms and R² is a hydrocarbyl
group containing 1 or 2 carbon atoms.

Alkylalkoxysilanes of formula R-Si-(OR²)₃ especially useful in
producing polyalkylsiloxanes in accordance with the present
invention are:
propyltrimethoxysilane; butyltriethoxysilane; butyltrimethoxysilane;
tert-butyltrimethoxysilane; propyltriethoxysilane;
isobutyltrimethoxysilane; tert-butyltriethoxysilane;
isopropyltrimethoxysilane; isobutyltriethoxysilane;
octyltriethoxysilane; isopropyltriethoxysilane;
secbutyltrimethoxysilane; butyltrimethoxysilane;
secbutyltriethoxysilane.

The polymerisation catalyst for the polyalkylsiloxanes is a
single compound or a mixture of two or more compounds.
Suitable catalysts in the present invention are the aliphatically
substituted benzenesulfonic acids, the aliphatically substituted
naphthalenesulfonic acids, the aliphatic sulfonic acids, aliphatically
substituted diphenylethersulfonic acids and silylalkylsulfonic acids.
The preferred catalysts are the aliphatically substituted
benzenesulfonic acids of the formula:

\[ R^4C_6H_4SO_3H \]

wherein \( R^4 \) is a monovalent aliphatic hydrocarbon substituent of at
least 6 carbon atoms. Suitable aliphatic hydrocarbon substituents
include hexyl, octyl, decyl, dodecyl, cetyl, myristyl, nonenyl,
phytanyl and pentadecadienyl. Preferably the \( R^4 \) radical contains at
least 8 inclusive carbon atoms, and most preferably at least 10.
The \( R^4 \) radical can be straight or branched chain. The \( R^4 \)
substituents are also illustrative of the substituents that can be
present in the other sulfonic acids useful herein. A mixture of
catalysts are generally employed, since these high molecular
weight acids are difficult to purify to a single species, and also
because mixtures function quite as well as single compounds.

The catalyst in this invention can be formed in situ from a
salt, such as the sodium salt of the aliphatic substituted
benzenesulfonic acid and an acid if so desired. The concentration
of catalyst can vary from 0.01 part by weight to a large amount.
However, the use of large amounts of catalyst can lead to a very
acidic polymerised product and the need to remove the catalyst in
order to obtain a very stable final silane/siloxane emulsion.

Polymerisation of the alkylalkoxysilane in this invention
proceeds satisfactorily at room temperature but can be carried out
at any desired temperature. The preferred temperature range is

20° to 95°C. The polymerised product is formed during a reaction
time of between 3 hours to 72 hours.
It should be noted that during the polymerisation process, alcohol will be produced and it may have an effect on the quality of the polymeric product as well as the stability of the emulsions. Therefore, it is preferable to remove any trace of alcohol formed in the polymerisation process. The solution of the polymerised product prepared by the method of this invention is acidic, having pH of about 2 to 4. For maximum stability of the emulsions, the neutralisation of the acid catalyst with a base in the solution of the stabiliser may be carried out.

Suitable silicone fluids useful in this invention include, but are not limited to, polydimethylsiloxanes which may be terminated as follows; silanol terminated; trimethylsiloxy terminated; acetoxy terminated; methylidiacetoxy terminated; methoxy terminated; ethoxy terminated; dimethylamine terminated; vinylidimethyl terminated; chlorine terminated; vinylphenylmethyl terminated; divinylmethyl terminated; monovinylidimethyl terminated; monotrimethylsilyl terminated; aminobutyldimethyl terminated; carboxypropylidimethyl terminated; carbinol terminated; or methacryloxypropyl terminated. A blend of polydimethylsiloxanes may also be used. The preferred silicone fluids are polydimethylsiloxanes with trimethylsiloxy termination, which have molecular weights ranging from 100 up to 400,000.

The emulsions prepared by the method of this invention include one to about thirty percent by weight of polyalkylsiloxane or silicone fluid, preferably two to twenty percent by weight.

The emulsifier is preferably an amine soap of an aliphatic carboxylic acid containing at least one olefinic double bond with a base.

Examples of carboxylic acids that may be utilised as an emulsifying agent in this invention are as follows:

Elaidic Acid  Erucic Acid  Isobutyric Acid
Azelaic Acid  Ricinoleic Acid  Valeric Acid
Pelargonic Acid  Aupanodonic Acid  Caproic Acid
Sebacic Acid  Behenolic Acid  Enanthic Acid
Caprylic Acid  Melissic Acid  Lactic Acid
Stearic Acid  Arotic Acid  Behenic Acid
Stearolic Acid  Gaidic Acid  Agaric Acid
5 Capric Acid  Aleurtic Acid  Brassic Acid
Undecanoic Acid  Muconic Acid  Margaric Acid
Lauric Acid  Myristic Acid  Enanthisia Acid
Oleic Acid  Linoleic Acid

However, other carboxylic acids may be utilised. It is most desirable for the carboxylic acid, whether it be aliphatic or aromatic, to provide an hydrophobic effect on the surface of the substrate.

Bases such as ammonium hydroxide, morpholine,
ethylamine, diethylamine, triethylamine, ethylenediamine,
butylamine, hexylamine, triethanolamine, diethylethanolamine, and alkylidimethylamine can be used to make the amine soap for emulsifying the emulsions in this invention. The preferred bases are ammonium hydroxide, morpholine and alkylidimethylamine. The emulsifier in this invention can be formed in situ from a salt of a fatty acid and an amine during the emulsifying process if so desired. The advantage of using an amine soap as an emulsifier in this invention is that this kind of emulsifier will be deactivated and cause no wetting effect when the emulsion is applied onto masonry surfaces.

The emulsions of this invention consist of up to about five percent by weight of the emulsifier, and preferably the emulsions include one half to three percent by weight of the emulsifier.

The emulsions of the present invention have a long shelf life and can be diluted to any appropriate concentration without changing their stability.
The following examples are set forth for the purpose of illustrating preferred aspects of the present invention. These examples are illustrative only and they are not to be constructed to limit the invention in any manner whatsoever.

The compositions prepared in the following examples represent the most preferred embodiments of the compositions of this invention. The final water repellent compositions can be prepared by diluting the concentrates prepared in the Examples with water to the appropriate concentration.

All parts and percentages described in the following examples are by weight, unless otherwise noted.

**EXAMPLE I**

40g of isobutyltrimethoxysilane, 0.5g of dodecylbenzenesulfonic acid, 5.5g of the sodium salt of dodecylbenzenesulfonic acid and 54g of water were placed in a 3 neck reactor and heated to 60°C with vigorous stirring. The system was held at that temperature with stirring for 24 hours. The system became a milky emulsion within 2 hours. During the polymerisation process alcohol was produced and recovered. The polymerisation was completed within 24 hours, and a polymeric product with fine particle sizes was obtained. The product was found to contain less than 1% of unpolymerised silanes by weight. The polymeric product was then used as the polyalkysiloxane in the next step of the process in this invention.

**EXAMPLE II**

The same procedure as in Example I was followed, however, the silane used in this example was isobutyltriethoxysilane. The polymerisation time was 48 hours at a temperature of 80°C.

**EXAMPLE III**

The same procedure as in Example I was followed, however, the alkylalkoxysilane used in this example is
isopropyltriethoxysilane. The process was carried out at a temperature of 60°C. The polymerisation time was 48 hours.

**EXAMPLE IV**

A mixture containing 10g of the polyalkysiloxane prepared from Example I, 2g of oleic acid and 48g of water was neutralised with ammonium hydroxide to a pH of approximately 7. 40g of isobutyltriethoxysilane was then added to the mixture and the system was stirred with a stirrer at the speed of 10,000 rpm for 10 minutes. A stable emulsion was produced, having particle sizes in the range between 0.1 and 1 μm.

**EXAMPLE V**

An emulsion of octyltriethoxysilane and the polyalkysiloxane from Example I was prepared as in Example IV.

**EXAMPLE VI**

Following the same procedure of Example IV, a mixture of two alkylalkoxysilanes such as isobutyltriethoxysilane and octyltriethoxysilane was used in this example. The ratio of isobutyltriethoxysilane and octyltriethoxysilane was varied from 1:4 to 1:1.

**EXAMPLE VII**

A mixture containing 10g of the polyalkysiloxane prepared from Example 1, and 50g of water was neutralised with ammonium hydroxide to a pH of approximately 7. 40g of isobutyltriethoxysilane was then added to the mixture and the system was stirred with a shear mixer at the speed of 10,000 rpm for 10 minutes. A stable emulsion was produced, having particle sizes in the range between 0.1 and 1μm.

**EXAMPLE VIII**

The same procedure as in Example VII was followed, however, the alkylalkoxysilane used in this example was iso-octyltriethoxysilane. The emulsion was found to be very fine and had a shelf-life of more than six months at room temperature.
EXAMPLE IX

A mixture containing 5g of a polydimethylsiloxane with a molecular weight of 13,650, 0.4g of oleic acid and 54.6g of water was neutralized with ammonium hydroxide to a pH of approximately 7. 40g of isobutyltriethoxysilane was then added to the mixture and the system was stirred with a shear mixer at the speed of 10,000 rpm for 5 to 20 minutes. A milky white emulsion was produced which had shelf life of more than 6 months at room temperature.

EXAMPLE X

A mixture containing 8g of a polydimethylsiloxane with a molecular weight of 9,430, 0.6g of oleic acid and 51.4g of water was neutralized with ammonium hydroxide to a pH of approximately 7. 40g of isobutyltriethoxysilane was then added to the mixture and the system was stirred with a shear mixer at the speed of 10,000 rpm for 5 to 20 minutes. A fine and stable emulsion was obtained.

EXAMPLE XI

A mixture containing 3g of a polydimethylsiloxane with a molecular weight of 17,250, 0.5g of linoleic acid and 56.5g of water was neutralized with ammonium hydroxide to a pH of approximately 7. 40g of isobutyltriethoxysilane was then added to the mixture and the system was stirred with a shear mixer at the speed of 10,000 rpm for 5 to 20 minutes. The product was a milky white emulsion which was stable for six months or more at room temperature.

EXAMPLE XII

A mixture containing 4g of a polydimethylsiloxane with a molecular weight of 28,000, 0.4g of oleic acid and 55.6g of water was neutralized with ammonium hydroxide to a pH of approximately 7. 40g of isobutyltriethoxysilane was then added to the mixture and the system was stirred with a shear mixer at the
speed of 10,000 rpm for 5 to 20 minutes. The emulsion prepared by this procedure was stable for more than six months at room temperature.

EXAMPLE XIII

A mixture containing 5g of a polydimethylsiloxane with a molecular weight of 13,650, 0.6g of linoleic acid and 54.4g of water was neutralized with ammonium hydroxide to a pH of approximately 7. 40g of octyltriethoxysilane was then added to the mixture and the system was stirred with a shear mixer at the speed of 10,000 rpm for 5 to 20 minutes. The above procedure produced a very stable emulsion.

EXAMPLE XIV

A mixture containing 7g of a polydimethylsiloxane with a molecular weight of 28,000, 0.5g of oleic acid and 52.5g of water was neutralized with ammonium hydroxide to a pH of approximately 7. 40g of octyltriethoxysilane was then added to the mixture and the system was stirred with a shear mixer at the speed of 10,000 rpm for 5 to 20 minutes. A stable emulsion which has a shelf life of more than six months was produced.

EXAMPLE XV

Following the same procedure as Example IX, a mixture of two alkylalkoxysilanes such as isobutyltriethoxysilane and octyltriethoxysilane was used in this example. The ratio of isobutyltriethoxysilane and octyltriethoxysilane was varied from 1:4 to 1:1.

EXAMPLE XVI

Following the same procedure as Example X, a mixture of two alkylalkoxysilanes such as isobutyltriethoxysilane and octyltriethoxysilane was used in this example. The ratio of isobutyltriethoxysilane and octyltriethoxysilane was varied from 1:4 to 1:1.
EXAMPLE XVII

Following the same procedure as Example XI, a mixture of two alkylalkoxysilanes such as isobutyltriethoxysilane and octyltriethoxysilane was used in this example. The ratio of isobutyltriethoxysilane and octyltriethoxysilane was varied from 1:4 to 1:1.

EXAMPLE XVIII

Following the same procedure as Example XII, a mixture of two alkylalkoxysilanes such as isobutyltriethoxysilane and octyltriethoxysilane was used in this example. The ratio of isobutyltriethoxysilane and octyltriethoxysilane was varied from 1:4 to 1:1.

EXAMPLE XIX

Water Repellency Test

The water repellency of permeable masonry was determined in accordance with the following procedure.

Concrete cubes of 50*50*45mm were obtained by cutting up larger manufactured concrete slabs. One side of the cube was immersed in the emulsion from Example IV or solution specified in Table 1, having different concentrations of alkylalkoxysilane. The time of immersion was 60 seconds in each case. After the immersion, the test samples were stored for two weeks at room temperature before their initial weights were recorded. The treated concrete cubes were then placed on a saturated sponge in a water bath (sponge test according to DIN 52617). After 14 days sitting on the saturated sponge, the test blocks were removed, blotted dry and immediately weighed. The percent weight gain of each concrete block was then determined by the following equation:

\[
\% \text{ weight gain} = \left(\frac{W_{\text{final}} - W_{\text{initial}}}{W_{\text{initial}}}\right) \times 100.
\]

The lower per cent weight gain values indicates more effective masonry water repellents.
The water repellency test was also carried out with cement mortar blocks, having dimensions of 50x50x30 mm. These cement mortar blocks were made according to DIN 1164 in which the cement/sand/water ratio was 1/3/0.5. They were allowed to cure at room temperature for 28 days before they were immersed in the emulsion from Example IV or solution of alkylalkoxysilane in hydrocarbon.

The substrate surface was washed with water using a metal brush, dried in an oven at 105°C and then allowed to cool to room temperature before impregnation. Therefore, the substrate surface was substantially dry and free of excess dirt, hydrocarbon deposits, and grease before it was impregnated.

The depth of impregnation was measured by breaking the impregnated blocks in half and wetting the fractured surfaces with water. The bright edge of the cross-section was then measured as the penetration depth of barrier penetrants. It should be noted that the depth of penetration depends on the substrate.

A solution containing the same concentration of the alkylalkoxysilane in mineral spirits was also prepared for comparison.
The test results are illustrated in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Penetrants</th>
<th>Conc. of Silane (%)</th>
<th>Substrate to be treated</th>
<th>Penetration Depth (mm)*</th>
<th>% Weight Gain. (after 14 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td>40</td>
<td>concrete</td>
<td>6</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>concrete</td>
<td>3</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>mortar</td>
<td>12.5</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>mortar</td>
<td>8.5</td>
<td>0.99</td>
</tr>
<tr>
<td>Solution</td>
<td>40</td>
<td>concrete</td>
<td>6</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>concrete</td>
<td>3.5</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>mortar</td>
<td>13</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>mortar</td>
<td>9.5</td>
<td>0.51</td>
</tr>
<tr>
<td>Control</td>
<td>untreated concrete</td>
<td></td>
<td></td>
<td>6.78</td>
</tr>
<tr>
<td>Control</td>
<td>untreated mortar</td>
<td></td>
<td></td>
<td>5.41</td>
</tr>
</tbody>
</table>

**EXAMPLE XX**

A different batch of concrete cubes and cement mortar blocks with dimensions as in Example XIX were prepared. The same procedure was carried out as in Example XIX using the emulsion from Example IX or the solution of alkylalkoxysilane in hydrocarbon solvent.
The test results are illustrated in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Penetrants</th>
<th>Conc. of Silane (%)</th>
<th>Substrate to be treated</th>
<th>Penetration Depth (mm)*</th>
<th>% Weight Gain. (after 14 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td>40</td>
<td>concrete</td>
<td>6</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>concrete</td>
<td>3</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>mortar</td>
<td>11</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>mortar</td>
<td>8</td>
<td>1.05</td>
</tr>
<tr>
<td>Solution</td>
<td>40</td>
<td>concrete</td>
<td>6.5</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>concrete</td>
<td>3.5</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>mortar</td>
<td>13</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>mortar</td>
<td>9.5</td>
<td>1.02</td>
</tr>
<tr>
<td>Control</td>
<td>untreated concrete</td>
<td></td>
<td></td>
<td>8.31</td>
</tr>
<tr>
<td>Control</td>
<td>untreated mortar</td>
<td></td>
<td></td>
<td>7.24</td>
</tr>
</tbody>
</table>
CLAIMS:

1. An aqueous silane/siloxane emulsion comprising
   (a) 4% to 50% by weight of an alkylalkoxysilane of the
   formula Rₙ-Si-R'₄-n, wherein,
   R is a hydrocarbyl group containing from 1 to 20
   carbon atoms;
   R' is an alkoxy group containing from 1 to 6 carbon
   atoms; and
   n is 1 or 2
   (b) 15% to 95% by weight of water;
   (c) 0% to 5% by weight of an emulsifier which is an
   amine soap; and
   (d) 1% to 30% by weight of a siloxane which is either
   a polyalkylsiloxane produced from a monomer of
   the general formula R-Si-(OR²)₃ where R is as defined
   above and R² is a hydrocarbyl group having 1 or 2
   carbon atoms; or
   a silicone fluid of the formula (R₃SiO)ₙ/₄⁺₂, where
   R is a hydrocarbyl group containing from 1 to
   6 carbon atoms, x is 1 or 2 and y is 2 or more;
   with the provisos that;
   when the siloxane is a polyalkylsiloxane and no
   emulsifier is present, a polymerisation catalyst which
   is a mixture of a benzenesulfonic acid and an alkali
   metal salt of a benzenesulfonic acid is employed to
   produce the polyalkylsiloxane; and
   when the siloxane is a silicone fluid at least 0.5%
   by weight of emulsifier is present in the emulsion.

2. An emulsion as claimed in claim 1 wherein the alkoxysilanes
   have a molecular weight between 135 and 600.

3. An emulsion as claimed in claim 1 wherein the
   alkylalkoxysilane is selected from the group consisting of
octyltriethoxysilane; isobutytriethoxysilane;
isobutyltrimethoxysilane; and octyltrimethoxysilane.

4. An emulsion as claimed in claim 1 wherein R$^1$ is ethoxy.

5. An emulsion as claimed in any one of the preceding claims wherein the amine soap is derived from an aliphatic carboxylic acid containing at least one olefinic double bond, and base.

6. An emulsion as claimed in claim 5 wherein the emulsifier is an amine soap derived from oleic acid or linoleic acid.

7. An emulsion as claimed in claim 5 wherein the base is selected from the group consisting of ammonium hydroxide, morpholine, ethylamine, diethylamine, triethylamine, ethylenediamine, butylamine, hexylamine, triethanolamine, diethylethanolamine, and alkylidimethylamine.

8. An emulsion as claimed in claim 1 wherein the polyalkylsiloxane is produced using dodecylbenzenesulfonic acid and its sodium salt as the polymerisation catalyst.

9. An emulsion as claimed in claim 1 wherein the polyalkylsiloxane is a polyisobutylsiloxane.

10. An emulsion as claimed in claim 1 wherein the siloxane fluid is a polydimethylsiloxane with trimethylsiloxy termination, having a molecular weight between 3780 and 28000.

11. An emulsion as claimed in claim 1 which additionally contains a biocidally effective amount of a biocide.

12. A method for treating permeable mineral building material comprising impregnating at least a surface of said permeable mineral building material with a composition as defined in claim 1.

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/AU 94/00767

A. **CLASSIFICATION OF SUBJECT MATTER**
   Int. Cl. C08L 83/06, C09D 183/06, C04B 41/49, 41/48

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

B. **FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC C08L 83/06, C09D 183/06, C04B 41/49, 41/48, IPC C09D 3/82

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU:IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT: WATER OR H2O OR AQUEOUS AND SOAP OR EMULSION
JAPIO: WATER OR H2O OR AQUEOUS AND SOAP OR EMULSION

C. **DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AU 16503/92 (WACKER CHEM GMBH) 12 November 1992 (12.11.92) page 2 lines 2-16; page 6 lines 1-9; page 8 lines 4-16</td>
<td>1-13</td>
</tr>
<tr>
<td>US 5250106 (WACKER CHEM GMBH) 5 October 1993 (05.10.93) column 2 lines 8-23; claims</td>
<td>1-13</td>
</tr>
<tr>
<td>EP 476452 (T.H. GOLDSCHMIDT AG) 25 March 1992 (25.03.92) See whole document</td>
<td>1-13</td>
</tr>
</tbody>
</table>

[X] Further documents are listed in the continuation of Box C.  

[X] See patent family annex.

- **Special categories of cited documents**:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means
  - "O" document published prior to the international filing date but later than the priority date claimed
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "X" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is taken alone
  - "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  - "&" document member of the same patent family

Date of the actual completion of the international search
17 March 1995 (17.03.95)

Date of mailing of the international search report
5 April 1995 (05.04.95)

Name and mailing address of the ISA/AU
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA

Authorized officer

GRANT MCNEICE

Facsimile No. 06 2853929

Telephone No. (06) 2832055

Form PCT/ISA/210 (continuation of first sheet (2)) (July 1992) copyhsw
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate of the relevant passages</th>
<th>Relevant to Claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 5091002 (T.H. GOLDSCHMIDT AG) 25 February 1992 (25.02.92) See column 3 line 36 - column 4 line 27, claims</td>
<td>1-13</td>
</tr>
<tr>
<td>A</td>
<td>US 4753977 (GENERAL ELECTRIC CO.) 28 June 1988 (28.06.88) See column 2 line 51 - column 3 line 3, claims</td>
<td>1-13</td>
</tr>
<tr>
<td>A</td>
<td>US 4525502 (GENERAL ELECTRIC CO.) 25 June 1985 (25.06.85) column 2 lines 45-65; column 3 lines 41-59; claims</td>
<td>1-13</td>
</tr>
<tr>
<td>A</td>
<td>US 5393330 (OSI SPECIALTIES, INC.) 4 January 1995 (04.01.95) See abstract and claims</td>
<td>1-13</td>
</tr>
<tr>
<td>A</td>
<td>US 4648904 (SCM CORPORATION) 10 March 1987 (10.03.87) See column 2 lines 5-47; claims</td>
<td>1-13</td>
</tr>
<tr>
<td>A</td>
<td>US 5037873 (PCR GROUP, INC.) 6 August 1991 (06.08.91) See column 2 lines 25-60, column 3 lines 30-60, claims</td>
<td>1-13</td>
</tr>
<tr>
<td>A</td>
<td>US 4937104 (HUELS AKTIENGESELLSCHAFT) 26 June 1990 (26.06.90) See column 4 line 57 - column 5 line 7, claims</td>
<td>1-13</td>
</tr>
<tr>
<td>A</td>
<td>US 4877654 (PCR, INC.) 31 October 1989 (31.10.89) See column 2 lines 15-35, column 2 line 64 - column 3 line 24, column 3 lines 56-66, column 6 lines 55-64, claims</td>
<td>1-13</td>
</tr>
</tbody>
</table>
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

<table>
<thead>
<tr>
<th>Patent Document</th>
<th>Patent Family Member</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cited in Search Report</td>
<td></td>
</tr>
<tr>
<td>AU 16503/92 DE 4114498</td>
<td>BR 9205828 CN 1069749</td>
</tr>
<tr>
<td>AU EP 582611</td>
<td>MX 9202068 JP 6081788</td>
</tr>
<tr>
<td>AU CA 2103354</td>
<td>CZ 9302504 US 5161650</td>
</tr>
<tr>
<td>US 5250106 EP 518324</td>
<td>AT 102912 CA 2070472</td>
</tr>
<tr>
<td>US DE 4119562</td>
<td>ES 2062850 JP 5155675</td>
</tr>
<tr>
<td>US NO 9922330</td>
<td></td>
</tr>
<tr>
<td>EP 476452 DE 4029640</td>
<td></td>
</tr>
<tr>
<td>US 5091002 DE 3911479</td>
<td>EP 392253</td>
</tr>
<tr>
<td>US 4753977 CA 1309539 E 63170484</td>
<td>DE 3778863 EP 275378</td>
</tr>
<tr>
<td>US JP 621197369</td>
<td>ZA 8707769</td>
</tr>
<tr>
<td>US 4525502 CA 1250983</td>
<td></td>
</tr>
<tr>
<td>US 5393330 EP 631999 CA 2125803 JP 7024298</td>
<td></td>
</tr>
<tr>
<td>US 4648904 AT 92452 AU 68657/87 CA 1277891</td>
<td></td>
</tr>
<tr>
<td>US DE 3688837 EP 234024 ES 2042492</td>
<td></td>
</tr>
<tr>
<td>US JP 621197369</td>
<td></td>
</tr>
<tr>
<td>US 5037873 EP 412516 JP 3088879</td>
<td></td>
</tr>
<tr>
<td>US 4937104 US 4433013</td>
<td></td>
</tr>
<tr>
<td>US 4877654 AT 91275 AU 28738/89 CA 1330691</td>
<td></td>
</tr>
<tr>
<td>US DE 68907439 EP 340816</td>
<td></td>
</tr>
</tbody>
</table>

END OF ANNEX