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(54) Titre : PRODUIT HYDROFUGE POUR MACONNERIE COMPRENANT DU SILOXANE DE METHYLE
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(54) Title: MASONRY WATER REPELLENT COMPOSITIONS COMPRISING METHYLHYDROGEN SILOXANES

(57) **Abrégé/Abstract:**

A method of rendering masonry architectural building materials water repellent by incorporating into the masonry architectural building material an additive which is a mixture of (i) a water soluble silane coupling agent and (ii) an emulsion which includes water, at least one surfactant and a siloxane fluid. The siloxane fluid is one of linear methylhydrogen siloxane polymers, linear methylhydrogen-methylalkyl siloxane copolymers, methyl-hydrogen cyclosiloxane polymers or methylhydrogen-methylalkyl cyclosiloxane copolymers. An inorganic porous mineral substrate including the mixture is also disclosed.



MASONRY WATER REPELLENT COMPOSITIONS COMPRISING METHYLHYDROGEN SILOXANES

ABSTRACT

A method of rendering masonry architectural building materials water repellent by incorporating into the masonry architectural building material an additive which is a mixture of (i) a water soluble silane coupling agent and (ii) an emulsion which includes water, at least one surfactant and a siloxane fluid. The siloxane fluid is one of linear methylhydrogen siloxane polymers, linear methylhydrogen-methylalkyl siloxane copolymers, methylhydrogen cyclosiloxane polymers or methylhydrogen-methylalkyl cyclosiloxane copolymers. An inorganic porous mineral substrate including the mixture is also disclosed.

MASONRY WATER REPELLENT COMPOSITIONS COMPRISING METHYLHYDROGEN SILOXANES

This invention relates to organosilicon masonry water repellent compositions and, more particularly, is directed to a water repellent composition for treating porous substrates which includes a mixture of a water soluble silane coupling agent and a siloxane fluid in the form of an emulsion containing a linear or cyclic methylhydrogen polymer or a copolymer such as a linear methylhydrogen-methylalkyl siloxane or methylhydrogen-methylalkyl cyclosiloxane.

Water resistance is an important factor in masonry construction. This is for the reason that moisture movement in masonry causes or contributes to problems such as expansion, shrinkage, cracking, staining, mildew, lowered resistance to freezing and thawing, chemical attack, corrosion of reinforcing steel and damage to structures from settling. Because of these problems, various techniques have been used to render masonry water resistant. Some of these methods include the surface treatment of structures with water repellents. Water repellents that have been used in the past are oils, waxes, soaps and resins and they have been applied to the masonry surfaces by brush, roller, air spray or airless spray techniques. One of the most prevalent category of repellent that has been used is organosilicon compounds and such compounds in organic solvents have been found to be useful for brick, concrete, stucco or terrazzo surfaces.

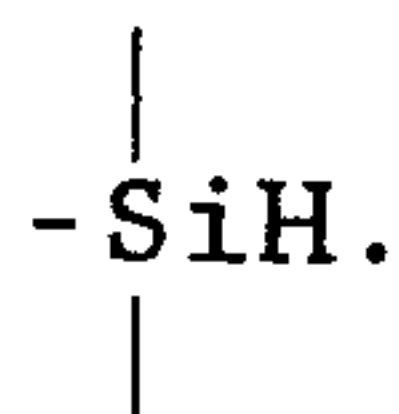
It is not new in the patent art to employ organosilicon compounds for the treatment of masonry surfaces in order to render such surfaces water repellent. For example, in U.S. Patent No. 4,002,800, issued January 11, 1977, there

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is disclosed a solution containing an alcohol or hydrocarbon solvent, an alkyltrialkoxysilane and an additive.

One category of organosilicon compound which has been used extensively is the alkoxysilane and representative of such masonry treatments with alkoxysilanes, and representative U.S. Patent No. 3,879,206, issued April 22, 1975; U.S. Patent No. 4,478,911, issued October 23, 1984; U.S. Patent No. 4,846,886, issued July 11, 1989; and U.S. Patent No. 4,874,431, issued October 17, 1989.

The compositions of the present invention differ from the compositions of the prior art in that they include a mixture of a water soluble silane coupling agent and an emulsion containing a siloxane fluid. The fluid has in the siloxane molecule the silyldyne radical



This is significant as will be pointed out hereinafter.

Of particular relevance to the present invention are U.S. Patent Nos. 3,879,206 and 4,002,800, noted above, each of which teach an alkyltrialkoxysilane such as butyltrimethoxysilane in combination with an additive such as aminoethylaminopropyltriethoxysilane. However, the combination is applied in a solvent such as ethanol rather than in the form of an aqueous solution as in the present invention. While U.S. Patent No. 4, 478,911, also noted above, includes an alkyltrialkoxysilane combined with an amine, the amine is an organic amine rather than an aminofunctional silane as in the present invention. Both U.S. Patent Nos. 4,846,886 and 4,874,431, noted previously, teach an alkylalkoxysilane and a beading agent which can be a material such as an aminofunctional silane of the formula $\text{H}_2\text{HCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$, however, the combination is applied in a carrier other than water such as an alcohol, glycol ether or mineral spirits and

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no aqueous solution is formed as in the present invention. Thus, there are significant differences between what is taught in accordance with the concept of the present invention and what is disclosed in the prior art as evidenced by the several patents noted and discussed above.

This invention is directed to a method of rendering masonry architectural building materials water repellent by incorporating into the masonry architectural building material an additive which is a mixture of (i) a water soluble silane coupling agent and (ii) an emulsion which includes water, at least one surfactant and a siloxane fluid. The siloxane fluid is selected from the group consisting of linear methylhydrogen siloxane polymers, linear methylhydrogen-methylalkyl siloxane copolymers, methylhydrogen cyclosiloxane polymers and methylhydrogen-methylalkyl cyclosiloxane copolymers.

The invention is also directed to a water repellent masonry architectural building material which is an inorganic porous mineral substrate having the above noted additive incorporated therein.

It is therefore an object of the present invention to chemically fix a water-repelling agent to a porous substrate in order to improve its resistance to the absorption of water as well as to impart to the substrate the ability to shed surface water.

It is a further object of the present invention to increase the density of an organosilicon matrix within a porous substrate in order to render the substrate water resistant and at the same time provide it with the property of shedding water.

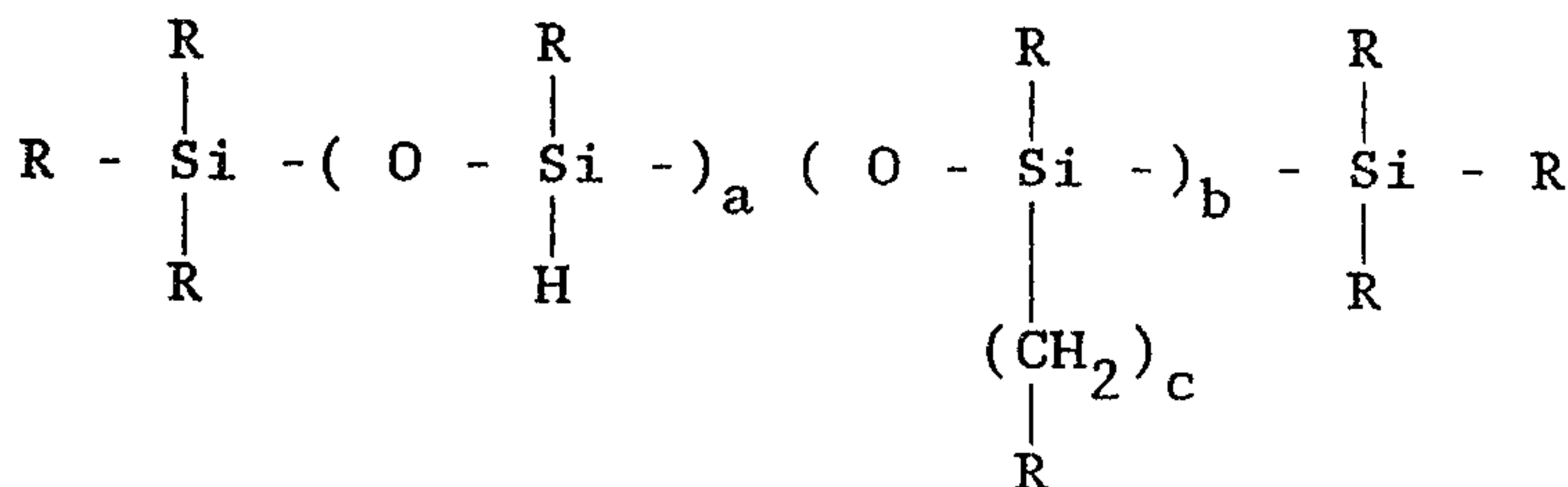
It is also an object of the present invention to provide a masonry water repellent composition for porous substrates in which the repellent not only renders the

substrate resistant to water penetration but in addition hinders the ingress of water at the surface.

These and other objects, features and advantages of the herein described invention will become more apparent from a consideration of the following detailed description thereof.

Masonry water repellents including alkylalkoxy-silanes impart water repellent properties to such porous substrates as concrete, mortar and stone. Such repellents function in this fashion because of the fact that they penetrate into the masonry prior to the time that they are transformed into immobile resinous materials. However, due to the penetration of the repellent into the porous substrate, the repellent does not leave behind much of a layer on the porous substrate. As a result, the repellent, though effective to render the substrate water resistant fails nevertheless to provide the substrate with coatings of any significant durability. The compositions disclosed herein are intended to overcome this deficiency and there can be achieved a good degree of water shedding function of the masonry structure because of polymer deposition on the masonry, in addition to the repellent formulation providing a deep section water barrier to water migration within the substrate itself.

A major advantage of the repellent compositions of the present invention is that the compositions are capable of being formulated into a form which complies with various state and federal regulations regarding volatile organic content (VOC). These regulations generally prohibit a volatile organic content for an architectural coating which is in excess of about four hundred grams per liter. In the case of the compositions of the present invention, no volatile component is liberated from the reaction of the



and $(\text{OSiRH})_d (\text{OSiRR}')_e$ where R is an alkyl radical having one to three carbon atoms; R' is the alkyl radical $(\text{CH}_2)_c \text{R}$; a is an integer having a value of from 3 to 35; b is an integer having a value of from zero to 32; c is an integer having a

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value of from one to seventeen; d is an integer having a value of from 3 to 10; and e is an integer having a value of from zero to seven.

The emulsion can include from about twenty to about sixty percent by weight of the siloxane and preferably, the emulsion includes forty to fifty percent by weight of the siloxane. Preferably, the integer a has a value of three or four; the integer b has a value of two or three; the integer c has a value of five, six or seven; the integer d has a value of three or four; and the integer e has a value of one or two.

The following examples are set forth for the purpose of illustrating the basic concepts of the present invention including the method of preparing the siloxane fluids of the present invention, as well as test data indicating the utility of masonry treatments with such compositions.

Example I

Into a 250 ml round bottom flask equipped with a reflux condenser and a heating mantle was placed a solution of 48 grams of $(\text{OSiMeH})_4$ and 16.8 grams of 1-hexene. One piece of eight mesh 0.5% Pt/C of 40 mg total weight or about 0.2 mg Pt was added to the solution and the contents of the flask were heated to reflux. An exotherm occurred during heating for about 10 minutes. The mixture was heated at reflux for an additional 15 minutes after which it was allowed to cool to room temperature. Fourier Transform Infrared Analysis of an aliquot of the mixture revealed the presence of SiH and the absence of olefin. Gas chromatography/mass spectrometry analysis revealed the product to be a mixture having the following composition:

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$(\text{OSiMeH})_4$	15%
$(\text{OSiMeH})_3/(\text{OSiMeC}_6\text{H}_{13})$	50%
$(\text{OSiMeH})_2/(\text{OSiMeC}_6\text{H}_{13})_2$	25%
$(\text{OSiMeH})/(\text{OSiMeC}_6\text{H}_{13})_3$	10%

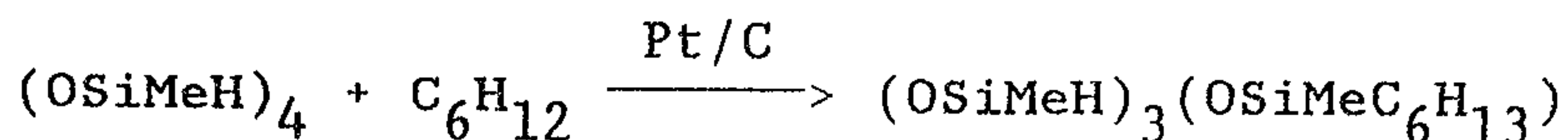
Example II

Following the same procedure as in Example I, a mixture of 75 grams of $\text{Me}_3\text{Si}-(\text{OSiMe}_2)_3(\text{OSiMeH})_5-\text{OSiMe}_3$ and 18.4 grams of 1-hexene was allowed to react in the presence of 0.2 mg Pt as 0.5% Pt/C.

Example III

A solution of 333 grams of $(\text{OSiMeH})_4$ and 210 grams of 1-dodecene ($\text{C}_{12}\text{H}_{24}$) was prepared by weighing the two compounds into a one liter bottle and stirring the contents for one minute. 100 grams of this solution was placed into a one liter round bottom flask equipped with a reflux condenser and a heating mantle. Two pieces of eight mesh 0.5% Pt on C (0.2 mg Pt each) were added to the flask and the mixture was heated to boiling. The remainder of the solution was poured into a 500 ml dropping funnel which was placed near the top opening of the reflux condenser. When the mixture in the flask started to boil, solution from the dropping funnel was added slowly through the reflux condenser. The fresh solution was added to the mixture at such a rate so as to maintain a gentle reflux in the flask. Addition of the solution in the dropping funnel required about 45 minutes. After all of the solution had been added, the mixture in the flask was heated at reflux for an additional 15 minutes. The mixture was allowed to cool to room temperature and filtered through diatomaceous earth.

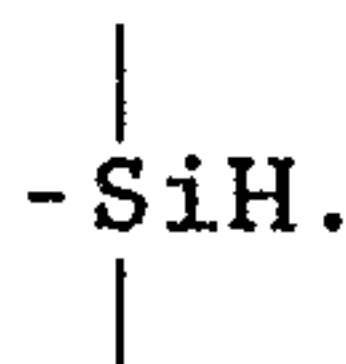
The reaction scheme for the process of preparing and using the composition of Example I can be seen as follows:



Thus, methylhydrogen cyclosiloxane is reacted with the olefin 1-hexene in the presence of a platinum-carbon catalyst to produce a low molecular weight siloxane penetrant having alkylmethylsiloxo and organohydrosiloxo groups. When applied to masonry, the low molecular weight siloxane having alkylmethylsiloxo and organohydrosiloxo groups of the formula $(\text{OSiMeH})_{0.75} (\text{OSiMeC}_6\text{H}_{13})_{0.25}$ is converted by hydrolysis and subsequent condensation to a copolymeric silicone resin of the formula $(\text{MeSiO}_{3/2})_{0.75} (\text{OSiMeC}_6\text{H}_{13})_{0.25}$. This resin is present on the surface and in the pores of the masonry and renders it resistant to water.

This hydrosilylation reaction of the olefin with a low molecular weight methylhydrogen siloxane does not usually produce a pure compound but a mixture of compounds is produced and this mixture is used as one of the waterproofing agents. It is not necessary to use pure compounds since upon application to masonry the penetrant hydrolyzes and condenses to form a silicone resin.

As previously noted, the compositions of the present invention differ from the compositions of the prior art in the presence in the siloxane molecule of the silyldyne radical



This difference is significant since the silyldyne radical of the masonry repellent of the present invention reacts with the hydroxide groups and moisture in the masonry substrate to form the copolymeric silicone resin described above. This resin is formed within the pores of the masonry substrate to

which the repellent composition is applied. The copolymeric silicone resin that is formed within the masonry substrate pores is hydrophobic and therefore readily resists the permeation of water onto and into the porous surface and interior of the masonry material. The compositions of the present invention have a relatively low viscosity and therefore are capable of diffusing into porous masonry substrates. When applied to a masonry substrate, the latent alkalinity of the masonry catalyzes the reactions of water and hydroxide groups with the silyldyne radical to produce SiOH and hydrogen. The alkaline masonry further catalyzes the condensation of SiOH groups to produce siloxane bonds and water and a resinous structure is ultimately produced.

As noted above, the repellent compositions of the present invention are capable of being formulated into coatings which comply with various state and federal regulations regarding volatile organic content (VOC). These regulations prohibit a volatile organic content architectural coating in excess of four hundred grams per liter. In the present invention, the volatile component liberated from the reaction of the repellent with masonry is hydrogen which is not a volatile organic compound. Prior art alkoxysilanes on the other hand liberate alcohol which is a volatile organic compound.

Accordingly, a masonry repellent can be formulated with the compositions of the present invention which complies with the volatile organic content regulations. Thus, a repellent in accordance with the present invention containing about forty-five to about fifty percent by weight solids will have a volatile organic content less than about four hundred grams per liter. Penetrants of the prior art which contain alkoxysilanes such as isobutyltrimethoxysilane have volatile organic contents about 650-700 grams per liter.

Although the alkyl group of the siloxanes described in the present invention contribute to the ability of the compound to render masonry hydrophobic, its presence is not always required. Thus, methylhydrogen siloxane may be used to waterproof masonry and the resulting silicone resin formed after complete hydrolysis and condensation is monomethylsilsequioxane or $\text{MeSiO}_{3/2}$. This material is substantially hydrophobic and readily renders masonry hydrophobic. However, there are advantages in using an alkylmethyl/methylhydrogen copolymeric material in lieu of the methylhydrogen siloxane. Thus, the olefins used to prepare alkylmethylsiloxane/methylhydrogen copolymers are less expensive than methylhydrogen siloxane from which these copolymeric materials are prepared. Hence material expense for alkylmethyl/methylhydrogen copolymeric compounds is less than methylhydrogen siloxane because the former is essentially the latter diluted with olefin. Even though the copolymeric materials require more processing than methylhydrogen siloxane, expense of the alkylmethylsiloxane/methylhydrogen copolymer are still lower than methylhydrogen siloxane. The copolymer also is less volatile and has a higher flash point than polymethylhydrogen siloxane.

The following examples illustrate details in the process for preparing low volatile organic content emulsion compositions of the instant invention.

The preferred starting material is a methylhydrogencyclosiloxane such as $(\text{OSiMeH})_4$. However, mixtures of these cyclic siloxanes are as effective as the pure cyclic compound. The preferred olefin is 1-hexene. Other olefins include 1-pentene, 1-heptene, 1-octene, 1-decene or 1-dodecene. Mixtures of these olefins can also be used. The ratio of SiH to olefin can be varied, but this ratio should be such that a minimum of three SiH groups per

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molecule is retained. For example, if pure $(\text{OSiMeH})_4$ is used, no more than one mole of olefin should be used per mole of cyclosiloxane. The method of hydrosilylation uses a heterogeneous catalyst such as 0.5 % Pt/C. A mixture of the SiH compound, olefin and catalyst is heated to reflux for approximately thirty minutes. If the batch size is large, it is advisable to reflux a small portion of the mixture while adding the remainder in small increments to control the highly exothermic reaction. The product from this reaction, a low viscosity oil, is a mixture of compounds having an average stoichiometry of $(\text{OSiMeH})_{0.75}/(\text{OSiMeR})_{0.25}$ wherein $\text{R}=\text{Me}$, C_6H_{13} or $\text{C}_{12}\text{H}_{23}$.

The low viscosity oil is homogenized with water and a surfactant to produce an oil in water nonionic emulsion having a solids content of about thirty percent by weight. As long as the pH of the emulsion is near neutral, hydrolysis of SiH is insignificant. When compositions of this invention are applied to a substrate, water evaporates to leave a low viscosity oil. When the substrate is alkaline, this alkalinity will catalyze reactions of hydrolysis/condensation. Specifically, SiH reacts with moisture and hydroxyls present in the substrate to produce $\text{SiOH} + \text{H}_2$. SiOH condenses to produce siloxane + H_2O . Since the silicone oil is multi-functional, a resinous structure will be formed with complete hydrolysis/condensation. This resin being highly hydrophobic waterproofs the substrate.

Example IV

A solution of 300 grams of $(\text{OSiMeH})_4$ and 105 grams of 1-hexene ($\text{C}_{12}\text{H}_{24}$) was prepared by weighing the two compounds into a one liter bottle and stirring the contents for one minute. 100 grams of this solution was placed into a one liter round bottom flask equipped with a reflux condenser and a heating mantle. Two pieces of eight mesh 0.5 %

Platinum on carbon (0.2 mg Pt each) were added to the flask and the mixture was heated to boiling. The remainder of the solution was poured into a 500 ml dropping funnel which was placed near the upper opening of the reflux condenser. When the mixture in the flask started to boil, solution from the dropping funnel was added slowly through the reflux condenser. The fresh solution was added to the mixture at such a rate so as to maintain a gentle reflux in the flask. Addition of the solution in the dropping funnel required about thirty minutes. After all of the solution had been added, the mixture in the flask was heated at reflux for an additional twenty minutes. The mixture was allowed to cool to room temperature and filtered through diatomaceous earth. FTIR analysis revealed the presence of SiH and the absence of olefin.

To 300 grams of this product was added six grams of the nonionic surfactant TERGITOL ® TMN-6 and 694 grams of distilled water. The mixture was stirred for thirty minutes and homogenized using a Gaulin laboratory homogenizer to produce an oil in water emulsion having a solids content of about 30 percent by weight. With the same procedure, $(\text{OSiMeH})_4$ was partially reacted with 1-dodecene using one mole of olefin to one mole of $(\text{OSiMeH})_4$ and the product was homogenized to obtain a 30% solids emulsion. $(\text{OSiMeH})_4$ was also emulsified using the above procedure to produce a 30% solids emulsion. Two-hundred gram portions of the three emulsions were diluted with water to produce emulsions having a solids content of 15% by weight.

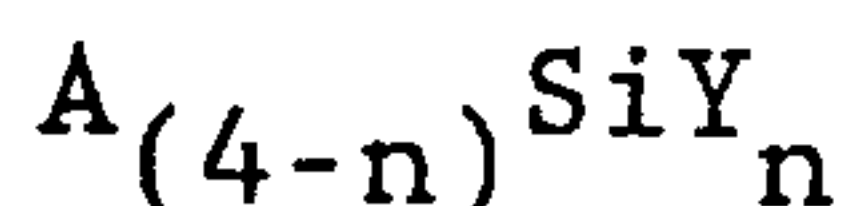
While a nonionic surfactant is shown in Example IV, other types of surfactants can be employed in accordance with the present invention. Thus, the emulsions of the present invention can be formulated with nonionic, cationic or amphoteric surfactants and mixtures thereof. The emulsions

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may also contain freeze-thaw additives such as polyglycols, representative of which are ethylene glycol, propylene glycol, butylene glycol, mixtures and copolymers thereof. Other techniques for preparing emulsions are applicable, for example as shown in U.S. Patent No. 4,620,878, issued November 4, 1986. The '878 patent also contains details of other suitable surfactants that may be employed. Reference is also made to the emulsion techniques and surfactants contained in U.S. Patent No. 4,501,619, issued February 26, 1985; U.S. Patent No. 4,631,273, issued December 23, 1986; and U.S. Patent No. 4,842,766, issued June 27, 1989. It is noted that the nonionic surfactant of Example IV is an ethoxylated trimethylnonanol with an HLB value of 11.7 and is a trademark and product of Union Carbide Corporation, Industrial Chemicals Division, Danbury, Connecticut.

Conventional silane coupling agents are well known in the art for bonding resins to fillers and substrates. Typically as part of the process of producing composite materials, reinforcing fillers are treated with silane coupling agents before being introduced into the uncured resin. The silane coupling agents form a coating on the filler and the coating interacts with the resin either chemically or through the formation of interpenetrating polymer networks to form a strong cohesive bond between the resin and filler. A significant benefit of silane coupling agents is the added hydrolytic stability they provide composite materials.

Various conventional highly water soluble silane coupling agents can be used in the present invention. Generally silane coupling agents are of the formula



where A is a monovalent organic radical, Y is a hydrolyzable radical and n is 1, 2 or 3, most preferably 3. A can be

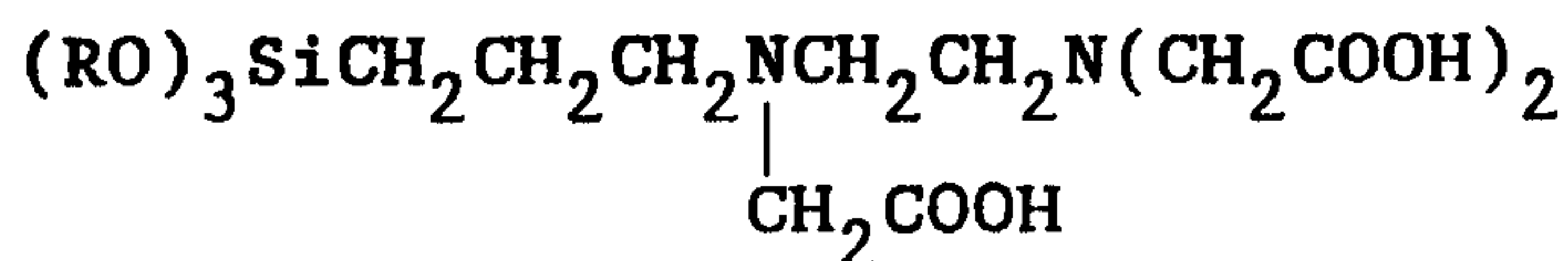
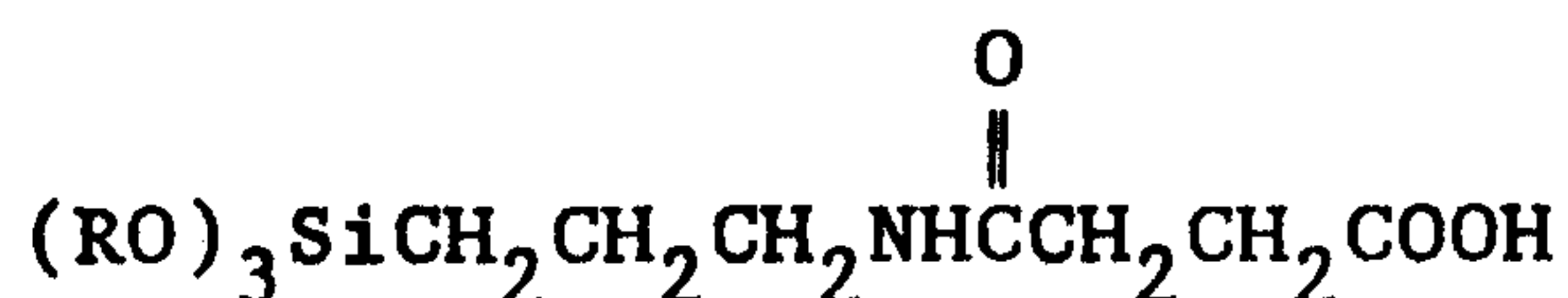
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various types of organic radicals including alkyl or aryl radicals. Y radicals hydrolyze in the presence of water and include acetoxy radicals, alkoxy radicals with 1 to 6 carbon atoms and alkylalkoxy radicals with 2 to 8 carbon atoms.

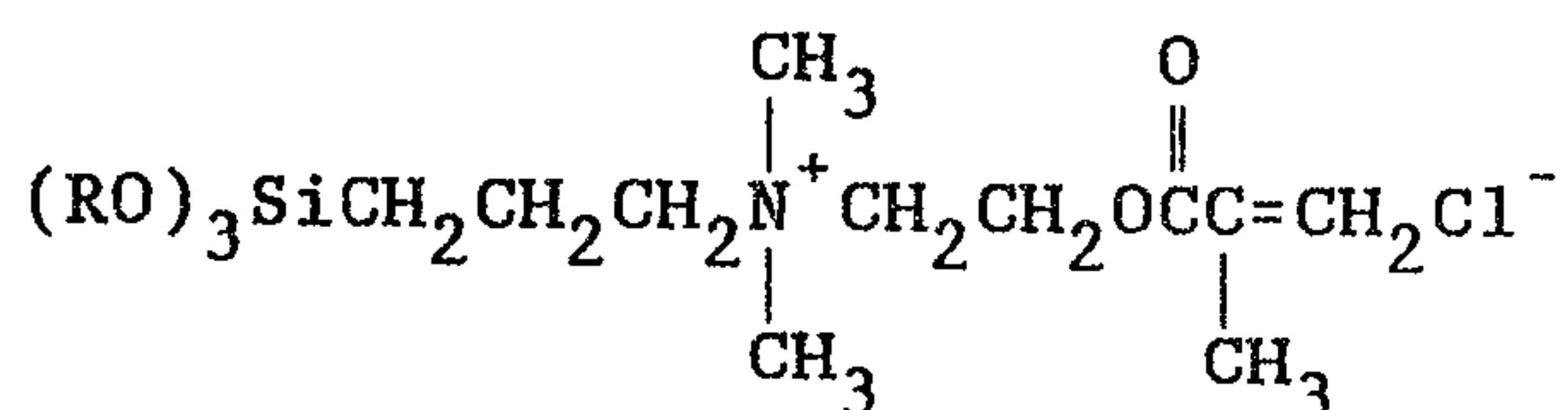
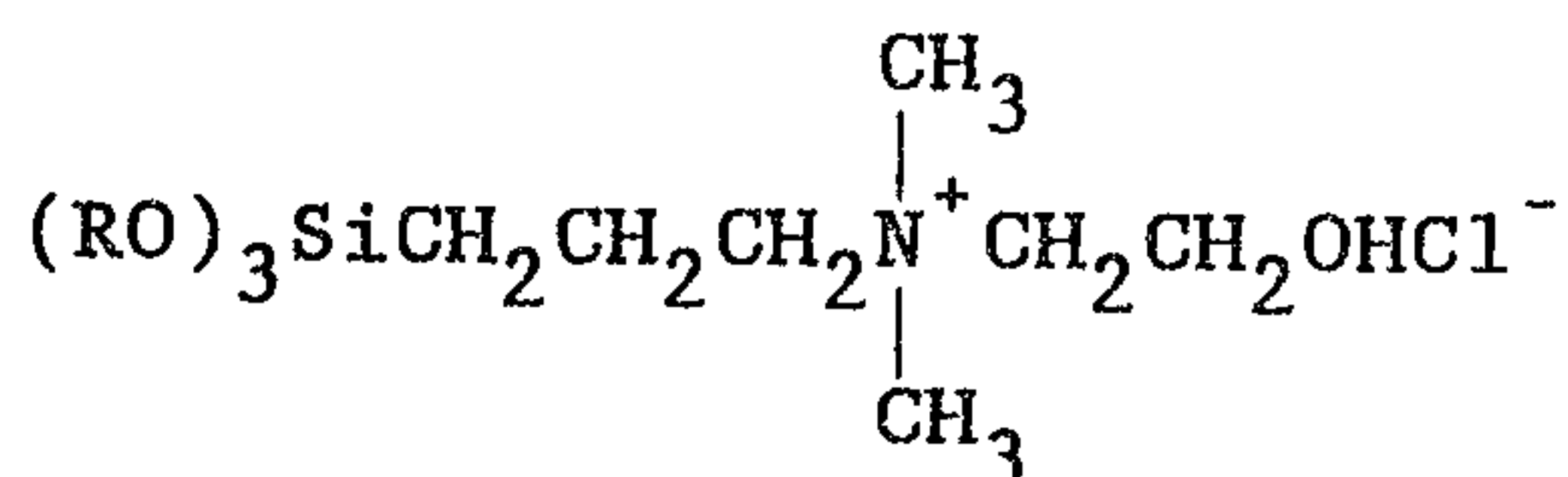
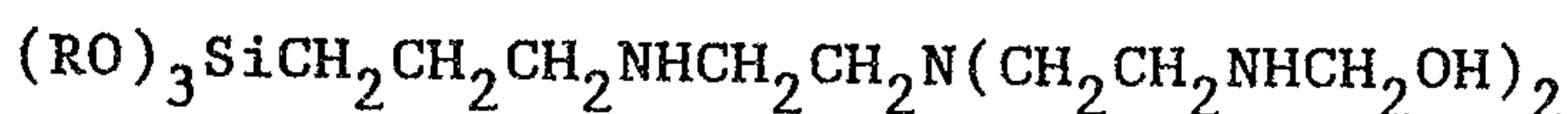
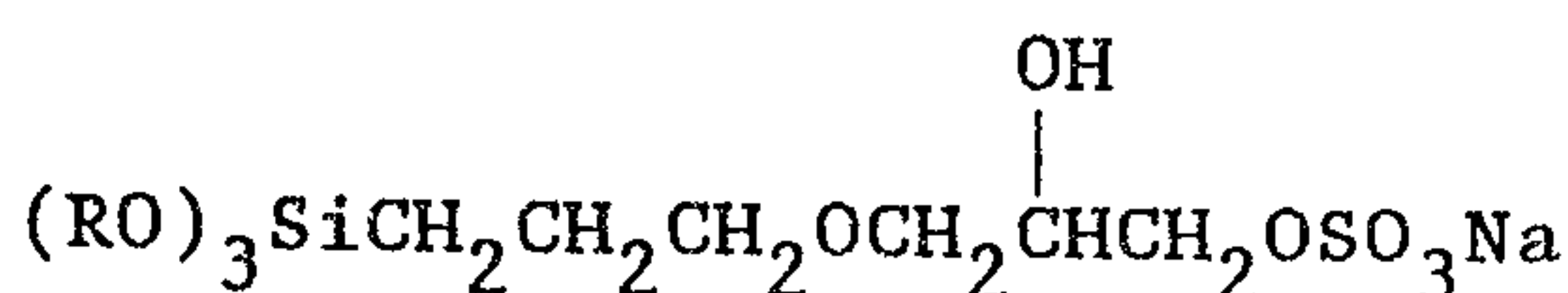
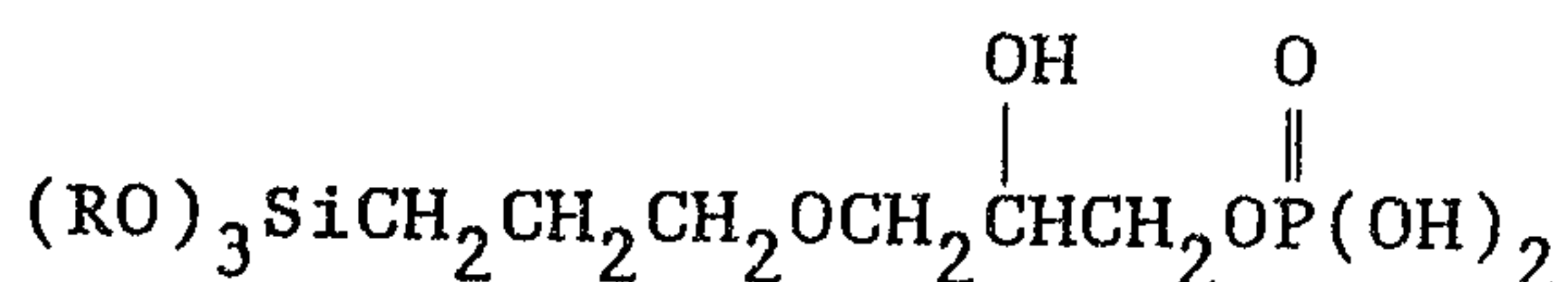
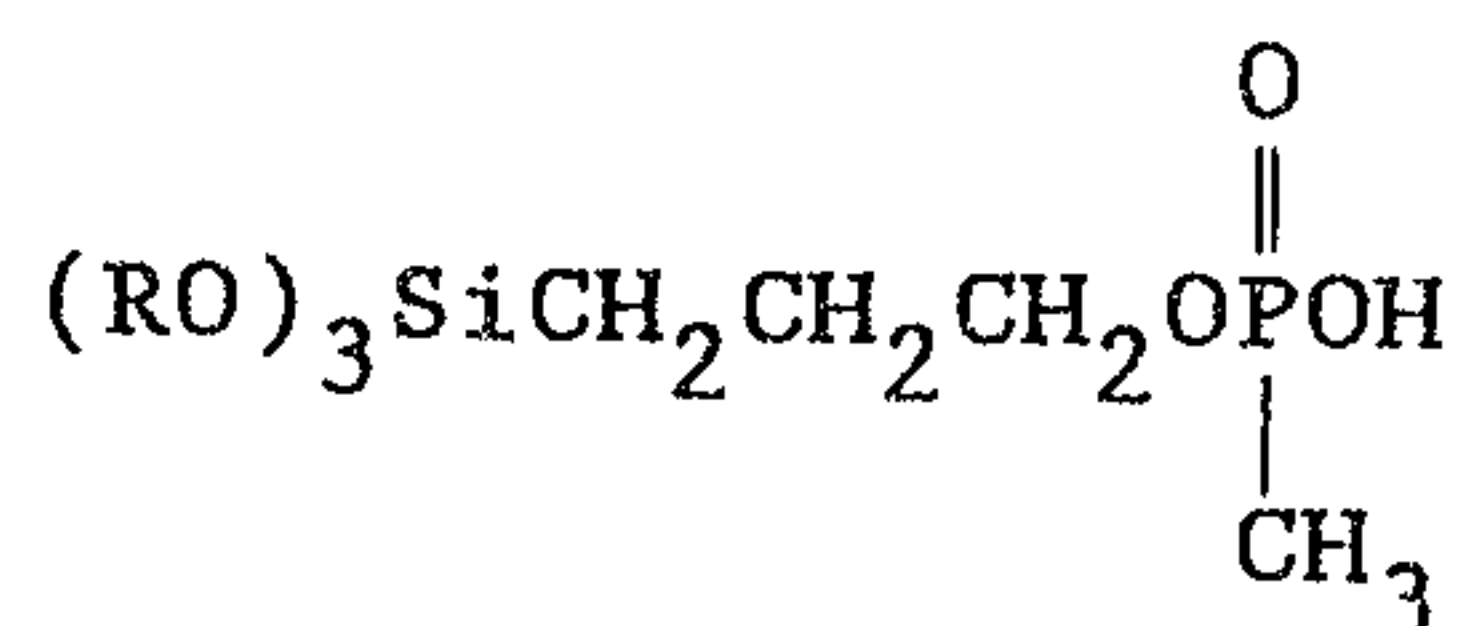
Specific silane coupling agents within the scope of the present invention include N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(aminoethylaminomethyl)-phenyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltris(2-ethylhexoxy)-silane, 3-aminopropyltrimethoxysilane, trimethoxysilyl-propyldiethylenetriamine, bis(2-hydroxyethyl)-3-aminopropyltrimethoxysilane and 2-methacryloxyethyl-dimethyl-[3-trimethoxysilylpropyl] ammonium chloride.

In particular, the most preferred silane coupling agents include N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane and the quaternary ammonium functional silanes. These silane coupling agents are commercially available. The other silane coupling agents are available commercially or their preparation is known in the art.

The silane coupling agents employed in accordance with the present invention should be highly water soluble silane coupling agents or hydrolyzed aqueous solutions thereof and exemplary of other of such materials are:



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The most preferred water soluble silane coupling agent is N-(2-aminoethyl)-3-aminopropyltrimethoxysilane of the formula $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$. This aminoalkyl functional silane is a low viscosity liquid having a viscosity of about six centistokes measured at 25°C. and is a reactive fluid containing an alkylamine organic group and a trimethoxysilyl inorganic group.

In accordance with the present invention, a method is provided for rendering masonry architectural building

materials water repellent. The method involves incorporating into the masonry architectural building material an additive which is a mixture of (i) a water soluble silane coupling agent and (ii) an emulsion which includes water, at least one surfactant and a siloxane fluid. The siloxane fluid may be one of a material such as a linear methylhydrogen siloxane polymer, a linear methylhydrogen-methylalkyl siloxane copolymer, a methylhydrogen cyclosiloxane polymer or a methylhydrogen-methylalkyl cyclosiloxane copolymer. Both the water soluble silane coupling agent and the emulsion have been described in detail above.

While the method of the present invention is applicable in general to masonry materials, the preferred masonry architectural building material includes gypsum and most preferably is in the form of gypsum wallboard. Gypsum is calcium sulfate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. When calcium sulfate dihydrate is heated to temperatures above about one hundred and 10°C ., moisture is evolved. The resulting product is plaster of paris often termed stucco. Plaster of paris has an approximate composition of $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ where the final temperature does not exceed about two hundred and 5°C . When plaster of paris is mixed with water it rehydrates and sets to a solid mass within a few minutes. Wallboard can be produced by layering slabs of the solid mass between sheets of fabric or tough paper.

The mixture which is employed in accordance with the present invention includes from about forty to eighty percent by weight of the emulsion and from about twenty to sixty percent by weight of the water soluble silane coupling agent. The most preferred mixture includes about seventy percent by weight of the emulsion and about thirty percent by weight of the water soluble silane coupling agent. The mixture is incorporated into the masonry architectural

building material in an amount of from about 0.1 percent by weight to about 0.8 percent by weight and may be incorporated into the masonry architectural building material by adding the mixture to a slurry of the gypsum prior to fabrication of the wallboard.

The following example is provided by way of additional illustration to further exemplify the concepts of the present invention.

Example V

A method for measuring the performance of moisture resistant gypsum wallboard was established and involved mixing a slurry, casting a standard sample, total immersion of the sample in water for a specified period and measurement of moisture uptake. Apparatus which was used included silicone rubber molds for casting two inch cube gypsum samples, a blender for mixing the slurry, an oven and a constant temperature water bath which included supports for the cubes. In each instance, five hundred grams of stucco and four hundred grams of water was used to form the slurry along with varying amounts of the organosilicon mixture. The organosilicon mixture was employed in amounts of 1.5, 3.0 and 6.0 grams, corresponding respectively to weight percentages of 0.16, 0.33 and 0.66%. Water was placed in the blender and the organosilicon mixture was added to the blender and mixed briefly. The stucco was added to the blender and allowed to soak for about ten minutes. The contents of the blender were mixed on high speed for fifteen seconds and poured into the molds. The molds were tapped to remove any entrapped air and leveled with a spatula. Following setting, the cubes were removed from the molds and dried at 40°C. overnight. The dried cubes were weighed and submerged in the bath at 22°C. The cubes were allowed to soak in the bath for about two hours and were removed, patted dry and weighed. The amount

of water absorbed was calculated. The average moisture absorption of a cube which did not contain the organosilicon mixture of the present invention was found to be forty-eight percent. The weight gain in percent due to moisture absorption is indicated in the accompanying tables along with the percent by weight of the components of the organosilicon mixture. Unless otherwise indicated, the amount of the mixture which was employed is three grams.

TABLE I

<u>Emulsion</u> <u>(Percent by weight)</u>	<u>Silane Coupling Agent</u> <u>(Percent by weight)</u>	<u>Moisture Pickup</u> <u>(Percent)</u>
75	25	6.1
50	50	4.6
100	--	31.7
--	--	48.0

Table I indicates that cubes containing the mixture of the emulsion and the silane coupling agent were far more effective at repelling moisture than cubes containing only the emulsion and significantly better than cubes which did not contain the organosilicon mixture.

TABLE II

<u>Emulsion</u> <u>(Percent by weight)</u>	<u>Silane Coupling Agent</u> <u>(Percent by weight)</u>	<u>Moisture Pickup</u> <u>(Percent)</u>
100	--	15.5
95	5	9.5
90	10	10.0
80	20	4.1
70	30	2.7
60	40	4.0
50	50	0.9
40	60	0.9
30	70	21.2
20	80	48.8
10	90	47.1
--	--	48.0

It can be seen from Table II that the most effective range can be found when the mixture contains from about forty to eighty percent by weight of the emulsion and from about twenty to sixty percent by weight of the water soluble silane coupling agent. The optimum blend has been found to be a mixture including about seventy percent by weight of the emulsion and about thirty percent by weight of the water soluble silane coupling agent. Data for Table II was obtained in accordance with the procedure of Example V. Table III shows the results of more detailed tests conducted in accordance with Example V and wherein organosilicon mixtures of varying proportions were employed.

TABLE III

<u>Emulsion(A)</u> <u>(% by wt)</u>	<u>Coupling Agent(B)</u> <u>(% by wt)</u>	<u>Moisture</u> <u>(%)</u>	<u>Grams A + B</u>
90	10	29.4	1.5
90	10	5.0	3.0
90	10	0.9	6.0
80	20	28.6	1.5
80	20	3.3	3.0
80	20	0.6	6.0
70	30	27.3	1.5
70	30	2.3	3.0
70	30	0.9	6.0
60	40	17.0	1.5
60	40	2.0	3.0
60	40	0.7	6.0
50	50	39.8	1.5
50	50	3.3	3.0
50	50	0.4	6.0
40	60	42.9	1.5
40	60	10.9	3.0
40	60	0.3	6.0
--	--	48.0	---

It will be apparent from the foregoing that many other variations and modifications may be made in the compounds, compositions, structures and methods described herein without departing substantially from the essential features and concepts of the present invention. Accordingly, it should be clearly understood that the forms of the invention described herein are exemplary only and are not intended as limitations on the scope of the present invention as defined in the appended claims.

Claims:

1. A method of rendering masonry architectural building materials water repellent comprising incorporating into the masonry architectural building material an additive which is a mixture of (i) a water soluble silane coupling agent and (ii) an emulsion which includes water, at least one surfactant and a siloxane fluid, the siloxane fluid being selected from the group consisting of linear methylhydrogen siloxane polymers, linear methylhydrogen-methylalkyl siloxane copolymers, methylhydrogen cyclosiloxane polymers and methylhydrogen-methylalkyl cyclosiloxane copolymers.

2. The method of claim 1 wherein the masonry architectural building material is a gypsum wallboard.

3. A water repellent masonry architectural building material comprising an inorganic porous mineral substrate for forming the masonry architectural building material and an additive incorporated into the inorganic porous mineral substrate for rendering the masonry architectural building material water repellent, the additive being a mixture of (i) a water soluble silane coupling agent and (ii) an emulsion which includes water, at least one surfactant and a siloxane fluid, the siloxane fluid being selected from the group consisting of linear methylhydrogen siloxane polymers, linear methylhydrogen-methylalkyl siloxane copolymers, methylhydrogen cyclosiloxane polymers and methylhydrogen-methylalkyl cyclosiloxane copolymers.

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4. The material of claim 3 wherein the masonry architectural building material is a gypsum wallboard.

5. A composition for rendering masonry architectural building materials water repellent comprising a mixture of (i) a water soluble silane coupling agent and (ii) an emulsion which includes water, at least one surfactant and a siloxane fluid, the siloxane fluid being selected from the group consisting of linear methylhydrogen siloxane polymers, linear methylhydrogen-methylalkyl siloxane copolymers, methylhydrogen cyclosiloxane polymers and methylhydrogen-methylalkyl cyclosiloxane copolymers.

6. The composition of claim 5 wherein the silane coupling agent is an aminofunctional silane coupling agent selected from the group consisting of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, trimethoxysilylpropyldiethylenetriamine, aminopropyltriethoxysilane and bis(2-hydroxyethyl)-3-aminopropyltrimethoxysilane.