

July 13, 1954

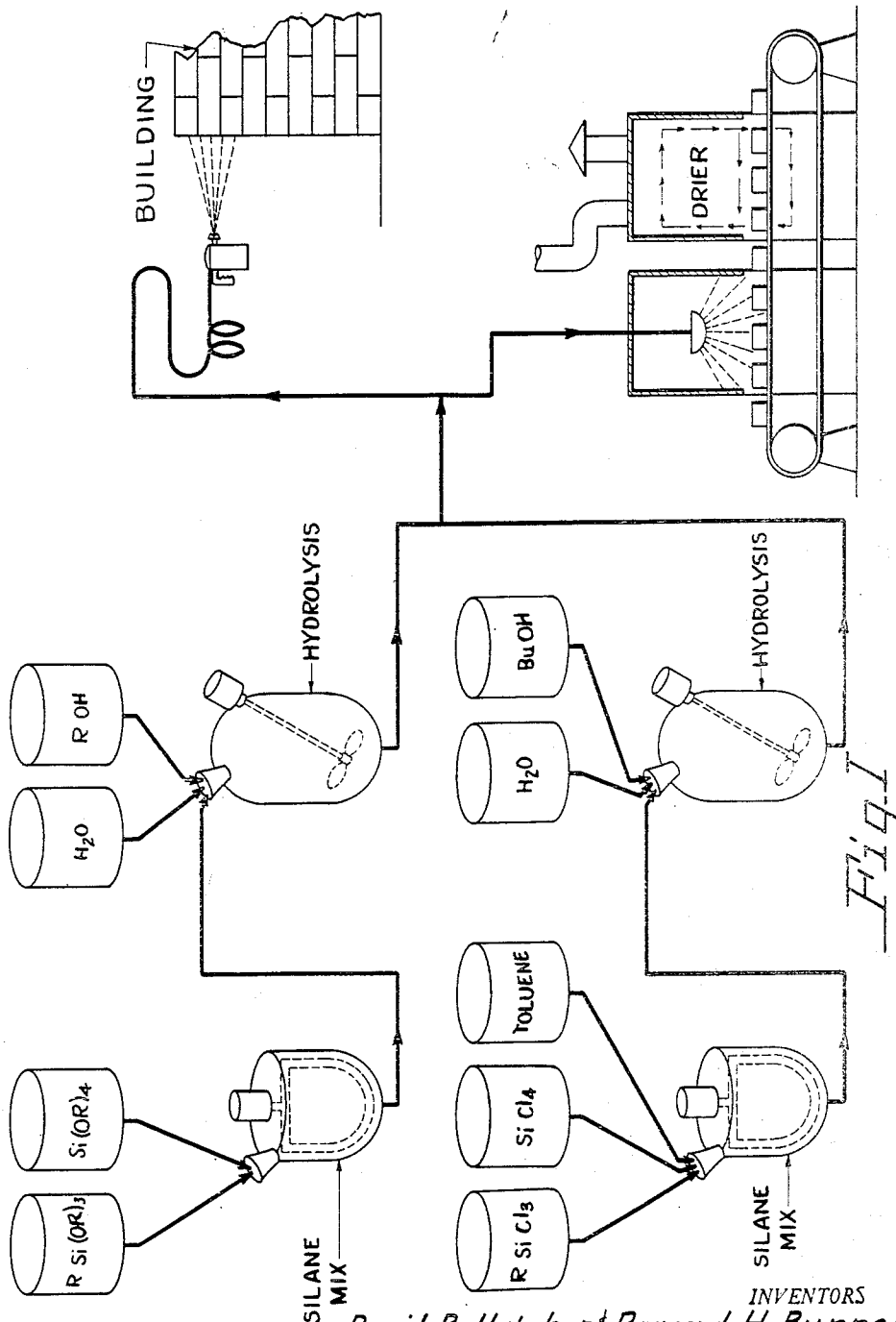
D. B. HATCHER ETAL

2,683,674

WATERPROOFING MASONRY WITH ALKYL POLYSILOXANES

Filed Aug. 7, 1950

2 Sheets-Sheet 1



INVENTORS
David B. Hatcher & Raymond H. Bunnell
BY

Marshall and Marshall
Attorneys

July 13, 1954

D. B. HATCHER ET AL

2,683,674

WATERPROOFING MASONRY WITH ALKYL POLYSILOXANES

Filed Aug. 7, 1950

2 Sheets-Sheet 2

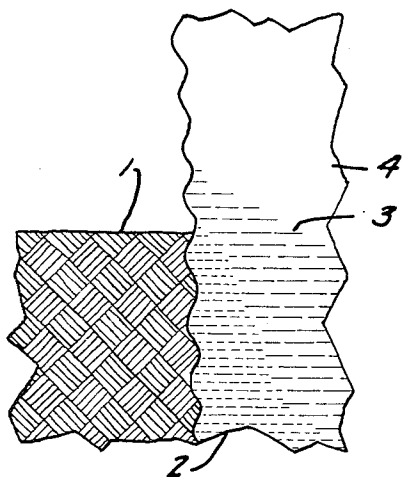


Fig. II

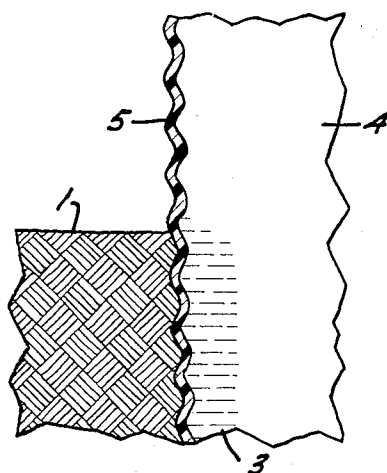


Fig. III

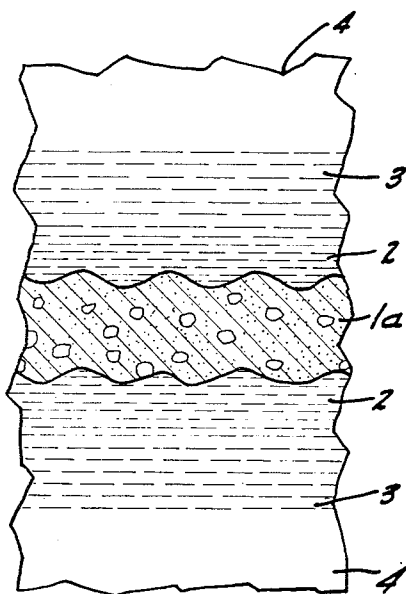


Fig. IV

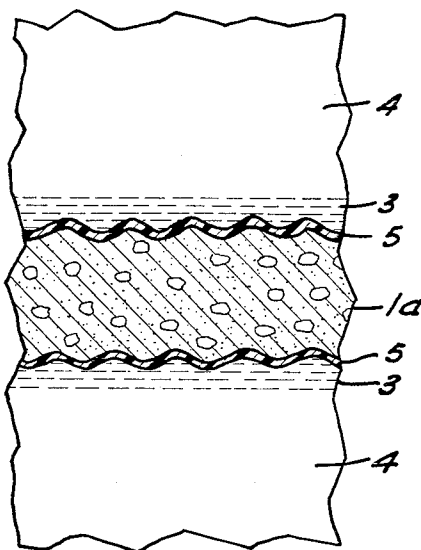


Fig. V

INVENTORS
David B. Hatcher & Raymond H. Bunnell
BY

Marshall and Marshall
Attorneys

UNITED STATES PATENT OFFICE

2,683,674

WATERPROOFING MASONRY WITH
ALKYL POLYSILOXANES

David B. Hatcher and Raymond H. Bunnell, Toledo, Ohio, assignors, by mesne assignments, to Allied Chemical & Dye Corporation, New York, N. Y., a corporation of New York

Application August 7, 1950, Serial No. 178,157

3 Claims. (Cl. 117—123)

1

2

The invention relates to the waterproofing of articles, particularly porous ceramic materials, by forming a water-repellent coating thereon.

The method heretofore used for increasing the water resistance of porous ceramic materials has consisted in applying to the surfaces of such ceramic materials a solution of aluminum stearate in a volatile solvent. Such treatment of the surfaces imparts water-repellency, but the water-repellency so imparted disappears after a relatively short period of months or years. Subsequent penetration of water, followed by freezing, then results in gradual weathering and disintegration of the ceramic material.

The principal object of the invention is the production of coatings of superior water-repellency. More specific objects and advantages are apparent from the description in which reference is had to the accompanying drawings illustrating preferred embodiments of the invention.

Figure I of the drawings is a diagram illustrating preferred methods of practicing the invention.

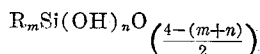
Figure II is an enlarged fragmentary cross-sectional view of a normal building foundation and moist earth adjacent thereto.

Figure III is a view that is the same as Figure II except that the foundation has been treated in accordance with the method of the invention.

Figure IV is an enlarged fragmentary cross-sectional view of masonry units held together by mortar as in a normal building structure.

Figure V is a view that is the same as Figure IV, except that the masonry units have been treated in accordance with the method of the invention.

A waterproofing composition embodying the invention, which is capable of forming coatings of superior water-repellency, comprises a substance having an average unit structure corresponding to the formula



wherein m is a number from 0.3 to 0.9; R is a primary aliphatic hydrocarbon radical having from three to nine carbon atoms; and not less than 30 per cent of the silicon atoms have such radicals attached thereto.

A substance having such an average unit structure is a substance of the type known as a siloxanol. The siloxanols that have been commonly known heretofore have been those containing lower alkyl radicals (usually methyl radicals and occasionally ethyl radicals). A silox-

anol having an average unit structure corresponding to the above formula would be a relatively unstable substance if R were methyl. Such a methyl siloxanol usually is prepared just before use and is cured by baking.

In contrast, the siloxanol in a waterproofing composition embodying the invention is a relatively stable substance, and after application to form a water-repellent coating, is allowed to remain in a partially condensed and uncured condition. Because of its stability, the siloxanol in a water-repellent coating produced in the practice of the invention does not become brittle, but remains substantially in its original condition and lasts indefinitely without cracking or crazing. Thus, the siloxanol in a water-repellent coating produced in the practice of the invention does not undergo appreciable further condensation upon exposure to the atmosphere.

If the value of " m " in the formula for the average unit structure of the siloxanol were below 0.3, the siloxanol would not be sufficiently stable. On the other hand, if the value of " m " were above 0.9, the siloxanol would produce unsatisfactory results because of its tendency to remain in a tacky condition.

A waterproofing composition embodying the invention is remarkably superior in effectiveness to a composition that is the same except that it contains a siloxanol in which the alkyl radicals are ethyl radicals, in that the same degree of water-repellency can be imparted by the application of a much smaller amount of solids per square foot in the use of a composition embodying the invention.

The striking improvement achieved in the waterproofing of porous ceramic materials using a volatile solvent solution of a composition embodying the invention has been demonstrated as follows:

Common sand mold bricks, which in the untreated state absorb a large amount of water, were treated on one flat side and on the four edges with one coat (approximately 10 grams) of one of the compositions specified in the first column of Table 1 below. The coating was applied to each brick using a paint brush one and one-half inches wide. After applying the coating to each brick, the brick was permitted to stand for 24 hours, weighed, and then placed with the flat, treated side down in a pan containing water at a depth of one-quarter inch. After four hours (practically all water absorption takes place in this time), the bricks were removed from the pans, wiped free of superficial moisture, and

weighed. From the increase in weight of each brick, the water absorbed by the brick was calculated as per cent of its former weight. (The terms "per cent" and "parts" are used herein to mean per cent and parts by weight unless otherwise designated.) Five bricks were used to test each composition specified in Table 1, and the average of the five results is given in Table 1 as the per cent of water absorbed. For the sake of comparison, untreated bricks were tested also in the same manner, the results being included in Table 1.

Composition A in Table 1 was a solution of a butylsiloxanol embodying the invention prepared by the following procedure:

A mixture of butyltrichlorosilane (310 grams), silicon tetrachloride (184 grams) and toluene (200 ml.) was added dropwise from a dropping funnel to a hydrolyzing solution consisting of water (1650 ml.), 1-butanol (425 ml.) and toluene (200 ml.) contained in a 4-liter beaker surrounded with ice water. The mixture in the beaker was stirred during the addition, and the rate of addition was adjusted so that the temperature of the solution never rose higher than 30 degrees C. When the addition from the dropping funnel, which required approximately one hour, was complete, the resinous layer was separated from the water layer in a separatory funnel, and the water layer was drawn off. The resin was washed with water (3 portions of 150 ml. each) containing enough salt to effect a more rapid separation (i. e., "salting out") of the resinous layer from the aqueous layer. The washed resin was then dried for sixteen hours over anhydrous sodium sulphate (about 35 grams). A commercial filter aid (10 grams of "Filtercel") was then added and the mixture was filtered. The filtrate was a clear water-white resin solution containing a solids content of 38.1 per cent.

Composition B in Table 1 was a solution of an ethylsiloxanol of approximately the same solids content which was prepared as described in the preceding paragraph except that ethyltrichlorosilane (392.4 grams) was used in place of the butyltrichlorosilane, and the amount of silicon tetrachloride employed was 102 grams.

Table 1

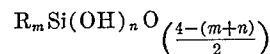
Waterproofing Composition	Percent Water Absorbed
A.....	0.53
B.....	8.55
None.....	19.5

From the results shown in Table 1, it is readily apparent that although a brick coated with an ethylsiloxanol solution (Composition B, which is in fact the best composition for waterproofing porous ceramic material heretofore known) absorbs considerably less water than an untreated brick, its water absorption is not nearly as low as the excellent water absorption of a brick coated with a composition of the invention (Composition A) when tested against a one-quarter inch head of water. (In the above demonstration the one-quarter inch head of water is roughly equivalent to a rain driven by a 20 miles per hour breeze.)

ALKYLSILOXANOL

For the sake of brevity, a substance having an

average unit structure corresponding to the formula



wherein m is a number from 0.3 to 0.9; R is a primary aliphatic hydrocarbon radical having from three to nine carbon atoms; and not less than 30 per cent of the silicon atoms have such radicals attached thereto is referred to hereinafter as an "alkylsiloxanol."

A primary radical having from three to nine carbon atoms (R in the above formula) may be a straight or branched chain primary alkyl radical having from three to nine carbon atoms such as, for example, a 1-propyl, 1-butyl, isobutyl, 1-pentyl, isoamyl, 1-hexyl, isohexyl, 1-heptyl, isoheptyl, 1-octyl, isooctyl, 1-nonyl or isononyl radical.

SILANE STARTING MATERIALS

An alkylsiloxanol embodying the invention may be produced by the controlled hydrolysis and condensation of a mixture of (1) one or more silanes having the general formula

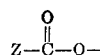


hereinafter referred to as alkylsilanes, and (2) one or more silanes having the general formula



hereinafter referred to as tetra-functional silanes, in which R is a primary alkyl radical having from three to nine carbon atoms, as hereinbefore described, x is an integer from one to three, Y is a hydrolyzable radical and Y' is a hydrolyzable radical or hydrogen. (Mixtures of alkylsilanes and mixtures of tetra-functional silanes may be employed.)

"Hydrolyzable radical" is used herein to include halo, alkoxy, amino, aroxy and acyloxy. The halo radical is any one having an atomic weight less than 80 (i. e., fluoro, chloro or bromo). The alkoxy radical is any primary or secondary alkoxy radical having from one to four carbon atoms (i. e., methoxy, ethoxy, propoxy, isopropoxy, n -butoxy, isobutoxy or secondary butoxy). Amino is simply the $-NH_2$ group. Aroxy radicals are any in which the aryl group is phenyl, or a mono-, di- or tri-substituted phenyl radical, each substituent being a primary, secondary or tertiary alkyl radical having from one to five carbon atoms, the total number of carbon atoms in the side chains being not more than five (i. e., the aryl radical is phenyl, or ortho-, meta- or para-methyl phenyl, any di- or tri-methyl phenyl, or any substituted phenyl in which the substituents are: one ethyl; one ethyl and one methyl; two ethyls; two methyls and one ethyl; two ethyls and one methyl; either propyl radical; either propyl radical and methyl; either propyl radical and two methyls; either propyl radical and ethyl; any butyl radical; any butyl radical and methyl; or any pentyl radical). The acyloxy radical has the general formula



in which Z is a saturated or unsaturated straight, branched or closed chain hydrocarbon radical having from one to eighteen carbon atoms, or phenyl or substituted phenyl, the substituents, if any, consisting of from one to three alkyl radicals each having from one to five carbon atoms, and all having a total of not more than five carbon atoms, as hereinbefore described.

Examples of alkyl that may be used as start-

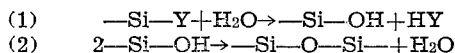
5

ing materials in the production of alkylsiloxanols embodying the invention include: 1-propyltrichlorosilane, 1-propyltrifluorosilane, 1-propyltriethoxysilane, dipropyldiethoxysilane, dipropyldichlorosilane, tripropylbromosilane, 1-butyltrichlorosilane, isobutyltrichlorosilane, 1-butyltriethoxysilane, isobutyltriethoxysilane, dibutyldifluorosilane, 1-butyltributoxysilane, 1-pentyltrichlorosilane, isoamyltrichlorosilane, 1-pentyltrifluorosilane, 1-pentyltriethoxysilane, diamyldifluorosilane, 1-hexyltrichlorosilane, 1-hexyltriethoxysilane, 1-heptyltrichlorosilane, and 1-octyltrichlorosilane.

Examples of tetra-functional silanes that may be used as starting materials in the production of alkylsiloxanols of the present invention include: ethyl orthosilicate, propyl orthosilicate, butyl orthosilicate, phenylorthosilicate, silicon tetrachloride, silicon tetrafluoride, silicochloroform, triethoxysilane, and silicon tetrabromide.

MOLECULAR STRUCTURE OF ALKYLSILOXANOL

The average number of hydrolyzable radicals determines, in part, the molecular structure that results after hydrolysis and condensation of silanes. ("Average number of hydrolyzable radicals," as used herein, signifies the total number of hydrolyzable radicals attached to the silicon atoms in the molecules of the silane starting materials divided by the total number of silicon atoms therein.) The reactions which occur during the course of the hydrolysis and condensation of silanes are understood to be represented by Equations 1 and 2 below:



in which Y is a hydrolyzable radical as hereinbefore described. Hydrolysis and condensation of a single silane having, attached to the silicon atom in the silane molecule, three hydrolyzable radicals yields cross-linked siloxanes; hydrolysis and condensation of a silane having two hydrolyzable radicals yields linear or cyclic siloxanes; while hydrolysis and condensation of a silane having one hydrolyzable radical yields disiloxanes. In general in a mixture of silanes the average number of hydrolyzable groups attached to the silicon atoms determines the molecular structure of the resulting siloxanes in much the same way. In the practice of the present invention only partial condensation of the products of the hydrolysis of the mixture of silanes is permitted to take place, so that the final hydrolysis products are not siloxanes but are partially condensed silanols (i. e., siloxanols).

The hydrolyzable radicals are removed from the silanes in the first step of hydrolysis so that it does not matter what hydrolyzable radicals are present in the silane starting materials. The significant radical for the purpose of the present invention is —OH, and any radical that is replaced upon hydrolysis by —OH can be used in the practice of the present invention. The least expensive and most readily available hydrolyzable radicals are usually preferred, but the by-products formed in the hydrolysis may also govern the choice of hydrolyzable radicals. For example, since highly toxic methyl alcohol is obtained in the hydrolysis of methoxysilanes, it is usually not desirable to hydrolyze silane mixture in which the hydrolyzable radicals are methoxy

6

radicals. The most desirable hydrolyzable radicals are ethoxy and chloro radicals.

It is desirable that all hydrolyzable radicals in any one mixture of alkylsilanes and tetra-functional silanes used in the production of compositions of the invention be the same. Halo radicals are more readily hydrolyzed than amino, acyloxy and alkoxy radicals so that the hydrolysis of, for example, a mixture of a butyltrihalosilane or butyldihaloethoxysilane with ethyl orthosilicate is not as readily controllable as the hydrolysis of, for example, a mixture of a butyltrihalosilane with silicon tetrachloride (or silicochloroform) or a mixture of butyltriethoxysilane with ethyl orthosilicate. Alkylsiloxanols embodying the invention cannot be readily prepared by the hydrolysis (and partial condensation) of a mixture of an alkyltriethoxysilane and silicon tetrachloride. The product of such hydrolysis gels since the silicon tetrachloride molecules hydrolyze and condense rapidly with each other before they can co-condense with hydroxy groups derived from the more slowly hydrolyzed alkyltriethoxysilane molecules.

As hereinbefore described the molecular structure of the siloxanols produced depends in part upon the average number of hydrolyzable radicals in the silanes used. This fact may be expressed in another way by saying that the molecular structure of the siloxanols depends upon the average number of non-hydrolyzable radicals attached to the silicon atoms in the silane molecules. The ratio r/Si in which r is the total number of non-hydrolyzable radicals attached to silicon atoms in the molecules of the siloxanols and Si is the total number of silicon atoms therein, represents the average number of non-hydrolyzable radicals. When the ratio of the total number of alkyl radicals to the total number of silicon atoms in the molecular structure of an alkylsiloxanol embodying the invention (i. e., the r/Si ratio or " m " in the formula given above corresponding to the average unit structure of an alkylsiloxanol) is too low, the siloxanol may not form a continuous flexible film when used as a waterproofing composition, but may form a film which cracks and becomes powdery. Furthermore, solutions of siloxanols of extremely low r/Si ratio tend to be so unstable as to be commercially unusable. In general, the r/Si ratio of an alkylsiloxanol embodying the invention is at least about 0.3 and it is preferable that it be at least about 0.4. It is most desirable that the r/Si ratio be at least about 0.5. When the r/Si ratio of an alkylsiloxanol is too high, such a siloxanol may not "dry" rapidly enough to be useful in the present method of waterproofing porous ceramic materials. In general the r/Si ratio of an alkylsiloxanol embodying the invention is not greater than about 0.9.

The distribution of the alkyl radicals attached to silicon atoms in the molecules of alkylsiloxanols is important. When less than 30 per cent of the silicon atoms in a mixture of an alkylsilane and a tetra-functional silane are attached to alkyl radicals, the product of the hydrolysis of the mixture ordinarily is not a partially condensed silanol but tends to be a gel, even if the hydrolysis is conducted at room temperature. Thus, at least 30 per cent of the silicon atoms in the molecules of an alkylsiloxanol embodying the invention are attached to alkyl radicals, and those alkylsiloxanols in which at least 50 per cent of the silicon atoms are attached to alkyl radicals are preferred.

PREPARATION OF ALKYL-SILOXANOL

In the preparation of alkylsiloxanols embodying the invention it is most desirable to hydrolyze a mixture of monoalkyl- and tetra-functional silanes, for the hydrolysis (and partial condensation) can be easily controlled to obtain siloxanols having any desired r/Si ratio within the limits hereinbefore specified. For example, hydrolysis (and partial condensation) of a mixture of 30 mole per cent of butyltriethoxysilane with 70 mole per cent of butyl orthosilicate may be conducted to yield a siloxanol having an r/Si ratio of about 0.3, whereas upon reversal of the molar proportions of silanes in the mixture, a siloxanol having an r/Si ratio of about 0.7 may be obtained. Although monoalkylsilanes may comprise from 30 mole per cent to 90 mole per cent of a mixture to be hydrolyzed which contains only tetra-functional silanes in addition to monoalkylsilanes, usually it is desirable that the monoalkylsilanes comprise from 50 to 90 mole per cent of such a mixture. Monoalkylsilanes are much less expensive to use than dialkyl- and trialkylsilanes, whose preparation is more expensive, even though the mole per cent of pure dialkyl- or trialkylsilane required in the hydrolysis of a mixture of such silane with a tetra-functional silane to obtain a siloxanol having a given r/Si ratio may be proportionately lower than the mole per cent of pure monoalkylsilane required to obtain the same r/Si ratio. Since not less than about 30 per cent of the silicon atoms in a mixture of alkyl- and tetrafunctional silanes to be hydrolyzed must have alkyl radicals attached thereto, a pure dialkylsilane cannot be hydrolyzed in admixture with a tetra-functional silane to obtain a siloxanol having an r/Si ratio less than about 0.6, and a pure trialkylsilane cannot be hydrolyzed in admixture with a tetra-functional silane to obtain a siloxanol having an r/Si ratio less than about 0.9. Furthermore, siloxanols prepared from mixtures containing dialkyl- and trialkylsilanes do not dry as rapidly as siloxanols produced from mixtures containing only monoalkylsilanes, in addition to tetra-functional silanes. It is more difficult to control the r/Si ratio of siloxanols prepared from mixtures containing dialkyl- and trialkylsilanes since some hexaalkyldisiloxane (when trialkylsilanes are used) and hexaalkylcyclotrisiloxane (when dialkylsilanes are used) usually tend to form, thus decreasing the yield of the desired alkylsiloxanol. Thus, alkylsiloxanols embodying the invention are most desirably prepared by a method that includes either (1) the hydrolysis of a mixture of an alkyltriethoxysilane and ethyl orthosilicate or (2) the hydrolysis of a mixture of an alkyltrichlorosilane and silicon tetrachloride (or silicochloroform), as shown in Figure I, the molar proportions of monoalkylsilane and tetra-functional silane being within the ranges hereinbefore described.

HYDROLYSIS

Both methods (1) and (2) are equally suitable for the preparation of alkylsiloxanols embodying the invention having an r/Si ratio of about 0.6 or higher. The hydrolysis of a mixture of an alkyltrichlorosilane and silicon tetrachloride is advantageous in that an alkyltrichlorosilane is more readily prepared than an alkyltriethoxysilane (which is usually prepared by reacting ethyl alcohol with the corresponding alkyltrichlorosilane). However, a dilute solution of hydrochloric acid is obtained as a by-product from

such a hydrolysis reaction, which causes disposal problems as well as loss of hydrogen chloride. On the other hand, although the hydrolysis of a mixture of an alkyltriethoxysilane and ethyl orthosilicate involves an extra processing step in the preparation of the ethoxysilane, anhydrous hydrogen chloride may be recovered from the preparation of the ethoxysilane and reused, for example, in the preparation of silicochloroform. Furthermore, alkylsiloxanols embodying the invention of any desired r/Si ratio may be prepared by hydrolysis of a mixture of an alkyltriethoxysilane and ethyl orthosilicate, whereas alkylsiloxanols having an r/Si ratio lower than 0.6 cannot be readily prepared by the hydrolysis of a mixture of an alkyltrichlorosilane and silicon tetrachloride since silicon tetrachloride hydrolyzes rapidly and gels when the number of hydrolyzable radicals in the mixture to be hydrolyzed is high.

In order to be useful in the method of the present invention, the alkylsiloxanols must be soluble in a volatile solvent, as hereinafter discussed. Thus, the average number of hydroxyl groups per silicon atom in the molecular structure of an alkylsiloxanol which may be used in the present method (i. e., as represented by " n " in the formula given above which corresponds to the average unit structure of an alkylsiloxanol) must be large enough for the siloxanol to be soluble. However, the resin must be sufficiently condensed so that it has the desired molecular weight and viscosity; i. e., " n " must not be too large. In general, the ratio between the hydroxy groups and the oxygen atoms attached to silicon atoms is variable, and although the proportion of hydroxyl groups attached to silicon atoms in a freshly prepared solution of an alkylsiloxanol may be relatively high, this proportion tends to decrease gradually upon application of the solution in accordance with the present method.

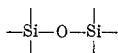
It is understood, of course, that when a tetra-functional silane whose molecule contains a hydrogen atom attached to a silicon atom (e. g., silicochloroform) is used in the production of the alkylsiloxanols of the invention, hydrogen atoms are present in place of some of the hydroxy groups which are represented in formula for the average unit structure of the siloxanols. No difference in the properties of the siloxanols can be detected, however, when hydrogen atoms are present in place of some of the hydroxy groups.

When the hydrolyzable radicals in a mixture of alkyl- and tetra-functional silanes to be hydrolyzed (and partially condensed) in the preparation of alkylsiloxanols embodying the invention are less readily hydrolyzable than halo radicals (e. g., ethoxy radicals in a mixture of an alkyltriethoxysilane and alkyl orthosilicate), a carefully controlled hydrolysis reaction may be conducted, as hereinafter described, in a hydrolyzing solution of an inorganic acid in water, using a mutual solvent for the silanes and the hydrolyzing solution.

When the hydrolyzable radicals in the mixture of silanes to be hydrolyzed (and partially condensed) in the preparation of siloxanols embodying the invention are readily hydrolyzable radicals such as halo radicals (e. g., chloro radicals in a mixture of an alkyltrichlorosilane and silicon tetrachloride) the hydrolyzing agent may be water alone, the hydrolysis being conducted in the presence of a suitable solvent for the silanes, as hereinafter discussed.

The carefully controlled hydrolysis reaction by which alkylsiloxanols embodying the invention are obtained may be conducted by adding the mixture of alkyl- and tetra-functional silanes to the hydrolyzing solution at a rate sufficiently slow that the exothermic hydrolysis reaction does not cause local overheating (e. g., at such a rate that one mol of silanes is added in from about 10 to about 20 minutes). It is usually desirable that the hydrolyzing solution be stirred during the silane addition; otherwise, local overheating may result in spite of a slow rate of silane addition. It is often desirable to hydrolyze halosilanes with a water-ice slurry; the hydrolysis producing a hydrohalic acid which then serves as a catalyst for further hydrolysis. The mineral acids that are used as hydrolysis catalysts for less readily hydrolyzable radicals such as alkoxy and aroxy radicals include hydrochloric, sulfuric and phosphoric, hydrochloric usually being preferred. The amount of hydrolyzing solution that is used includes at least enough water to effect complete hydrolysis of the silanes (i. e., at least one gram mol of water for every two gram atoms of hydrolyzable radicals in the silanes to be hydrolyzed). When the mixture of silanes contains hydrolyzable radicals that are halo radicals, it is usually advantageous to use an excess of water, e. g., from 5 to 10 gram mols for every two gram atoms of hydrolyzable radicals, in order to dilute the hydrohalic acid that is formed, but it is ordinarily not advantageous to use more than about 20 gram mols of water for every two gram atoms of hydrolyzable radicals.

When a mixture of an alkyltrichlorosilane and silicon tetrachloride is hydrolyzed in the production of an alkylsiloxanol having an r/Si ratio between about 0.6 and about 0.9, it is necessary to conduct the hydrolysis in the presence of certain solvents in order to avoid gelling of the products of the hydrolysis. Suitable solvents include any alcohol which is substantially insoluble in water but has some miscibility in water (e. g., 1-propanol, 1-butanol or a higher alcohol having up to eight carbon atoms, or mixtures thereof) used in admixture with any aromatic hydrocarbon which is ordinarily employed as a solvent for silanes (e. g., benzene, toluene, or xylene) or mixtures thereof. In general, about equal parts by volume of the aromatic hydrocarbon (preferably toluene) and alcohol (preferably 1-butanol) are used, as shown in Figure I. Usually it is desirable initially to divide the aromatic hydrocarbon solvent equally between the silane mixture and the hydrolyzing solution. (It is believed that the partially miscible alcohol solvent avoids confining the hydrolysis of chlorine atoms attached to silicon atoms to an interphase (between water and a solvent insoluble in water), at which there is an insufficiency of water which results in the rapid formation of



bonds and subsequent gelling. An aromatic hydrocarbon such as toluene acts as a diluent to prevent local high concentration of silicon tetrachloride and resultant gelation. (Toluene is insoluble in water and cannot be used alone without causing the reaction to take place at the interphase between the toluene and the water.) Higher ketones such as methylisobutylketone, methylisoamylketone, and amylethylketone, may also be used as solvents for the silanes without danger of gelling of the hydrolysis products. A

higher ketone is sufficiently miscible with water that it prevents the reaction from taking place at an interphase, but requires no diluent for the silanes since it does not react with the silanes as an alcohol does.)

A mutual solvent (i. e., a solvent for both the hydrolysing solution and the silanes) which is used for the carefully controlled hydrolysis of a silane mixture containing less readily hydrolyzable radicals than halo radicals may be a lower ketone (e. g., acetone, methylethylketone or diethylketone) or a lower alcohol (e. g., ethanol, 1-propanol or 1-butanol).

It is usually desirable to use a substantial amount of a solvent or solvents for just the silanes (e. g., from about 100 to about 300 ml. of solvents per gram mol of silanes, or even more when the silane mixture is particularly easy to hydrolyze), although for silane mixtures that are hydrolyzable only with comparative difficulty (e. g., a mixture of an alkyltriethoxysilane and ethyl orthosilicate, with which a mutual solvent is preferred), considerably less solvent may be used (e. g., approximately 70 ml. per gram mol of silanes).

It has been found that the hydrolysis is usually substantially complete within from about 5 to about 10 minutes after the addition of the silane to the hydrolyzing solution has been completed. (Apparently, leaving the silane in contact with the hydrolyzing solution for longer periods of time has no deleterious effect on the resulting products.)

When a two-phase hydrolysis reaction has been conducted (i. e., using a solvent or mixture of solvents for just the silanes as, for example, in hydrolyzing a mixture of an alkyltrichlorosilane and silicon tetrachloride), the silane layer is allowed merely to separate from the water layer (e. g., in a separatory funnel) and the water layer is drawn off. The separated organic solution of the hydrolysis products (i. e., siloxanols) is then washed with water and dried (e. g., over a drying agent such as anhydrous calcium chloride or anhydrous sodium sulfate). The drying agent is then removed (e. g., by filtration).

When the hydrolysis reaction is conducted with a mutual solvent and is considered to be approximately complete, the mixture of liquid is separated into two components (e. g., by solvent extraction using a solvent which is not miscible with water, such as diethyl ether). It is usually desirable then to extract the water layer again. In the hydrolysis of a mixture of ethyl orthosilicate and an alkyltrialkoxysilane, it is desirable to use only the amount of water theoretically required to hydrolyze all of the silanes so that a separation into two components is not necessary. The mixture, after addition to the hydrolyzing solution, is allowed to stand for at least twelve hours and preferably about twenty-four hours to permit completion of the hydrolysis (and partial condensation) reaction. The preparation of alkylsiloxanols by the hydrolysis of a mixture of an alkyltriethoxysilane and ethyl orthosilicate is advantageous in that siloxanols of any desired r/Si ratio may be prepared without danger of gelation merely by mixing the desired amount of the silane reactants with water and a mutual solvent and allowing the mixture to stand for at least twelve hours. Since ethanol is formed during the hydrolysis, it is usually desirable to use ethanol as the mutual solvent.

In addition to the alkylsiloxanols hereinbefore described, compositions embodying the invention

may comprise other substances. For example, the mixture of silanes which is hydrolyzed in the preparation of compositions of the invention may contain small quantities of methylsilanes, ethylsilanes and arylsilanes, e. g., methyltrichlorosilane, ethyltrichlorosilane and phenyltrichlorosilane. However, such silanes should comprise not more than about 20 mole per cent and preferably not more than about 10 mole per cent of the silanes to be hydrolyzed, since their use may make a waterproofing coating too brittle. The ethylsilanes and particularly the methylsilanes have the added disadvantage that they produce serious difficulties by causing an excessive tendency to gel during hydrolysis of such mixtures. Furthermore, the silanes used in the preparation of alkylsiloxanol compositions of the invention may comprise halo-substituted alkylsilanes in which there are not more than three halogen atoms per alkyl radical, and in which each halogen has an atomic weight less than 80 and is attached to a carbon atom which is not in the beta-position in an alkyl radical. (Beta-haloalkylsilanes cannot be used, since under the hydrolysis conditions hereinbefore described they tend to decompose, with the splitting off of an olefin from the silane molecule.) Halo-substituted alkylsilanes which may be used in the preparation of compositions embodying the invention include: alpha-chloropropyltrichlorosilane, alpha-chlorobutyltrichlorosilane, gamma-chloropropyltrichlorosilane, gamma-chlorobutyltrichlorosilane and delta-chlorobutyltrichlorosilane. Such silanes should comprise not more than about 20 mole per cent and preferably not more than about 10 mole per cent of the silanes to be hydrolyzed. The use of such silanes in larger amounts should be avoided in the preparation of a composition of the invention which may be applied as a water-repellent coating on a ceramic material, since there is danger that such silanes may liberate HCl, which would, of course, be harmful to the ceramic material.

The alkylsiloxanol compositions embodying the invention are particularly useful in the present method of waterproofing porous ceramic materials, which comprises applying a coating of a volatile solvent solution of an alkylsiloxanol, as hereinbefore defined, on the porous ceramic material and drying the coated material.

POROUS CERAMIC MATERIAL

The term "ceramic materials" includes all products which are manufactured entirely or chiefly from raw materials of an earthy nature, as distinguished from those of a metallic or organic nature, and in whose manufacture a high-temperature treatment is involved. The present method of waterproofing is applicable to porous ceramic materials, the word "porous" being used herein to mean a material having sufficient porosity that upon standing in one-quarter inch of water at room temperature for 24 hours it absorbs more than 1 per cent of its weight in water. Thus, the term "porous" distinguishes ceramic materials to which the present method is applicable from glazed ceramic materials which may be classified as glass, pottery or enameled metals. Porous ceramic materials include: structural ceramics such as common brick, paving brick, face brick, sewer pipe, drain tile, hollow block, terra cotta, conduits, roofing tile, and flue lining; cements and plastics such as Portland cement, calcined gypsum products (i. e., molding and building plaster and stucco), and magnesia cement; and insulation products such

as electrical insulators (porcelain spark plugs, etc.) and thermal insulators (diatomaceous earth brick). The present method is most applicable to masonry, i. e., to all articles and architectural structures of such porous ceramic materials as stone, brick, tiles, artificial stone, adobe, etc., and to ceramic articles, particularly masonry units (i. e., bricks, pieces of stone, etc.), which in masonry are generally held together or made a single mass by mortar, plaster or earth.

The porous ceramic materials should be dry when treated with a waterproofing composition by the present method.

METHOD OF WATERPROOFING

In accordance with the present method, a volatile solvent solution of an alkylsiloxanol embodying the invention may be applied to a porous ceramic material by spraying, brushing, dipping, or any other method by which the solution can be conveniently applied to coat the surface of the porous ceramic material. The volatile solvent serves the same function in a waterproofing composition used in the present method as the solvent in any resinous coating composition, i. e., it dilutes the composition so that it can be readily applied by spraying, brushing, dipping or any of the usual methods of application. In general, the amount of solvent should be sufficient to dilute the siloxanol solution to a concentration of from about 5 to about 35 per cent solids, and preferably from about 8 to about 10 per cent solids. (It has been preferable to apply ethylsiloxanol solutions, which have been used in the best method heretofore known for the waterproofing of porous ceramic materials, in higher solids content, for example, from about 15 to about 25 per cent). It is usually impractical to use a solution of higher concentration, not only from the standpoint of economy, but also because a solution of too high a concentration may form a thick coating which may seal the pores of a ceramic material such as masonry and prevent "breathing" of the masonry. Evaporation of water from the surface, i. e., "breathing" or transpiration, is believed to be important in maintaining the integrity of ceramic materials, particularly masonry structures. For example, if through a break in the mortar, water gets into a masonry structure whose pores are sealed, the structure may crack when the temperature drops below freezing, since the water cannot escape by evaporation through the pores at the surface of the masonry. A coating applied to a porous ceramic material in accordance with the present method does not seal the pores of the material but penetrates the pores to form a water-repellent coating therein, and thus does not prevent the free passage of water vapor through the material. Water in its liquid form, however, cannot readily penetrate the highly water-repellent coating. Thus, a ceramic article embodying the invention which has been rendered water-repellent in accordance with the present method is still porous and is capable of "breathing."

The fact that a water-repellent coating applied to a porous ceramic material in accordance with the present method penetrates the pores of the material has been demonstrated as follows: A common sand mold brick was coated on all six sides with a solution of the butylsiloxanol hereinbefore referred to as composition "A." The brick was broken in half, and immersed in a pan of water for a few hours with the uncoated broken surface down. Examination of the brick upon removal from the water showed that the entire

cross-section of the brick except for a narrow (about $\frac{1}{8}$ inch) margin around the cross-section of the brick was dark from the impregnation of water. The narrow margin around the cross-section of the brick was dry because the alkylsiloxanol solution had penetrated the pores of the brick and thus prevented the passage of liquid water into the coated pores. In Figures II, III, IV and V the portion 4 of a porous ceramic material which contains only the amount of water vapor that is normally breathed from the atmosphere through the pores is indicated by the absence of dashed lines. A high concentration of liquid water is represented by more dense dashed lines 2 and a high concentration of water vapor is represented by less dense dashed lines 3. Thus, Figure II shows that in an ordinary building foundation, a layer 2 of liquid water penetrates the portion that is adjacent a moisture source 1 (i. e., the earth) and that although this layer of liquid water diminishes gradually as the distance from the moisture source increases (some of it vaporizes through the pores that are not adjacent the moisture source) to form a surrounding layer 3 of highly concentrated water vapor, so much liquid water is able to penetrate the foundation that a layer of actual water 2 is retained in the interior of the foundation material.

On the other hand, as shown in Figure III, liquid moisture from the earth 1 cannot penetrate a foundation which has been treated with a water-repellent coating 5 in accordance with the present method. Although a light layer of highly concentrated water vapor 3 exists at the points of direct contact of the earth with the foundation, the water-repellent coating prevents penetration of liquid water into the foundation material. The foundation material treated in accordance with the present method is still porous so that the light vaporous layer 3 "breathes off" through the pores of the foundation material and is not retained in the material.

An important embodiment of the present invention is a porous ceramic article, particularly a masonry unit, which has been treated in accordance with the present method. As indicated in Figure I, the present method comprises applying a waterproofing composition preferably prepared by the hydrolysis of either a mixture comprising an alkyltrichlorosilane and silicon tetrachloride or a mixture comprising an alkyltriethoxysilane and ethyl orthosilicate to a masonry structure (e. g. a building), or to the masonry units themselves which are then dried. The advantages in the use of masonry units which have been rendered water-repellent before they are used in masonry construction are readily apparent. For example, during the construction of masonry in hot, dry climates, it is ordinarily necessary to keep wetting the newly erected masonry in order to prevent the masonry units from drawing moisture from the mortar (such withdrawal of moisture would prevent the mortar from setting properly). The use of water-repellent masonry units embodying the invention eliminates the necessity for keeping the units wet, for the water from the mortar is no longer soaked up by the water-repellent masonry units, and the only loss of water is the small amount which evaporates at the edges of the mortar joints, this slight loss taking place so slowly as not to interfere with the setting of the mortar. As shown in Figure IV, water from a moisture source 1a (i. e., mortar) readily penetrates ordinary masonry units. The high concentration of

liquid water 2 at the mortar joint diminishes gradually as the distance from the joint increases (some of it vaporizes through the pores that are not adjacent the moisture source) to form a layer of highly concentrated water vapor, but some moisture impregnates nearly the whole masonry unit and is retained in the interior of the unit. On the other hand, as shown in Figure V, liquid moisture from mortar cannot penetrate masonry units which have been treated with a water-repellent coating 5 in accordance with the present method. No liquid water is soaked into the masonry units and the light layer of highly concentrated water vapor which forms at the mortar joints evaporates through the pores of the masonry and does not remain in the interior of the units.

Although the ethylsiloxanol solutions applied in accordance with the best waterproofing method heretofore known, like the resins of the present invention, do not seal the pores of a ceramic material but penetrate the pores to form a water-repellent coating therein such resins are not nearly as effective waterproofing agents as the resins of the invention used in the present method, as hereinbefore demonstrated. Furthermore, the solutions of the alkylsiloxanols embodying the invention in general are much more stable than the solutions of ethylsiloxanols heretofore known for the waterproofing of porous ceramic materials. Coatings produced from ethylsiloxanol solutions tend to cure to brittle films more rapidly than coatings of the alkylsiloxanols of the invention, and may crack and form non-continuous coatings within a shorter period of time than coatings of the present resins.

The amount of a volatile solvent solution of an alkylsiloxanol embodying the invention required to form a water-repellent coating upon a porous ceramic material depends, of course, upon the porosity of the ceramic material and the severity of the weathering conditions to which the material is exposed. In general, the maximum required amount of a solution having a solids concentration within the ranges hereinbefore described is not more than about one gallon per 25 square feet of area, and usually it is not more than one gallon per 75 to 100 square feet of area. In some cases as little as one gallon per 200 square feet may be highly effective, although usually it is preferable to apply not less than one gallon per 125 square feet. Such limitations are, of course, arbitrary and may be varied widely when the ceramic materials employed are relatively dense or extremely porous, the optimum amounts of waterproofing resin solutions in such cases being best determined by experiment. In any event, the resin solutions employed in the present method have such good penetrating power that a single coat is sufficient to impart excellent water repellency. In contrast, aluminum stearate solutions which have been among the best waterproofing agents heretofore known, do not penetrate a porous ceramic material and are absorbed too slowly to be effective when applied in a single coat. That is, since an aluminum stearate solution does not penetrate the pores of a ceramic material, a single coat is soon worn off the material. Furthermore, a coating of aluminum stearate cannot be applied to a porous ceramic material in cool weather, e. g., at temperatures below 50 degrees F., because a solution of aluminum stearate at lower temperatures tends to be so stiff and gel-like that it does not have even the slight penetrating power it has when applied at higher temperatures.

Coatings of alkylsiloxanols embodying the invention dry to a non-tacky state, upon exposure to the atmosphere, rapidly enough to be commercially useful in the present method of waterproofing porous ceramic materials. The solvents in which the present alkylsiloxanols are used in waterproofing should, of course, be sufficiently volatile to permit the water-repellent coatings applied to porous ceramic materials in accordance with the present method to dry rapidly to a non-tacky state. Although it is only necessary that the volatility of a solvent used in the present method be such that the solvent will evaporate at atmospheric temperatures within about one week, ordinarily it is preferable that the solvent evaporate within about two days, and it is most desirable that the solvent evaporate more rapidly, e. g., within about twenty-four hours, so that an alkylsiloxanol used in such a solvent hardens in place before it has a chance, in its diluted, low viscosity state, to run down and thus form an uneven coating upon the ceramic material to which it is applied.

The volatile solvent solutions of alkylsiloxanols employed in the present method may contain a pigment (or pigments) suspended therein (i. e., the waterproofing solution may be a paint composition). Ordinarily such compositions are those in which the resin solids concentration is within the upper part of the ranges hereinbefore described and the proportion of pigment is approximately equal in weight to the proportion of resin solids in the volatile solvent solution. In the case of a waterproofing composition used in the present method which contains a pigment, the volatility of the solvent should be sufficiently great so as to prevent "flooding" of the pigment (i. e., a change in color at the surface of the paint film caused by a concentration at the surface of the paint film of one of the ingredients of the pigment portion).

All of the solvents hereinbefore described which may be used in the preparation of alkylsiloxanols embodying the invention are suitable solvents in which to apply such resins in the waterproofing of porous ceramic materials by the present method. Thus, the alkylsiloxanol solution, as prepared, may have the proper concentration to be used directly in the present method, or may only require further dilution with the solvent (or mixture of solvents) in which it was prepared, or further concentration (e. g., by evaporation of part of the solvent) if too dilute upon preparation. If desired, however, the solvent (or mixture of solvents) in which the alkylsiloxanol is prepared may be removed and replaced with any solvent which is sufficiently volatile to be used in the present method. (For example, it is preferable to use ethanol as a solvent in the hydrolysis of a mixture of an alkyltriethoxysilane and ethyl orthosilicate since ethanol is also obtained as a by-product from such a reaction. Because ethanol has such a low flash point, it may be desirable in the practice of the present method to recover the pure ethanol by vacuum distillation and substitute a less hazardous solvent in which to apply an alkylsiloxanol as a water-repellent coating.) Suitable volatile solvents in addition to those hereinbefore described for use in the preparation of alkylsiloxanols embodying the invention include, for example, ethers, such as diethyl, ethylpropyls, dipropyls and propylbutyls and cyclic ethers such as dioxane, and hydrocarbon solvents such as benzene, toluene, xylenes, hexanes, heptanes and octanes. These

solvents may not be desirable, however, for the alkylsiloxanols of low (e. g., less than 0.6) r/Si ratio (prepared by the hydrolysis of a mixture of an alkyltriethoxysilane and ethyl orthosilicate) which tend to be somewhat unstable in nonpolar solvents. For example, a sample of a 1-butylsiloxanol resin solution having an r/Si ratio of about 0.5 (prepared as described in Example 1a, below) which is distilled under reduced pressure to remove all ethanol solvent, and is then diluted with xylene to about a 50 per cent solids concentration, gels within five days upon standing at atmospheric temperatures. On the other hand, three other samples of the same resin which are distilled under reduced pressure to remove all ethanol and are then dissolved in 1-butanol (60 per cent solids), methylethylketone (40 per cent solids) and a mixture of 25 per cent of methylethylketone and 75 per cent of toluene (40 per cent solids), respectively are stable for six months or longer at atmospheric temperatures. Ordinarily, however, it is preferable to employ any alkylsiloxanol embodying the invention in a volatile solvent (or mixture of solvents) in which it may be prepared, since removal of the solvent (e. g., by distillation under vacuum) always involves danger of gelling the hydrolysis products during the distillation.

Upon drying to a non-tacky state, a water-repellent coating of an alkylsiloxanol applied in accordance with the present method forms a continuous flexible film that prevents the ingress of any appreciable amount of water into a porous ceramic material. Furthermore, the flexibility of the film deposited in the crevices of the porous ceramic material (e. g., masonry units such as brick or stone) allows expansion and contraction of the material in hot and cold weather without cracking of the film. The ability of the resin solutions employed in the present method to penetrate porous ceramic materials results in water-repellent coatings that have excellent permanency. For example, whereas an aluminum stearate coating applied to a porous ceramic material which is subjected to certain weathering conditions might have to be replaced within two or three years in order to retain the maximum waterproofing effect (and probably would need to be applied in two coats, for reasons hereinbefore explained), a single coat of one of the resin solutions which may be employed in the present method applied to a similar porous ceramic material and subjected to similar weathering conditions would last at least two or three times as long as the aluminum stearate coating, for example five to eight years, and might be highly effective for a considerably longer period.

Not only are the waterproofing compositions embodying the invention useful in the present method of waterproofing porous ceramic materials, but they are also highly effective in the waterproofing of paper, leather, and textiles. For example, a very dilute (approximately 1 to 5 per cent solids concentration) solution or emulsion of a waterproofing composition embodying the invention may be applied to paper in accordance with any standard method employed in the art of coating paper. Since a rapid cure is usually desirable, a lead drier may be used with the waterproofing composition in order to obtain a coating which cures at a temperature of about 100 to 150 degrees C. in five minutes or less. The cured paper has good water-repellency. Very dilute solutions or emulsions of compositions of the invention may be applied to textiles to impart

water-repellency. Again it is usually desirable to incorporate a lead drier in the composition in order to permit the coated material to cure in a few minutes at a temperature of about 100 to 120 degrees C.

The waterproofing compositions of the invention are also useful as electrical insulating varnishes. For example, paper may be re-coated (e. g., from two to four times) by the procedure described above until the desired thickness of a hard, flexible coating is obtained. The resulting coated paper has good electrical properties which make it useful in many applications, e. g., as a cable wrap.

The following examples illustrate the practice of the invention:

Example 1

Butylsiloxanol waterproofing compositions embodying the invention having various r/Si ratios are prepared as follows:

(a) A butylsilane (0.25 mol of 1-butytriethoxysilane), a tetra-functional silane (0.25 mol of ethyl orthosilicate), a solvent (39.4 grams of "Shellacol", a denatured alcohol consisting of 92.5 per cent of ethanol and 7.5 per cent of water) and an acid hydrolyzing solution (13.8 ml. of a solution prepared by diluting 1 part by volume of 37 per cent hydrochloric acid with six parts by volume of water) are mixed and the mixture is allowed to stand at room temperature for twenty-four hours. The resulting resin has an r/Si ratio of about 0.5

(b) The procedure described in (a) is repeated using the following proportions of the ingredients to obtain a resin having an r/Si ratio of about 0.3:0.15 mol of 1-butytriethoxysilane; 0.35 mol of ethyl orthosilicate; 40 grams of "Shellacol"; and 15 ml. of the acid hydrolyzing solution.

(c) The procedure described in (a) is repeated using the following proportions of the ingredients to obtain a resin having an r/Si ratio of about 0.4:0.2 mol of 1-butytriethoxysilane; 0.3 mol of ethyl orthosilicate; 40.26 grams of "Shellacol"; and 13.93 ml. of the acid hydrolyzing solution.

(d) The procedure described in (a) is repeated using the following proportions of the ingredients to obtain a resin having an r/Si ratio of about 0.7:0.35 mol of 1-butytriethoxysilane; 0.15 mol of ethyl orthosilicate; 40.94 grams of "Shellacol"; and 12.46 ml. of the acid hydrolyzing solution.

Example 2

Propylsiloxanol waterproofing compositions embodying the invention having various r/Si ratios are prepared as follows:

(a) A propylsilane (0.25 mol of 1-propyltriethoxysilane), a tetra-functional silane (0.25 mol of ethyl orthosilicate), a solvent (39.16 grams of "Shellacol"), and 13.63 cc. of the acid hydrolyzing solution prepared as described in Example 1(a), are mixed and the mixture is allowed to stand for twenty-four hours. The resulting resin has an r/Si ratio of about 0.5. A film of the resin on a glass plate dries tack-free at room temperature.

(b) The procedure described in (a) is repeated using the following proportions of the ingredients to obtain a resin having an r/Si ratio of about 0.3:0.15 mol of 1-propyltriethoxysilane; 0.35 mol of ethyl orthosilicate; 39.24 grams of "Shellacol"; and 14.47 ml. of the acid hydrolyzing solution.

(c) The procedure described in (a) is repeated using the following proportions of the ingredients to obtain a resin having an r/Si ratio of about 0.8:0.4 mol of 1-propyltriethoxysilane; 0.1 mol of ethyl orthosilicate; 39.05 grams of "Shellacol"; and 12.11 ml. of the acid hydrolyzing solution.

(d) A mixture of 1-propyltrichlorosilane (74.55 grams), silicon tetrachloride (47.6 grams) and toluene (50 ml.) is added dropwise from a dropping funnel to a hydrolyzing solution consisting of water (412 ml.), 1-butanol (106 ml.) and toluene (50 ml.) contained in a 4-liter beaker surrounded with ice water. The mixture in the beaker is stirred during the addition, and the rate of addition is adjusted so that the temperature of the solution never rises higher than 30 degrees C. When the addition from the dropping funnel, which requires approximately one hour, is complete, the resinous layer is separated from the water layer in a separator funnel, and the water layer is drawn off. The resin is washed with water (3 portions of 50 ml. each) containing enough salt to effect a more rapid separation of the resinous layer from the aqueous layer. The washed resin is then dried for sixteen hours over anhydrous sodium sulfate (about 20 grams). A commercial filter-aid (5 grams of "Filtercel") is then added, and the mixture is filtered. The filtrate is a clear water white resin solution, having an r/Si ratio of about 0.6. A film of the resin on a glass plate dries tack-free at room temperature in about 35 minutes.

Example 3

A nonylsiloxanol waterproofing composition embodying the invention is prepared by the following procedure:

A mixture of higher alkylsilanes, in which the alkyl radicals contain not more than nine carbon atoms, containing a substantial proportion of 1-nonyltrichlorosilane (55.1 grams), in admixture with silicon tetrachloride (34 grams) and toluene (30 ml.), is added dropwise from a dropping funnel to a hydrolyzing solution consisting of water (250 ml.), 1-butanol (64 ml.) and toluene (30 ml.) contained in a 4-liter beaker surrounded with ice water. The mixture in the beaker is stirred during the addition, and the rate of addition is adjusted so that the temperature of the solution never rises higher than 30 degrees C. When the addition from the dropping funnel, which requires approximately one hour, is complete, the resinous layer is separated from the water layer in a separatory funnel, and the water layer is drawn off. The resin is washed with water (3 portions of 35 ml. each) containing enough salt to effect a more rapid separation of the resinous layer from the aqueous layer. The washed resin is then dried for sixteen hours over anhydrous sodium sulfate (about 10 grams). A commercial filter-aid (5 grams of "Filtercel") is then added, and the mixture is filtered. The filtrate is a clear water white resin solution having an r/Si ratio of about 0.5.

Example 4

A hexylsiloxanol waterproofing composition embodying the invention is prepared by the following procedure:

A mixture of N-hexyltrichlorosilane (131 grams), silicon tetrachloride (63 grams) and toluene (81 ml.) is added dropwise from a dropping funnel to a hydrolyzing solution consisting of water (666 ml.), 1-butanol (172 ml.) and toluene (81 ml.) contained in a 4-liter beaker sur-

rounded with ice water. The mixture in the beaker is stirred during the addition, and the rate of addition is adjusted so that the temperature of the solution in the beaker never rises higher than 15 degrees C. When the addition from the dropping funnel, which requires approximately fifty minutes, is complete, the resinous layer is separated from the water layer in a separatory funnel, and the water layer is drawn off. The resin is washed with water (3 portions of 50 ml. each) containing enough salt to effect a more rapid separation of the resinous layer from the aqueous layer. The washed resin is then dried for sixteen hours over anhydrous sodium sulfate (about 20 grams). A commercial filter-aid (5 grams of "Filtercel") is then added, and the mixture is filtered. The filtrate is a clear water white resin solution, having an r/Si ratio of about 0.6.

The solids concentrations of the resin solutions prepared as described in Examples 1 through 4 above may be adjusted to within a range from about 8 to about 10 per cent by addition of more of the solvent. A single coat of any of the resulting resin solutions may be applied to a porous ceramic material (e. g., a wall of unit masonry construction) in accordance with the present method to produce effective waterproofing. For example, upon application of a coat of the nonylsiloxanol solution prepared as described in Example 3 to a common sand mold brick, and immersion of the brick in a pan containing water at a depth of one-quarter inch (by the procedure hereinbefore described), the per cent of its weight in water absorbed by the brick after four hours is negligible (0.60 per cent).

What is claimed is:

1. A method of waterproofing porous masonry that comprises applying thereto a volatile solvent solution containing from 5 to 35% by weight of a siloxanol derived by the complete hydrolysis and incomplete condensation of a mixture consisting of a mono-alkyl silane in which three hydrolyzable groups and a single primary alkyl radical having from 3 to 9 carbon atoms are

attached to silicon and of a tetrafunctional silane having 4 hydrolyzable groups attached to silicon, the proportions of monoalkyl and tetrafunctional silanes in said mixture being such as to yield a siloxanol upon hydrolysis having from 0.3 to 0.9 primary alkyl radicals per silicon atom and not less than 30 per cent of said silicon atoms having such alkyl radicals attached thereto, said solution being applied to said masonry in amounts ranging from 25 to 125 square feet of surface per gallon of said solution, and air drying.

2. A method as claimed in claim 1 wherein the average number of said primary alkyl radicals is from 0.5 to 0.9, not less than 50% of said silicon atoms have such radicals attached thereto and said solution contains from 5 to 10% by weight of said siloxanol.

3. A method of waterproofing as claimed in claim 1 wherein the solution is applied to bricks, wherein the siloxanol is a butyl siloxanol having an average of 0.6 to 0.90 butyl groups per silicon atom and which is derived by the hydrolysis of mixtures consisting of butyltrichlorosilane and silicon tetrachloride.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,258,218	Rochow	Oct. 7, 1941
2,482,276	Hyde	Sept. 20, 1949
2,486,162	Hyde	Oct. 5, 1949
2,505,431	Rust et al.	Apr. 25, 1950
2,521,673	Britton et al.	Sept. 16, 1950
2,574,168	Brick	Nov. 6, 1951

FOREIGN PATENTS

Number	Country	Date
290,717	Great Britain	May 16, 1928

OTHER REFERENCES

Rochow, Chemistry of the Silicones, Wiley 1946, pp. 83 to 88 and 112.

The Chemical Age, February 26, 1949, pp. 322 to 326.