Hydrophobe VII *7th International Conference on*
Water Repellent Treatment and Protective Surface Technology for Building Materials
A.Elena Charola and J. Delgado Rodrigues, Editors
LNEC (Laboratório Nacional de Engenharia Civil), Lisbon: 2014 (19-28)

Silicon hydrides as water repellents, a lower VOC alternative to alkoxysilanes and alkoxy functional polysiloxanes

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SUMMARY: The use of silicon hydrides, molecules containing Si-H moieties as reactive groups, is a non VOC alternative to the alkoxy chemistry currently used in alkoxysilane and alkoxy functional polysiloxane water repellents. Alkyl Si-H materials, as n-octylsilane ($C_8H_{17}SiH_3$) or methyloctyl-co-methylhydrogen siloxane copolymers are considered useful for the protection of concrete. Linear and cyclic materials were synthesized and their depth of penetration into concrete was measured. The weight loss for treatments on concrete was shown to be significantly lower than for n-octyltriethoxysilane. Water absorption values and depth of penetration into porous substrates results indicate a performance close to that of the currently used alkyltrialkoxysilanes.

KEY-WORDS: Silicon hydrides, n-Octylsilane, n-Octyltriethoxysilane, Concrete, VOC

INTRODUCTION

The trend in the coating industry is to use lower VOC (volatile organic compound) products which is also of concern in the case of water repellents. Silicone water repellents are widely used in construction given their ability to form chemical bonds with most of the building substrates. In general this is achieved via the use of alkoxy functional materials that however, leads to the formation of alcohols as side products. This formation of alcohols makes it impossible to formulate zero VOC treatments using the alkoxy functional silanes or siloxanes which are currently the state of the art. Presently the limit of accepted VOC level of a coating depends on the national VOC regulation.

Silicon hydride containing silicon compounds are widely used as intermediates in the silicon industry. Their addition reaction to olefins, called hydrosilylation, is especially useful for the production of silicone gels, elastomers or alkylmethylsiloxanes.

Most hydride containing siloxanes are polymethylhydrides or copolymers containing the CH_3SiH-O- unit. These polymers are available in different molecular weights and contain generally trimethylsilyl end groups. In the construction industry they find use as water repellents for gypsum plasterboard and in some general purpose water repellents as one of the active ingredients. These polymethylhydrogensiloxanes are however not suited for concrete protection due to their low depth of penetration and limited stability against high pH. The general structure of a linear polymethylhydrogensiloxane is shown in Fig. 1.

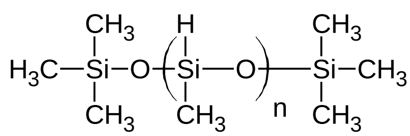

Figure 1. Polymethylhydrogensiloxane (PMHS).

Less common are cyclic methylhydrogensiloxanes which are available as tetra (Fig. 2) and penta cyclosiloxanes.

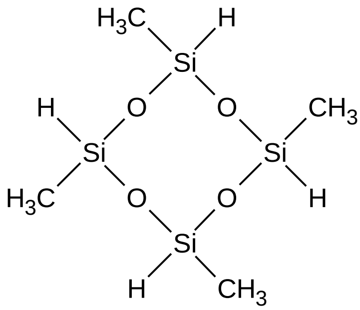

Figure 2. 1,2,3,4-Tetramethylcyclotetrasiloxane.

Monoalkylsilanes are the simplest class of silicon hydride hydrophobing agents but have not yet found any industrial use to the knowledge of the author. The structure of n-octylsilane is illustrated in Fig. 3 below.

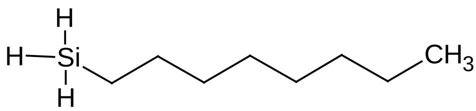

Figure 3. n-Octylsilane.

What all these materials have in common is the hydrogen bonded to the silicon atom that can react with water (or other compounds containing active hydrogen) forming silanols. While these reactions are generally highly exothermic, the reactions with water or alcohols are however slow under neutral conditions and are catalysed by acids or bases [1]. These silanols can further condensate to Si-O-Si bonds exactly as the traditional alkoxysilanes do. As an example the reaction of n-octylsilane with water is shown in Fig. 4.

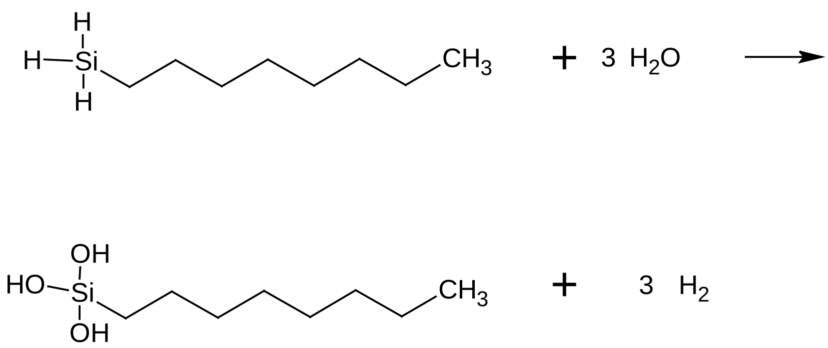

Figure 4. Reaction of n-octylsilane with water to form a silanol.

The only side product of this reaction is hydrogen gas which is not a VOC. Since this reaction is catalysed by bases, it will proceed rapidly when fresh concrete or mortar is treated with SiH containing molecules. Some more details on the reactivity of SiH groups are found in the literature [2,3].

The hydrolysis of n-octyltriethoxysilane (shown in Fig.5), a molecule widely used in silicone water repellent formulation, will lead to the formation of ethanol.

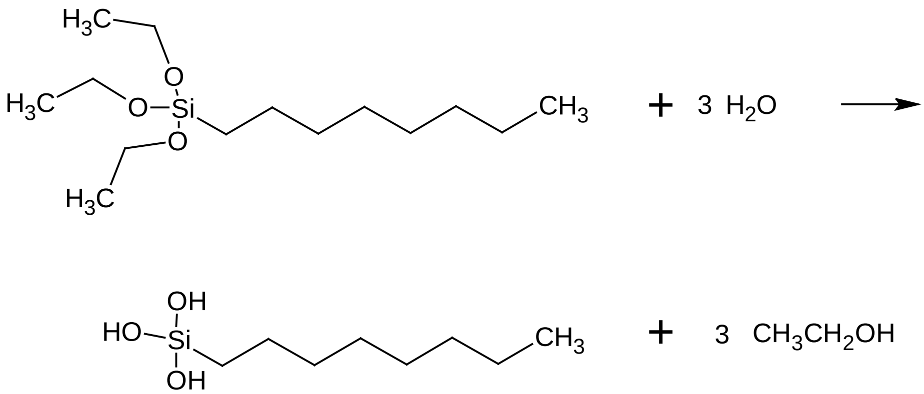

Figure 5. Reaction of n-octyltriethoxysilane with water to form a silanol and ethanol.

In the case of applying 1kg of n-octyltriethoxysilane to concrete, 499 g of ethanol (VOC) are formed, assuming complete hydrolysis of the alkoxy groups.

Recent patent publications [4,5,6] suggest that reaction products of linear and cyclic methylhydrogen siloxanes with 1-octene as well as n-octylsilane are good performing water repellent products for concrete. The general idea behind all structures is that the octyl group will provide good water repellency and the SiH moieties will react with the cementious materials.

EXPERIMENTAL

Materials

Tetramethylcyclotetrasiloxane, pentamethylcyclopentasiloxane, polymethylhydrogen-siloxane with a viscosity of 15cst (PMHS 15cst), n-Octyltriethoxysilane and Pt catalyst (Platinum-divinyltetramethylsiloxane complex 3-3.5%Pt) were supplied by ABCR GmbH Germany. 1-Octene (98%) was supplied by Sigma Aldrich Germany. N-Octylsilane was supplied by ChemPur Germany. Polymethylhydrogensiloxane with a viscosity of 30cst (PHMS 30cst) was supplied by Dow Corning under the name 1107 fluid. All materials were used as received.

Synthesis

Hydrosilylation was carried out by mixing the SiH component with the desired amount of olefin (5g in total) in 10ml bottles. To this one drop of catalyst solution (diluted 1:10 in the olefin) was added. After a short induction period the samples start to warm up due to the exothermic reaction. Bottles were put for 30 minutes into a water bath (~15°C) to control the exothermic reaction. Afterwards the materials were put in an oven for 2 hours at 80°C in order to complete the reaction and then applied without any further purification. It should be noted that this procedure is only suited for small quantities and it would be dangerous to scale it up.

The reaction is illustrated in Fig. 6 below for a cylic siloxane reacted with 2 mols of 1-octene.

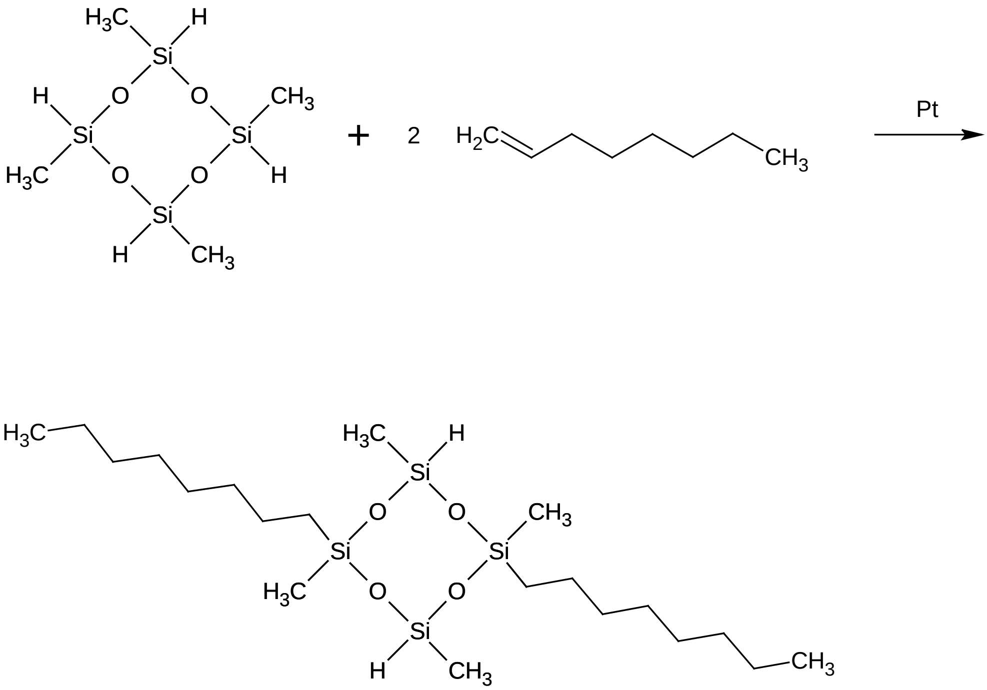

Figure 6. 1,2,3,4-tetramethyl 1,3-dioctylcyclotetrasiloxane (compound 2) made by the reaction of 1,2,3,4-tetramethylcyclotetrasiloxane with 1-octene.

It should be noted, that the reaction products are mixtures of isomers and not pure components. Table 1 summarizes the materials synthesized.

Table 1. Formulations used for the synthesis.

Compound	SiH	Olefin	Molar ratio SiH:Olefin
1	Tetramethylcyclotetrasiloxane	1-octene	4:1
2	Tetramethylcyclotetrasiloxane	1-octene	2:1
3	Pentamethylcyclopentasiloxane	1-octene	5:2
4	PMHS 15 cst	1-octene	4:1
5	PMHS 15 cst	1-octene	2:1
6	PMHS 30 cst	1-octene	4:1
7	PMHS 30 cst	1-octene	2:1

Depth of penetration

The surface of concrete blocks (6 x 6 x 4 cm) was treated with an amount of silicone corresponding to $500 g/m^2$. The depth of penetration (DOP) was determined after 1 week storage at room temperature by splitting the treated concrete blocks and wetting the newly formed surface with ink. The distance of the line formed between wet and dry concrete to the surface was measured with a ruler giving the DOP in mm.

Weight change

The concrete blocks used for the determination of depth of penetration were weighed using an analytical balance (0.001g). The weight was recorded before, directly after (~30s), 1 day after and 7 days after the treatment. The weight change was calculated as % of the amount applied. For SiH materials the weight change can be above 100% since reaction of SiH groups with moisture from the air leads to a weight increase.

Water repellency

The water repellency of Compound 2 for a treatment of $500 g/m^2$ was measured using a horizontal Rilem (or Karsten) tube. The concrete sample was identical to the one used in the DOP measurement. This concrete has a water absorption of 4.0% when tested in a 24hour immersion test. The amount of water absorbed was recorded after 1, 4 and 24 hours. The measurement was done 1 week (storage at room temperature) after treating the concrete.

RESULTS AND DISCUSSION

Depth of Penetration

A crucial parameter controlling the performance of penetrating sealers for the protection of reinforced concrete is the depth of penetration (DOP). This is described together with the factors controlling the DOP in the literature [7]. The main focus on performance of the silicon hydride treatment on concrete was therefore the measurement of the DOP.

The results obtained in the scope of this study are summarized in the following Table 2. The application rate was 500g/m^2 unless indicated otherwise.

Table 2. DOP values for methylhydrogen materials and n-octyltriethoxysilane.

Treatment	DOP (mm)
Tetramethylcyclotetrasiloxane	16
Pentamethylcyclopentasiloxane	11
PMHS 15 cst	16
PMHS 30 cst	8
Compound 1	14
Compound 2	14
Compound 3	8
Compound 4	16
Compound 5	7
Compound 6	6
Compound 7	3
n-Octyltriethoxysilane	24
n-Octyltriethoxysilane 250g/m^2	18
n-Octylsilane	28

It can be seen from the DOP values in the Table 2 that some of the products can penetrate well beyond 10 mm into the concrete used but not as deeply as n-octyltriethoxysilane which was used as a reference. However it should be noted, that the speed of absorption varies significantly and is generally lower for the compounds synthesized than for the n-octyltriethoxysilane.

Weight change

As an indication of the volatility of the treatments during an application the weight change of the concrete blocks was measured after 1 and 7 days (Table 3). These values do not strictly correspond to VOC values according to regulations since these are based on boiling points and vapour pressure. They are however a good indication for the volatility and reactivity with the substrate.

Table 3. Weight change of the treated samples after 1 and 7 days.

Treatment	after 1 day (%)	after 7 days (%)
Tetramethylcyclotetrasiloxane	68.0	71.9
Pentamethylcyclopentasiloxane	55.5	54.0
PMHS 15 cst.	97.6	102.4
PMHS 30 cst.	98.3	103.9
Compound 1	89.3	90.1
Compound 2	92.7	95.7
Compound 3	92.8	96.8
Compound 4	97.1	103.9
Compound 5	93.1	96.8
Compound 6	97.3	101.0
Compound 7	96.8	99.8
n-Octyltriethoxysilane	92.1	79.4
n-Octyltriethoxysilane 250g/m^2	88.7	70.5
n-Octylsilane	33.2	31.1

Tetramethylcyclotetrasiloxane, pentamethylcyclopentasiloxane and n-octylsilane are volatile in this test, and are not suited as low VOC materials since they substantially evaporate prior to reaction with the concrete. PMHS is not resistant to a high alkalinity environment and therefore not suitable for a durable concrete protection despite the low volatility. The increase in weight seen for most silicon hydrides between the 1 and 7 day values is explained by the increase in molecular weight when silanols are formed from the reaction of SiH with humidity from the air. The higher weight change seen for a lower treatment rate in case of the n-octyltriethoxysilane may be explained by the difference in DOP observed. The higher DOP value at a higher rate can lead to more complete hydrolysis and less evaporation of unreacted n-octyltriethoxysilane.

Cyclic methylhydrogen-methyloctyl siloxanes

The products (compounds 1-3) formed from a reaction of the cyclic siloxanes with 1-octene are characterized by a lower DOP versus the methylhydrogen siloxanes. This can be easily understood on the basis that addition of the bulky n-octyl groups increase the size and reduce the mobility of the molecules. The weight change can be increased to levels above 95%. Considering that the compounds were used without purification and therefore may contain some unreacted starting materials, which are volatile, it can be concluded that a structure shown in Fig. 6 is indeed not volatile at all when used as treatment for concrete.

Water repellency testing with the Rilem tube for compound 2 gave the following results shown in Table 4.

Table 4. Result of the Rilem test for compound 2.

	1h	4h	24h
Compound 2	0.05ml	0.1ml	0.2ml
Untreated reference	>4ml	n.a.	n.a.

During the measurement small bubbles of hydrogen are formed at the concrete surface indicating that the cure of the silicon hydride was not complete at this point in time. The values show that excellent water repellency is achieved in this test.

Data for the reaction products of mixtures of cyclic methylhydrogen-siloxanes (containing approx. 52 % of tetramethylcyclotetrasiloxane, 43% of pentamethylcyclo-pentasiloxane and 5% of hexamethylcyclohexasiloxane) with 1-octene and 1-dodecene were reported to have VOC levels of less than 50g/l according to ASTM 5095 [4]. Mortar cubes treated with some of the mixtures described had water exclusion rates of above 90% in a 24 hours immersion test.

Strong bases are known to polymerize cyclic siloxanes by ring opening [8]. It is unclear if this kind of reaction can occur during the treatment of concrete and what the final chemical structure of the silicone applied will be.

Linear methylhydrogen-methyloctyl siloxanes

The reaction of PMHS with 1-octene leads to random copolymers (compounds 4-7) with the following structure.

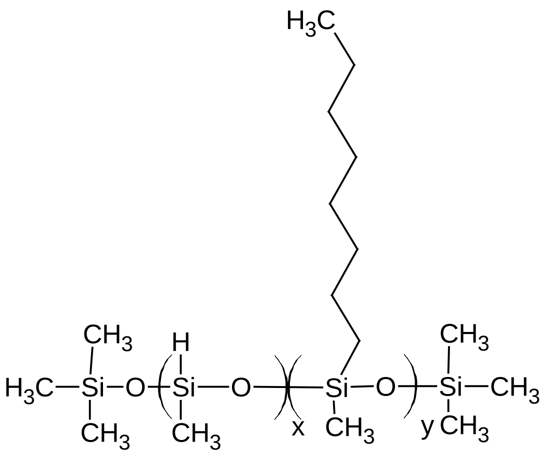

Figure 7. Polymethylhydrogen-co-methyloctylsiloxane made by the reaction of polymethylhydrogensiloxane with 1-octene.

As seen for the cyclic compounds the reaction of PMHS with 1-octene leads to a reduction in DOP. In case PMHS 30cst was used to prepare the copolymer the lowest DOP observed in this study was obtained.

Therefore, care must be taken to select as starting material a PHMS that has a chain length short enough to yield compounds still useful for protection of reinforced concrete.

For this class of materials (in form of an emulsion) durability data are reported [5] showing that no change in performance occurred after 2000 hours of QUV weathering and a VOC level of less than 100g/l according to ASTM 5095.

A treatment will lead to a linkage of the octyl group via two silicone atoms to the substrate since octyl group and silanol formed from SiH hydrolysis are located on neighboring Si atoms in the molecule. This is shown in Fig. 8 on the right. The Si-O- bond to the substrate is therefore only "indirectly" shielded by the octyl group through steric hindrance against hydrolytic attack at high pH values as seen in concrete. It is therefore yet unknown if this kind of treatment has the same chemical durability as conventional silanes.

Monoalkylsilanes

A surface treatment with an alkylhydrogensilane (RH_3Si) is in principle chemically identical to a treatment made with an alkoxyalkylsilane ($R(OR')_3Si$) leading to a linkage shown on the left in Fig. 8 for the case of n-octyl materials.

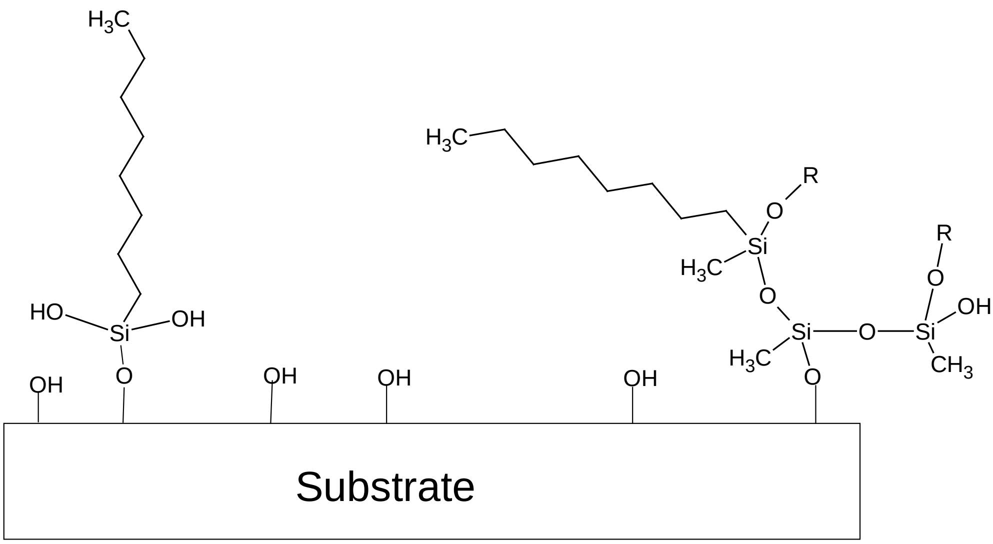

Figure 8. N-octyl groups chemically bonded to a substrate via different silicone linkages.

The potential use of long chain monoalkylsilanes as water repellents was already proposed decades ago [9]. In a recent patent application it was published that n-octylsilane applied to concrete shows good performance. For an application amount of 200g/m^2 a 7mm DOP was reported. The water repellency tested with the Rilem method showed less than 1ml absorption after 24 hours [6].

In the present study n-octylsilane showed the highest DOP value. This can be explained by the fact that it was the smallest molecular size material tested. However the high volatility shown in the weight change tests makes n-octylsilane unsuited as a low VOC water repellent for concrete.

Whichever route is used to obtain monoalkylsilanes, the reduction of monoalkyltrichlorosilanes or hydrosilylation of monosilane with olefins, production of these materials is expensive and difficult to implement on a large scale process.

CONCLUSIONS

The hydrolysis of molecules containing Si-H moieties as reactive groups and octyl chains as hydrophobic part allows the generation of silanols without the formation of volatile organic side products. These silanols can then undergo condensation reactions forming a hydrophobic treatment which is chemicaly bonded to a suited subtrate such as concrete. Due to the relative high molecular weight the treatment is almost completely retained without evaporation losses.

Cyclic and short linear methyloctyl-methylhydrogen-siloxanes are able to penetrate deeply into porous substrates making them potentially suitable for the protection of structural concrete. The depth of penetration in concrete is however inferior to the one obtained with n-octyltriethoxysilane. The materials can conveniently be synthesized using the hydrosilylation reaction starting from intermediates available on an industrial scale.

The silicon atom linked to the substrates is not the one containing the bulky octyl group as in case of octylsilanes. A better fundamental understanding about the hydrolytic stability of this linkage at high pH would be therefore desirable.

N-octyl silane is not easily available or synthesized on a larger scale. The molecule itself has a boiling point of 162°C and is therefore a VOC by itself. Its potential usage as a water repellent in construction applications is for the time being only of academic interest.

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