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NEW APPROACHES TO WATERPROOFING OF SPACE SHUTTLE INSULATING MATERIALS

SRI Project 1292

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SUMMARY

Future reusable space vehicles will be in service much more frequently than current space shuttles. Therefore, rapid reconditioning of spacecraft will be required. Currently, the waterproofing of space shuttles after each re-entry takes 72 hours and requires substantial labor. In addition, the currently used waterproofing reagent, dimethylethoxysilane (DMES), is considered toxic, and ethanol fumes are released during its hydrolytic activation. Consequently, a long time period, which is not acceptable for future operations, is needed to ensure that all the excess volatile compounds are removed before further maintenance of the space vehicle can be performed.

The objective of this project was to assist NASA Ames in finding improved waterproofing systems by identifying suitable waterproofing agents that can be applied by vapor phase deposition and will be less toxic, bond more rapidly to the insulation material surface, and potentially have higher thermal stability than the DMES system.

Several approaches to achieve faster waterproofing with less toxicity were assessed using the following alternatives:

- Reactive volatile compounds that are rapidly deposited by chemical bonding at the surface and leave no toxic volatiles.

- Reactive reagents that are the least toxic.

- Nonvolatile reagents that are very reactive and bond strongly to the insulating material surface.

Three specific types of potential reagents were chosen for evaluation in this project:

1. Volatile reagents with Si-Cl functional groups for vapor deposition

2. Volatile reagents with Si-H functional groups for vapor deposition

3. Nonvolatile oligomeric or polymeric reactive siloxanes that are assumed to have higher thermal stability and/or strong bonding to the insulating material.

The chemistry involved in the project was targeted at the generation of intermediates having reactive Si-OH bonds for the formation of either volatile species or polymeric species that bond rapidly to the surface and also cure rapidly. We focused on two chemical reactions—hydrolysis of Si-Cl bonds and catalytic dehydrocoupling of Si-H bonds.

The project results revealed primarily that volatile alkylchlorosilanes can provide an efficient gas-phase deposition approach for waterproofing of spacecraft insulating materials. This system possesses some advantages—such as relatively high volatility, very rapid hydrolysis rates to form the Si-OH containing species, and low toxicity—associated with excellent waterproofing properties (assuming that the by-product, HCl, can be easily removed prior to exposure of reagents to the insulating material). In fact, the presence of acid vapor at low concentration may be advantageous for accelerating the deposition rates of the silanol intermediates. We also found that the formed silanol intermediates can be stable and volatile enough to be delivered from a "generator reservoir" to the target surface.

Other sources for silanols have been identified to provide additional options for choosing the best reagent or mixture of reagents. Various leaving groups can be used as precursors to the silanol intermediates. The choice of reagents should be based on: (a) ease of application, (b) reagent and intermediate volatility, (c) kinetics of generating the silanol intermediate, (d) rate of chemical bonding to the surface, (e) toxicity, and (e) other hazards. Most attractive are reagents possessing Si-H bonds because they are more volatile than similar reagents with other hydrolyzable groups and do not release toxic by products. However, the conversion of Si-H to Si-OH functional groups in the presence of moisture by catalytic dehydrocoupling is not fast enough at the currently used conditions. Acceleration of the dehydrocoupling reaction is achievable.

The study results combined with existing literature on coupling agents strongly indicate that chemical bonding between the reagent and the surface is required. Physical deposition of condensed species at the surface of the fibrous material is not sufficient enough.

If the toxicity of silanes prevents the use of volatile monomeric silanes, then an alternative approach can be developed by spraying nonvolatile siloxanes having a significant degree of alkoxy or silanol functional groups. This system requires a spray approach and a significant amount of a delivery solvent which is disadvantageous. However, once the reagents are delivered to the insulating materials, there are no concerns about the toxicity of volatile silanes. In this case, the only environmental concern is the solvent evolved from the solution and the relatively small levels of alcohol released when an alkoxysiloxane reagent is used.

Our results, combined with NASA's reports and the literature search, strongly indicate that kinetics and, primarily, the bonding rates of the silanol reagent to the surface of the insulating material are the main issues in developing a rapid waterproofing system.

The laboratory work conducted in this project is very preliminary. Additional development associated with extending the fundamental understanding of the hydrolysis-condensation kinetics

of gas-phase waterproofing reagents and chemical bonding of reagents to the insulating material surface will result in the development of a practical, rapid-replenishment process to waterproof re-entered space vehicles.

The following recommendations are suggested for further exploration of the gas-phase deposition approach:

- Screen the options of using other reagents beside hydrido, chloro, and alkoxy silanes tested thus far, after assessing their potential hazards and/or corrosive effects.

- Develop a better understanding of the hydrolysis (or dehydrocoupling) and condensation mechanisms of typical reagents on the basis of currently available literature and assumed processes.

- Identify areas where current model studies are not sufficient to extrapolate the existing kinetics developed for solution systems to the gas-phase system.

- Focus on approaches to accelerate the condensation of volatile silanols formed by hydrolysis or dehydrocoupling, and develop convenient chemistries that will favor surface bonding over self-condensation of the silanol intermediates.

- Develop a better understanding of the characteristics of the chemical species bonded to the insulation material surface that provide good and stable waterproofing systems.

- Assess potential negative effects of condensation catalysts directly deposited at the surface or in the gas phase on the degradation of the insulating materials and possibly other spacecraft surfaces.

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OBJECTIVES AND BACKGROUND

OBJECTIVES

SRI International is assisting NASA Ames Research Center examine the option of gas phase deposition of suitable reagents for more effective waterproofing of space craft. The overall objective is to identify methods and reagents that will reduce the time needed for waterproofing (currently 72 hours), have less toxicity during deposition, and produce a waterproofing layer that is more thermally stable. The objectives of this preliminary study were to

- Identify suitable waterproofing agents that can be deposited from the vapor phase and replace the current DMES system which is toxic, and slow to bond to the surface.[1]

- Explore new waterproofing agent systems that may have higher thermal stability and/or lower toxicity at the time of deposition.

BACKGROUND

Future space vehicles will be in service much more frequently than the current space shuttles and the duration between flights is anticipated to be as short as one week. This scenario requires rapid reconditioning of the space vehicle. Currently, the space shuttles need to be waterproofed after each re-entry, using a process which takes 72 hours. Each tile is injected in two place[5] with dimethylethoxysilane (DMES), a low boiling point liquid which provides very good protection against water uptake from rain. Besides the long period and substantial labor required to complete the injection, time is also required to cure ("age") the thin film (assumed to be of the order of a few monolayers). Before curing by chemical bonding to the surface, the compound is susceptible to evaporation or self-condensation. Consequently, it may easily be washed off the surface by rain. Aging is required to bond the reagent to the surface through the formation of Si-O-Si or Si-O-Al bonds.. Further bonding of DMES to form polymeric siloxane species is also assumed.

DMES is considered to be toxic and ethanol fumes are released during activation and chemical bonding. A prolonged period is required to make sure that all volatiles are removed before further maintenance of the space vehicle.

Gas phase deposition of suitable reagents is being considered by NASA. Gas phase deposition will reduce process time and similar waterproofing efficacy may be achievable with smaller amounts of deposited material. Recently, NASA researchers have been able to improve the process and accelerate aging by depositing a platinum catalyst at the surface of a bag (simulating the waterproofing chamber) covering the insulation during gas phase deposition. DMES was found to be an efficient reagent, as were other volatile compounds containing Si-H bonds.[2]

However, a considerable time was still required to achieve adequate bonding of the reagent to the surface. As discussed in this report we assume that the catalyst is responsible for activating a dehydrocoupling reaction in which Si-H groups react with moisture to form Si-OH groups which interact rapidly with the insulation surface. This reaction requires direct contact between the reagent and catalyst. Kinetic factors probably inhibit this reaction.

APPROACH

SRI assessed several approaches to achieve faster waterproofing with less toxic reagents. We assumed that the following reagents would be suitable alternatives to the current system:

- Reactive volatile compounds that are rapidly deposited by chemical bonding at the surface and leave no toxic volatiles.

- Reactive reagents that are the least toxic.

- Nonvolatile reagents that are very reactive and bond strongly to the insulating material surface.

Three specific types of compounds were chosen for this feasibility study. In all three cases Si-OH intermediates are formed to facilitate bonding between the reagents and the surface as well as with themselves where more than a single monolayer is deposited:

1. Volatile reagents with Si-Cl bonds for vapor deposition

2. Volatile reagents with Si-H bonds for vapor deposition

3. Nonvolatile oligomeric or polymeric reactive siloxanes that are assumed to be thermally stable and/or to bond strongly to the insulation material.

The chemical approach involves forming reactive Si-OH bonds, to promote either the formation of volatile species or polymeric species that bond rapidly to the surface and cure quickly. Primarily, we used two chemical reactions described below: hydrolysis of Si-Cl bonds and dehydrocoupling of Si-H bonds.

HYDROLYSIS OF ALKYLCHLOROSILANES

Volatile reagents containing Si-Cl group(s) were reacted with Si-OH group(s) (Reaction 1) to form what were assumed to be volatile derivatives:

$$R_3SiCl + H_2O \longrightarrow R_3Si\text{-}OH + HCl \qquad (1)$$
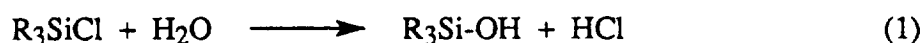
Si-Cl groups are rapidly hydrolyzed by water (moisture) to form Si-OH. Alkylchlorosilanes having low boiling points are preferred, but another critical need is that the silanol intermediate

should be volatile by itself if produced away from the insulating material surface. These requirements limit the choices for this approach. Another major consideration , described below, is that hydrolyzed Si-OH bonds tend to condense rapidly to form Si-O-Si bonded oligomeric species if the concentration is high or in the presence of acidic and, especially, basic environments (as happened in our experiments).

The following reagents were considered because of their volatility before and after hydrolysis and their commercial availability:

1. Dimethylchlorosilane (DMCS), $(CH_3)_2SiHCl$; b.p. 37°C

2. Dimethyldichlorosilane (DMDCS), $(CH_3)_2SiCl_2$; b.p. 71°C

3. Trimethylchlorosilane (TMCS), $(CH_3)_3SiCl$; b.p. 58°C

4. Methyldichlorosilane (MDCS), $(CH_3)SiHCl_2$; b.p. 41°C

5. Triethylchlorosilane (TECS), $(CH_3CH_2)_3SiCl$; b.p. 145°C.

DMCS is, in fact, the reagent used to form DMES. DMDCS and MDCS have the capability to form two Si-OH species. In this case, double-linking to the surface is feasible and would result in higher stability of the deposited reagents. Polymerization of these reagents at the surface is also feasible. However, the potential intermediates may be too reactive or too dense to be transported as gases.

Although DMES has the potential to form two Si-OH bonds, further catalytic activation of the Si-H or Si-OEt bonds is required, and such activation is slow and requires either transition metal or strong base catalysts. TMCS and TECS can form only a single Si-O-surface bond and are anticipated to form only a single-monolayer waterproofing film. Ethyl-silicon groups (found on TECS) provide lower surface tension with water than methyl-silicon and hydrido-silicon groups. TECS is also attractive because it provides a stable Si-OH derivative, which can be isolated. Nevertheless, both the original reagent or its derived silanol may not be volatile enough for vapor deposition.

DEHYDROCOUPLING OF SILICON COMPOUNDS CONTAINING SI-H BONDS

Using a transition-metal catalyzed dehydrocoupling reaction, explored at SRI, Si-H groups on oligo- and polysiloxanes can convert to Si-OH or Si-OR by reacting with H_2O or ROH, respectively.[3]

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$$R_3Si\text{-}H + H_2O \longrightarrow R_3Si\text{-}OH \text{ (in the presence of Ru catalyst)} \qquad (2)$$
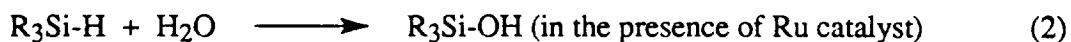
This reaction allows the use of waterproofing reagents, including alkyl silanes or oligomeric and polymeric siloxanes, that originally have Si-H groups, and which are catalytically converted to reactive intermediates prior to bonding to the surface. It is assumed that in the new gas phase deposition approach currently being investigated by NASA Ames researchers, the dehydrocoupling reaction is responsible for the activation of the DMES and similar reagents with Si-H bonds. In this system, a Pt catalyst is deposited inside the bag chamber used for the vapor deposition experiments.

The advantages of this concept are as follows:

- Monomeric reagents having Si-H group(s) are more volatile than any equivalent compounds containing other hydrolyzable groups.

- More efficient and stable coatings can be obtained if a compound like DMES generates more than one Si-O-M bond with the surface.

- Water and hydrogen are the only vapor by-products (beside the reagent itself); however, the reagent is expected to interact rapidly with the surface when Si-OH is formed.

- When oligosiloxanes or polysiloxanes with multiple Si-H bonds are used, no toxic volatiles are evolved except the solvent used to transfer the reagent to the surface of the fibers.

Dehydrocoupling of Volatile Silanes

Only minimal work has been conducted on this topic at SRI during this phase because of the priorities established. We have limited the work in this area because of the parallel activities at NASA Ames. However, as discussed later in this report, we believe that further exploration of this concept will provide fundamental understanding and lead to the development of a faster deposition system than is currently possible with this approach.

Thus far, only diethylsilane (DES) has been tested and only $Ru_3(CO)_{12}$ has been used as a catalyst at SRI.

Dehydrocoupling of Nonvolatile Siloxanes

Over the past six years, SRI has investigated and applied dehydrocoupling reactions to polysiloxane systems having multiple Si-H bonds. Such systems can be used as low-molecular-

weight cyclomers or polymers. Both are liquids with relatively low viscosity (10-20 cps). They can be activated directly at the surface, if mixed with an effective catalyst or if an effective catalyst is deposited at the surface first. Transition metal catalysts, primarily some Ru and Pt catalysts, were found to be most active. However, bases and, to a lesser extent, acids can also activate this reaction.

Since it is desirable to avoid any deposition of catalysts at the surface of the insulating fibers, for fear that the deposited catalysts will degrade the fiber strength at high temperature, these polymers or oligomers must be activated and modified prior to deposition. In this project, we synthesized and used low-molecular-weight cyclohydridomethylsiloxane (CHMS), $[CH_3SiHO]_n$ with $n_{avg} = 5$ by catalytic decomposition of linear polysiloxane. We also used commercially available polyhydridomethylsiloxane (PHMS) having the same monomeric units as the cyclomers. A $Ru_3(CO)_{12}$ catalyst was used for substitution of Si-H on the cyclomer and polymers by ethoxy and hydroxyl groups to form ethoxy modified cyclomers (CHMS-OEt) and ethoxy and hydroxy modified polymers (PHMS-OEt and PHMS-OH, respectively). The following polymeric intermediates were used as dilute solutions:

- 0.5, 1, and 2% PHMS-OEt in ethanol
- 0.5, 1, and 2% PHMS-OH in ethanol
- 0.5, 1, and 2% CHMS-OEt in ethanol.

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METHODS AND RESULTS

TYPES OF INSULATING MATERIALS TESTED

Two types of insulators were used in the waterproofing experiments: one made of silica based fibrous material, and the other made of alumina (the majority) and silica fibers.

EVALUATION METHOD

We used a water pickup test similar to that used by NASA Ames. In this test, waterproofed samples are immersed in distilled water for 15 min, shaken or gently wiped to remove surface external droplets, and then reweighed. Water pickup is calculated as the wt% increase over the dry weight. In most cases, the 15-min immersion test was repeated on a sample over a period of days and weeks to check the stability of the waterproofing layer.

Chemistries involved with the various reagents were also monitored by using proton nuclear magnetic resonance (NMR) techniques, especially to assess the formation and stability of Si-OH species.

HYDROLYSIS OF Si-Cl CONTAINING REAGENTS

Experiments were performed by first passing nitrogen as a carrier gas through the selected reagents and then passing the saturated gas through the hydrolysis medium. Various hydrolysis media were used, including water, solutions of sodium hydroxide (NaOH) and disodium phosphate (Na_2HPO_4), solid sodium hydroxide pellets, and others. The activated volatile intermediate was then transferred into a bag containing an insulator specimen as shown in Figure 1. A double-bag (bag-in-bag) technique was used, similar to the experimental set-up used at NASA Ames. The flow rate of the carrier gas was monitored by a flow meter. Temperatures of the reagent reservoir and the hydrolysis media were adjusted by placing each of them in cooling baths of salt/ice water or ethylene glycol/dry ice. The exposure times of the specimens to the flowing reagents and the hold (aging) periods for the bagged specimens after delivery of reagent was completed were recorded.
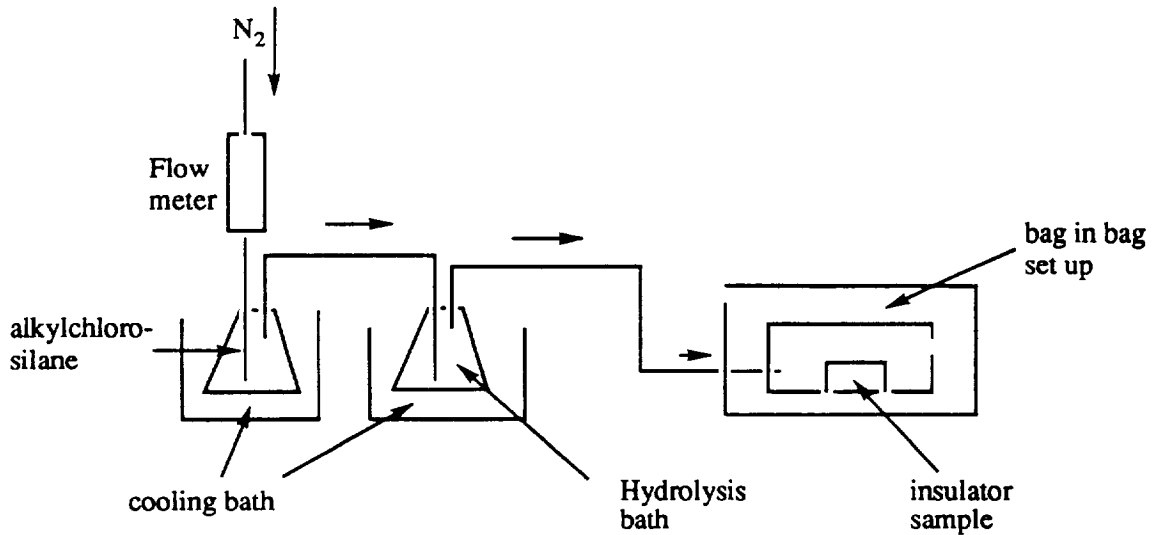
Figure 1. Waterproofing reagent delivery experimental set-up.

Tables 1 through 5 present the waterproofing results as a function of hydrolysis medium and its temperature, flow rate, exposure period, hold period (aging) before the holding bag was opened, and type of insulation material. Bold lettering in the tables indicates runs providing good or acceptable results according to NASA criteria.

Our experiments revealed that all the tested alkylchlorosilanes formed very good waterproofing films on the SiO_2 insulating material when they were directly deposited on the insulation material without passing through hydrolysis medium. In this case, the hydrolysis takes place by direct interaction with the Si-OH groups at the insulator surface or by reacting with adsorbed moisture. However, such direct deposition results in the high HCl levels, which are assumed to be unacceptable because of environmental and corrosion concerns.

Table 1

WATERPROOFING EXPERIMENTS WITH DIMETHYLCHLOROSILANE (DMSC)

Activation Pass (Temp.)[a]	Flow Rate (mL/min)	Exposure/ Hold Time	HCl Detection[b]	Water Pickup (%/days)	Type of Insulator	Comments
Water (RT)	20	60 min/2 h	No	450/1	SiO_2	No sign of coating,[c] condensed silicone layer covers the water
Water/ice water	19	60 min/0 h	At the end	30.8/1	SiO_2	Well coated[d]
Water (0°C)	35	90 min/1 h	No		SiO_2	Partially coated[e]
Water/ice (3°C)	35	60 min/0 h	No	Turbid water	SiO_2	No sign of coating
Water (-12°C)	35	60 min/1 h	No	Turbid water[f]	SiO_2	No sign of coating
NaOH(s) (70°C)[i]	12	40 min/10 h	No	543/1	Al_2O_3	No sign of coating
NaOH(s) (RT)	22	60 min/ >10 h	At the end	450/1	Al_2O_3	Slightly better than Run #1
NaOH(s) (RT)	14	40 min/1 h	No	495/1	SiO_2	Partially coated
NaOH(s) (RT)	21	70 min/2 h	No	400/1	SiO_2	No sign of coating, condensed silicone layer covers the water
NaH$_2$PO$_4$(s) (RT)	20	60 min/60 h	No	367/1	SiO_2	Barely coated[g]
NaH$_2$PO$_4$(s)/ ice water	**20**	**60 min/0 h**	**At the end[h]**	**15/1**	**SiO_2**	**Well coated**
NaH$_2$PO$_4$(s)/ice water	15	90 min/0 h	At the end	143/1	SiO_2	Mostly coated
NaOH (RT)[j]	21	70 min/2 h	No	397/1	SiO_2	No sign of coating, condensed silicone layer covers the water

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Table 1

WATERPROOFING EXPERIMENTS WITH DIMETHYLCHLOROSILANE (DMSC)
(continued)

Activation Pass (Temp.)[a]	Flow Rate (mL/min)	Exposure/ Hold Time	HCl Detection[b]	Water Pickup (%/days)	Type of Insulator	Comments
NaOH (RT)	19	70 min/2 h	No	343/1	SiO$_2$	Partially coated, condensed silicone layer covers the water
NaOH (-3°C) (both)	33	60 min/0 h	At the end		SiO$_2$	No sign of coating
NaOH/ice water	20	60 min/0 h	No	322/1	SiO$_2$	Slightly coated dimer layer
NaOH/ice water	30	60 min/0 h	At the end		SiO$_2$	Partially coated
NaOH (-3°C)	25	60 min/0 h	At the end		SiO$_2$	Slightly coated
NaOH (-3°C)	30	90 min/0 h	At the end	29/1	SiO$_2$	Well coated
NaOH (-3°C) (both)	33	60 min/2 h	At the end		SiO$_2$	Well coated
NaOH (-8°C) (both)	3 5	60 min/0.5 h	At the end	16/1 19/3	SiO$_2$	Well coated
NaOH (-12°C) (both)	35	60 min/1 h	At the end	16/1	SiO$_2$	Well coated
NaOH (-12°C) (both)	3 5	120 min/10 h	At the end	22/1 22/3 21/8	SiO$_2$	Well coated
NaOH (-12°C) (both)	3 5	120 min/10 h	At the end	19/1 19/4 19/8 18/11	SiO$_2$	Well coated

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Table 1

WATERPROOFING EXPERIMENTS WITH DIMETHYLCHLOROSILANE (DMSC)
(concluded)

Activation Pass (Temp.)[a]	Flow Rate (mL/min)	Exposure/ Hold Time	HCl Detection[b]	Water Pickup (%/days)	Type of Insulator	Comments
NaOH (-12°C) (both)	35	60 min/10 h	At the end	24/1 23/4 22/10	SiO_2	Well coated
NaOH (-12°C) (both)	30	60 min/10 h	At the end	22/1 21/4	SiO_2	Well coated
NaOH (-12°C) (both)	35	90 min/1 h	At the end		Al_2O_3	No sign of coating

[a]RT = room temperature. Temperature for ice water is about 0-3°C. Ice-salt and ethylene glycol/dry ice baths were used to achieve low temperatures and followed by thermometer reading.

[b]Wet pH paper was put inside the bag. In most cases, the pH paper indicated acidic conditions close to the end of exposure.

[c]"No sign of coating" means no waterproofing effect.

[d]"Well coated" means that the entire surface is coated as indicated by the visual hydrophobicity of the surface.

[e]"Partially coated" means that only part of surface is coated and exhibits hydrophobicity.

[f]"Turbid water" means that nonbonded condensed siloxane physically deposited at the fibrous surface was washed off and emulsified by the water. Usually, this means that the waterproofing does not work well.

[g]"Barely coated" means that only a very small portion of the surface is coated, possibly at localized areas.

[h]Signs of acid seen inside deposition chamber only at the end of the purging step; the litmus paper in the chamber turned red.

[i]"(s)" means that the reagent was passed through a column packed with solid pellets of base.

[j]Base solution consists of ~25 wt% of NaOH.

Table 2

WATERPROOFING EXPERIMENTS WITH DIMETHYLDICHLOROSILANE (DMDCS)

Activation Pass (Temp.)[a]	Flow Rate (mL/min)	Exposure/ Hold Time	HCl Detection[b]	Water Pickup (%/days)	Type of Insulator	Comments
NaOH[e] /ice water	20	45 min/0 h	No	260/1	SiO_2	Some coated[c]
NaOH (40°C)	37	30 min/1 h	Yes		SiO_2	No sign of coating[d]
NaOH (RT)	37	30 min/4 h	Yes		SiO_2	Most parts not coated
NaOH (20°C)	37	35 min/10 h	Yes		SiO_2	No sign of coating
NaOH /tap water	37	40 min/2 h	Yes		SiO_2	No sign of coating
Na_2HPO_4[f] /ice water	16	60 min/0 h	At the end	99/1	SiO_2	Mostly coated, no washable layer
Na_2HPO_4 /ice water	16	60 min/0 h	No	96/1	SiO_2	Mostly coated
Na_2HPO_4 /ice water	**26**	**60 min/0 h**	**Yes**	**17/1**	**SiO_2**	**Well coated**
NaOH /ice water	22	60 min/0 h	No	175/1	SiO_2	Mostly coated
NaOH /ice water	21	60 min/0 h	No	286/1	SiO_2	Partially coated
NaOH /ice water	37	60 min/1 h	At the end		SiO_2	Mostly coated
NaOH /ice water	37	60 min/0.2 h	At the end	29/1	SiO_2	Mostly or partially coated
NaOH /ice water	**37**	**30 min/10 h**	**At the end**	**13/1 17/4 18/15 17/20**	**SiO_2**	**Well coated**

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Table 2

WATERPROOFING EXPERIMENTS WITH DIMETHYLDICHLOROSILANE
(DMDCS) (concluded)

Activation Pass (Temp)[a]	Flow Rate (mL/ min)	Exposure/ Hold Time	HCl Detection[b]	Water Pickup (% /days)	Type of Insulator	Comments
NaOH /ice water	37	30 min/2 h	At the end		SiO$_2$	Mostly or partially coated[c]
NaOH /ice water	37	30 min/1 h	At the end	66/1	SiO$_2$	Mostly or partially coated
NaOH /ice water	35	35 min/10 h	At the end		SiO$_2$	No sign of coating[d]
NaOH (0°C)	37	40 min/0.7 h	At the end		SiO$_2$	Partially coated
NaOH (-10°C)	35	90 min/1.5 h	At the end		SiO$_2$	Mostly coated
NaOH (-12°C)	35	90 min/10 h	At the end		SiO$_2$	Mostly coated

[a]RT = room temperature. Temperature for ice water is about 0-3°C. Ice-salt and ethylene glycol/dry ice
  baths used to achieve low temperatures are followed by the thermometer reading.
[b]Wet pH paper was put inside the bag. In most cases, the pH paper indicated acidic conditions
  close to the end of exposure.
[c]"Partially coated" means that only part of surface is coated.
[d]"No sign of coating" means no waterproofing effect.
[e]25 wt% NaOH solution.
[f]10 wt% NaH$_2$PO$_4$.

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Table 3
WATERPROOFING EXPERIMENTS WITH TRIMETHYLCHLOROSILANE

Activation Pass (Temp)[a]	Flow Rate (mL/min)	Exposure/ Hold Time	HCl Detection[b]	Water Pickup (% /days)	Type of Insulator	Comments
NaOH (RT)	18	60 min/0 h	No	387/1	SiO$_2$	No sign of coating[c]
NaOH (RT)	15	80 min/0 h	No	350/1	SiO$_2$	No sign of coating
NaOH (10°C)	**27**	**40 min/0.3 h**	**At the end**	**18/1**	SiO$_2$	**Well coated[d]**
NaOH (10°C)	29	30 min/10 h	At the end		SiO$_2$	Partially coated[e]
NaOH /ice water	**18**	**60 min/0.3 h**	**Yes in the end**	**18/1**	SiO$_2$	**Well coated**
TAEPA[f] /ice water	18	45 min/0 h	No		SiO$_2$	No sign of coating
NaOH (0°C)	37	35 min/10 h	Yes		SiO$_2$	Partially coated
NaOH (-12°C)	35	60 min/1 h	Yes		SiO$_2$	No sign of coating

[a]RT = room temperature. Temperature for ice water is about 0-3°C. Ice-salt and ethylene glycol/dry ice baths used to achieve low temperatures are followed by thermometer reading.

[b]Wet pH paper was put inside the bag. In most cases, the pH paper indicated acidic conditions close to the end of exposure.

[c]"No sign of coating" means no waterproofing effect.

[d]"Well coated" means that entire surface is coated.

[e]"Partially coated" means that only part of surface is coated.

[f]TAEPA = Tetraaminoethylenepentaamine.

Table 4

ALKYLCHLOROSILANES DIRECTLY DEPOSITED BY GAS PHASE FLOW[a]

Reagent[b]	Activation Pass (Temp)[b]	Flow Rate (mL/min)	Exposure/ Hold Time	HCl Detection[c]	Water Pickup (%/days)	Type of Insulator	Comments
DMES	RT	13	40 min/2 h		568/1	Al_2O_3	No sign of coating[d]
DMES	RT	13	70 min/2 h		33/1	SiO_2	Well coated[e]
DMES	RT	18	40 min/0 h		17/1 25/4[f]	SiO_2	Well coated
TECS	RT	30	40 min/0 h	At the end	20/1	SiO_2	Well coated
TMCS	RT	18	30 min/0 h	At the end	15/1	SiO_2	Well coated
DMDCS	RT	16	30 min/0 h	At the end	17/1	SiO_2	Well coated
DMCS	RT	16	40 min/0 h	At the end	16/1	SiO_2	Well coated

[a]The reagents were not passed through hydrolyzing solution; thus, HCl was also released to the chamber and accelerated the reagent bonding to the surface.

[b]DMES: Dimethylethoxysilane; DMDCS: dimethyldichlorosilane; TMCS: chlorotrimethylsilane; TECS: Triethylchlorosilane.

[c]Wet pH paper was put inside the bag. In most cases, the pH paper indicated acidic conditions close to the end of exposure.

[d]"No sign of coating" means no waterproofing effect.

[e]"Well coated" means that entire surface is coated.

[f]Waterproofing was reduced over time.

Table 5

**COATING CONDITIONS FOR GOOD WATERPROOFING WITH
VARIOUS CHLOROSILANES[a]**

Reagent[a]	Activation Pass (Temp)[b]	Flow Rate (mL/min)	Exposure/ Hold Time	HCl Detection[c]	Water Pickup (% /days)	Type of Insulator	Comments
DMCS	Na₂HPO₄ ice water	20	60 min/0 h	At the end	15/1	SiO₂	Well coated
DMCS	NaOH (-8°C) (both)	35	60 min/0.5 h	At the end	16/1 19/3	SiO₂	Well coated
DMCS	NaOH (-12°C) (both)	35	120 min/10 h	At the end	19/1 19/4 19/8 18/11	SiO₂	Well coated
DMDCS	Na₂HPO₄ ice water[c]	26	60 min/0 h	Yes	17/1	SiO₂	Well coated
DMDCS	NaOH ice water	37	30 min/10 h	At the end	13/1 17/4 18/15 17/20	SiO₂	Well coated
TMCS	NaOH ice water	18	60 min/0.3 h	At the end	18/1	SiO₂	Well coated

[a]DMDCS: dimethyldichlorosilane; TMCS: chlorotrimethylsilane; DMCS: dimethylchlorosilane.
[b]Temperature for ice water is about 0-3°C. Ice/salt and ethylene glycol/dry ice baths were used to achieve the desired low temperature.
[c]Wet pH paper was put inside the bag. In most cases, the pH paper indicated acidic conditions close to the end of exposure.

All the tested alkylchlorosilanes exhibited no waterproofing effect after activation by passing through NaOH solutions at room temperature. However, all the reagents demonstrated good waterproofing after passing through NaOH solutions at low temperature before deposition on the silica-based insulating material. In contrast, waterproofing films were not obtained on alumina-based material under the same conditions.

The following experimental factors showed important effects in providing good waterproofing films:

- Boiling point of the alkylchlorosilane

- Flow rate of the carrier gas

- Type of hydrolysis solution

- Temperature of hydrolysis solution

- Exposure period

- Post delivery holding (aging) period of the specimen inside the deposition bag.

We also found that the weight gain of the insulating materials after a successful waterproofing film has been deposited is negligible. This observation is significant for future operations, where hundreds of flights per shuttle will require many repetitions of the waterproofing treatment.

We noticed that rapid condensation of the in-situ formed Si-OH groups occur in the hydrolyzing solution under the following conditions: (a) in the presence of strong bases or acids as catalysts; and (b) at certain temperatures above 0°C when catalysts are present. When the condensation reaction occurs in the hydrolyzing solution, the solution becomes turbid and an oligomeric oil formed as a thin fiber at the solution surface and the side walls of the tubing connecting the hydrolysis container to the deposition bag. Under these conditions, no significant waterproofing is achieved. The condensation reaction can be well controlled by lowering the temperature of the hydrolyzing (activating) solution through which the alkylchlorosilanes are passed. In general, temperatures close to or below 0°C are required to stabilize the Si-OH groups prior to vaporization. The optimal temperature varies from one reagent to another primarily as a function of the intermediate silanol vapor pressure.

The above conclusions were confirmed by ^{1}H-NMR analysis of DMCS samples collected after they had passed through various basic solutions. A peak derived from Si-OH at around 5.1-5.3 ppm in D_6-DMSO (d^6-dimethyl sulfoxide) is typically observed for the collected product.

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VOLATILE REAGENTS ACTIVATED BY DEHYDROCOUPLING OF Si-H BONDS

The dehydrocoupling of diethylsilane (DES) was conducted under two different sets of conditions. We first attempted to use a heterogeneous system in which $Ru_3(CO)_{12}$, used as a very efficient homogeneous dehydrocoupling catalyst, was deposited on high-surface-area SiO_2 powder, molecular sieves, or dissolved in mineral oil. Nitrogen was bubbled as a carrier gas through liquid DES at room temperature and passed through the catalytic bed at room temperature into a flask containing alcohol cooled by ice water. The reagent was collected and analyzed for Si-OH by NMR (using d^6-DMSO as a solvent). The NMR analysis did not identify any Si-OH groups, and we concluded that activation of the reagent had not occurred.

Although we discontinued the effort to perform dehydrocoupling on a "time-of-flight" basis to focus on further explorations of chlorosilane activation systems, this approach should be revisited to gain a more fundamental understanding. The use of other catalysts such as heterogeneous platinum and palladium, or heating the catalyst bed (as tried in this effort) are valid approaches to dehydrocoupling. Other hydridosilane candidates should also be tested.

The second approach was to use a solution for the catalytic dehydrocoupling reaction. DES was dissolved in either ethanol or dioxane containing the Ru catalyst. The solutions were refluxed for 2 h to activate the catalyst and allow the hydrosilane to interact with the residual moisture in the solution. Hydrogen was released, and formation of Si-OH was confirmed by ^{1}H-NMR analysis. However, no silanol species were vaporized when nitrogen was bubbled through these solutions.

Though work on this approach was discontinued, it still shows good potential, especially if an intermediate silanol, having a higher vapor pressure, can be used. This approach will require a more focused effort in future studies in order to develop the necessary reaction parameters.
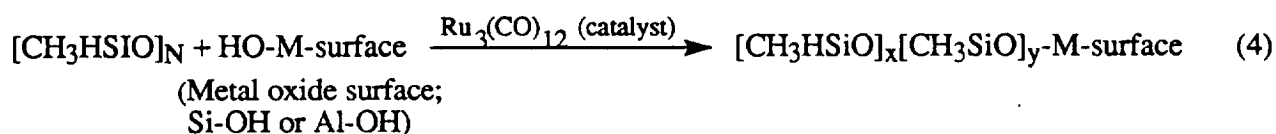
NONVOLATILE REAGENTS ACTIVATED BY DEHYDROCOUPLING OF Si-H BONDS

For reasons of improved thermal stability, we considered originally the use of nonvolatile silicon-based waterproofing polymers that bond strongly to surfaces. However, this approach fit also with the revised objectives of this project, i.e., acceleration of the waterproofing process and elimination of toxic silane. In this approach, nonvolatile oligomers and polymers are used in solutions based on the least toxic solvents (such as hydrocarbons) or non-VOC solvents (such as water/acetone and siloxanes).
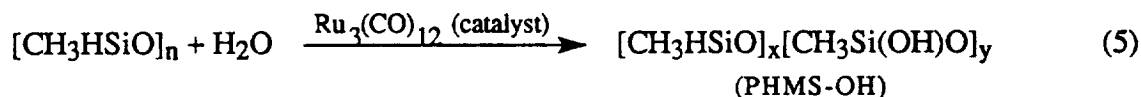
This concept is based on dehydrocoupling cyclomers and low-molecular-weight hydridomethylsiloxane polymers which have [CH3HSiO] monomeric units. The cyclomers and polymers are easily synthesized by reacting CH3HSiCl2 with water:

$$CH_3HSiCl_2 + H_2O \longrightarrow [CH_3HSiO]_n \qquad (3)$$
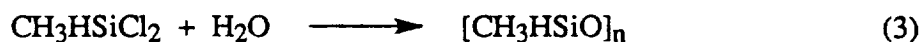
These polymeric species are very low-viscosity liquids (thin oils), which can be dehydrocoupled easily in the presence of 10-500 ppm of Ru3(CO)12 or other transition metal catalysts, including Pt. This reaction can be conducted *in situ* directly with the surface hydroxyl groups, as illustrated in Reaction (4).
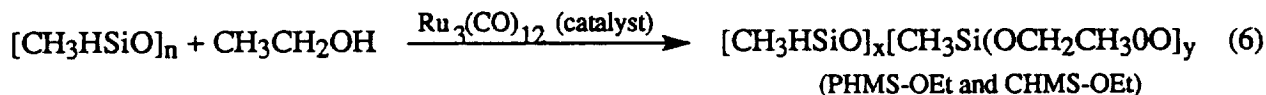
$$[CH_3HSIO]_N + HO\text{-}M\text{-}surface \xrightarrow{\text{Ru}_3\text{(CO)}_{12}\ \text{(catalyst)}} [CH_3HSiO]_x[CH_3SiO]_y\text{-}M\text{-}surface \qquad (4)$$
$$\text{(Metal oxide surface;}$$
$$\text{Si-OH or Al-OH)}$$

Alternatively, the polymer can react with water in an appropriate solvent before deposition to form PHMS-OH, as illustrated in Reaction (5).

$$[CH_3HSiO]_n + H_2O \xrightarrow{\text{Ru}_3\text{(CO)}_{12}\ \text{(catalyst)}} [CH_3HSiO]_x[CH_3Si(OH)O]_y \qquad (5)$$
$$\text{(PHMS-OH)}$$

Though siloxanes containing multiple Si-OH units tend to condense rapidly and form insoluble gels, we have found conditions in which such polymers remain stable in appropriate solutions for a long time, even after all the original Si-H bonds have been consumed. The resultant product is reactive, bonds easily to surfaces through Si-O-M bonds, and cures rapidly.

A third option with this system is to use alcohols to dehydrocouple cyclomers or polymers with multiple Si-H bonds, forming PHMS-OEt and CHMS-OEt, as shown in Reaction (6). The resultant alkoxy species are reactive in the presence of moisture, especially under acidic or basic conditions.

$$[CH_3HSiO]_n + CH_3CH_2OH \xrightarrow{\text{Ru}_3\text{(CO)}_{12}\ \text{(catalyst)}} [CH_3HSiO]_x[CH_3Si(OCH_2CH_3O)O]_y \qquad (6)$$
$$\text{(PHMS-OEt and CHMS-OEt)}$$

We assessed the potential of the products of Reactions (5) and (6), PHMS-OH, polyhydridomethylsiloxane ethoxide (PHMS-OEt), and cyclohydridomethylsiloxane ethoxide (CHMS-OEt). These modifications of CHMS and PHMS were made from commercially-available starting materials. NMR and IR analyses revealed that about 60% of the Si-H groups were replaced by Si-OEt in Reaction (6) and 70% were replaced by Si-OH in Reaction (5).

Coatings were made by dipping specimens in the solutions, then drying the dipped specimens in open air at room temperature overnight. No bagging is needed for curing (aging) the coatings in this case. Water pickup is the weight change after immersion of coated samples in distilled water for 15 minutes. The results are summarized in Table 6.

Table 6

WATERPROOFING RESULTS USING HYDRIDOSILOXANES

Solution	Insulation Material	Water Pickup wt% (%/Days)
0.5% PHMS-OEt	SiO_2	Picks up water
1% PHMS-OEt	SiO_2	9.5/1; 15/4; 20/7; 20/11; 19/14; 20/30
1% PHMS-OEt	Al_2O_3	Picks up water
2% PHMS-OEt	SiO_2	12.5/1; 17/4; 21/7; 15/11; 21/14; 20/30
2% PHMS-OEt	Al_2O_3	Picks up water
0.5% CHMS-OEt	SiO_2	Picks up water
1% CHMS-OEt	SiO_2	Picks up water
1% CHMS-OEt	Al_2O_3	Picks up water
2% CHMS-OEt	SiO_2	14/1; 8.3/4; 13/7; 9/11; 9/14; 9/14
2% CHMS-OEt	Al_2O_3	Picks up water
0.5% PHMS-OH	SiO_2	Picks up water
1% PHMS-OH	SiO_2	Picks up water after 1 day: 15/2; 16/3
0.5% PHMS-OH	Al_2O_3	10/1, 12/4
1% PHMS-OH	Al_2O_3	15.7/1; 13.5/3; 15/7; 12/10; 10.5/20
2% PHMS-OH	Al_2O_3	13.6/1; 13.5/4; 13.3/7; 13.7/11; 13.7/14; 14/30

aTypical curing conditions: 95°C/3 h.

The results indicate that

- CHMS-OEt and PHMS-OEt provide good waterproofing coatings on silica-based insulation material although not on the alumina insulating blanket.

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- In general, PHMS-OEt seems to perform better than CHMS-OEt. This observation can be explained if we assume that the chemical bonding of the cyclomer (CHMS-OEt) to the surface is more difficult because of steric hindrance kinetics and fewer reactive sites.

- PHMS-OH coatings made from low concentration solutions provide good waterproofing for both alumina and silica insulating materials, especially for alumina-rich materials.

- To obtain good waterproofing results on silica, the coatings had to be "aged" for more than one day. With a shorter aging period, the material still picked-up water.

- Even when the waterproofing reagents are not volatile, the kinetics of bonding the reagents to the insulator surface still seems to be critical. If chemical bonding does not occur, the waterproofing reagent can be washed off the surface.

- One major advantage of this system relative to the gas deposition system is that aging can occur in an open environment because no toxic waterproofing agents are released.

- Optimization of these coatings and acceleration of the curing kinetics by catalytic effects after deposition are expected to provide a good waterproofing system.

DISCUSSION
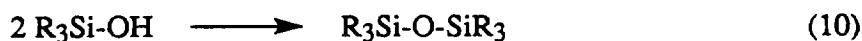
GENERAL CONSIDERATIONS

The results of this project, combined with the known performance characteristics of DMES[1] and recent results reported by NASA's researchers,[2] strongly indicate that the main issues in obtaining sufficient waterproofing are the kinetics of the reagent hydrolysis [Reactions (7) and/or (8)], the condensation (bonding) reaction to the surface [Reaction (9)], and condensation with other molecules of the hydrolyzed reagent [Reaction (10)]:

$$R_3Si\text{-}X + H_2O \longrightarrow R_3Si\text{-}OH + HX \qquad (7)$$
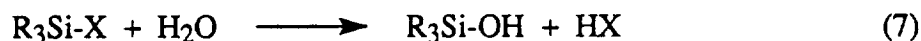
In this case, X is H, OEt, Cl, or NHSiMe$_3$.

$$R_3Si\text{-}X + HO\text{-}M\text{-}surface \longrightarrow R_3Si\text{-}O\text{-}M\text{-}surface + HX \qquad (8)$$

HO-M-surface represents pendant hydroxyl functional groups found at the surfaces of the insulation materials.

$$R_3Si\text{-}OH + HO\text{-}M\text{-}surface \longrightarrow R_3Si\text{-}O\text{-}M\text{-}surface \qquad (9)$$

$$2\ R_3Si\text{-}OH \longrightarrow R_3Si\text{-}O\text{-}SiR_3 \qquad (10)$$

For gas-phase deposition of waterproofing reagents the following are major factors in determining the efficiency and speed of reagent transport and chemisorption (by covalent bonding to surface) and in eliminating toxic reagents, by either self-condensation or rapid evacuation of excess volatile reagents:

- Vapor pressure (volatility) and flow rates of the reactants or the intermediates.

- Dilution of the reactant (or intermediate) in a reacting (hydrolyzing) solution or in the gas phase.

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- Activation rates of hydrolyzable latent reactivity groups in solution or as they pass through or near a heterogeneous catalytic bed.

- Rate of silanol intermediate condensation with the surface, in comparison with the rate of its self-condensation.

- Level of reagent bonding to surface (number of covalent bonds between a reagent and the surface).

- Types and numbers of hydrophobic groups on the organosilicon reagent.

Discussion of a few cases follows. In the basic operation, currently used for waterproofing the space shuttle, DMES is injected as a liquid directly into the tiles and locally transferred inside the tile "cell" by vapor phase redeposition. The bonding to the surface in this case is assumed to result from activation of the Si-OEt groups according to Reactions (7) and/or (8) followed by the condensation reactions illustrated in Reactions (9) and (10). Though we could not find any literature that specifically addressed the kinetics of the hydrolysis-condensation reactions of DMES, valuable information about these reactions can be extracted from in-depth studies about the deposition of coupling agents of the type $R_nSi(OR')_{4-n}$ used to bond inorganic surfaces to organic materials (such as fiberglass reinforced epoxy composites)[4] and, more recently, in various sol-gel studies in which $Si(OR')_4$ and $R_nSi(OR')_{4-n}$ are hydrolyzed and condensed to silica.[5] These articles are helpful in understanding the chemistry involved also in gas-phase waterproofing systems.

The hydrolysis/condensation reactions are dramatically enhanced in the presence of acid or base (nucleophilic) catalysts. In the current system, to the best of our knowledge, such catalysts are not used. Thus, the deposition rates are relatively slow and may be affected by the following factors:

- Amount of moisture or adsorbed water at the insulating surface [for Reaction (7)].

- Number of M-OH bonds at the surface and the kinetics of Reaction (8) as a function of electronegativity of the metallic element.

- Acidity or basicity of the insulator surface that can activate Reactions (8) or (9).

- Temperature.

In the absence of a strong base or a transition metal catalyst such as Pt, Pd, Ru, Rh, Sn, or Zn, we assume that the Si-H bond of DMES is not activated, only a single bond between the waterproofing reagent and the surface is formed, and the remaining Si-H groups contribute to the

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hydrophobicity of the waterproofed surface. Based on these assumptions, the deposited species at the end of the process will be:

$$[(CH_3)_2HSi-O-M-surface]$$
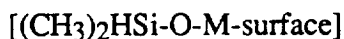
Information received from NASA as well as observations from this project indicate that these types of reagents provide good waterproofing for silica-based surfaces but not for alumina. In our study we also found that bonding to different surfaces varies even when the reagents already have Si-OH bonds at the time of deposition. This evidence supports the assumptions that bonding to the surface strongly depends on the surface chemistry.

The transition metal catalytic approach, currently being studied by NASA Ames, activates the Si-H bond instead of the Si-OEt bond because of gas-surface interactions with the catalyst on the bag surface. This process is slow, as evidenced by the relatively long aging process required to achieve waterproofing. If DMES is used, for example, it is anticipated that first the alkoxy silane is deposited at the surface, and only later is the alkoxy group hydrolyzed to form species that are double bonded to the surface:

$$[(CH_3)_2(EtO)Si-O-M-surface \longrightarrow [(CH_3)_2Si-(O-M-surface)_2] + EtOH \quad (11)$$

Table 7 compares some typical hydrolyzable monomeric silanes (having hydrolyzable Si-X groups) that should be considered as waterproofing reagents if they have sufficient volatility before and after hydrolysis.[6] The chlorosilanes can be replaced by bromo and iodo analogs, but these analogs are expected to be heavier and typically are not commercially available. Methoxy silanes are included in the table as more volatile analogs of the ethoxysilanes but are less suitable for use in this application because the released alcohol (methanol) is more toxic. A similar situation exists for the formyloxy analogs of the acetoxy silane reagents.

Table 7 indicates the dependence of volatility on the substituent, according to the following order:

$$H > CH_3 > Cl > OCH_3 > N(CH_3)_2 > OCH_2CH_3 > O_2CH > O_2CCH_3$$
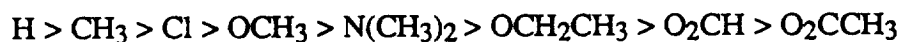
However, the kinetics of the hydrolysis of each functional group is also critical for rapid waterproofing, as discussed earlier. The preference in this regard is expected to be as follows:[7]

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$$Cl > O_2CH > O_2CCH_3 > N(CH_3)_2 > OCH_3 > OCH_2CH_3 > H$$

This order is semi-quantitative because we could not find a good reference that systematically and quantitatively compared all of the functional groups listed above. The hydrolysis of halosilanes can occur even at temperatures as low as - 80°C. The carboxylate silanes are also very sensitive to hydrolysis and serve as excellent catalysts to promote the hydrolysis of themselves and alkoxy groups. The aminosilanes are less reactive but still provide a self-catalytic effect as well as catalytic enhancement for the hydrolysis of alkoxy and Si-H bonds.

Table 7
BOILING POINTS OF POTENTIAL SILANE-BASED WATERPROOFING REAGENTS

Reagent	b.p. (°C)
$(CH_3)_3SiH$	7
$(CH_3)_3OMe$	56
$(CH_3)_3SiCl$	57
$(CH_3)_3SiOEt$	76
$(CH_3)_3SiNMe_2$	86
$(CH_3)_3SiO_2CH$	87
$(CH_3)_3OH$	99
$(CH_3)_3Si(OAc)$	103
$(CH_3)SiH_3$	-58 (explosive)
$CH_3SiH_2(OMe)$	0/127
$CH_3SiH(OMe)_2$	61
$(CH_3)SiH_2Cl$	9
$(CH_3)SiHCl_2$	41
$CH_3SiH_2(OEt)$	143
$CH_3SiH(OEt)_2$	95
$CH_3SiH(NMe_2)\ (OEt)$	100
$CH_3SiH_2(NMe_2)$	?
$CH_3SiH_2(O_2CH)$	?
CH_3SiH_2OH	?
$CH_3SiH_2(OAc)$	?

Table 7
**BOILING POINTS OF POTENTIAL SILANE-
BASED WATERPROOFING REAGENTS**
(concluded)

Reagent	b.p. (°C)
$(CH_3)_2SiH_2$	-20
$(CH_3)_2SiH(OMe)$	?
$(CH_3)_2SiHCl$	36
$(CH_3)_2SiH(OEt)$	54
$(CH_3)_2SiH(NMe_2)$	67
$(CH_3)_2SiH(O_2CH)$	?
$(CH_3)_2SiHOH$	?
$(CH_3)_2SiH(OAc)$	?
$CH_3(OMe)_3$	103
CH_3SiCl_3	66
$CH_3Si(OEt)_3$	142
$CH_3Si(NMe_2)_3$	55/17
$CH_3Si(O_2CH)_3$	?
$CH_3Si(OH)_3$	Cannot be isolated
$CH_3Si(OAc)_3$	MP 40.5
$(CH_3)_2Si(OMe)_2$	82
$(CH_3)_2SiCl(OMe)$	77
$(CH_3)_2SiCl_2$	70
$(CH_3)_2Si(OEt)_2$	114
$(CH_3)_2Si(NMe_2)_2$	?
$(CH_3)_2Si(O_2CH)_2$	?
$(CH_3)_2Si(OH)_2$	MP 100
$(CH_3)_2Si(OAc)_2$	165

The hydridosilane bond is actually inert in the absence of an appropriate catalyst. Transition metal catalysts based on the elements Pt, Ru, Rh, and Pd are most effective for activating the dehydrocoupling of Si-H with H-OH bonds and releasing hydrogen (which can be considered in this case as a "hydrolysis" reaction). Bases, for example, metal hydroxides, and to a

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lesser extent amines such as (CH₃)₂NH, can also be dehydrocoupling catalysts but are not as effective as the transition metals. This catalytic effect is currently being applied (using Pt as the catalyst) in the study reported by NASA Ames.[2] However, the catalyst in this case was deposited at the surface of the covering bag and not on the insulating material itself. Therefore, the coating process is less efficient and the distance of the activated hydrolyzed intermediates from the target surface favors intercondensation of the reagents with themselves rather than with the surface.

It is currently believed that the presence of a transition metal catalyst at the surface of the insulating material will be harmful to the mechanical properties of the fibers once they are exposed to elevated temperature during the space shuttle's re-entry to the atmosphere. We feel that this assumption should be investigated more thoroughly before complete dismissal of such an approach, because ppm levels of dehydrocoupling catalyst deposited at the surface may tremendously increase the hydrolysis and condensation reactions with the surface and allow use of minimal quantities of the delivered reagent.

The release of hydrochloric, formic, and acetic acids and amines should be considered potentially corrosive to some sensitive surfaces of the space shuttle. However, we assume that all the shuttle-building materials are chosen for their substantial durability and are not sensitive to relatively low levels of gaseous HCl. The organic acids and amines should present even less of a problem.

Hydrogen can also represent a potential problem because of its flammability. We think that the concentration of the released hydrogen in the gas phase will be too low to generate a hazard, and the hydrogen can be easily removed or diluted as rapidly as it is formed. However, calculations should be made to ensure the safety of such a system.

Of coarse, environmental issues relevant to the deposition process are a major concern in developing an optimal waterproofing system. An educated judgment suggests the following ranking of hydrolyzable functional groups from a toxicity point of view:[8]

$$H < OCH_2CH_3 < O_2CCH_3 < Cl < O_2CH < OCH_3 < N(CH_3)_2$$
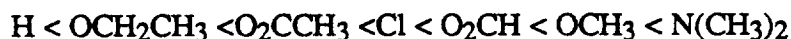
Hydrogen is completely nontoxic, and ethanol and acetic acid at low concentrations are only irritants. More information about the toxicity and other environmental issues and hazards (including compatibility with other materials) of these released gases will be given to NASA in a separate package of information gathered and analyzed by SRI's Environmental Health and Safety Department.

SILANOL INTERMEDIATE CONDENSATION

Our study and the NASA study indicate that even rapid hydrolysis is not sufficient to obtain good waterproofing. The hydrolyzed intermediates must condense with the surface hydroxyl groups at an efficient rate. For example, even when we used a polysiloxane containing a high concentration of Si-OH, we had to age the coatings to achieve good bonding to the surface. Also, it is clear that bonding to alumina is less favorable to silica surfaces.

We found that volatile intermediates with Si-OH functional groups can be stable enough under certain conditions to be delivered from a "generator" reactor in the deposition chamber without self-condensation. We found that the waterproofing effect could be achieved in less than 1 h once slightly acidic conditions are achieved inside the deposition bag (a sign of escape of either free HCl or chlorosilane from the generator). A few hours were required to achieve similar waterproofing properties when acid was not detected inside the bag.

It is well known that condensation of Si-OH groups can be accelerated by acid or base catalysts through an S_N2 nucleophilic reaction mechanism.[9] In sol-gel condensation reactions, for example, basic conditions are traditionally used. However, other nucleophiles, such as fluoro or acetic anions, are excellent condensation catalysts. We therefore believe that the presence of such nucleophiles in catalytic quantities will enhance the bonding of the silanol waterproofing reagent to the surface of the insulating materials.

The condensation reaction with the surface ("chemisorption") competes with the self-condensation of the hydrolyzed species. The latter reaction results in the formation of oligomers that can be physically deposited at the surface but are not chemically bonded to it. The physically adsorbed particles can be easily washed from the surface. Several good studies in this field have been conducted with active organoalkoxysilanes, $R_nSi(OR)_{4-n}$, used as coupling agents for composite materials.[4] These studies showed the correlation between the hydrolysis and various condensation reactions under acidic and basic conditions. However, all these studies are based on dilute solution systems and not gas phase reactions, in which the type of solvent, R and RO groups, water and alcohol concentrations, as well as pH conditions, have a major impact on the kinetic values. We could not find in the literature specific correlations between the hydrolytic and condensation kinetics for typical alkoxysilanes and silanes having the other leaving groups discussed above.

Assuming that the presence of a catalyst would enhance the condensation reaction, a few concepts can be developed. First, it is important that the catalyst be either in the gas phase or volatile enough to be removed during the waterproofing process to prevent any undesired

deposition that would degrade the fibrous material at elevated temperature. Second, the catalyst should be relatively harmless in terms of toxicity and corrosion. Our studies showed that a low level of HCl in the waterproofing chamber significantly accelerated the deposition rates of chlorosilane systems. Acetic acid, ammonia, or other volatile amines are also good candidates, if present in very low concentrations.

Catalysts can be delivered to the insulation material in the gas phase before or during transport of the gaseous waterproofing reagent. Physical adsorption of such a catalyst may be enough to accelerate condensation with the fiber surface. In fact, such a situation may be preferable because of competition between the chemisorption and self-condensation of the reagents. A catalyst deposited at the surface may enhance the surface bonding and will not affect the self-condensation in the gas phase. Another attractive option is to bleed low levels of gaseous silane having chloro, amino, or acetoxy groups together with the hydrolyzed or alkoxy reagent. In this case, the released leaving group will serve as an auto-condensation catalyst.

CHLOROSILANES AS WATERPROOFING REAGENTS

This project revealed that chlorosilanes can serve as excellent waterproofing reagents without the need to expose the insulation material (or other parts of the spacecraft or the operating environment) to significant amounts of HCl, which is released during hydrolysis of the Si-Cl bond. A simple way to achieve the hydrolyzed intermediates is to bubble them through water solutions. We assumed that basic conditions would enhance this reaction as well as prevent the release of HCl to the atmosphere. The presence of different bases and their concentration in solutions seem to be important too. We found that it was critical to control the level of basicity to avoid condensation of the hydrolyzed reagents during their passage through the water solution. A more efficient way to prevent condensation in the water solution is to cool the water.

Another critical factor is the residence time of the hydrolyzed intermediate in the water solution. Residence time is controlled by the pathway length, the volume of the solvent container, and the rate the carrier gas is passed through the solution. Of course, the specific vapor pressure of each type of intermediate contributes.

We also discovered that if the water temperature is low enough, it is feasible to generate hydrolyzed intermediates and release them into the deposition chamber even in the absence of a base. The low temperature keeps the released HCl in solution. Only at the end of the process have we sometimes been able to detect (by litmus paper) the evolution of HCl into the deposition

chamber. We assume that careful process development will eliminate any accidental volatilization of the corrosive gas to the spacecraft environment.

Nevertheless, we have found that after the hydrolyzed reagent has been delivered a low level of HCl in the waterproofing chamber enhances the rate of deposition of the silane at the surface, and completion of waterproofing can be obtained in less than 1 h. In contrast, we found that without this slightly acidic environment, a few hours are required to "age" the waterproofing reagent; otherwise, the waterproofing is inadequate. This observation prompted our consideration about the value of a condensation catalyst, as discussed in the section above.

The hydrolysis reaction of the alkylchlorosilanes can take place quickly at very low temperature (below -55°C). However, we found that the self-condensation reaction is much slower at temperatures below -3°C even in the presence of a strongly basic solution. This observation provides the possibility of achieving efficient hydrolysis while therminally inhibiting the condensation reactions.

We found an optimum temperature range for each reagent used in the study. This range depends on the molecular structure of the reagents. For example, a good waterproofing layer is obtained with TMCS at temperatures above 0°C when NaOH solution s used. However, a good coating is obtained with DMCS only when the temperature is below -3°C, when the same solution and other processing conditions are used. This variation in behavior is explained by the higher stability of the trimethylsilanol intermediate relative to dimethylsilanol.

The temperature of the hydrolysis reaction should not be too low because the vapor pressure of the silanol intermediate is reduced and even solidifies products in some cases. For example, TMCS and DMDCS gave inadequate coatings when the solution temperature was reduced to -12°C. Thus far, the best temperature range for each of the reagents passed through NaOH solution is as follows:

DMCS: -15 to -3°C
TMCS: -10 to 8°C
DMDCS: -10 to 3°C

Another important factor is the type of solution. Different types of solutions will affect the rates of condensation as a result of the pH or the type of catalytic nucleophile. At this stage, we focused on using NaOH solution, which is a strong basic solution, although other bases were also tried. For example, Na_2HPO_4, a weak base, gave a better waterproofing results when higher temperatures were used (0-3°C). A solution containing organic amino groups was also tested, but

waterproofing was not successful because the increased solubility of the alkylsilanol in the organic amine/water solution enhanced the self-condensation reaction in the hydrolyzing solution.

When water was used alone (containing some NaCl) as the medium for DMCS, the alkylsilanol intermediate remained in the solution, which became turbid even at relatively low temperature (-5 to -10°C). In contrast, the NaOH solution always remained clear and the generated alkylsilanol was vaporized to the deposition area by the carrier gas. We conclude that more work needs to be done to identify the best hydrolysis media for the systems.

Another factor is the contact time of the chlorosilane (or alkylsilanol) with the hydrolysis solution. Shorter residence periods lead to better waterproofing results. Higher flow rates of carrier gas than the 13 to 18 mL/min used with DMES gave much better results for the chlorosilane systems because of the short contact time of the intermediates with the solution and with each other.

Higher flow rates also assist the delivery of the silanol intermediates. For example, TMCS has a boiling point of 57.6°C, but its corresponding silanol has a boiling point of >90°C, so a high flow rate is required. Nevertheless, when higher flow rates are used with chlorosilanes having low boiling points, it is important to cool the reservoir to avoid delivery of large amount of the chlorosilanes into the hydrolysis solution in a short period (for example, in the case of DMCS). We found that a one hour exposure time was adequate for a good waterproofing coating when DMCS was used as a reagent and delivered at a flow rate of 30-35 mL/min. The hold time after delivery is also important. More work is required to determine the best conditions for exposure and the optimal hold time.

The current study focused on an approach where the hydrolysis reaction occurs in a water-based solution. Other modified systems may provide better and more convenient hydrolysis chambers. For example, a system comprising gas phase hydrolysis of chlorosilanes with controlled level of moisture, then passage of the intermediate products through a solid base medium to trap the released HCl, may be advantageous and eliminate the need to control the solution temperature.

HYDRIDOSILANES AND ALKOXYSILANES AS WATERPROOFING REAGENTS

Similar considerations to those discussed above in relation to the chlorosilane approach can be used for hydridosilane and alkoxy silane reagents. The differences between these three types of reagents are their relative volatility before hydrolysis and the hydrolysis (or dehydrocoupling) rates.

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Hydrosilanes

Hydridosilanes are advantageous because of their higher volatility and inert by-products (assuming rapid dilution of the released hydrogen). However, activation requires contact with a transition metal catalyst. We predict that both solution and solid catalyst systems can be developed. We anticipate that activation of the hydridosilane before transfer into the waterproofing chamber (in contrast to current procedures used at NASA Ames) will be advantageous in minimizing the aging period. Currently, catalytic activation occurs only at the surface of the waterproofing chamber, so the initial reagent must move out to and away from the chamber walls. We also do not want to rule out the option that a zinc, tin, or some other transition metal catalyst could be deposited at the surface first to assist direct condensation with the surface hydroxyl groups. These catalysts may not harm the fibers at elevated temperature and may even evaporate at high temperature. However, the deposition of such a catalyst may slow the waterproofing process.

Alkoxysilanes

Alkoxysilanes are heavier and less reactive in hydrolytic conditions than the corresponding chlorosilanes. However, they may be good candidates for hydrolytic solution operation. Acidic conditions that are unfavorable for catalyzing condensation (typically pH 4) may accelerate the hydrolysis rates enough to provide efficient hydrolysis during the residence time of the reagent in the solution. The only disadvantages of this system relative to the chlorosilane analogs are the lower hydrolysis rates and the release of alcohol to the waterproofing chamber.

POLYSILOXANES AS WATERPROOFING REAGENTS

Polyalkoxysiloxanes and polysilanols gave good waterproofing coatings on silica, but only polysilanols also provided adequate waterproofing coatings on alumina-based material. We can conclude that bonding directly to the alumina material is achievable, but the kinetics of this reaction are much slower than for bonding to a silica surface and even further slower than for the self-condensation reaction. The polysilanols successfully bond to the alumina surface because of their high local concentration after deposition and the local steric hindrance of the polymer itself, which inhibits self-condensation in full capacity.

Of coarse, the disadvantage of using alkoxysiloxanes and polysilanols is their non-volatility; they must be applied by solution spraying, which is not an attractive approach as vapor deposition.

CONCLUSIONS

This project revealed primarily that volatile alkylchlorosilanes can provide another efficient gas-phase deposition approach for waterproofing of spacecraft insulating materials. This system has process advantages—such as relatively high volatility, very rapid hydrolysis, and low toxicity—associated with excellent waterproofing properties, assuming that the by-product, HCl, can be easily removed from the vapor phase. In fact, a slight bleeding of acid may be advantageous for accelerating the deposition rates of the silanol intermediates.

We also found that silanol intermediates can be formed and be both stable enough and volatile enough to be delivered from a "generator reservoir" to the target surface. In fact, in the absence of an adequate condensation catalyst, a hold period is required to ensure good chemical bonding between the waterproofing reagent and the surface.

The study results combined with existing literature on coupling agents strongly indicate that chemical bonding between the reagent and the surface is required. Physical deposition of condensed species at the surface of the fibrous material is not sufficient.

Other sources for silanols have been identified to provide additional options for choosing the best reagent or mixture of reagents. Various groups can be used as precursors to the silanol intermediates. The choice of reagents should be based on: (a) ease of application, (b) reagent and intermediate volatility, (c) kinetics of generating the silanol intermediate, (d) rate of chemical bonding to the surface, (e) toxicity, and (e) other hazards.

If the toxicity of silanes prevents the use of volatile monomeric silanes, then an alternative approach is to spray nonvolatile siloxanes having a significant degree of alkoxy or silanol functional groups. This system has the disadvantage of using a spray and therefore a significant amount of solvent. However, once the reagents are delivered to the insulating materials, there are no concerns about the toxicity of volatile silanes. In this case, the only environmental concern is the solvent evolved from the solution and the relatively small levels of alcohol released when an alkoxysiloxane reagent is used.

Our results, combined with NASA's reports and the literature search, strongly indicate that kinetics and, primarily, the deposition rates of the silanol reagent at the insulation material surface are the main issues in developing a rapid waterproofing system. Although good studies have been

conducted about the kinetics of hydrolysis and condensation of typical coupling agents and their chemical bonding to surfaces (including silica),[4] this literature information does not completely answer all our questions. All the publications are based on using very dilute solutions, catalytic conditions (acidic or basic), and larger functional groups than the methyl group used for waterproofing the spacecraft insulation materials. Therefore, these studies can serve only as basic guidelines. Our literature survey did not identify any relevant literature regarding similar dynamics of gas-phase-hydrolyzable silanes.

The laboratory work conducted in this project is very preliminary. Additional development associated with extending our fundamental understanding of the hydrolysis-condensation kinetics of gas-phase waterproofing reagents will result in the development of a practical, rapid process to replenish the waterproofing on space vehicles after re-entry

RECOMMENDATIONS

The development of a gas-phase deposition system for rapid replenishment of waterproofing on spacecraft is feasible. Such a process is heavily dependent on the volatility of the silane reagent and its silanol derivative, the rate of hydrolysis, and the rates of condensation to the surface. It is also dependent on the relative efficiency of the deposited hydrophobic film (i.e., the minimal level of material needed to be deposited at the surface to provide sufficient waterproofing). At the same time, the development of this approach needs to consider the toxicity of the silane reagent, its silanol intermediates, and by-products. Because the toxicity is only a problem of the presence of the reagents and their silanol intermediates in the gas phase, rapid hydrolysis and especially condensation rates are required. Another concern, besides toxicity, is the potential corrosivity or flammability of the released by-products of the hydrolysis reaction.

The studies at both NASA Ames and SRI reveal the feasibility of several gas-phase deposition systems. The studies indicate that hydrolysis-condensation kinetics play a major role in this approach, and these reactions need to be faster than currently achieved. The Discussion section in this report offers various ways to accelerate the reactions and to eventually develop practical deposition technology. However, a significant amount of information remains unknown about the chemical behavior of each suggested type of reagent, their hydrolytic and kinetic characteristics, and especially how to condense them rapidly by direct bonding to the surface (rather than self-condensation).

The silane toxicity can be eliminated if a nonvolatile, soluble reagent capable of condensation with the surface is applied by spraying. However, in this case the solvents used as a vehicle for the waterproofing reagent become a critical issue. This approach should be kept in mind as an alternative, but not as a primary approach for rapid waterproofing.

The following recommendations are suggested for further exploration of the gas-phase deposition approach:

- Screen other reagents beside hydrido, chloro, and alkoxy silanes tested thus far, after assessing their potential hazards and/or corrosive effects.

- Develop a better understanding of the hydrolysis (or dehydrocoupling) and condensation kinetics of typical reagents on the basis of currently available literature.

- Identify areas where current model studies are not sufficient to extrapolate published kinetics developed for solution systems to the gas-phase system.

- Focus on approaches to accelerate the condensation of volatile silanols formed by hydrolysis or dehydrocoupling, and develop convenient chemistries that will favor surface bonding over self-condensation of the silanol intermediates.

- Develop a better understanding of the characteristics of the chemical species bonded to the insulation material surface that provide good and stable waterproofing systems. This understanding will reflect the combination of using the best reagents for rapid bonding to the surface and using the minimal levels of reagents required for bonding to the surface.

- Assess potential negative effects of condensation catalysts directly deposited at the surface or in the gas phase on the degradation of the insulating materials and possibly other spacecraft surfaces. This effort is needed because it is assumed that much more efficient systems can be developed if a solid catalyst (sometimes at ppm levels) can achieve rapid chemisorption of the reagents to the insulating material surface.

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