# FINAL REPORT

## Replacement of Isocyanate Chemistry for Polyurethane-Like Topcoats

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This project attempted to establish a non-isocyanate polymerization-crosslinking platform for a high-performance exterior topcoat that replaces the use of environmentally hazardous isocyanate chemistry used in state-of-the-art polyurethane (PU) topcoats. The original technical approach consisted of hydrosilylation platform including the synthesis of adequate intermediate building blocks having either multiple Si-H or multiple terminal alkene sites. The technical approach was successfully modified to a combination of hydrosilylation-dehydrocoupling platform in the last year of the project in an effort to overcome several drawbacks identified during the performance of the hydrosilylation-only platform.

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# LIST OF ACRONYMS

| | |
|---|---|
| A-187 | epoxy functional silane |
| ASTM | American Society for Testing and Materials |
| ASTM 4366 | Koenig hardness test |
| ASTM D3363-74 | pencil hardness test |
| ASTM D3359-02 | cross-hatch adhesion test |
| ASTM E2546 | microhardness test |
| ATMS | allyltrimethoxysilane |
| BMS10-11 | Boeing; Corrosion and Fluid Resistant Primers |
| Boeing | The Boeing Company |
| BS 3900:E8 | Koenig hardness test |
| CA7502 | PPG commercial aerospace epoxy primer |
| DFT | dry film thickness |
| DIM 53157 | Koenig hardness test |
| DMA | dynamical mechanical analysis |
| DMS-V03 | Gelest silicone resin (lowest molecular weight version) |
| DMS-V22 | silicone resin (Gelest) |
| DMS-V22 | silicone resin (Gelest) |
| DSC | differential scanning calorimetry |
| DTT | dry to touch |
| ene | alkene (vinyl groups) |
| FTIR | Fourier transformed infrared spectroscopy |
| H-NMR | hydrogen-nuclear magnetic resonance |
| HAP | hazardous air pollutant |
| HMDI | hexamethylene diisocyanate |
| HPDMS-R-HPDMS | Hydro terminated polydimethylsiloxane-organic-polydimethylsiloxane |
| IPDI | isophorone diisocyanate |
| IR | infrared spectrometry |
| ISO 14577-1 | micro hardness test |
| ISO 1522 | Koenig hardness test |
| MEK | methyl ethyl ketone (butatone) |
| MIL | Military specifications |
| MIL-PRF-85285E | Type I, Type II, Type III, and Type IV Polyurethane Topcoats |
| MW | molecular weight |
| NAVAIR | Naval Air Systems Command |
| NMR | nuclear magnetic resonance |
| OEM | original equipment manufacturer |

| | |
|---|---|
| PDMS | polydimethylsiloxane |
| PHMS-OH | polyhydromethylsiloxane-hydroxylated |
| PPG | PPG Industries, Inc. |
| ppm | parts per million |
| Pt | platinum |
| PU | polyurethane |
| R21 | cyclic Si-H polymer (produced at SRI) |
| R32 | multi-vinyl polymer (produced at SRI) |
| R44 | tetrakis Si-H polymer (produced at SRI) |
| R60 | higher molecular weight variation of the Si-H functional polymer (produced at SRI) |
| R71 | higher molecular weight variation of the Si-H functional polymer (produced at SRI) |
| RB | round-bottomed (flask) |
| RR-94 | HMDI-based urethane acrylate |
| RT | room temperature |
| SDS | Safety Data Sheet |
| SERDP | Strategic Environmental Research & Development Program |
| Si-H | silicon hydride |
| Ene | compound containing a double bond |
| TGA | thermal gravimetric analysis |
| THF | tetrahydrofurane |
| UV | ultraviolet |
| VIN C50 | Siltech® tri-functional high-molecular-weight silicone pre-polymer with reactive vinyl groups |
| VIN J10 | Siltech® multi-functional high-molecular-weight silicone pre-polymer with reactive vinyl groups |
| VOC | volatile organic compound |
| VTAS | vinyltriacetoxysilane |
| VTMS | vinyltrimethoxysilane |
| XRR | IPDI-based urethane |
| RR-94 | HMDI-based urethane acrylate |

# KEYWORDS

Topcoat, aerospace paint, paint industry polyurethane (PU), isocyanate, urethane, hydrosilylation reactions, platinum catalysts, hydro-silane, vinyl, terminal alkenyl, dehydrocoupling reactions, curing, silanol chemistry, silanol condensation, alkoxysilane hydrolysis, crosslinking, condensation reactions, paint characteristics, coating performance, aerospace aluminum alloys, primer paints, hardness, adhesions, paint stability, and pot life.

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SRI International led this project and teamed with PPG, a leading global paint supplier, and Boeing, the leading global aircraft manufacturer and a main military aircraft supplier.

# ABSTRACT

**Objective.** The objective of this project was to establish a non-isocyanate polymerization-crosslinking platform for a high-performance exterior topcoat to replace the use of environmentally hazardous isocyanate chemistry used in state-of-the-art polyurethane (PU) topcoats. SRI International (SRI) led a team, including PPG and Boeing, to develop a new chemistry platform for ultraviolet (UV) and weathering-stable aircraft topcoats based on organosilane chemistry traditionally used for silicone-based sealants and elastomers. The topcoat was to be a thermoset hybrid resin coating consisting of nonaromatic organic and siloxane segments that are cured at room temperature (RT) or very moderate temperatures.

**Original Technical Approach.** The synthesis of adequate intermediate building blocks for achieving the desired topcoats utilized the highly efficient hydrosilylation reaction between Si-H and terminal alkene sites, a reaction also employed to cure the derived coating formulations. This synthesis approach can utilize many commercially available reagents, can be scaled up, and is applied using common manufacturing methods.

**Modified Technical Approach.** The technical approach was modified in the last year of the project to overcome several drawbacks of our original approach identified during the program. The modified approach began with the synthesis of multiple Si-OH-containing intermediates via hydrosilylation (as was the case in the original approach), followed by dehydrocoupling reactions to efficiently convert Si-H groups to Si-OH in the presence of water and/or Si-OR in the presence of alcohol. The intermediates were then cured by catalyzed Si-OH condensation. This modified approach overcame major challenges associated with the original approach, and we recommend further development using the modified approach.

**Results.** The project focused on nonaromatic formulations known to be significantly more stable during long-term exposure to UV light, as required for aerospace applications. The SRI team synthesized more than 100 intermediates and screened more than 450 formulations as clear and pigmented topcoats over aircraft aluminum alloys or aircraft-certified primers deposited on aluminum alloys. Most of the hydrosilylation syntheses were found to be very versatile and simple to process (even in the absence of solvents) if we included 10 to 20 ppm of an extremely efficient Pt catalyst. The catalyzed reaction was less useful in amine and isocyanate functional groups (complete deactivation of the catalyst) and acrylic and other vinyl groups in proximity to carbonyl group (much slower reactions at low temperatures). However, the main problems identified with the hydrosilylation system occurred during the curing of the evolved formulations as coatings. Nevertheless, the reactions could be easily scaled up from 10 to1000 g quantities.

Curing in this system relies on additional hydrosilylation reaction in the presence of the live platinum remaining from the intermediate synthesis step. In most cases, we had to add about 30 ppm of a fresh catalyst to accelerate the curing reaction at RT and 50°C. The original approach demonstrated curing capability at 50°C with adequate hardness and adhesion when down-selected formulations of intermediates were deposited as coatings over aluminum and chromated aluminum surfaces. However, we encountered various challenges, which required us to seek solutions and redirect the project's approach at month 22. The main shortcoming associated with curing the coating formulations occurred during their deposition over primers. The amine content at the surface of the cure primers was sufficient enough to poison the Pt

catalyst. An additional major hurdle was the very short pot life after mixing the Si-H and vinyl intermediates once the additional catalyst required for curing was added. In contrast, the lack of additional catalyst led to insufficient curing even at 50°C. These shortcomings are described in detail in this report. Although we have solved or mitigated some of these problems, the solutions were not elegant and added more steps, solvents, and surface pretreatments than desired.

We switched to the modified approach in the last year of the project. We took a few of the multiple Si-H-bonded intermediates and efficiently converted all their Si-H into Si-OH via a dehydrocoupling reaction with water. This is a very efficient reaction, in which a commercially available ruthenium carbonyl catalyst is used at the level of 100 ppm. During the synthesis of the best Si-OH intermediate (down-selected for the final sets of testing), some condensation of the Si-OH into Si-O-Si (+$H_2O$) was observed, and it extended the degree of polymerization and consequently the molecular weight of the Si-OH intermediate and its viscosity. The higher viscosity was found to be advantageous for paint formulations and applications. Curing the formulation based on the Si-OH intermediates was very efficient at RT when a base (amine) catalyst was added; this yielded high hardness and adhesion values that far exceeded the values achieved with the hydrosilylation system. The pot life was extended to the range of4 to 20 h, which is a very realistic time frame for thermoset coatings. The amine content of the primers that was so detrimental to Pt-catalyzed hydrosilylation curing was advantageous for curing and bonding of the Si-OH system.

We had only enough time to evaluate six different Si-OH intermediates, and we down-selected one for scale-up and formulation. Thus, we are clearly far from an optimization stage. Indeed, a number of other formulas can be synthesized and evaluated if additional studies are performed. The down-selected intermediate was scaled up to 2 L of ready-to-use solutions. Although we evaluated a single intermediate in the standard tests of aviation-grade topcoats (according to MIL-PRF-85285E and Boeing's commercial standards), some of the early formulations passed many of the required tests. We still need to improve the bending and impact resistance of the coatings according to the MIL specs (even though they were adequate for Boeing's tests). Weathering stability can also be improved by using appropriate additives that have not yet been studied in a systematic manner.

**Benefits.** The hydrosilylation-deydrocoupling intermediate approach provides intermediates that are good candidates for further R&D activities focusing on topcoats for aircraft and non-aircraft applications. In contrast, the hydrosilylation-only system is not adequate for top-coating applications. Nevertheless, we encourage assessment of the intermediates (which are simple to make with the hydrosilylation reaction) because we believe they are excellent candidates for gas separation of organic compounds when tailored-affinity membranes are used.

The benefits of the proposed hydrosilylation-dehydrocoupling system are its versatile intermediate synthesis capabilities, the chemical stability of the derived coatings, and the fact that there are many suitable commercially available reagents for obtaining good intermediate candidates based on this approach. Given the very low levels of transition-metal catalysts and the capability to recover them via sorbing materials, the overall cost of the formulations will be similar to or less than that of currently produced topcoats (polyurethanes) for aircraft applications.

# OBJECTIVE

## STATEMENT OF NEED

The project aimed at developing a non-isocyanate polymerization crosslinking platform through hydrosilylation and a combination of hydrosilylation-dehydrocoupling reactions to produce nonaromatic polymers typical for aircraft grade PU that (1) eliminates the use of environmentally hazardous isocyanate chemistry and (2) improves the weather stability of the topcoat. The development of replacement products for PU is of growing interest and demand for both military and commercial applications due to the health hazards associated with the isocyanate chemistry. The specific objective was to develop an aircraft-grade topcoat that meets the specifications for polyurethanes as defined in MIL-PRF-85285E, titled "Performance Specification, Coating: Polyurethane, Aircraft and Support Equipment (12-JAN-2012)".

## TECHNICAL APPROACH

This project established a non-isocyanate polymerization-crosslinking platform for a high-performance exterior topcoat that (1) eliminates the use of environmentally hazardous isocyanate chemistry and (2) simultaneously improves the weather stability of the topcoat. The SRI team worked on a topcoat technology for producing polymers containing the typical nonaromatic building blocks incorporated in aircraft grade PU but having different polymerization/crosslinking chemistry than isocyanate. Building blocks that are easily produced by current manufacturing capabilities are polymerized and crosslinked by efficient hydrosilylation and a combination of hydrosilylation-dehydrocoupling reactions. The project focuses on nonaromatic formulations known to be significantly more stable during long-term exposure to ultraviolet (UV) light conditions, as desired for aerospace applications. However, it is highly feasible to expect even better coating intermediates and subsequent coating performance with intermediates containing aromatic functional groups.

The investigated hydrosilylation-deydrocoupling synthesis approach and the derived versatile intermediates developed in this project provide a platform for intermediates that can be further explored and optimized for aircraft and non-aircraft topcoats. In addition, the original hydrosilylation-only system that was found to be inadequate for top-coating applications can be very useful as an approach for making for gas separation having tailored-affinity for organic gases.

Siloxane compounds and polysiloxanes ("silicones") are known to be environmentally safe due to their bioinert nature and chemical stability. They are also heat and fire resistant and have been used for many years in surgical inserts and implants. There is a growing market for polysiloxanes as materials for kitchen appliances that operate at high temperature in contact with food. Volatile cyclosiloxanes are used as ingredients in a number of personal health and beauty products in contact with human skin, including deodorants, antiperspirants, cosmetics, shampoo, and body lotions. These volatile compounds are also used as environmentally friendly dry-cleaning solvents and in industrial cleaning.[8] A 2011 report commissioned by the Canadian Government[9] regarding decamethylcyclopentasiloxane (siloxane D5) concluded that there are no environmental issues related to volatile siloxanes and indicated benign health effects in rats.[10]

## POTENTIAL BENEFITS

The advantage of the explored hydrosilylation-dehydrocoupling system is its versatile synthesis capabilities, the chemical stability of the derived coatings, and the use of many suitable, commercially available reagents for obtaining good intermediate candidates based on this approach. Given the very low levels of transition-metal catalysts and the capability to recover them via sorbing materials, the overall cost of the formulations will be similar to or less than that of currently produced topcoats (polyurethanes) for aircraft applications.

The topcoat platform developed in this project consists of nonaromatic organosilane curable (thermoset) resins that are historically considered as components of nontoxic and environmentally safe materials.

Our development involves the formulation of paints exclusively consisting of only nonvolatile siloxane and organic crosslinkable intermediate. The Safety Data Sheet (SDS) for silicone (polysiloxane) oils (also used in cosmetics) does not indicate any known health hazard issues. Examples are SDS documents for dimethicone (a cyclooligamer of dimethysiloxane that is broadly used by the cosmetic industry) and polydimethylsiloxanes that are used in many medical products and implants that are inserted into the body or in contact with its skin. The ppm levels of the Pt catalyst residing in hydrosilylated silicone elastomers in breast implants have been examined, and no hazards were found that were associated with Pt. Even higher daily exposure to Pt compounds via industrial products and automotive catalytic convertor emissions have not been linked with any health risks.[11]

The effort focused on liquid intermediates with repatively low viscosity. It allowedthe minimization of volatile organic compounds (VOCs) and the use of VOC-exempt solvents and eliminated hazardous air pollutant (HAP) solvents. The Si-OH intermediates developed after the modification of the chemistry platform are stilllow viscosity fluids but they require the presence of a polar organic solvent to prevent self-crosslinking. Minimization of the solvent content has not been addressed yet.

The evolved technology is a viable approach for high-end topcoats while eliminating the growing health concerns regarding exposure to isocyanate compounds currently classified as potential human carcinogens and known to cause asthma and irritation of mucous membranes and skin. Additional potential advantages of the chemistry include improved UV stability, and reduced flammability and toxic combustion products in the event of fire. A significant development effort is still required to bring this technology to fruition.

# BACKGROUND

## POLYURETHANE (ISOCYANATE) VERSUS HYDROSILYLATION REACTIONS

Polyurethanes (PUs) are the preferred polymeric materials for many high-end coating and foam applications for military and civilian use, including most durable topcoats.[1-3] However, the health hazards associated with isocyanate compounds used as active building blocks for PU—especially hexamethylene diisocyanate (HDI), which is currently used for state-of-the-art nonaromatic PU topcoats—are cause for increasing concern.[4-7] Other concerns are (1) the potential for exposure to toxic fumes generated when PUs are exposed to thermal degradation and fire; (2) added maintenance cost; (3) operation downtime; and (4) generation of hazardous waste as a result of depainting or repainting necessitated by premature changes in the appearance of the coating (e.g., color fading, loss of gloss, chalking) caused by environmental exposure.

PU topcoats improve the appearance and lifespan of many military systems. On vehicles, they give the exterior a high gloss, improve color retention, and provide resistance to scratches and corrosion. In the aerospace arena, PU coatings protect external parts of aircraft during the extreme temperature fluctuations that occur when a plane leaves a hot runway and ascends to below-freezing temperatures at cruising altitudes. In addition, they also help protect the skin of the plane from rust and pitting. Other types of PU coatings are used in construction; for example, building floors, steel trusses, and concrete supports are spray-coated with PU to improve their appearance, make them more durable and easier to clean, and reduce corrosion and associated maintenance costs. The basic reaction of isocyanate during the formation of PU is shown in Figure 1, which can be compared with the hydrosilylation reaction (Figure 2) assessed in this project.

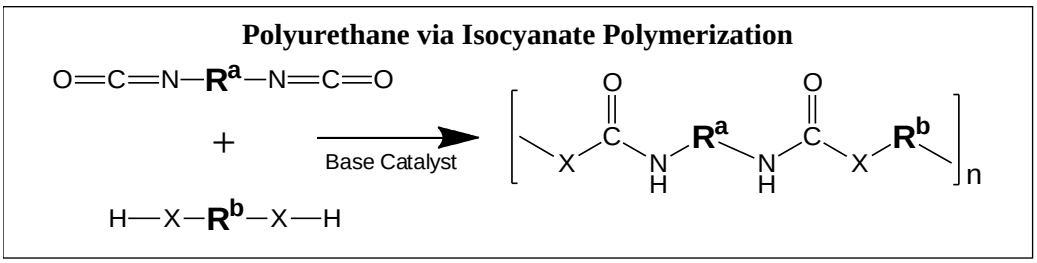



***Figure 1.*** *A typical reaction of isocyanate with X-H containing groups to form PU; typical Ra & Rb groups are illustrated in Figure 3. X group is an NR, O, or $CO_2$ functional group. For UV-stable topcoats both Ra & Rb preferably contain only aliphatic organic groups and no aromatics.*

It should be noted that both the isocyanate and the hydrosilylation reactions are defined as "addition reactions" in which a double bond is inserted into X-H (isocyanate) or Si-H (hydrosilylation) bonds. Figure 3 shows typical $R^a$ & $R^b$ building blocks for industrial PU systems. In the proposed study we focus on building blocks consisting of linear oligomeric aliphatic, ether, ester, and siloxane chains, which are significantly more stable than the aromatic building blocks under UV conditions and more elastomeric in their nature.

Polyurethanes have been in commercial use since the mid-1950s and are still considered to be the high-end products for durable paints and varnishes. Other PU products have been commercialized in the forms of elastomers and foams.[2,3]

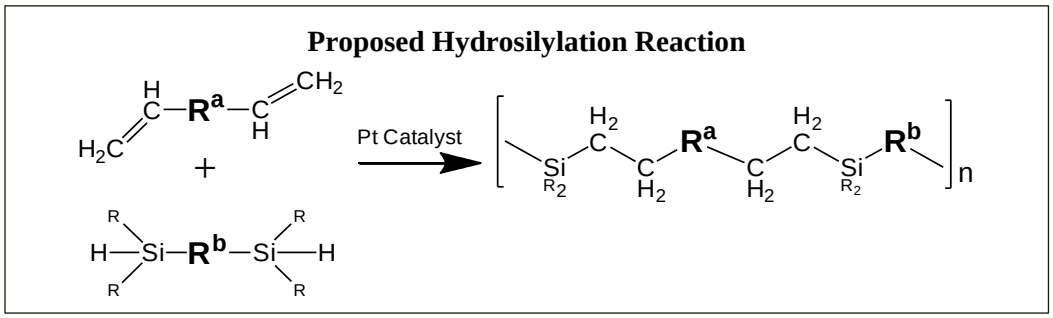



***Figure 2.*** *The proposed hydrosilylation reactions of terminal alkene sites with Si-H to form polymers consisting of newly formed chemically stable Si-C bonds. Ra&Rb groups can be the same as in PU, but the polymerization-curing chemistry is not based on isocyanates.*

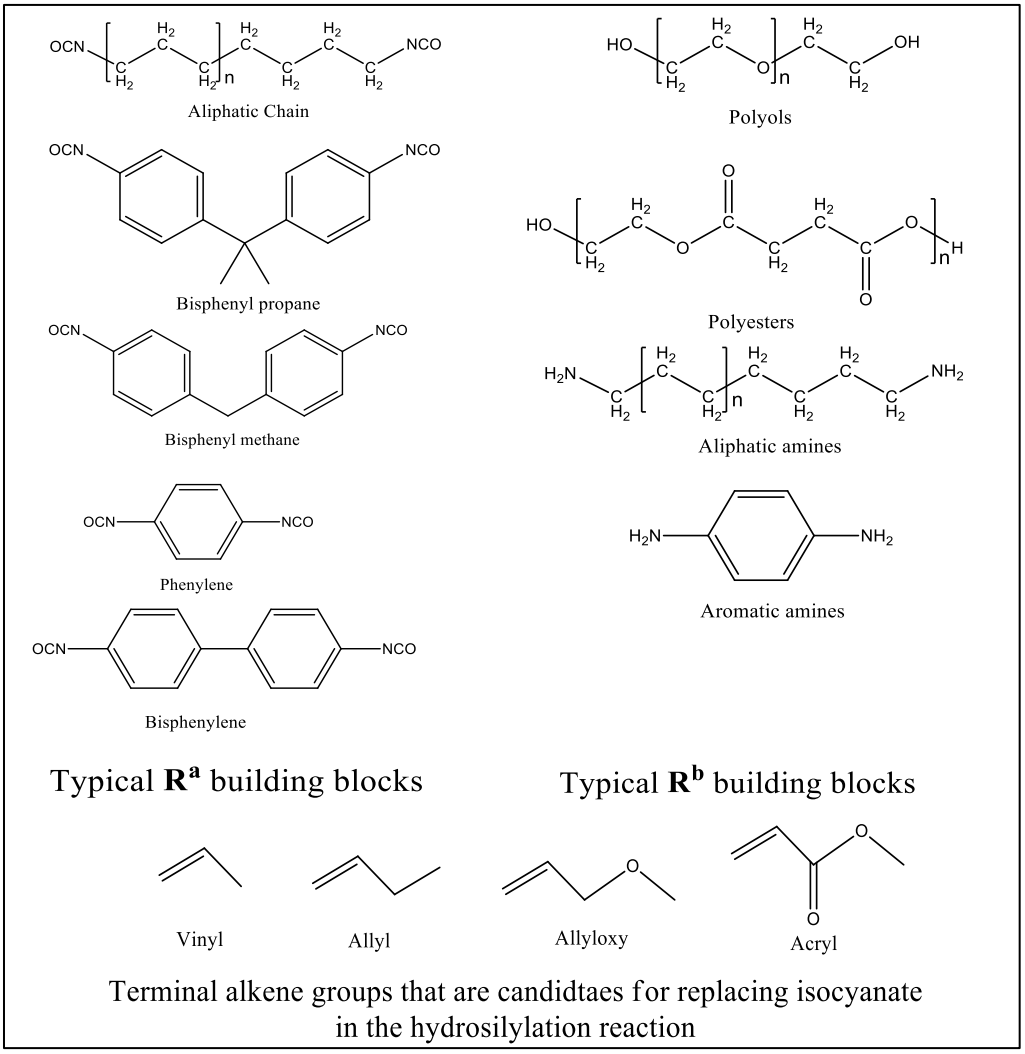



***Figure 3.*** *Typical building blocks used as "Part A" and "Part B" in PU formulations. Various terminal alkene groups can replace the isocyanate functional groups.*

## HEALTH HAZARD ISSUES WITH POLYURETHANES

PU synthesis, use, storage, processing, and decomposition may result in exposure to isocyanates, which can cause skin irritation, asthma, or even cancer. Therefore, diisocyanate compounds have become increasingly regulated as dermal and inhalation sensitizers and irritants. The possibility of hazardous release of hydrogen cyanide during thermal decomposition is still under debate.[4-6] The isocyanate group is produced by a reaction with phosgene, which is highly toxic and reactive, and therefore highly regulated.[7] PU systems must be kept moistureless until their deposition to avoid unintentional foaming and curing due to their reactivity with water, which causes release of $CO_2$.[12]

## TECHNICAL APPROACH: REPLACING ISOCYANATE CHEMISTRY WITH (a) HYDROSILYLATION AND (b) HYDROSILYLATION-DEHYDROCOUPLING

The isocyanate alternative chemistry considered initially to achieve the project objectives was based solely on hydrosilylation reaction which is efficiently used by the organosilicon and polysiloxane industry. Along the course of the project, we realized that the hydrosilylation is a great technique for the designed synthesis of intermediates but it faced significant challenges during the paint formulation, deposition, curing and post-curing properties. We solved these challenges by modifying the chemistry approach and using a combination of hydrosilylation followed by dehydrocoupling reactions during the synthesis step. The combined chemistry can be implemented as a "one pot reaction". Below, we discuss the background of the two platforms that were used in this project as replacement for the isocyanate cuemistry – (a) hydrosilylation and (b) hydrosilylation-dehydrocoupling.

### (A) Hydrosilylation Platform

For this project we originally proposed to replace the isocyanate polymerization-crosslinking chemistry with catalytic hydrosilylation coupling of compounds containing two or more alkene sites with compounds containing multiple Si-H groups, as illustrated in Figure 4 and Figure 5. The organic building blocks represented by $R^a$ & $R^b$ in Figure 2 can be the same or alternative to the organic compounds constituting current PU and epoxy systems or simple derivatives thereof.

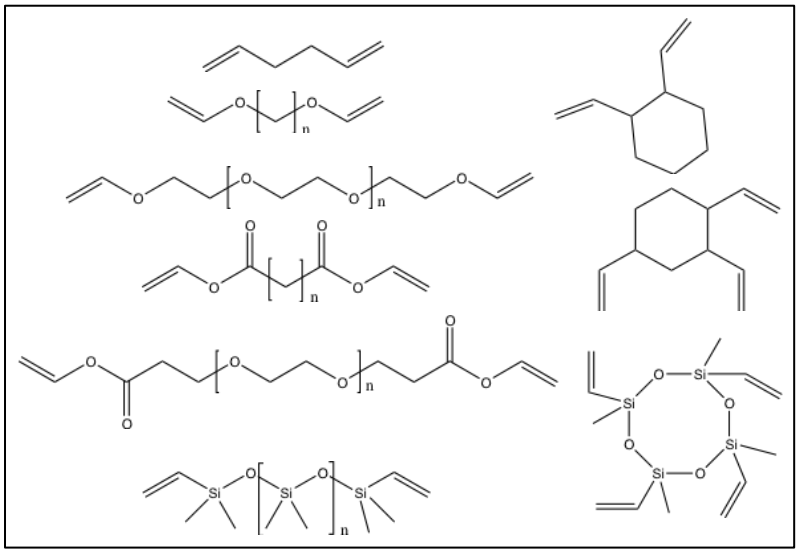


***Figure 4.*** *Potential multi-alkene nonaromatic compounds ("Part A") that can replace isocyanate compounds in the proposed hydrosilylation platform.*

Hydrosilylation is one of the most efficient and stable reactions known in homogeneous organometallic catalysis. It is commonly used by the silicone (polysiloxane) industry.[13] Although hydrosilylation has been in use

for more than 50 years, it is rarely incorporated with conventional organic materials, most likely due to industrial culture barriers between industries.[14-16]

Our aim was to develop isocyanate-free chemistry for topcoat formulations that can encompass a broad range of organic building blocks already practiced in current industrial polymers and resins. We have focused on nonaromatic building blocks that are used today for state-of-the-art PU topcoats facing severe weathering conditions. We first generated nonvolatile intermediates by hydrosilylation and then crosslinked formulations of "Part A' plus "Part B" via the same highly efficient hydrosilylation reactions. The Pt catalysts can be used at the very low level of 20 to 50 ppm on a molar basis (Figure 5).

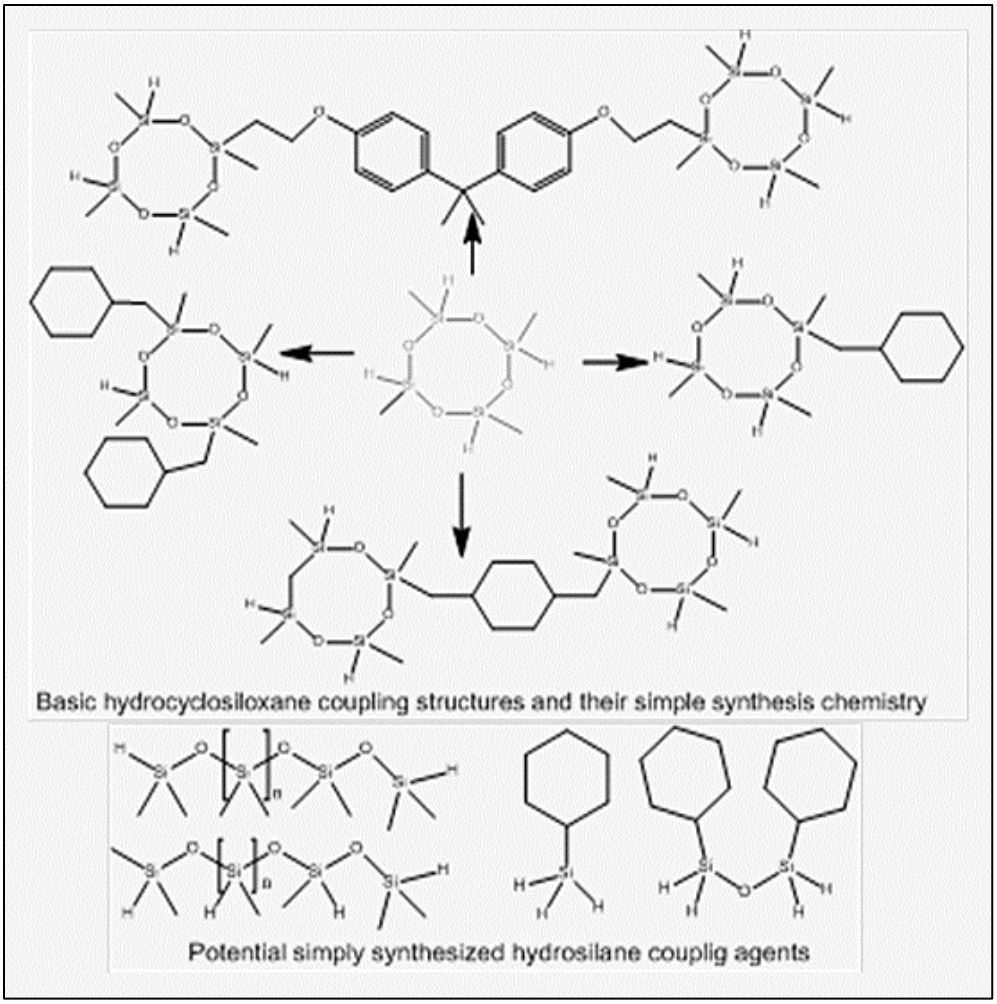



***Figure 5.*** *Examples of multihydrosilane compounds and their derivatives that can be used as extended crosslinkable units in the proposed platform ("Part B").*

Many of the predominant organic building blocks, utilized in either industrial urethane or epoxy systems, will be good candidates for forming topcoat formulations and other resin applications with similar or better performance than current urethane systems. Also, vinyl, allyl, and acryl compounds that are mass-produced for commodity polymeric systems can be utilized as grafted modifiers to create the active polymerization/curing reactivity sites.

In general, we have planned to avoid the incorporation of amine- and nitrogen-containing species that are sensitive to oxidation (causing yellowing and aging effects). The Si-C bonds generated during hydrosilylation are significantly more stable under UV exposure and thermal and hydrolytic conditions than any of the evolved bonding units in PU systems. The incorporation of siloxane groups via stable Si-C bonds into the final organic-rich resin is anticipated to add resistance to moisture, UV, heat, and fire. They can also enhance the hydrophobicity. The silicon-based crosslinking reagents can be designed and easily synthesized to enhance the degree of crosslinking (to provide harder coatings) or reduce it (to yield more elastomeric, flexible coatings), depending on need. They can contain additional crosslinking elements for sequential curing mechanisms. Alternatively, linear oligosiloxanes with terminal Si-H sites can serve as thermally, hydrolytically, and UV-stable, as well as highly hydrophobic, replacements of organic polyols and esters that are currently used in common aliphatic polyurethane topcoat systems. A few nonaromatic options that are feasible with the proposed chemistry platform are illustrated in Figure 4. For practical formulations and spray-coating applications, as well as for unknown environmental issues, we planned use nonvolatile compounds containing multiple Si-H functional groups. Examples of attractive multi-Si-H building blocks and crosslinkers are illustrated in Figure 5. We used nonaromatic multi-Si-H compounds in our studies.

Although it is preferred to avoid using nitrogen-containing species in topcoat formulations due to their inferior weathering performance it is assumed that urethane and urea functional groups (as well as similar functional groups such as carbonate, amide, or ester) attribute to the overall performance characteristics of the cured topcoat. Such attributes may include chemical interactions affecting the physical and chemical durability, flexibility, gloss, and other characteristics of the coatings. In this case it is feasible to introduce such groups into dialkene (olefinic) building blocks via conventional industrial chemistry, as shown in Figure 6. For example, if urethane (carbamate) functionality is found to be highly desired, we can synthesize a carbamate intermediate with the desired terminal sides that fit the selected curing chemistry.

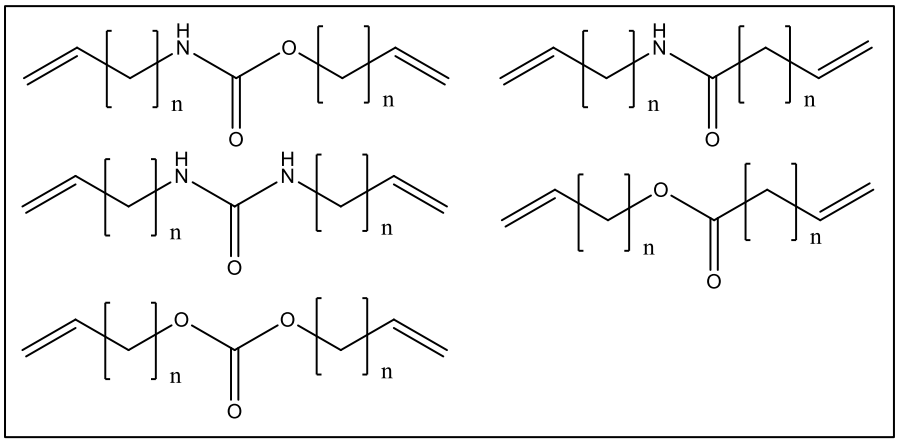


***Figure 6.*** *Dialkenes with functional urethane and similar functional groups that can be easily synthesized industrially.*

**(B) The Hydrosilylation-Dehydrocoupling Platform**

The Si-H chemistry allows additional versatilities of the overall system including the grafting of other crosslinking functional groups such as epoxy, cyclocarbonate, and hydroxyl. The Si-H functional groups can also react efficiently before or after their incorporation to the topcoat formulations to further react with water or alcohols (including moisture) in the presence of transition metal catalysts (e.g., Ru and Pt complexes) via an efficient dehydrocoupling reaction (shown in the equations below).[17-20]

$$\text{Si-H} + H_2O \longrightarrow \text{Si-OH} + H_2 \quad (1)$$

$$\text{Si-OH} + \text{Si-OH} \longrightarrow \text{Si-O-Si} + H_2O \quad (2)$$

$$\text{Si-OH} + \text{Si-H} \longrightarrow \text{Si-O-Si} + H_2 \quad (3)$$

The produced Si-OH or Si-OR has been proven to be stable in other paint formulations. They can then be activated thermally or even at room temperature in the presence of a condensation catalyst to provide additional curing. Currently, the assessment of such paints that are highly inorganic in their content, is aimed at robust corrosion-resistant industrial and automotive applications. More recently, these paints became of interest for aerospace applications as well. The original platform is based on robust preceramic polymers that consist of an inorganic skeleton as the major weight component and some organic side-groups that allow fabrication processes similar to those of organic-based paints. The platform chemistry is based primarily on efficient catalytic dehydrocoupling reactions that were developed at SRI,[16-20] which may also involve hydrosilylation steps, similar to the reactions studied in the current project**.** Figure 7 shows the platform chemistry. The monomeric unit shown in the red circle is the predominant one in our currently evaluated formulation ("PHMS-OH," polyhydromethylsiloxane-hydroxylated).

The polymers are curable even at ambient temperature and can be converted to ceramic products ("polymer derived ceramics"). However, if only low-temperature curing is performed, they maintain their inorganic-organic hybrid characteristics at temperatures exceeding 300°C. The polymers and their derived paint formulations fall under the definition of "inorganic-organic hybrids."

SRI's preceramic coating platform consists of inexpensive preceramic polymers and can be applied by conventional low-cost processing techniques using currently practiced industrial coating lines. The coatings can be tailored to provide various combinations of mechanical, chemical, environmental, thermal, or electronic characteristics, including:

- High-temperature stability (exceeding 300°C)
- Oxidation protection at elevated temperature
- Abrasion, scratch, and impact resistance due to hardness exceeding 6H (up to 9H)
- Moisture barrier sealing
- Low dielectric insulating layers (but can be filled with conductive fillers as necessary)
- Plastic protection against mechanical and chemical degradation
- Complete UV stability
- Excellent adhesion to many substrates.

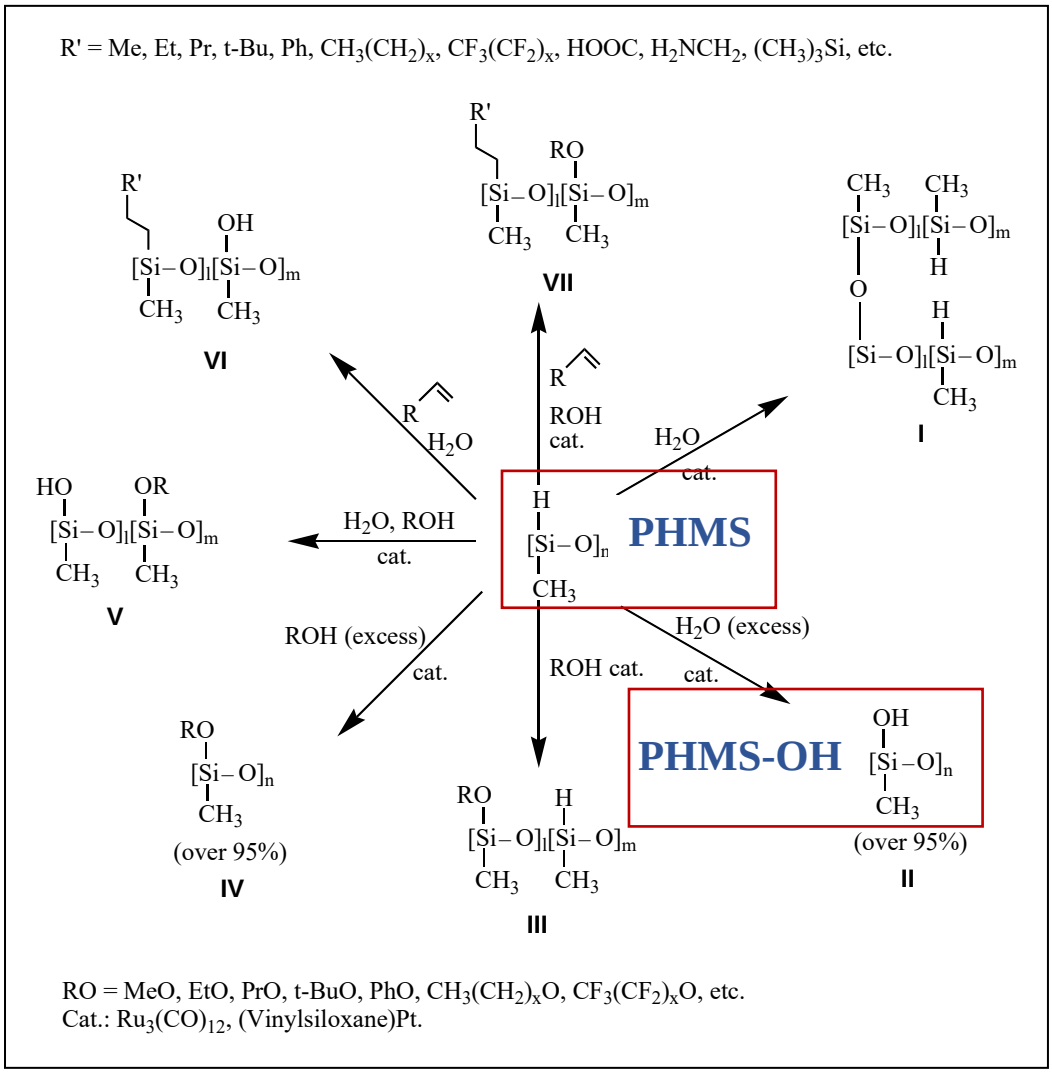



***Figure 7***. *SRI's preceramic polymer platform based on dehydrocoupling and hydrosilylation-dehydrocoupling combinations. PHMS-OH is the mostly used polymer in current commercial evaluations and consists of the illustrated units circled in red.*

Clearly, the abrasion, scratch, impact, moisture, and UV resistance make such coatings good candidates for aircraft topcoats. The potential drawbacks with the currently used version (PHMS-OH) is limited thickness per layer of coating (~20-30 µm) and flexibility during bending due to the high degree of crosslinking of this specific system. These issues can be circumvented, if needed, by (a) modification of the polymer with alkyl side groups (see Figure 7); (b) adding polydimethylsiloxane segments that will reduce the degree of crosslinking; and (c) blending with other polymer intermediates containing Si-OH or Si-OR groups.

The platform provides a wide range of options for altering the physical and chemical properties of the polymeric coatings by tailoring the composition and structure of:

- The inorganic backbone network (providing the main durability aspects)
- The organic substituents and skeletal components (providing functionalities such as low surface tension, bonding to surface, and elasticity if necessary)
- The crosslinking reagents (providing the controlled hardness-flexibility characteristics and adaptation to industrial processes)
- Selected fillers that synergistically enhance the overall performance due to their interactions with the inorganic polymer (for enhancing hardness and toughness, improving chemical barrier performance, and matching coefficients of thermal expansion).

The incorporation of Si-OH functional groups on the synthesized polymers provides a unique capability for chemical bonding of the polymers to surfaces such as steel, aluminum, glass-ceramics, and certain plastics. The Si-OH groups are also instrumental in creating a high degree of crosslinking after the coating is applied and cured by condensation catalysts or heat, in a manner similar to sol-gel chemistry. The Si-OH groups also interact with the inorganic filler surfaces constituting reinforced-composite microstructures.

The platform is currently evaluated for corrosion-resistant coatings in robust environments, serving primarily as multifunctional coatings that do not require a combined primer/topcoat/clear coat strategy. This platform is also based on organosilicon reactions, but in this case the presence of amines in the primer should be advantageous, as the RT curing mechanism of this system involves the use of amines as efficient curing catalysts. Although never assessed before as a topcoat over primer, this system is clearly a good candidate to meet many of the Mil specifications associated with robust and weather resistance coatings.

The examples shown in Figure 8 are grey "metallic" and black paint formulations that passed severe corrosion testing. The silver-colored paint passed a 1000 h salt fog test. Notice that the uncoated area of the metallic-like coating is heavily corroded, but no recession or delamination of the coating is observed at the edge between the coated and the uncoated areas, demonstrating the good chemical bonding of the coatings to the substrate. Also, no degradation is observed

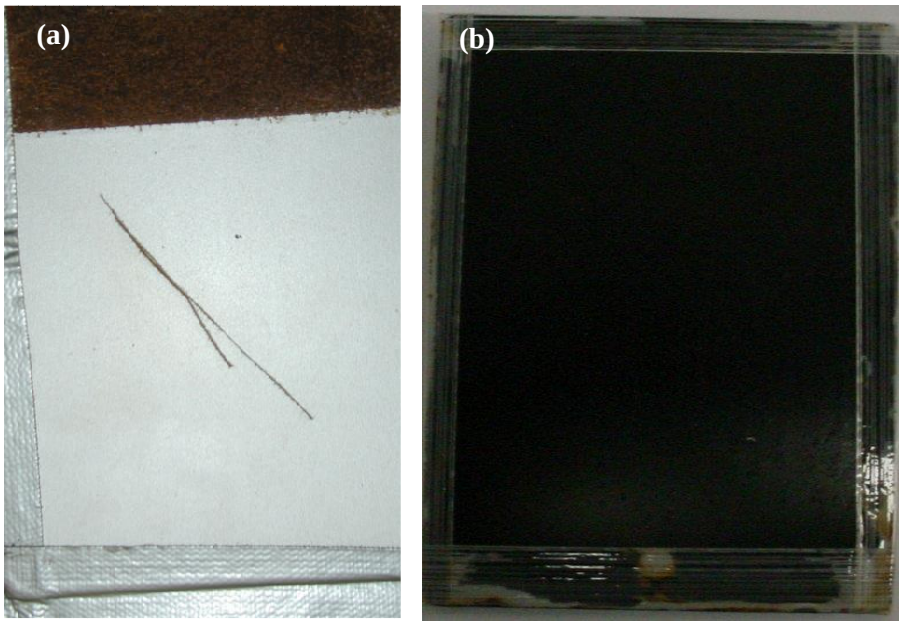



***Figure 8.*** *Preceramic polymer formulations coated over steel. (a) Metallic-like coatings after 1000 h of salt fog test. (b) Black coating heated at 350°C for 12 h followed by 500 h of salt fog test.*

at the intentional scratch scored in the middle of the coated area. The black coating was soaked at 350°C (~700°F) for 12 h and then tested in a salt fog chamber for 500 h. The testing revealed that the above performance can be obtained with coatings that are 15 µm thick—much thinner than conventional organic protecting paints.

Paint formulations have shown stability for over 20 months in ambient warehouse conditions. There is still a volatile organic compound (VOC) component in the current paint formulations in the form of low-molecular-weight alcohols and other common paint solvents. However, the VOC level has been reduced to 0.3 lb/gal, well below any regulated limits for standard or high-performing paints.

Regarding external coatings for aircraft applications the main drawback of the base SRI platform is the low elasticity of the cured products, due to very high degree of crosslinking. Hence the system that is currently evaluated for heavy automotive application is not suitable because it cannot meet the flexibility and bending requirements for aircraft applications. There is a need to develop polymers that possess multiple Si-OH but at the same time have long segments that do not crosslink.

# MATERIALS AND METHODS

## ORIGINAL PLAN AND PROPOSED TASKS

Originally, we proposed a three-phase, 3-year project to develop non-isocyanate, non-nitrogen-containing topcoats with performance characteristics similar to or better than polyurethanes that fulfill or exceed the specifications described in MIL-PRF-85285E (Coating, Polyurethane, Aircraft and Support Equipment). The proposed plan focused on achieving the following main requirements:

- Good adhesion to both aluminum alloys and primers certified for aircraft coatings (4B)
- Adequate hardness (2 to 4H)
- Resistance to water, solvent, hydraulic fluids, fuel, and weather
- Flexibility during bending and freezing that meet the aircraft standards
- Recoatability, gloss, and infrared reflectance
- Appropriate shelf life before mixing of components and good pot life afterward.

Each of the phases was planned to include the following integrated tasks, which covered the range from synthesis through formulations, short- and mid-term testing, and technology transfer planning. Project tasks, subtasks, and lead assignments are listed below.

**Task 1: Synthesis and Modification of Building Blocks and Intermediates *(SRI)***

Task 1.1: Initial Reactivity Assessment

Task 1.2: Modified Reagent Synthesis and Testing (Iterations

Task 1.3: Assessment of Other Hydrosilylation Catalysts

**Task 2: Curing and Structure-to-Property Assessment *(SRI)***

Task 2.1: First Iteration Coatings

Task 2.2: Second Iteration Curing

Task 2.3: Third Iteration Curing

**Task 3: Topcoat Formulations and Screening *(SRI)***

Task 3.1: Formulation First Iteration

Task 3.2: Formulation Second Iteration

Task 3.3: Formulation Third Iteration

**Task 4: Screening and Development of Candidate Formulations *(PPG, assisted by SRI and Boeing)***

**Task 5: Adaptation to Specific Aircraft Needs and Practices *(Boeing, assisted by SRI, PPG and NAVAIR)***

**Task 6: Technology Transfer Planning *(SRI, Boeing, PPG and NAVAIR)***

**Task 7: Management and Reporting *(SRI with inputs from PPG and Boeing)***

Figure 9 illustrates the interrelations between the tasks and the team participants.

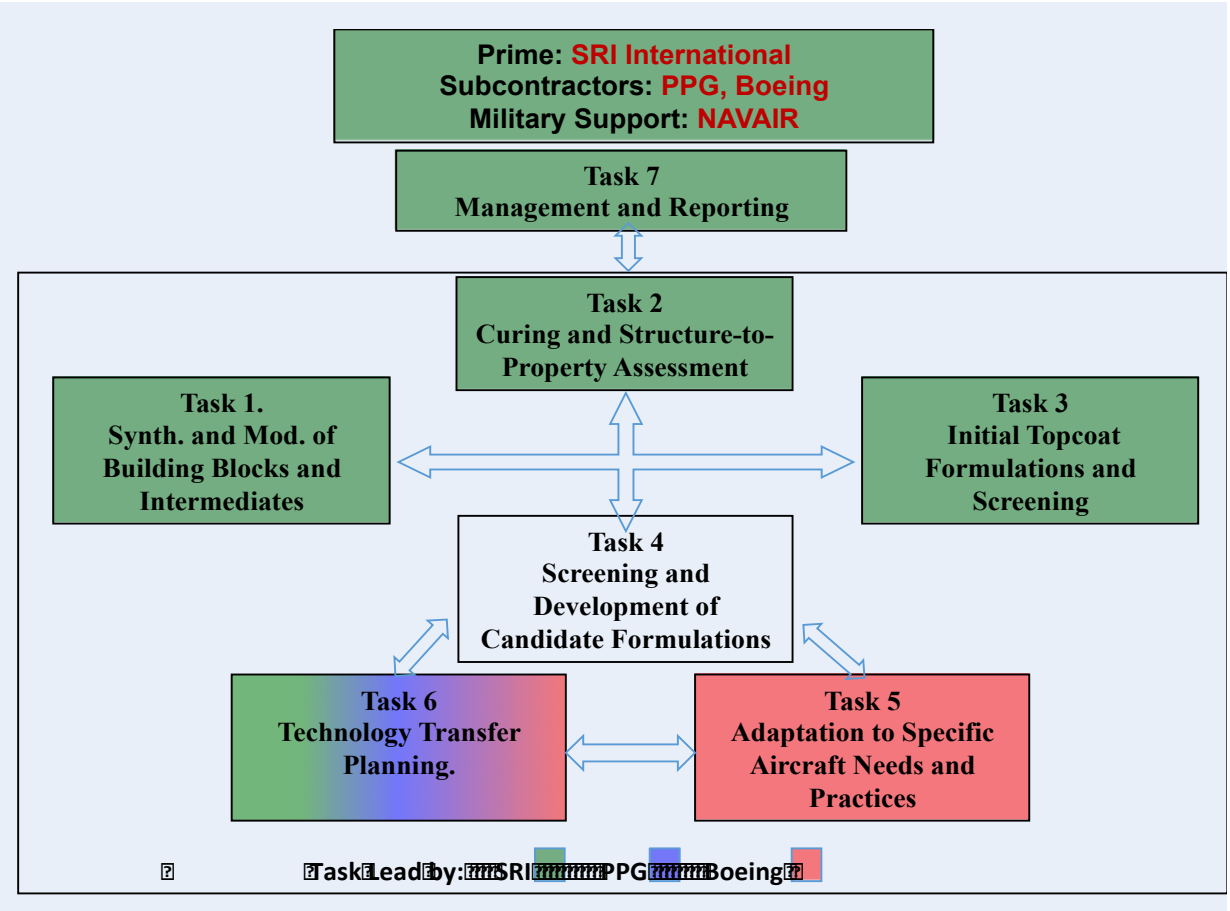



***Figure 9.*** *Project tasks, team member assignments, and their interconnections throughout the project performance.*

The project team included expertise that is critical for (1) development of a new coating system, (2) adequate guidance throughout the R&D activities, and (3) enhanced technology transfer:

**SRI International's Chemistry and Materials Laboratory** was responsible for addressing the chemistry aspects of the synthesis, curing, adhesion compatibilities, pot life, intermediate characteristics, early-stage formulation, and initial assessment of coatings.

**PPG's Corporate Research** guided the team in meeting the practicality of the developed system, formulation development and assessment, and scalability. (PPG has replaced Deft, a small aircraft paint manufacturer that was acquired by PPG during the negotiation period of the project).

**Boeing's Materials and Process Technology** for commercial airplanes guided the team based on their OEM experience, needs, and overall painting facility capabilities. They tested the evolved paint platform using facilities and procedures associated with aircraft specifications (MIL specs and Boeing's).

**NAVAIR's Materials Engineering Division** at Naval Air Systems Command provided some additional guidance associated with the adaptation of paints to military operations, needs, and requirements. They performed their own tests on selected formulations at the end of the project.

## REAGENTS AND GENERIC SYNTHESIS

The bulk of the descriptions of experimental procedures and testing are provided later in this report. In this section we provide a few examples for the synthesis of intermediates generated via hydrosilylation and a combination of hydrosilylation and dehydrocoupling reactions. The literature contains numerous examples of the reactions utilized, and therefore it is unnecessary to go into specific detail for each reaction conducted.

In the course of this work, materials to be included in a formulation were designated a Reactant number (R#); for example, R71 is generated from a cyclic aliphatic divinyl ether and tetramethyl-tetracyclosiloxane. The reactants were then combined to generate a resin, and these were designated with an X#; for example, resin X138 is composed of reactants R71 and R31. In the later stages of the project, dehydrocoupling was used to convert some of the silane (Si-H)-containing reactants to silanol (Si-OH)-containing reactants. In these instances, the reactant is designated with an –OH in the label; for example, R71 becomes R71-OH. As will be discussed later, the R#-OH reactants are capable of undergoing a condensation reaction, effecting cross linking without the need of an additional reactant to the formulation.

All of the organic reagents were purchased from Sigma-Aldrich or VWR, and all of the siloxane and organosilane reagents were purchased from Gelest. Platinum catalyst was purchased from Gelest as a 2.2% solution in toluene and diluted by a factor of at least 50:1 with dry toluene to generate a catalyst solution that contains 5 $x10^{-4}$g Pt per gram of solution. In some smaller scale reactions, dilution to 100:1 or greater has been utilized. Ruthenium catalyst employed in the dehydrocoupling reaction was purchased from Alfa-Aesar.

In a typical hydrosilylation reaction to generate reactants, the silane and vinyl reagents are mixed without solvent and brought to temperature (35-40°C), and aliquots of 5-20 ppm Pt catalyst are added. Note that the amount of catalyst added is relative to the reagent that is completely consumed. For example, in the reactions cited below, the limiting reagent in generating R51 is the cyclomer as it is completely functionalized. Therefore, the ppm catalyst used in this experiment is relative to the weight of the cyclomer on a weight Pt/weight cyclomer basis. In the case of the example of the synthesis of R60, the limiting reagent is the diene and hence any catalyst addition is expressed as weight Pt/weight diene basis. The reaction progress is easily followed using FTIR analysis of a thin film of the reaction mixture. The silane (Si-H) functional group exhibits a distinct and strong absorbance in the 2200-2000 $cm^{-1}$ region of the spectrum, and the vinyl also exhibits a strong signal in the 1600 $cm^{-1}$ region. As the endpoint in all reactants involves the complete reaction of either a silane or vinyl component, the endpoint determination is straightforward. Structure determination is then conducted utilizing NMR spectroscopy.

Examples of the FTIR of the silane and vinyl components and the reaction mixture after reaction completion for the generation of R51and R60 are shown later in the results. The specific reactions are shown in Figure 10.

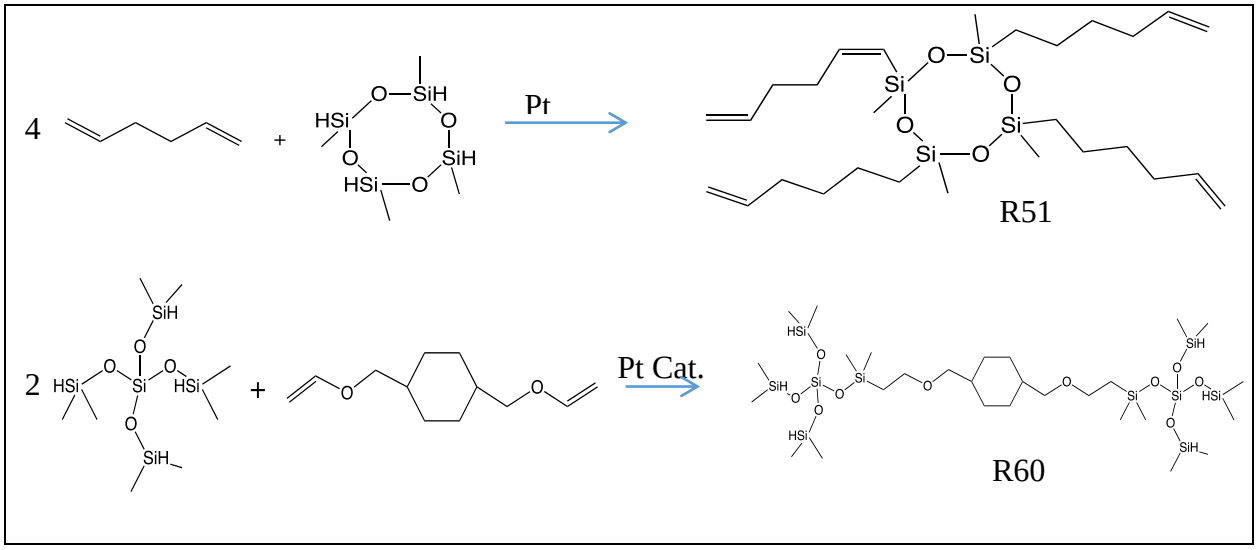



***Figure 10.*** *The synthesis of R51 and R60*

In the example of R51, we used the following experimental protocol:

1) In a 100 ml single-neck round-bottomed flask fitted with a stir bar and a drying tube, add 10 g tetramethyl-cyclotetrasiloxane (0.042mol, 240.5g/mol).
2) Add 15.0 g of 1,5-hexadiene (0.18 mol, 10% mol excess) and place the flask in a 35°C water bath.
3) Add 0.125 g of Pt catalyst solution (5 ppm, conc = $4x10^{-4}$ g Pt/g solution); the reaction mixture rapidly heats as the exothermic reaction proceeds.
4) After cooling to room temperature, analyze the mixture by casting a thin film on an intrinsic silicon wafer and observing the FTIR spectrum.

In the example of R60, we used the following protocol:

1) In a 100 ml single-neck round-bottomed flask fitted with a stir bar and a drying tube, add 10 g of 1,4-cyclohexanedimethanol divinyl ether (0.051 mol, 196.3g/mol).
2) Add 5.0 g of tetrakis(dimethylsilyl) orthosilicate (0.051mol, 196.3g/mol) and place the flask in a 35°C water bath.
3) Add 0.125 g of Pt catalyst solution (5ppm, conc = $4x10^{-4}$ g Pt/g solution) and stir the reaction mixture as the reaction proceeds.
4) After several hours at 35°C cooling to room temperature, analyze the mixture by casting a thin film on an intrinsic silicon wafer and observing the FTIR spectrum.

The FTIR and NMR analyses are discussed further in the Results section.

The other synthetic tool utilized in this project was a dehydrocoupling reaction that converts the silane functional groups (Si-H) to silanol (Si-OH). The silanol groups can then undergo a condensation reaction forming a siloxane linkage and water. A solvent is required for the dehydrocoupling reactions, as opposed to the hydrosilylation reaction. Previous experience has shown that alcohols and alcohol water mixtures are excellent solvents. The experimental details for dehydrocoupling reactions very similar to those conducted in the course of this project have been reported, and only brief examples of the experimental details will be presented here.

The conversion of the silane functionalities to silanols can be easily monitored by FTIR. As indicated earlier, the silane (Si-H) functional group exhibits a distinct and strong absorbance in the 2200-2000 $cm^{-1}$ region of the spectrum. There is also a band in the FTIR at 1200-1280 $cm^{-1}$ associated with the silicon-methyl ($Si-CH_3$) functionality that is ubiquitous on all of the silanes employed in this project. This band can be utilized as an internal reference because it tends to exhibit little if any variation as the silanes are converted to silanols. As such, this gives us an internal reference to guage the extent of silane to silanol conversion. In general, conversion efficiencies of silane to silanol conversion are in the range of 95-100%.

An example of the protocol for the dehydrocoupling reaction to convert R71 to R71-OH is:

1) Set up a 1 L three-neck round-bottomed (RB) flask fitted with a mechanical stirrer, a condenser with a gas outlet adapter connected to a bubbling tube, and a glass stopper, and place the flask in a heating mantle.
2) To 450 g 1-butanol, add 116 g R71 (1.03 mols Si-H@ 677.3g/mol and 6 Si-H per mol)
3) Add 25 g water (1.56 mol, 50% mol excess relative to Si-H)
4) Heat mixture to 75°C
5) Add 10 mg $Ru_3(CO)_{12}$ dissolved in 5 ml $CH_2Cl_2$ (aliquot 1)
6) Monitor gas generation through bubbler (hydrogen is evolved in the dehydrocoupling reaction)
7) When gas evolution slows, repeat steps 5 and 6 until 4 aliquots of catalyst have been added
8) Check FTIR
9) Adjust catalyst addition as needed until FTIR indicates >95% of silanes converted to silanol
10) Cool to room temperature
11) Filter through steel wool
12) Determine weight percent solids and refrigerate.

It is also possible to conduct the hydrosilylation reaction(s) and the dehydrocoupling reactions in a sequential manner as the hydrosilylation reactions are conducted neat and require no purification prior to conducting the dehydrocoupling reaction. As an example of this, we describe the utilization of two sequential dehydrocoupling experiments, followed by a hydrosilylation reaction conducted in the same flask with no purification other than filtering. The reaction scheme is shown in Figure 11.

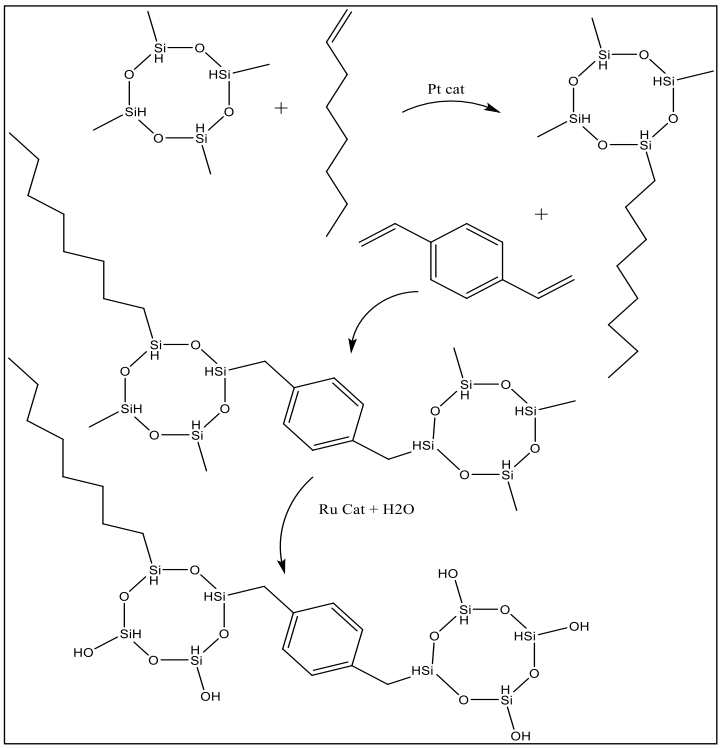



***Figure 11.*** *Synthesis of modified R71-OH, with lower level of Si-OH and additional organic conte*

**Preparation of (mono-Octyl-TMCS)DVB**

*1-octene modified cyclomer*

1) Add 100 g tetramethylcyclotetracyloxsane (0.416 mols, 240.5 g/mol) to 1-L RB flask
2) Add 11.7 g 1-octene (0.104 mols, 112.2 g/mol) and mix well
3) Place drying tube over mixture
4) Add 5x10-4 g Pt catalyst (5ppm based on TMCS) and mix well
5) If solution does not become warm (reaction is exothermic), place in 40°C oil bath for 30 min
6) Remove and cool to room temperature
7) Check FTIR to confirm reaction completion

*Reaction with TVC*

8) Add 22.5 g of divinylbenzene (0.208 mols, 2:1 cyclomer:DVB) and mix well
9) Add 5x10-4 g Pt catalyst (5 ppm based on DVB) and mix well
10) Place in 40°C oil bath for 60 min
11) Check FTIR to confirm reaction completion

*Conversion of silane to silanol*

12) Add 400 g 1-butanol
13) Add 20 g $H_2O$ (1.25 mols, 50% excess relative to remaining Si-H)
14) Warm mixture to 75°C
15) Add 10 mg $Ru_3(CO)_{12}$ dissolved in 5 ml $CH_2Cl_2$ (aliquot 1)
16) Monitor gas generation through bubbler (hydrogen is evolved in the dehydrocoupling reaction)
17) When gas evolution slows, repeat steps 5 and 6 until 4 aliquots of catalyst have been added
18) Check FTIR
19) Adjust catalyst addition as needed until FTIR indicates >95% of silanes converted to silanol
20) Cool to room temperature
21) Filter through steel wool
22) Determine weight percent solids and refrigerate

After reactants are generated, they are stored in the refrigerator and monitored for gellation. Characterization of reactants is provided in the Results section.

# RESULTS AND DISCUSSION

Below we provide results and discussion for each of the research tasks. We systematically separate the efforts into the two periods in which we focused on first (a) the hydrosilylation platform and then (b) the hydrosilylation-dehydrocoupling platform). Some of these activities were performed in parallel.

## TASK 1. SYNTHESIS & MODIFICATION OF BUILDING BLOCKS & INTERMEDIATES

### (a) The Hydrosilylation Platform

Figure 12, which shows the different compounds grouped based on their functional groups. The purpose of the various reaction combinations was to:

a) Establish a baseline reactivity using Karstedt's catalyst (a platinum complexed with divinylsiloxane; significantly used by the polysiloxane and silane reagent industry, shown in Figure 12 and Figure 13.
b) Assess which types of multi-Si-H or vinyl compounds are very active or inactive ("poisonous") in their reactivity.
c) Begin generating linear and crosslinking components for potential resin systems. Assess whether low-molecular-weight, as-received commercial reagents (some volatile) can serve "as is" in paint formulations. (This potential use of the starting compounds was discarded at an early stage of the research, resulting in the effort toward the formation of intermediates with higher viscosity and no volatility.)
d) Assess the effect of functional groups in addition to the Si-H and vinyl on miscibility, curing, pot life, and adhesion to substrates. (This part served as a prelude for further paint formulation in later stages of the project.)

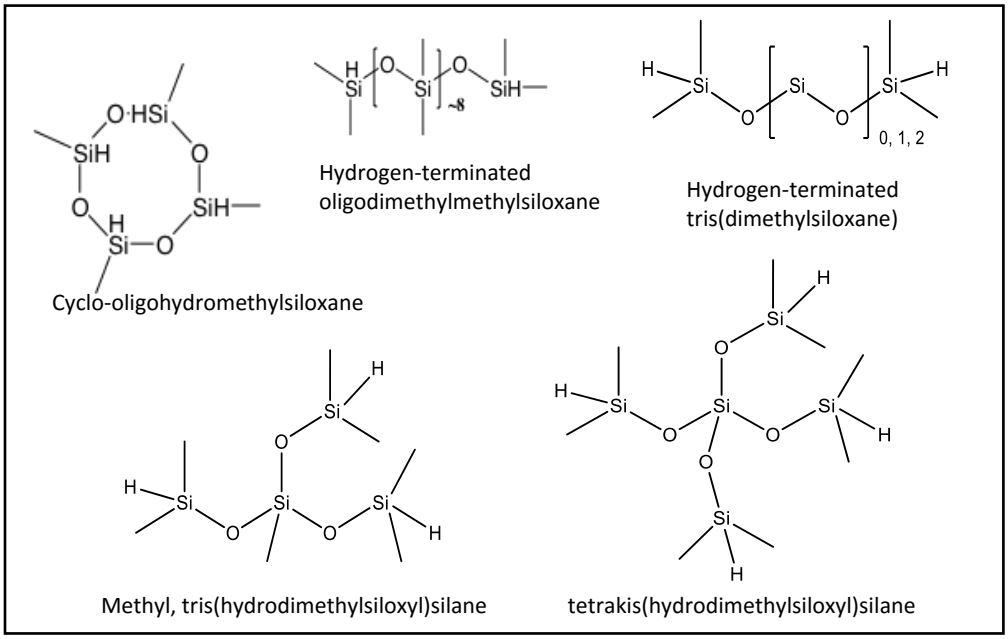



***Figure 12.*** *Various compounds with multiple Si-H that were used as reagents to form intermediates via hydrosilylation reactions.*

The initial synthetic work consisted of assessing a series of commercially available multi-vinyl reagents with linear, cyclomeric, and branched multi-Si-H reagents in their hydrosilylation reactivity. The structures of the various reagents already assessed in the study are drawn in Figure 12 and 13.

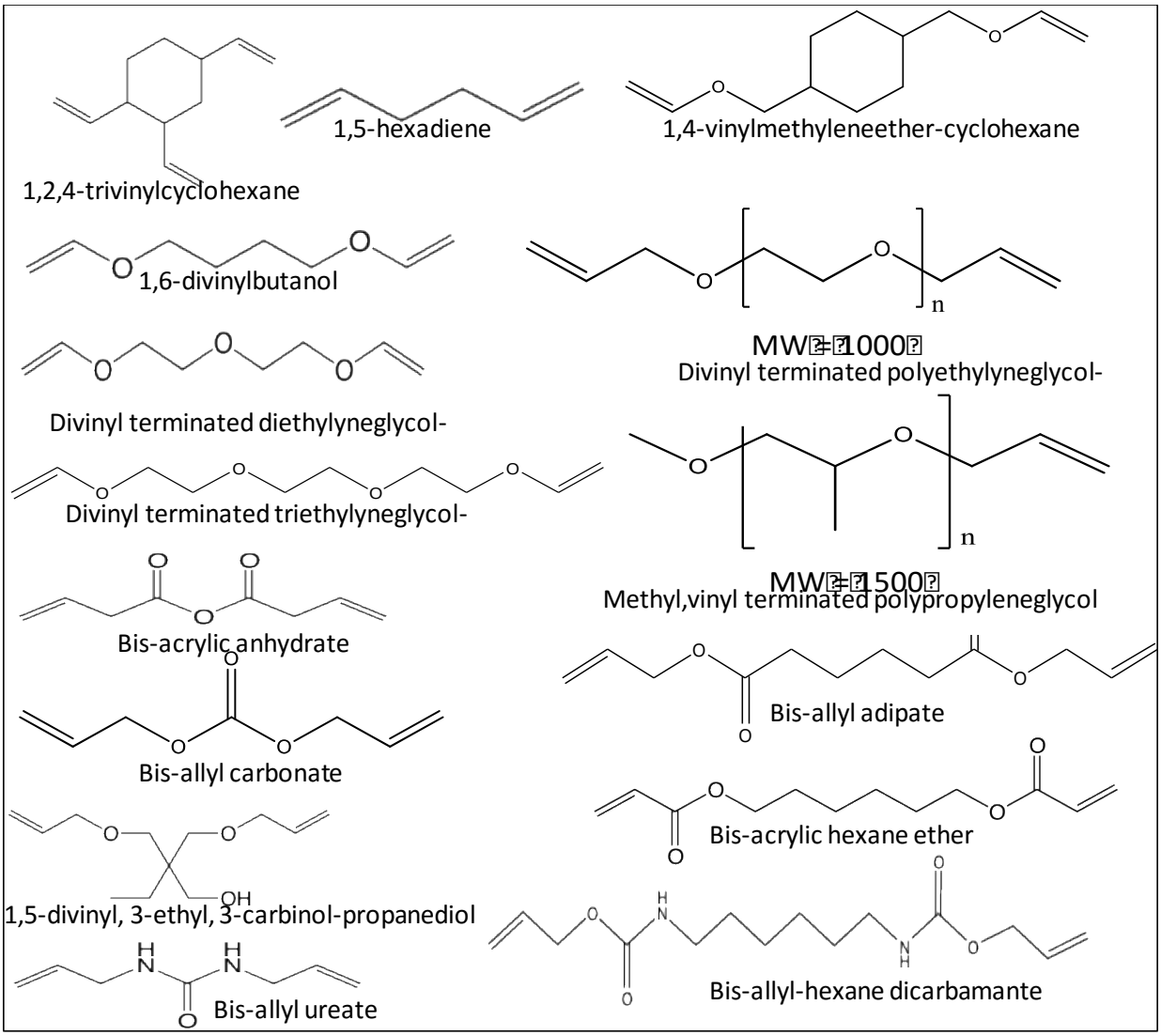



***Figure 13.*** *Various compounds with multiple vinyl sites that were used as reagents to form intermediates via hydrosilylation.*

### *Reactivity Efforts*

The base Si-H compounds were all small (relatively volatile) siloxanes consisting of linear, cyclomeric, and branched structures. All were assessed later as reagents for our major intermediate synthesis effort.

The vinyl compounds were all organic with various additional functional groups in between the vinyl sites. Most of the commercial vinyl compounds possess only two terminal vinyl sites. The

only compound containing three vinyl groups was trivinyl-cyclohexane. Later, we synthesized intermediates with more than two vinyl groups by reacting the divinyl and trivinyl compounds with compounds containing three and four Si-H groups. The intermediate products in this case contained between three and eight vinyl groups.

A variety of polysiloxanes also possess vinyl groups as terminal sites and as pendant groups. These polysiloxanes are commercially available in a broad range of molecular weights. We have not included these vinyl siloxanes in our study, since this chemistry is used for making typical elastomeric "silicones" via room temperature vulcanization (RTV). However, it may be of interest to assess such compounds in the context of the dehydrocoupling-hydrosilylation approach, as discussed later.

We performed reactions with known stoichiometric ratios of the terminal alkene functionalities to Si-H functionalities to avoid crosslinking during the formation of the intermediates. In most cases the tractable intermediates were obtained without any difficulties and the intermediates were still low viscosity.

The catalytic activity of the homogenous platinum catalyst was extremely efficient. We have used 10 to 50 ppm of the Pt compound, compared to the vinyl and hydride mixture. Due to the low viscosity, there was no need to add a solvent to the reactions. The catalyst was added in a highly diluted solution to control the reactivity.

The reactions were monitored by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (H-NMR) analyses of aliquots extracted during the reactions. As necessary, we added more catalyst or solvent, or made other adjustments such as an increase/decrease of reaction temperature.

In both spectroscopic analyses we can easily follow the disappearance of the Si-H and vinyl bonds. In H-NMR the monitoring is quantitative, and we can also monitor quantitatively the formation of the Si-$CH_2$-$CH_2$- and Si-CH(-$CH_3$)- bonds, since the methylene group adjacent to the Si has a distinct shift at around ~0.5-0.8 ppm, which is different from the conventional methyl groups of $CH_3$-Si that have shifts around 0.0 ppm. Most spectra are taken from samples diluted in deuterated chloroform.

The FTIR monitoring is more qualitative in its nature but allows a rapid feedback for assessing the reaction progress. Thin films of reaction aliquots are placed on an intrinsic silicon wafer (IR % transmittance >50%; thickness = 200 microns; resistivity > 20,000 ohm square, University Wafer, Boston, MA) and the FTIR spectrum is collected in a transmittance mode. The predominant observation is the reduction in the signal intensity of the spectral features due to the carbon-carbon double bond and the Si-H. The alkene-based stretches are observed in the 1500 $cm^{-1}$ to 1620 $cm^{-1}$ region, and specific location is confirmed with a spectrum of the neat reagent. The hydrosilane stretches are found at 2128 $cm^{-1}$ and 2175 $cm^{-1}$ for the linear silane and cyclomeric silane, respectively. In the case of the diacrylate, a band in the carbonyl region at 1685 $cm^{-1}$ is observed to grow in with some reduction in the parent carbonyl band at 1731 $cm^{-1}$.

In the case of the Si-H intermediates, the extent of reaction can be quantitatively followed by monitoring the decrease in the Si-H stretch relative to the Si-$CH_3$ stretch observed at 1260 $cm^{-1}$ for both the linear and cyclomeric silanes used in this study. This signature remains relatively constant during the hydrosilylation reaction, and hence it is used as an internal reference to gauge

the extent of silane reacted. However, we observed that the majority of the assessed organic reagents have substantial overlap of the spectral features in the same region as the Si-$CH_3$ stretch. Therefore, the quantitative capability of this technique is not as accurate relative to the H-NMR analysis.

Figure 14 and Figure 15 illustrate typical FTIR spectra during and after completion of the formation of a vinyl and a hydride intermediate, respectively. Typical H-NMRs during and after formation of vinyl and hydride intermediates are respectively illustrated in Figure 16 and Figure 17**.** The typical Si-H shift is in 4.7 ppm. It becomes smaller compared to the $CH_3$-Si during the hydrosilylation in the case of forming a Si-H intermediate. Most characteristics in the synthesis of such Si-H intermediates is the complete disappearance of the vinyl shifts at around 6.4-6.5 ppm and the appearance of new $CH_3$Si- shifts at 0.1 ppm and –$CH_2$-Si- at 0.9 ppm.

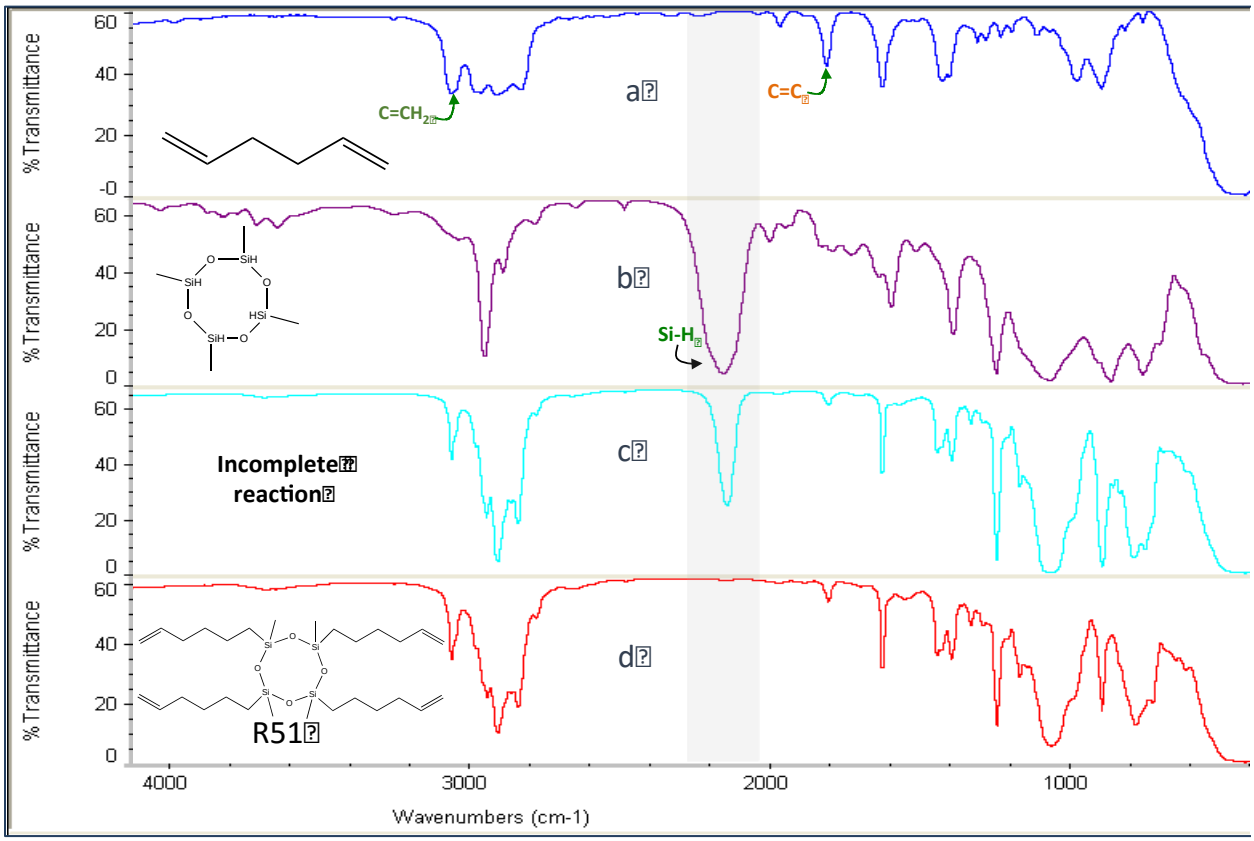



***Figure 14.*** *FTIR of (a) multi-vinyl and (b) multi Si-H reagents, (c) incomplete reaction and (d) final multi-vinyl product (R51).*

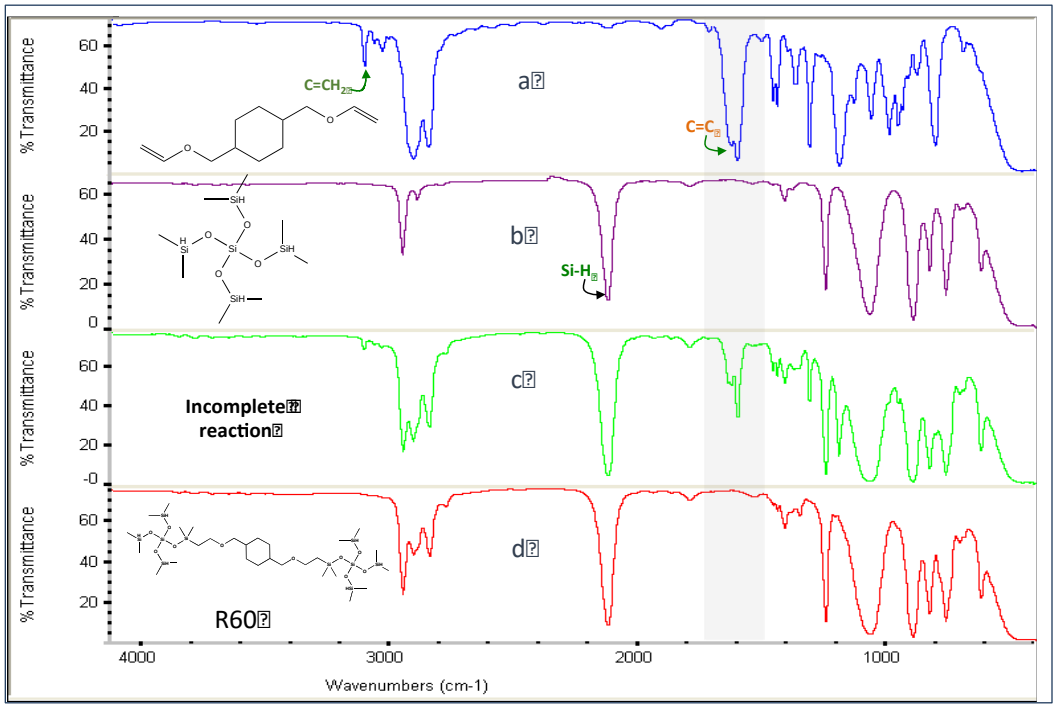



***Figure 15.*** *FTIR of (a) multi-vinyl and (b) multi Si-H reagents, (c) incomplete reaction and (d) final multi Si-H product (R60).*

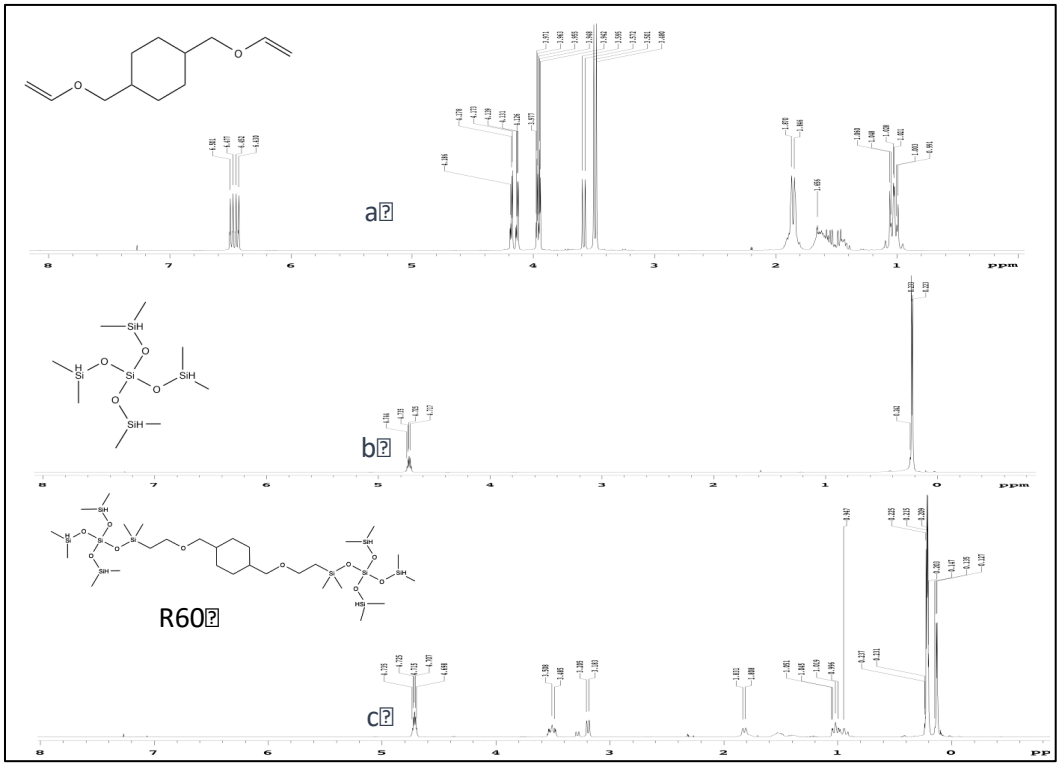



***Figure 16.*** *H-NMR of (a) multi-vinyl and (b) multi Si-H reagents and (c) final multi Si-H product (R60).*

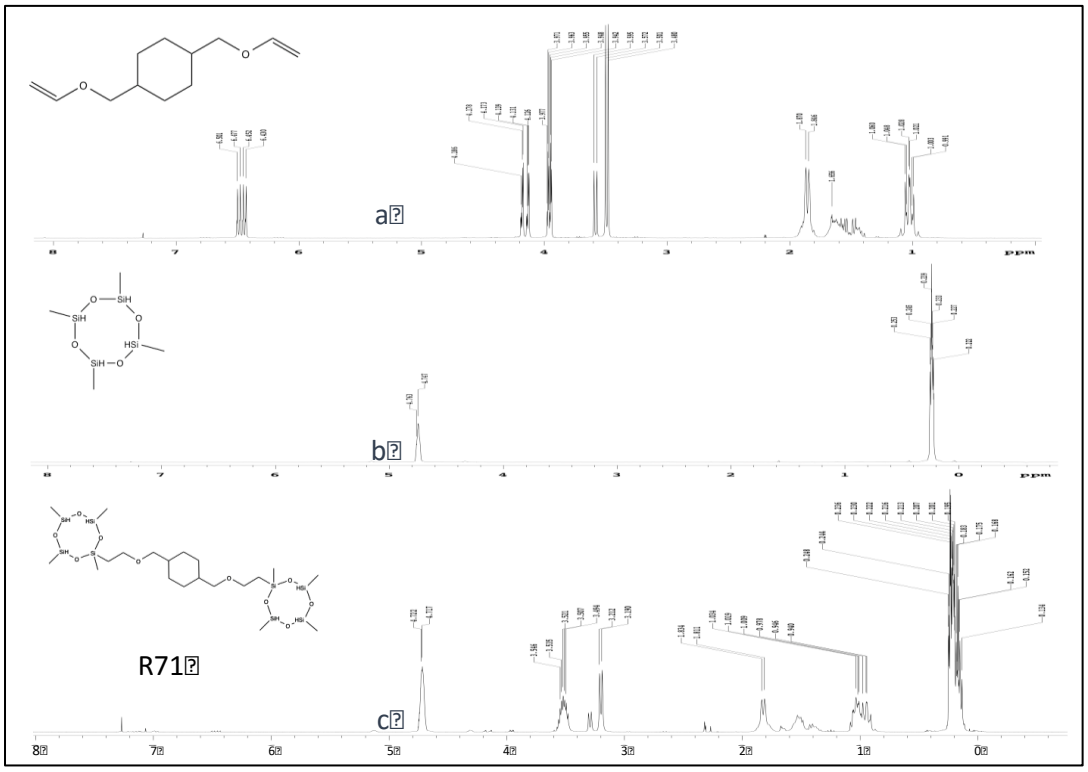



***Figure 17.*** *H-NMR of (a) multi-vinyl and (b) multi Si-H reagents and (c) final multi Si-H product (R71).*

### *Intermediate Synthesis*

All the Si-H compounds are reactive as expected. Their reactivity is similar when the compounds are small with a slight preferential reactivity in the order of $CH_3$-Si(O)$_2$-H (cyclomer) > $(CH_3)_2$Si(O)-H (branched) > $(CH_3)_2$Si(O)-H (linear).

The various multi-vinyl compounds included alkanes, cycloalkanes, di- and polyethers, acrylates, esters, carbonate and urethane (carbamate, NH-(C=O)-O), ureate (NH-(C=O)-NH) functionalities. The vinyl compounds show significant differences in reactivity based on the additional functional groups. Most active were the alkenes. Di- and polyether compounds were also active, with reduced activity as the linear ether chain grew longer. In contrast, compounds based on acrylic functionality in which the vinyl group is in a β position from the carboxylic group were very slow or inactive. We concluded that the acrylic groups and, to a lesser extent, vinyl groups adjacent to carbonyl groups, inhibit the Pt catalyst by their strong complexation to the Pt.

Compounds containing nitrogen, including carbamate or ureate units (synthesized at SRI), did not react at all because of amine-group poisoning of the catalyst. In future research activities we recommend to reassess these functional groups with other hydrosilylation catalysts.

Compounds containing esters (not acrylates) showed mixed reactivity, in which the further the carboxylic (or carbonate) groups are away from the vinyl groups, the faster the kinetics of the hydrosilylation. Most of the hydrosilylation products with the esters are solids with crystalline appearance associated with the formation of crystalline centers around the ester functional

groups. This observation was significantly different from the rest of the products, which are all liquids, even where relatively high molecular weight is obtained. We recommend revisiting this issue by trying other catalysts that are less sensitive to chelation ion inhibition.

Over 80 different intermediates (most with more than two active sites) have been synthesized, mostly in conjunction with the progress in formulation and coating curability, solvent resistance, hardness, and adhesion screening of formulations performed in Tasks 2 and 3. Figure 18 through Figure 22 illustrate all the different products that were synthesized during the three iteration phases. They are grouped by their functional groups or functioning purposes. The performance of this task is slowed down at this stage of the project, according to the original plan, but we expect the need and the ability to synthesize additional new intermediates if there is a renewed interest in such organic-siloxane resins for applications other than coatings (e.g., selective membranes). Appendix A.1 summarizes all the synthesis reactions that were carried out during the project. Another table (A.2) summarizes the screening formulations between various Si-H and Si-vinyl intermediates.

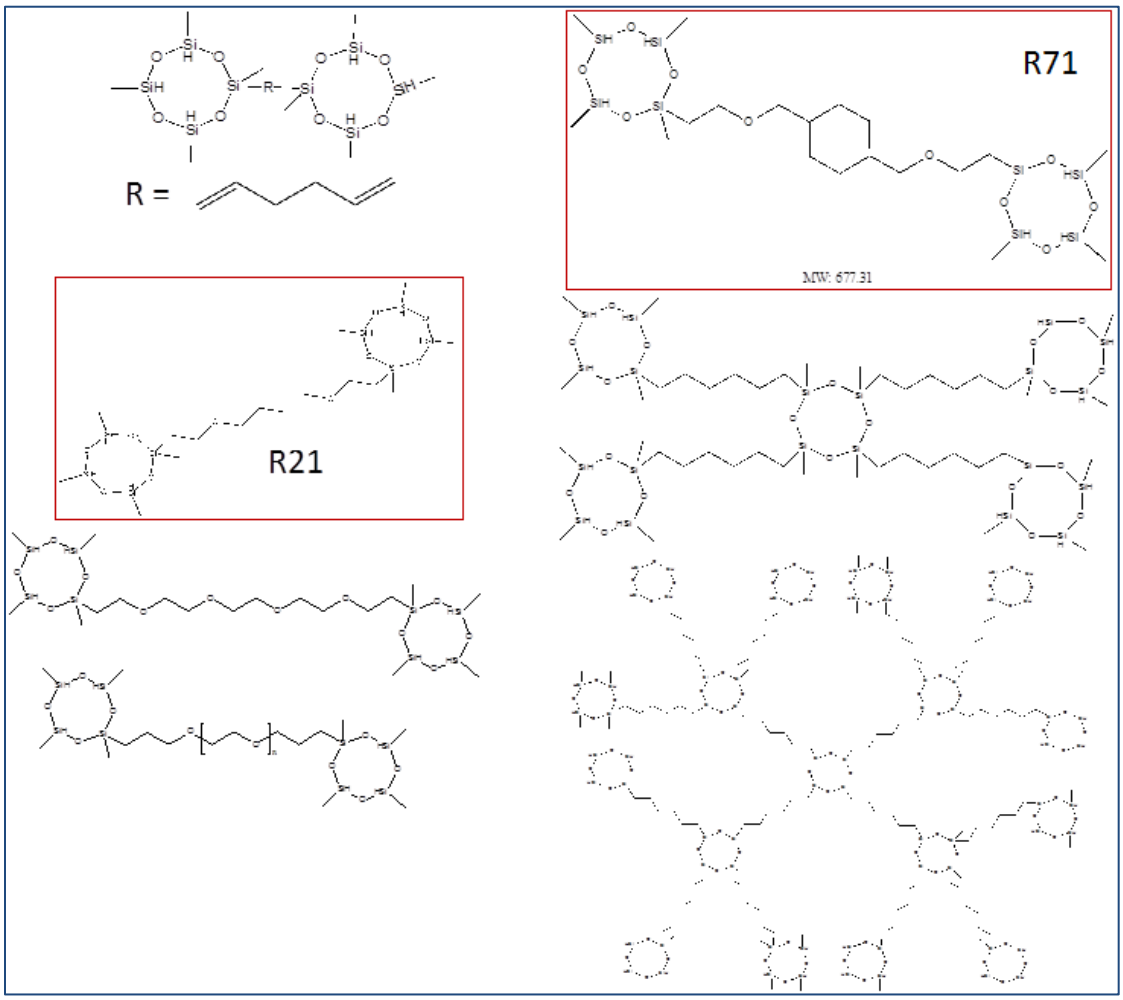



***Figure 18.*** *Various intermediates containing multiple Si-H groups synthesized in the project. The intermediates in the red boxes were selected and scaled up for further evaluation.*

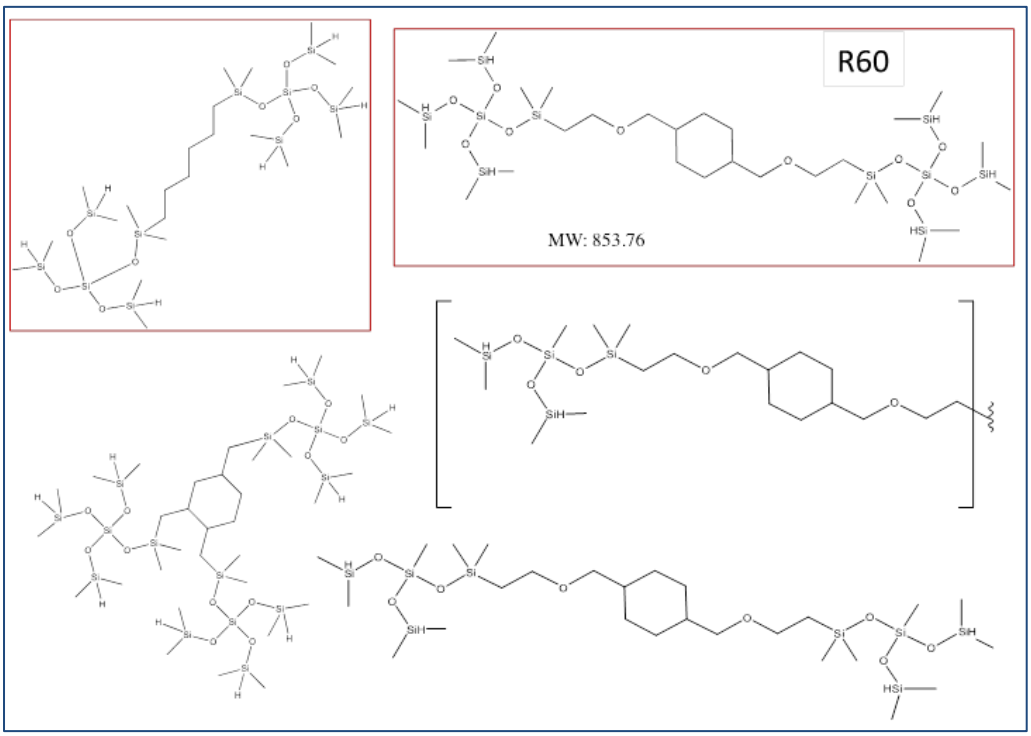



***Figure 19.*** *Additional intermediates containing multiple Si-H groups synthesized in the project. The intermediates in the red boxes were selected and scaled up for further evaluation.*

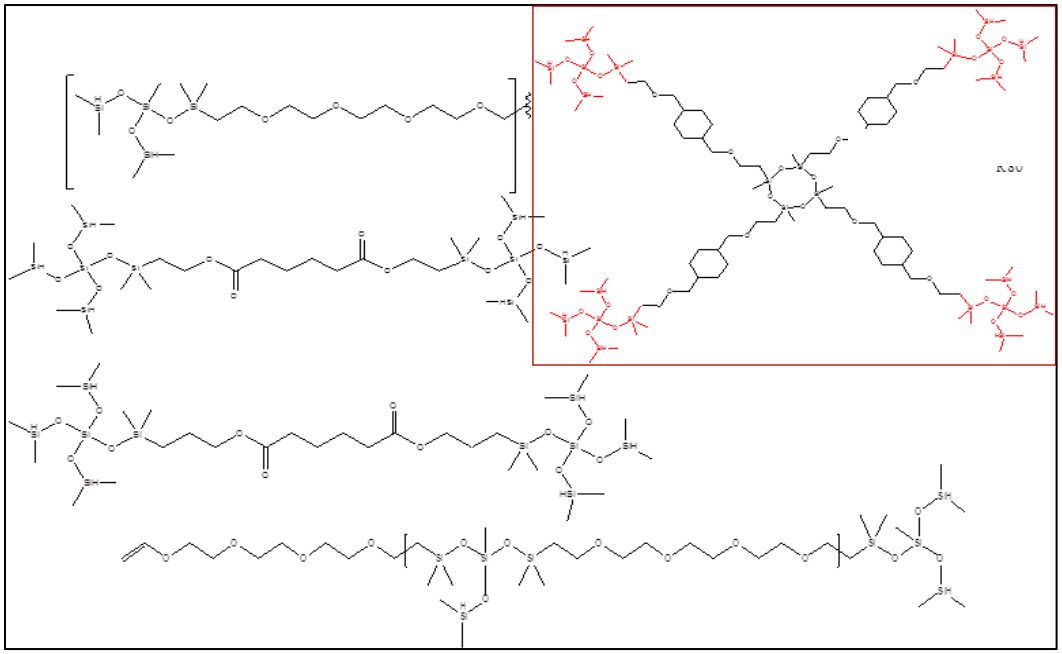


***Figure 20.*** *Additional intermediates containing multiple Si-H groups synthesized in the project. The intermediates in the red boxes were selected and scaled up for further evaluation.*

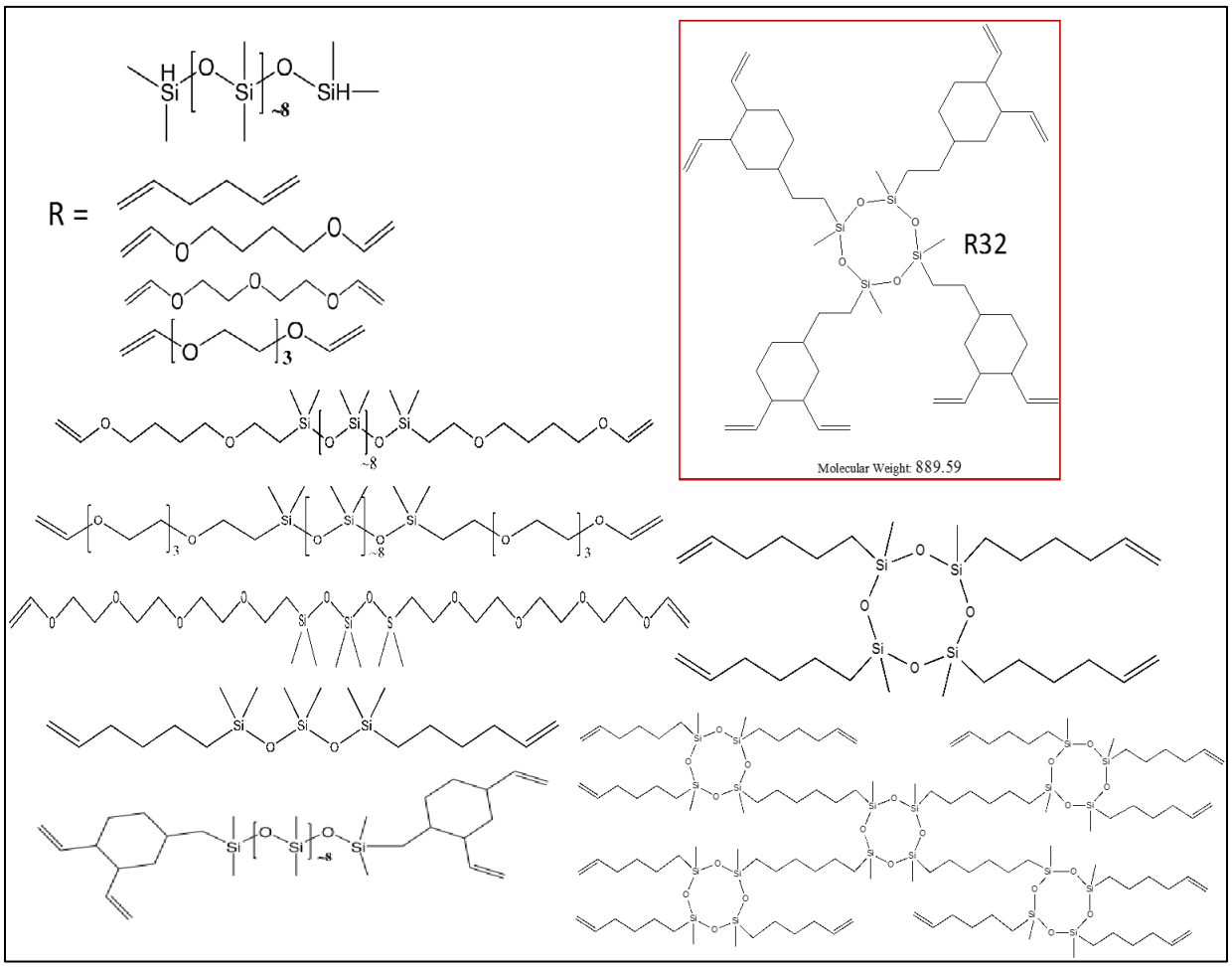



***Figure 21.*** *Various intermediates containing multiple vinyl groups that were synthesized in the project. The intermediates in the red boxes were selected and scaled up for further evaluation.*

The efforts toward developing practical intermediates focused on relatively low molecular weight products that provide either multiple hydrosilylation functional groups or linear chain extenders. We primarily used the linear and cyclomeric silanes coupled with the alkane-based products. In a few cases we produced intermediates with higher molecular weights by making several "generations" in which we alternated between excess of Si-H and excess of vinyl groups.

To avoid crosslinking during these reactions, we reacted one of the two types of the reagents ("Reagent A") with an excess amount of the other type ("Reagent B") in a stoichiometry that is suitable to saturate all the functional groups of "A" with mole equivalents of "B", adjusted to saturate "A", while only one functional group of "B" is reacted. The end result is that "B" still possessed multiple unreactive sites after all the sites of the first reagents were saturated, and crosslinking and gelation were avoided. Another measure to prevent crosslinking was to add "A" dropwise into a flask containing all "B". Therefore, all the active sites of "A" were easily saturated with the significantly higher concentration of "B". After each alternate step, the excess sof the vinyl or the Si-H reagent was evaporated.

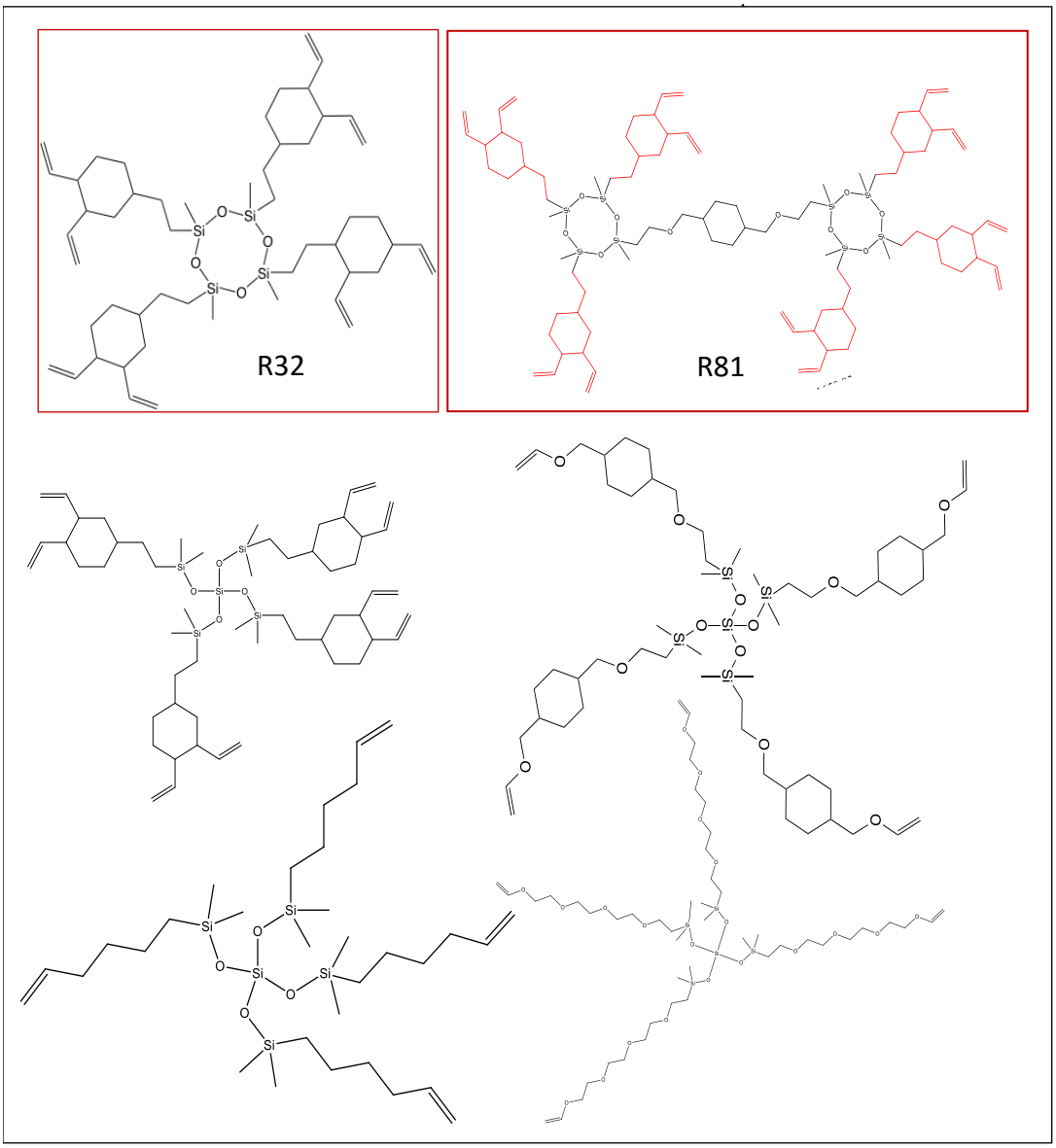



***Figure 22.*** *Additional intermediates containing multiple vinyl groups that were synthesized in the project. The intermediates in the red boxes were selected and scaled up for further evaluation.*

### *Crosslinkers*

Most of the intermediates synthesized, thus far, can be defined as "crosslinkers" because they possess more than two reactive sites (Si-H or vinyl) per intermediate molecule. However, the ones that were found to perform best have typically 6 to 8 such functional groups. It is expected that not all the reactive sites react during the curing at ambient temperature or even at 120˚F (50˚C). Utilizing the reactivity observed during the initial stage, SRI synthesized a series of intermediates that were extensively explored as crosslinkable reagents. With a few exceptions, the strategy emphasized the use of intermediates that possess more than two Si-H or vinyl groups.

In the case of the materials generated with the cyclotetrasiloxane, the structures consist of two cyclomers, bridged by one of the following groups: 1,5-hexadiene, 1,4-butanediol divinyl ether, di(ethylene glycol) divinyl ether or tri(ethylene glycol) divinyl ether. Very low levels of Karstedt's catalyst, in the range of 5-10 ppm, were utilized to obtain these crosslinkers, and the low viscosity liquids obtained appear to be stable when stored neat.

In the case of the 1,2,4-trivinylcyclohexane-based crosslinkers, we synthesized components that have alkene groups or silane groups as the pendant functional moieties. The crosslinker with alkene pendant functionalities was prepared by bridging two of the trivinylcyclohexanes with an oligomeric (short-chain) hydrogen-terminated PDMS. The derived product is a crosslinker with two alkene functionalities on either end. The crosslinker with the silane pendant functionalities was prepared by using an excess of the hydrogen-terminated PDMS with 1,2,4-trivinylcyclo-hexane, resulting in (after removal of excess silane) three hydrogen-terminated PDMS links extending from the cyclohexane ring.

### *Linear Extenders*

Linear extenders are long-chain intermediates having only two terminal Si-H or $-CH=CH_2$ groups that by themselves do not provide crosslinking capabilities. Such compounds were synthesized to be added as fractions in an overall formulation for enhancing the flexibility of the highly cured networks. We did not see any positive effect by using these linear extenders. However, we have tried only a few options, and we assume that having such optional intermediates will be useful.

When coupled with the crosslinking intermediates of the other hydrosilylation functional groups they did not perform well, and the hardness was significantly reduced relative to formulations without the extenders. More attempts will be made in that direction in the future.

### *Miscellaneous Intermediates*

Another effort for increasing the viscosity was synthesizing intermediates that are more polymeric in their nature. The main difficulty is to prevent gelation during the formation of such extended multifunctional compounds. Higher generations of intermediates were synthesized by alternately using one of the reagents (either Si-H or vinyl groups) in excess, followed by removal of the excessive compound by evaporation after saturation. We have been able to form up to four generations before the intermediate gelled (see Figure 20 – Figure 22). The viscosity indeed increased significantly from generation to generation, before the product gelled. As expected these products are highly branched, which is another reason for the increased viscosity.

In addition, we tried to synthesize viscous polymers by reacting multisite reagents with linear compounds containing only a single reactive site. By adjusting the stoichiometries between the two reagents, we have been able to obtain a few highly viscous reagents. However, these high-viscosity reagents did not provide good coatings, due to either separation from the formulation solutions or by being too viscous.

Bisalkenyl reagents with diester and carbonate functionalities were also evaluated. The idea was to add viscosity to the coating formulations and then form crystalline centers, enhancing the mechanical performance of the final coating. Indeed, these intermediates are solid at room temperature or at slightly lower temperatures. However, all the synthesized intermediates of this type induced a very sluggish curing and did not make the cut for advanced formulations of this system.

***Scale-up***

The initial synthesis quantities were of the order of 10 to 20 g. Intermediates selected for further studies were scaled up to 50-to-100-g scale. These products were submitted to PPG and Boeing for their own evaluations. Batches sent to both companies were initially in the range of 60 to 75 g per batch. Later, we scaled up the synthesis to the 0.5-kg level for larger scale formulation of the hydrosilylation curing systems. During the scale-up it was important to control better the overall temperature due to the volume increase. Since the hydrosilylation is an exothermic reaction, we did not use external heating unless we observed sluggish reactivity or incomplete one.

Once we switched the work to the hydrosilylation-dehydrocoupling system, we scaled up the synthesis of the down-selected intermediate (R71-OH, see discussion later) to 1 kg per batch, which required the synthesis of 1 kg of hydrosilylated material. No major issues have been noticed in scaling up this step, which is performed in the temperature range of RT to 80°C.

**(B) The Hydrosilylation-Dehydrocoupling System**

As discussed in detail in Tasks 2 to 4, we have encountered numerous problems with the hydrosilylation curing system, once we began using it as the leading chemistry to cure coating formulations. Sluggish curing and curing catalyst (Pt compound) poisoning when deposited over epoxy primers, and inversely a very short pot life, led to unsatisfactory results.

After a significant effort in solving the above and other problems with certain but not satisfactory solutions we decided to switch to an Si-OH curing system via the formation of intermediates with free Si-OH bonds instead of the active sites of Si-H that can react with the surface and crosslink via self-condensation reaction. This revision follows a parallel SRI activity of forming a practical resin for robust painting by synthesizing $[MeSi(OH)O]_x$ (PHMS-OH) from $[MeSi(H)O]_x$ (PHMS), which can nicely react with metallic substrates and crosslink via condensation mechanism. The dehydrocoupling platform for utilizing the commercially available PHMS is illustrated in Figure 7.

However, polymethylhydroxysiloxane (PHMS-OH) itself and its paint formulations provide hard and therefore brittle coatings with very limited elongation before feathering, while aircraft coating standards call for a high level of stretching, as manifested by the bending test requirements for aircraft coating MIL specs.

The dehydrocoupling synthesis performed in this project was geared toward making intermediates with a much lower degree of crosslinking than PHMS-OH. It still counted on the ease of the hydrosilylation reaction as the first step for making intermediates possessing multiple Si-H bonds. The Si-H bonds were then transformed to Si-OH by the catalytic dehydrocoupling reaction with water. There are plenty of other intermediates that can be synthesized by this approach by design. However, due to time and budget constraints, we limited ourselves to the utilization of only Si-H intermediates synthesized earlier in the project.

The hydrosilylation-dehydrocoupling reaction starts with the same (a) hydrosilylation approach to form intermediates containing multiple terminal sites of Si-H bonds (some canalso be in the middle of polymerized intermediate chains) followed by (b) catalytic dehydrocoupling reactions, hence quantitatively converting the Si-H to Si-OH as shown in the following reaction:

$$(H\text{-}Si)_{n-1}R^1\text{-}Si\text{-}CH_2\text{-}CH_2\text{-}R^2\text{-}CH_2\text{-}CH_2\text{-}\ R^1(Si\text{-}H)_{n-1} + H_2O \longrightarrow$$

$$(HO\text{-}Si)_{n-1}R^1\text{-}Si\text{-}CH_2\text{-}CH_2\text{-}R^2\text{-}CH_2\text{-}CH_2\text{-}\ R^1(Si\text{-}OH)_{n-1} + \text{oligomers of the Si-OH intermediate} + H_2$$

The dehyrocoupling reaction consists of catalytic and very efficient conversion of Si-H to Si-OH, a process developed at SRI,[17-20] which enables formulations that can be efficiently cured later at RT via a condensation reaction in the presence of a variety of base, acid, or organometallic catalysts:

$$2\text{Si-OH} \longrightarrow \text{Si-O-Si} + H_2O$$

The best dehydrocoupling catalyst we have discovered thus far is the commercially available $Ru_3(CO)_3$, although there are monomeric derivatives consisting of $L_xRu(CO)_y$ that are more active; however, their synthesis from the $Ru_3(CO)_{12}$ requires additional steps. Better, lower-cost catalysts are anticipated with further research in the field. Recovery of the catalyst is also feasible. Nevertheless, at the low levels of catalyst we currently use, the cost of the catalyst is not an issue for current commercialization activities of the PHMS-OH platform.

Intermediates synthesized based on the hydrosilylation-dehydrocoupling combinations are illustrated in

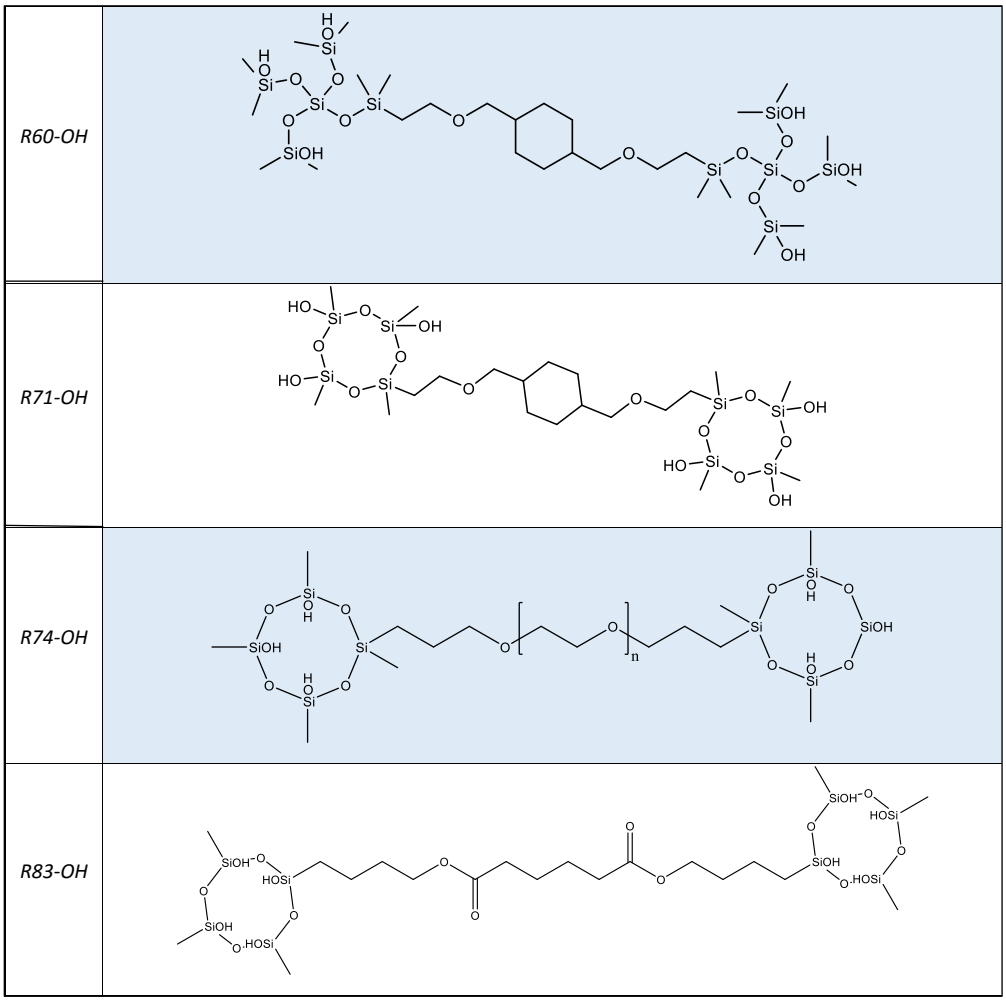



***Figure 23.*** *Si-OH intermediates synthesized and tested in paint formulation. R71-OH was down-selected for all the remaining formulation and coating evaluation.*

Figure 23. Due to the limited duration we have down-selected R71-OH as the only intermediate for intensive formulation studies with and without the addition of PHMS-OH. Its synthesis is illustrated in Figure 24. It should be noted that the intermediate is not staying as a "monomer" only. Gel permeation chromatography (GPC) analysis reveals significant polymerization via Si-OH condensation that occurs during the synthesis, as shown in Figure 25. This is a positive effect since a medium level of viscosity is desired for paint formulations to avoid dripping before the curing progresses and to minimize the curing reaction on a molar basis, since curing is associated with an exotherm and coating shrinkage. In fact, polymerized intermediates are the common practice in polyurethanes and epoxy resins.

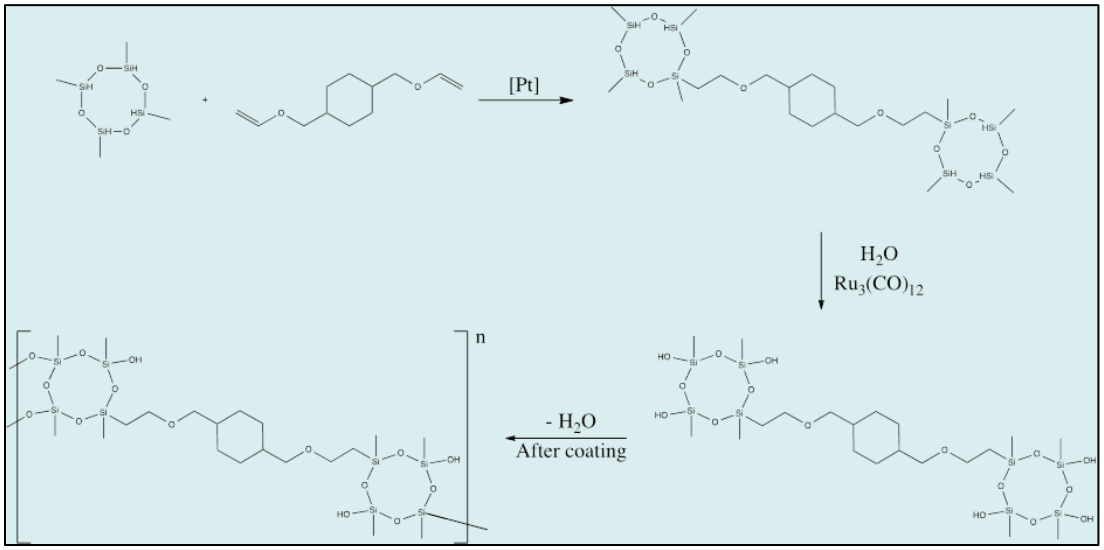
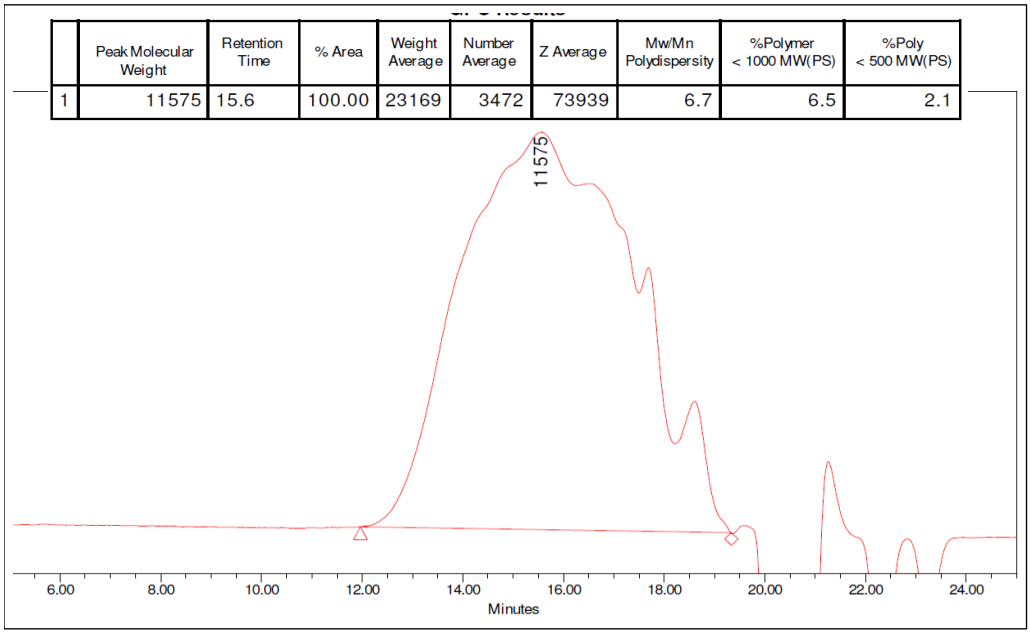



***Figure 24.*** *The synthesis and curing of R71-OH.*



| | Peak Molecular Weight | Retention Time | % Area | Weight Average | Number Average | Z Average | Mw/Mn Polydispersity | %Polymer < 1000 MW(PS) | %Poly < 500 MW(PS) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 11575 | 15.6 | 100.00 | 23169 | 3472 | 73939 | 6.7 | 6.5 | 2.1 |



***Figure 25.*** *GPC analysis of a synthesized batch of R71-OH, indicating significant polymerization by condensation of Si-OH to Si-O-Si groups*

The derived liquid polymer is not gelled when stored as 25 wt% solution in alcohols at ambient temperature in spite of the relatively high concentration of the Si-OH groups. This observation was correct for most of the prepared batches. However, the first scaled-up batch gelled rapidly even when stored in the refrigerator. Analysis of this batch revealed excessive level of extension, which actually means crosslinking. Other batches showed stability in solution even at RT for months.

The stability of the intermediates as well as PHMS-OH in solutions in spite of the high concentration of the reactive Si-OH is associated with the neutral pH of the solution, while the presence of basic or acidic pH accelerates the gelation of similar systems.

Both the hydrosilylation and the subsequent dehydrocoupling can be done in a one-pot reaction and then directly used for formulations without any purification step for the intermediates.

In order to control stability, we have various synthesis variables that can be further used to adjust the overall stability as well as performance. One approach is to block some of the Si-OH by alkylating the intermediate via hydrosilylation of a monovinyl compound prior to the dehydrocoupling. This approach may negatively affect the curing and the adhesion at the formulation stage. Another approach is to block some of the Si-OH sites by initially reacting the Si-H compound with alcohol during the dehydrocoupling reaction. In this case we form mixed Si-OH/Si-OR functional groups. The reduction of the Si-OH concentration and the steric hindrance imposed by the alkoxy groups result in enhancing the stability of the intermediate solutions and allow increase the intermediate concentration if needed for formulation purposes. The capability to control the ratio of the Si-OH/OR and maintain it in solution is important to further increase the shelf life of the ingredients and the pot life of the active formulation, if necessary. However, there is typically a tradeoff in the curing rates at room temperature.

A few of the reactions discussed above are illustrated in Figure 26.

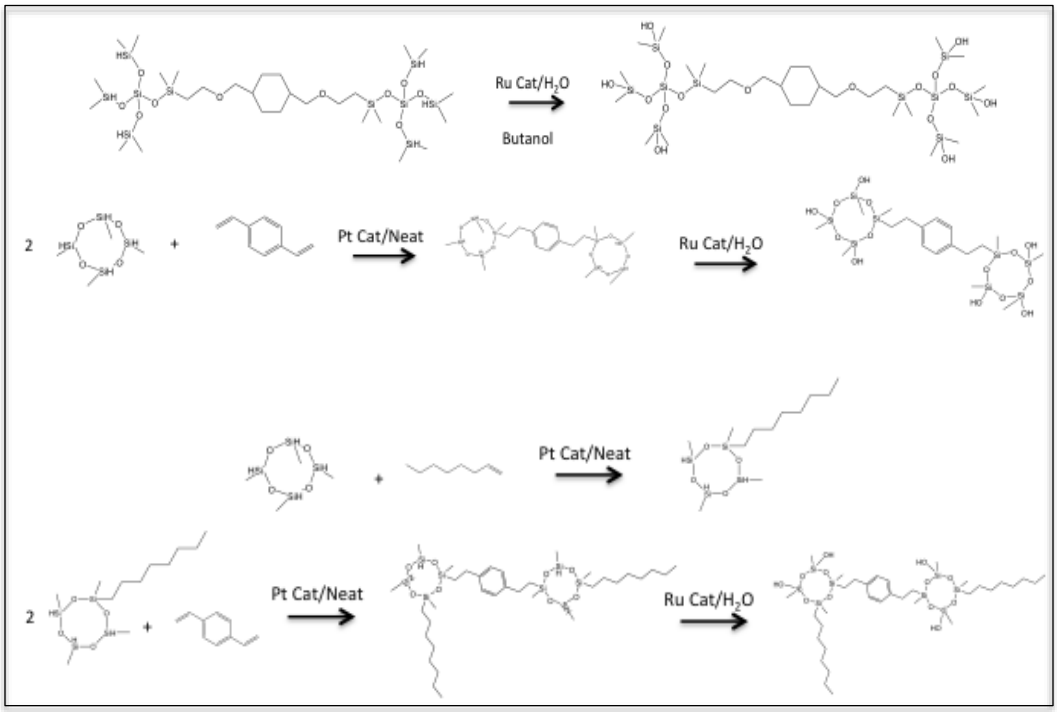



***Figure 26.*** *The synthesis reaction of Si-OH intermediates*

***Synthesis and Characterization of R71-OH***

Since R71-OH is the only Si-OH intermediate that we have extensively evaluated in the third year of the project, we provide in this section more information about its synthesis and characterization.

The conversion of the silane to silanols was readily achieved in butanol at temperatures in the range of 75-80°C. Figure 27 represents the FTIR of R71 and R71-OH after completion of the dehydrocoupling reaction. The strong signal due to the Si-H functionality at 2100-2200cm$^{-1}$ is seen to drastically reduce and integration of this band relative to the Si-$CH_3$ signal at 1250cm$^{-1}$ indicates >95% conversion.

There is some indication that a small amount of butoxide formation is beneficial to the shelf life of the R71-OH material. The butoxide will form if no water is present and is the result of a dehydrocoupling reaction using the solvent, butanol. Efforts to elucidate the ability of butoxide formation to extend the shelf life of the material in a quantitative sense were not successful as the ability to quantitate any butoxide formation proved difficult as it is impossible to get rid of any residual solvent without causing the R71-OH to cross-link to itself via condensation making analysis impossible. It should be noted that in those formulations where it is speculated that there is 10-20% butoxide formation the shelf life of R71-OH at room temperature is greater than one year.

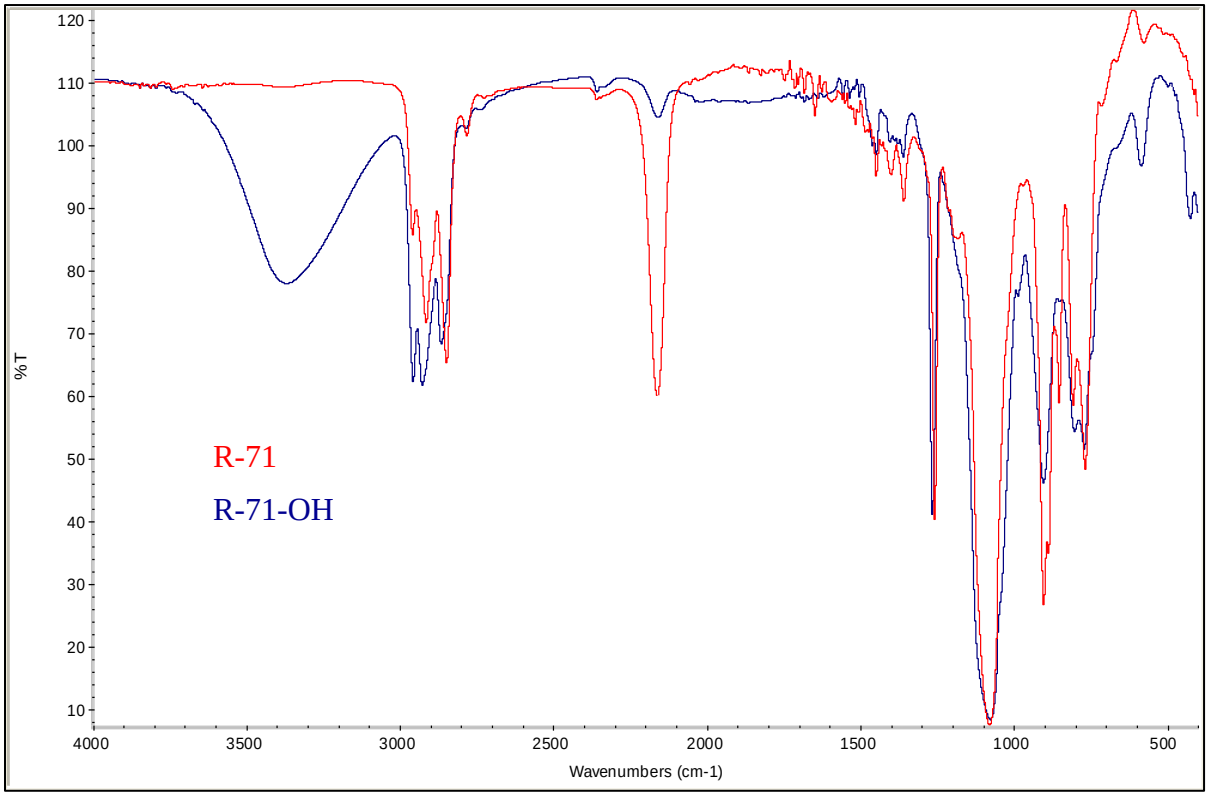



***Figure 27.*** *FTIR of R71 and its derived R71-OH after dehydrocoupling.*

## TASK 2. CURING & STRUCTURE-TO-PROPERTY ASSESSMENT

Most of the initial formulations, catalytic curing experiments and evaluation of the cured materials were originated at SRI. Once advancement was achieved with selected formulations, the selected intermediates were submitted to PPG and Boeing for their own analysis and modifications. In this section we discuss the accumulated information about the curing studies. As in all other tasks we separate between the hydrosilylation only and hydrosilylation-dehydrocoupling systems.

### (A) Formulations based on Hydrosilylation Only Reactions

The curability (crosslinking reaction) of paint formulations via the same hydrosilylation reaction used to form the various series of intermediates is the essence of the originally proposed platform. Thus, this activity began soon after we started the intermediate synthesis work. Most of the screening studies have been performed and further developed at SRI. However, selected intermediates were also submitted to PPG and Boeing for self-evaluation. Initially, we performed curing reactions at RT in vials using formulations consisting of 1:1 mol equivalents of Si-H:vinyl. However, as the work has progressed, we have studied the curing capability of formulations after their deposition by casting thick films of the various formulations over aluminum alloy plates and later on over selected epoxy primers. Coatings with thickness aiming at 50μm were evaluated.

A major reason for the shift in mode of curing assessment from vial to a coating configuration is associated with the discovery that the curing is slower (at least at room temperature) in the format of coatings versus the bulk ("pot" storage). This is because the hydrosilylation reaction is exothermic and the in-situ generated heat after formulation accelerates the curing rate of the bulk material inside the container. In contrast, the heat can be easily dissipated in a coating form and the crosslinking reactivity slows down at RT. In fact, the issue of too fast reactivity of formulations in a pot vs. adequate or even sluggish curability of coatings became a major issue for investigations performed during the second half of the project, as discussed later in Task 3. Thus, most of the observations associated with this task are described in Task 3 activities.

A typical procedure for assessing the curability of a couple of Si-H/ene intermediates is provided below for reactions X36 and X40, which represent the first two down-selected couples for further studies in Tasks 3 and 4.

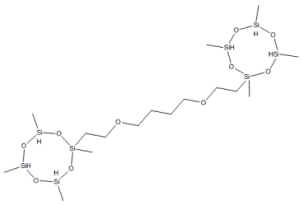
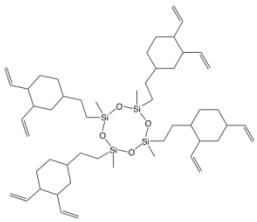
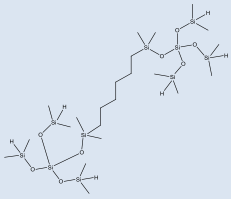
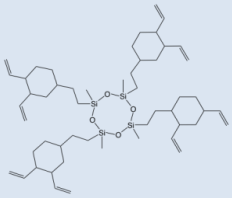
**1) Formulation Mix**

a) Table 1 below represents the stoichiometric ratio of the Si-H and vinyl intermediates, where the stoichiometry is defined by the molar weight of each intermediate. Notice that this is not a stoichiometric ratio of the Si-H and the vinyl groups.

b) While the reagents are still cold, the desired amounts are weighed out into a scintillation vial or a flask with a stopper while vigorously stirring (preferably with magnetic stirring)

c) The mixture should be homogeneous. If not, a compatibilization solvent such as cyclohexane, heptane, toluene or xylene can be added.

***Table 1:*** *The main formulations used for the initial curing studies*

| Form. # | A = Si-H part | B =Ene Part (A:B ratio) | BASE ratio A:B equivalents *(A/B weight ratio)* | Suggested 1st modification for A:B |
|---|---|---|---|---|
| **X36** |  <br>MW=623.2 g<br>1 equiv.=623.2/6=**103.9g**<br>***R21*** |  <br>MW=889.6 g<br>1 equiv. =889.6/8=**111.2 g**<br>***R32*** | 1:1<br>*(0.93)* | 1:0.5<br>*(1.87)* |
| **X40** |  <br>MW=739.6 g<br>1 equiv.=739.6 /6=**123.3g**<br>***R44*** |  <br>MW=889.6 g<br>1 equiv. =889.6/8=**111.2 g**<br>***R32*** | 1:1<br>*(1.11)* | 1:0.5<br>*(2.22)* |

**2) Catalyst strategy**

a) Starting first without the addition of a catalyst counting on the internal catalyst already in parts A and B. It may be enough already; there may be an aging issue, thus it is possible that there will be batch to batch variations.

b) If the room temperature dry to touch (DTT) is sluggish then 0.1 g of the 0.05% catalyst solution are added per 1.0 g of mixed formulation (A + B).

c) The catalyst can be added in two ways:

i) Added to part B (ene) first <u>before</u> it is combined with Part A (Si-H) while stirring the solution

ii) Added to a combined formulation when it is cold (around or below 0°C) by slowly adding drops of the catalyst solution to a vigorously stirred (magnetically) solution.

d) If the added amount catalyst is too much, then it is cut it by half.

e) If it is still sluggish double the amount of catalyst.

**3) Deposition over Substrate**

a) Spreading the formulation onto an aluminum plate with the desired thickness.

b) Watching for the wettability of the formula.

c) If the wetting is not good, sometimes it is better to age the formulation a bit, if it is not too reactive.

**4) Curing**

a) At RT for slow curing. (Checking after 1 day and then every 3-4 days for increased hardness).

b) At 50C for a duration of 1 to 4 hours. (Checking every hour for hardness)

***Catalyst Efficiency Assessment***

One significant aspect of the curability was to assess the efficacy of the live Pt catalyst which remained within the synthesized intermediates (between 10 to 75 ppm of Pt catalyst, depending on the hydrosilylation reactivity during the intermediate synthesis). We wanted to understand if it remains active enough to complete the curing without additional catalyst. The observations varied depending on:

a) The activity of the mixed intermediates,

b) The residual amount of active catalyst from the intermediate synthesis, and

c) The time passed from the synthesis of the batch ("aging").

The latter observation (c) is associated with the decomposition or transformation of the catalyst remaining in the stored intermediate, which reduces or stops the catalytic activity. Later on, it brought up the topic whether it is better to remove the catalyst from the intermediate after the synthesis and add a fresh catalyst only when the paint formulation is prepared for actual deposition. This way the pot-life and curing rates of the formulations can be much more reliable and repeatable.

The concept of removing the catalyst prompted a lab activity to demonstrate efficient removal of the live catalyst or its selective "poisoning" (thus, the poisoning agent does not poison additional catalyst when added prior to coating deposition). The "poisoning" occurs if some organic or inorganic compounds or ions have strong affinity to the Pt catalyst and compete with the Si-H and/or Si-CH=$CH_2$ in complexation bonding to the catalyst's metal core. In the case of a poisoning compound, it is bonded irreversibly to the Pt atom, while in a catalytic situation the bonding can be reversal and the reaction product tend to leave easily from the catalytic site. Amines, ammonia, sulfur, and thiols are known as Pt poisoning elements. Potentially, the live catalyst "poisoning" can be also associated with leaching of trace amounts of compounds from the storage containers, hence deactivating the live catalyst as a function of aging.

The curing studies were performed at both RT and 50°C (~120°F). The higher temperature was selected because it is within the operating practices at Boeing painting hangars where the entire facility is heated up to this temperature to accelerate drying and curing of the deposited paints (defined by Boeing as an "accelerated" ambient temperature).

The initial curing is detected by the conversion of the formulation from a liquid (oily) form into a gel ("dry to touch"). Since most of the formulations are made without additional solvent, the "dry" stage is solely related to curing and not to solvent evaporation, which is the case in many conventional paint formulations. The curing inside the formulation container is manifested by the formation of a soft gelled material. The gelation in the pot is also achieved without any additional catalyst. Most of the formulations that were cured in the container without additional catalyst contained no more than 30 ppm (by weight) of the catalyst remained from the synthesis of the intermediates. The addition of a fresh catalyst to a total range of 50 to 75 ppm (including

the synthesis catalyst) was required for RT curing of deposited coatings. Some formulations can be adequately cured at 50°C without the addition of catalyst. Yet, enhancing the hardness of the coating (extended curing stage) requires the additional amount of fresh catalyst.

It is important to realize that we are dealing with extremely low levels of catalyst, since for most thermoset paints, it is required to add amounts of 1 to 5 wt% (10,000 to 50,000 ppm) of various catalysts (i.e., 3 to 4 orders of magnitude higher than we added for the curing vs hydrosilylation). Increasing the amount of catalyst and temperature accelerates the reactivity of this system in an exponential fashion because the reaction is exothermic, generating internal heat, which in-tern accelerates the reaction rates once activated.

Most of the intermediates and their mixtures are colorless. One exception is R32 (shown in in Table 1, which was selected as our preferred vinyl intermediate for the curing and formulation studies. R32 is slightly yellow in appearance with some haziness. The color and haziness indicate transformation of the catalyst.

We evaluated formulations of mixed intermediates mostly without adding solvents, since most of the good intermediate performers had low viscosity by themselves, typically in the molecular weight range of 400 to 800. Since the viscosity is relatively low compared to standard paints, we have shifted our synthesis focus to the synthesis of intermediates that have higher molecular weight or molecular structure that impose higher viscosity. In particular we found that the derivatives of bis-(vinyl-methane ether)-cyclohexane enhance the viscosity of relatively low molecular weight intermediates.

Formulations with increased viscosity components may present another issue, which is miscibility and separation of the components after coating deposition. This post-painting separation can increase the curing time and make uneven coatings. Addition of compatibilizing solvent is not always helpful, since we still observed phase separation after the solvent evaporation and prior to curing. This situation may be eliminated once we add pigments (fillers) to the formulations, as they may prevent the phase separation by good wetting of the intermediates over the surface of the incorporated particles. Another approach to avoid separation with viscous intermediates is to age the mixed formulation, hence allowing some bonding between the Si-H and Si-vinyl intermediate to occur.

As indicated above and further discussed in Tasks 3 and 4, the curability with added Pt catalyst is adequate for achieving curing even at RT and extends the curing to achieve significant hardness. However, the pot life is relatively short or very short after such an addition, which hampers the practicality of the platform. Therefore, we have added the following assessments after April 2015 in search of slowing down the pot reactivity after the coating formulation but allowing the reactivity to proceed at low temperature after the formulation is coated:

a) Replacing the curing catalyst with a less active one.
b) Adding a solvent that reduces the concentration of catalyst and hence increases pot life.
c) Adding a reversible volatile inhibitor to the solution. In this case the bonding of the inhibitor in the formulation solution will reduce its hydrosilylation reactivity in the pot, but once it is deposited as a coating it can be volatilized while the catalyst is reactivated.

Option (a) was not successful at all. The potential catalysts that were assessed did not provide good enough hydrosilylation activity at RT, except the Pt ones, which did not prolonged the pot

life over the formulations with the original Pt catalyst. It should be noted that there are many potential catalysts consisting of Pt, Rh and Pd that were not assessed due to effort limitation and the later-on decision to switch the effort to Si-OH based intermediates.

Option (b) may provide an adequate solution to the problem. We found that conventional alcohols (methanol, ethanol, etc.) indeed enhance the pot-life to beyond the 4h threshold as shown in Table 2. However, they negatively affected the dry time and the completeness of the curing after the solvent has been removed. It is possible that traces of these solvents still affect the catalyst reactivity by strong complexation. Methanol seems to be the best inhibitor since it provides hard coatings when cured at 50C. However, it does not adhere well to the substrate. The addition of 5 wt% vinyltrimethoxylsilane, together with the alcohol increase the adhesion to the substrate, while still maintains adequate pot life and significant hardness after curing.

***Table 2:*** *Inhibition effects of various reagents, solvents and complexation components.*

| Solvent/ Inhibitor | Pot Life (h) | Hardness at 50°C* | Adhesion at 50°C* | Hardness at RT | Adhesion at RT |
|---|---|---|---|---|---|
| **~1 wt% solvent and ~30 ppm of Pt catalyst** | | | | | |
| Methanol | 4<x<72 | 3-4H | 0B | 2H | NA |
| Ethanol | 4<x<72 | 2H | 2B | <H | NA |
| Isopropanol | <4.5 | 2H | 0B | H | NA |
| *50C for 4 hours and RT for 3 days | | | (gelled over the weekend) | | |
| **20ul of the inhibitor/solvent and 42 ppm of Pt catalyst and 5wt% allyltrimethoxysilane (ATMS)** | | | | | |
| Methanol | 4<x<24 | 4-5H | 1-2B | 2H | |
| Ethanol | 4<x<24 | 4H | 1-2B | <H | |
| Isopropanol | 4<x<24 | 4H | 0-1B | <H | |
| (gelled overnight) | | | | | |
| **1 wt% solvent and 43 ppm of Pt catalyst and 4wt% vinlyltrimethoxysilane (VTMS)** | | | | | |
| Methanol | 4<x<72 | 5H | 2B | 4H | 1-2B |
| Ethanol | 4<x<72 | 5H | 3-4B | 4H | 2-3B |
| Isopropanol | 4<x<72 | 5H | 3-4B | 3-4H | 2-3B |
| *50C for 4 hours and RT for 2.5 days | | | (gelled over the weekend) | | |
| **1ml of the inhibitor/solvent and 30 ppm of Pt catalyst** | | | | | |
| Benzothiazole (460 ppm) | < 5min | 4H | 1-2B | 3H | 1-2B |
| Xylene | < 5min | 5H | 4B | 3H | 2-3B |
| Acetone | < 5min | NA | NA | NA | NA |
| **44 ppm of Pt** catalyst and 4wt% VTMS | | | | | |
| Vinyltrimethoxysilane (VTMS) | >4h | 5H | 3B | sticky | NA |

Most known hydrosilylation inhibitors require heat for removing them from the formulation and reactivating the catalyst. These include compounds containing conjugated carbonyl-alkene functional groups, such as fumarate, maleate, and volatile aminosilanes. Ketones and diketones are also potential candidates.

Room temperature curing is assessed in time frames of days and weeks as anticipated in the case of conventional paints for achieving maximum curability and subsequent performance. Curing at 50°C was assessed at 1 h and 4 h of baking in an oven. In general, as discussed in Tasks 3 and 4, the heat cure provides improved characteristics relative to the RT curing concerning the curing extension for obtaining coatings with adequate hardness and improved adhesion. An interesting point is that the cyclomeric and branched Si-H groups have reversed order of reactivity between the initial synthesis of the Intermediates and their formulation curing. During synthesis, the cyclomeric units are more reactive. However, the curability of the branched Si-H reagents tested thus far is faster. This "anomaly" can be used strategically in future formulations, if the technology is used for making products outside the field of aircraft coatings (for example, selective membranes).

Curing over primer became another major issue that will be discussed in later tasks. However, it should be mentioned here that curing of coatings over a standard aerospace-certified primer coating is not adequate, and is sluggish even with additional Pt catalyst, in contrast to the same formulation coatings over pretreated metals. It seems that the problem is associated with the fact that epoxy primers and urethane formulations contain intermediates and curing catalysts that are amine based. Amines tend to inhibit or poison the hydrosilylation activity of Pt catalysts, especially the Pt(0) (Karstedt catalyst) used, thus far. This is another incentive to assess other hydrosilylation catalyst in the near future, aside the issue of short pot life.

Before abandoning the hydrosilylation only approach, we have tested the catalysts illustrated in Figure 28. All these catalysts were reported for their capability to hydrosilylate and are commercially available. However, none of them except the chloroplatinic acid was really active in the formulation/ environment conditions used in this study.

Table 3 and Table 4 summarize the comparative results of using the various potential catalysts. They were evaluated for their curability as a function of time and temperature as well as for their progressive curing at RT as a function of time. The pot life (P) of the formulations with various catalysts was assessed aside the hardness (H) and the bonding (B) of each.

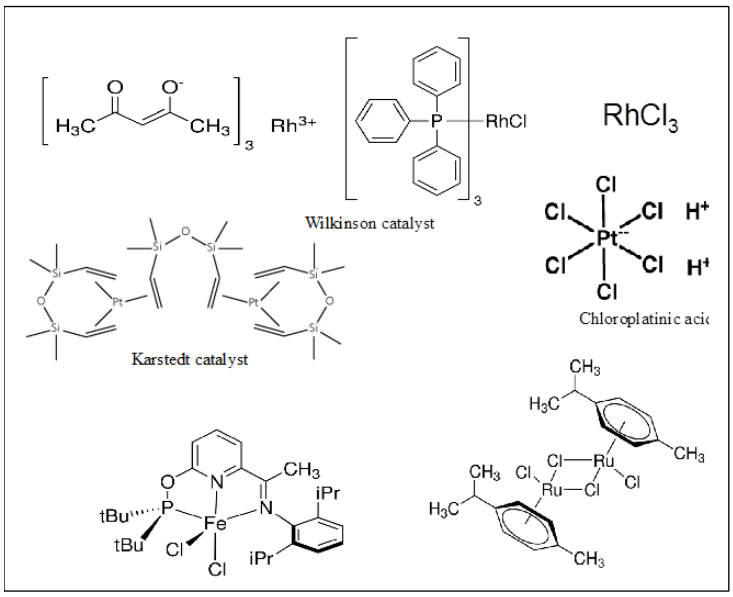



***Figure 28.*** *Various hydrosilylation catalysts to be assessed as curing catalysts.*

***Table 3:*** *The reaction between R71 and R32 – cured at 50 ℃*

| 1:1 R71:R32 + Catalyst | 32 ppm | | 67 ppm | | 100 ppm | | 191 ppm | | 355 ppm | |
|---|---|---|---|---|---|---|---|---|---|---|
| **50°C/ 4hr** | **H*** | **B**** | **H** | **B** | **H** | **B** | **H** | **B** | **H** | **B** |
| **Tris(dibutylsulfide)rhodium trichloride** | 2 | 1 | 4 | 2 | 3 | | 5 | 1-2B | 4 | 0 |
| **Chloroplatinic acid hydrate** | 2 | 3 | 4 | 2-3B | 4 | 0 | 4 | 0-1B | 4 | 1-2B |
| **(tBu)PNN(iPr)$FeCl_2$** | 2 | 3 | 4 | 3 | NC | NC | NC | NC | x | x |
| **Tris(triphenylphosphine)rhodium(I) chloride** | 2 | 1 | 4 | 0 | 1 | | 5 | 3 | 4 | 4 |
| **Rhodium(III) acetylacetonate** | 2 | 2 | 4 | 0 | 4 | | 4 | 2 | 2 | 3-4B |
| **Di-µ-chlorobis[(p-cymene) chlororuthenium (II)]** | 2 | 2 | 2 | 2 | <H | | 5 | 0 | 2 | 3-4B |
| **Pt-Karstedt catalyst (control) no additional of external catalyst** | 5 | 0 | 2H/0B | | | | | | | |

***Table 4:*** *The reaction between R71 and R32 – room temperature curing*

| 1:1 R71:R32 + Catalyst | 32 ppm (1d) | | | 67 ppm (4d) | | | 100 ppm (3d) | | | 191 ppm (3d) | | | 355 ppm (2d) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Room Temperature curing** | **H** | **B** | **P** | **H** | **B** | **P** | **H** | **B** | **P** | **H** | **B** | **P** | **H** | **B** | **P** |
| **Tris(dibutylsulfide)rhodium trichloride** | NC | | | NC | | | NC | | 3h | NC | | ≤3 | NC | | ≤2 |
| **Chloroplatinic acid hydrate** | <H | | | 2 | | | 1 | 2 | 3h | 1 | | ≤2h | 1 | | 2h |
| **(tBu)PNN(iPr)$FeCl_2$** | NC | | | NC | | | NC | | NC | NC | NC | NC | x | x | x |
| **Tris(triphenylphosphine) rhodium(I) chloride** | NC | | | NC | | | NC | | >3 | NC | | >1wk | NC | | ≤2 |
| **Rhodium(III) acetylacetonate** | NC | | | NC | | | NC | | >3 | NC | | >1wk | NC | | >2 |
| **Di-µ-chlorobis[(p-cymene)chlororuthenium(II)]** | NC | | | NC | | | NC | | >3 | NC | | ≤1wk | NC | | >2 |
| **Pt-complex (control) no additional catalyst** | 2 | | <2m | Control: NC (17d) | | | | | | | | | | | |

*H: hardness; B: adhesion; NC: not cured; P: pot life (shown as days)*

Table 5 follows the progress of curing and adhesion as a function of long curing periods at RT. Only the Pt catalysts show adequate results. However, the regular catalyst we have used as the primary one (Karstedt's) was found to be more effective and active than chloroplatinic acid. The latter one may be more active for a few of the intermediate syntheses.

***Table 5:*** *The reaction between R71 and R32 – after prolonged period*

| **1:1 R71:R32 + Catalyst** | **32 ppm (1 mo)** | | **67 ppm (1 mo)** | | **100 ppm (1 mo)** | | **191 ppm (3wk)** | | **355 ppm (17 d)** | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Room Temperature** | **H** | **B** | **H** | **B** | **H** | **B** | **H** | **B** | **H** | **B** |
| **Tris(dibutylsulfide)rhodium trichloride** | NC | | <H | | NC | | NC | | NC | |
| **Chloroplatinic acid hydrate** | <H | | 3 | 2-3 | 4 | 2 | 4 | 1-2 | 4 | 2 |
| **(tBu)PNN(iPr)$FeCl_2$** | NC | | NC | | NC | | NC | | X | X |
| **Tris(triphenylphosphine) rhodium(I) chloride** | NC | | <H | | NC | | NC | | NC | |
| **Rhodium(III) acetylacetonate** | NC | | H | | NC | | NC | | NC | |
| **Di-µ-chlorobis[(p-cymene)chlororuthenium(II)]** | <H | | H | 4-5 | H | | <H | | NC | |
| **Pt-complex (control): no additional catalyst** | 4 | 4 | Control: 17d - NC | | | | | | | |

**H: hardness; B: adhesion; P: pot life (shown as hours if not noted otherwise)*

***Inconsistency Due to Aging***

During the study we have noticed an inconsistency in the curing rates between different batches of the vinyl and the Si-H intermediates. Especially, it was noticed during the assessment of R32 vinyl functional polymer and R44 Si-H functional polymer (Reaction X40). It was also noted that the cure response, as evaluated by solvent resistance had fallen off dramatically as a function of aging of the intermediates. When fresh batches of the same intermediates were evaluated, the cure time and performance characteristics were consistent. This inconsistency can be explained if the "living" catalyst (the platinum complex), which is not removed from the intermediates and later participates in the curing stage, gradually degrade as a function of aging. In this scenario, it would be difficult to count on the presence of pre-blended catalyst.

A series of tests was designed to determine if the varied performance were due to batch-to-batch variations of the starting materials. In all, 3 batches of the R32 and 3 batches of the R44 were tested in a round robin analysis. Each of the batches was ordered by the date that it was received, Thus, the lower the batch number, the older the batch. The systems were compared based on dry time, gel time, and solvent resistance. The data of the experiments are captured in in Table 6, and a direct comparison of dry time for different R44 batches is illustrated in Figure 29.

***Table 6:*** *Batch Comparative Observations*

| Batch R44 | Batch R32 | Dry to Touch Time (h) | Pot Life (h) | 24 h Solvent Resistance |
|---|---|---|---|---|
| **2*** | 2* | Did not dry | Did not gel | Not tested |
| **3** | 2 | Did not dry | Did not gel | Not tested |
| **4** | 2 | Did not dry | Did not gel | Not tested |
| **2** | 3 | 3 | 2 | Fail 5 |
| **3** | 3 | 2.5 | 2.5 | Fail 25 |
| **4** | 3 | 2.5 | 2 | Fail 10 |
| **2** | 4 | 1 | 10 min | Fail 45 |
| **3** | 4 | 1 | 10 min | Pass |
| **4** | 4 | 1 | 10 min | Pass |

** Batch number; The degree of failure is marked by the number of strokes required by a cloth soaked with MEK to breach the coating integrity after curing for 24h; Pass means no breaching after 100 strokes.*

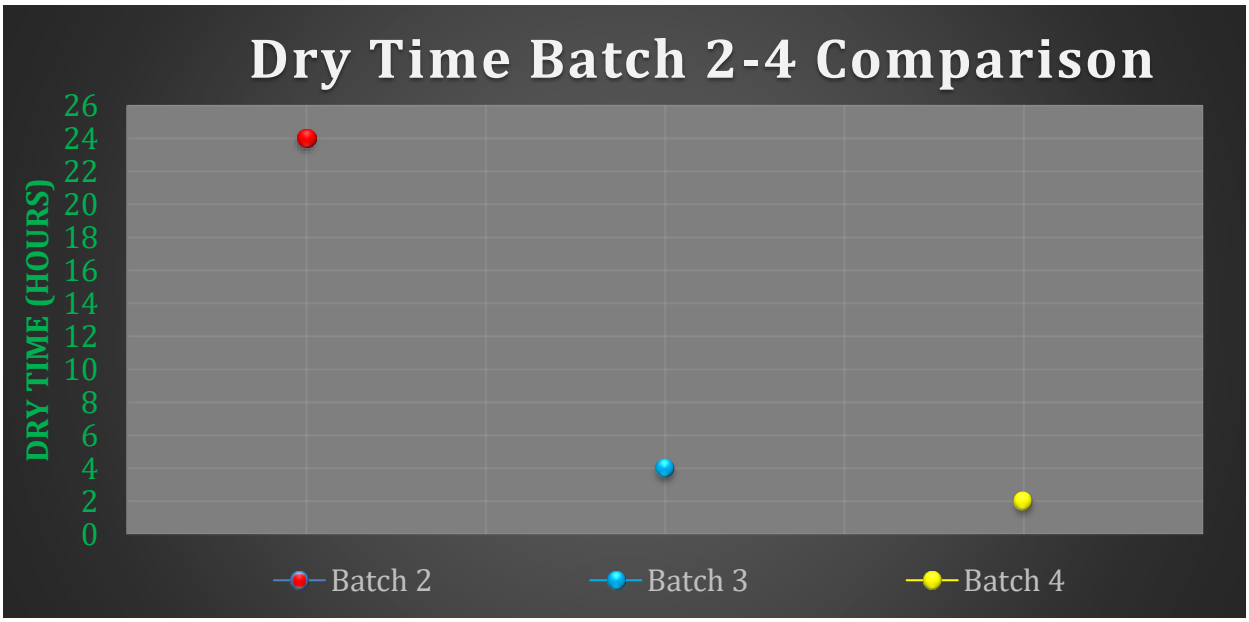



***Figure 29.*** *Dry Time Batch Comparison of R44*

The series analysis reveals that newer batches provide better crosslinking as manifested in faster dry time and better solvent resistance after 24h. It is also associated with much shorter life time. Older batches reveal an opposite behavior – long pot life, little or no crosslinking, and no solvent resistance at 24 hours. Closer analysis indicates that the main problem is the aging of the catalyst in R32, i.e. the multi vinyl compound.

It is well known and also reassessed in the current study that the Pt form much more stable complexation with vinyl groups via π donation, while the complexation of Si-H via oxidative addition (forming Si-Pt-H species) is less stable. For example, mixed intermediates in which the molar ration of Si-H to vinyl is >1 will be more reactive than if the ratio is <1.

IR spectra were run on the batches of both R44 and R32 to determine, if differences in the intermediate molecular structures could be noted. See Figure 30 and Figure 31.

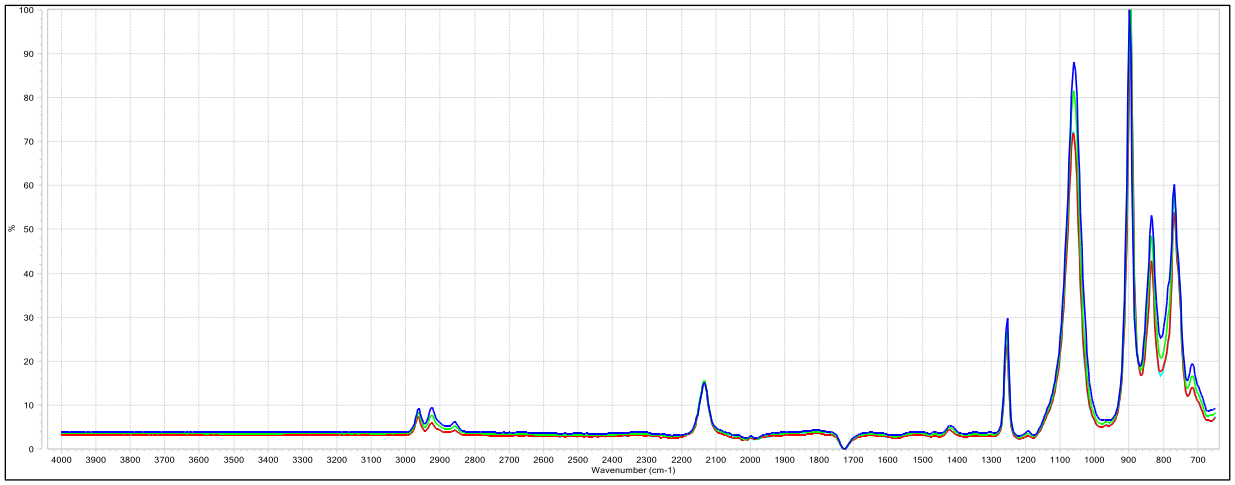



***Figure 30.*** *IR of different Batches of R44*

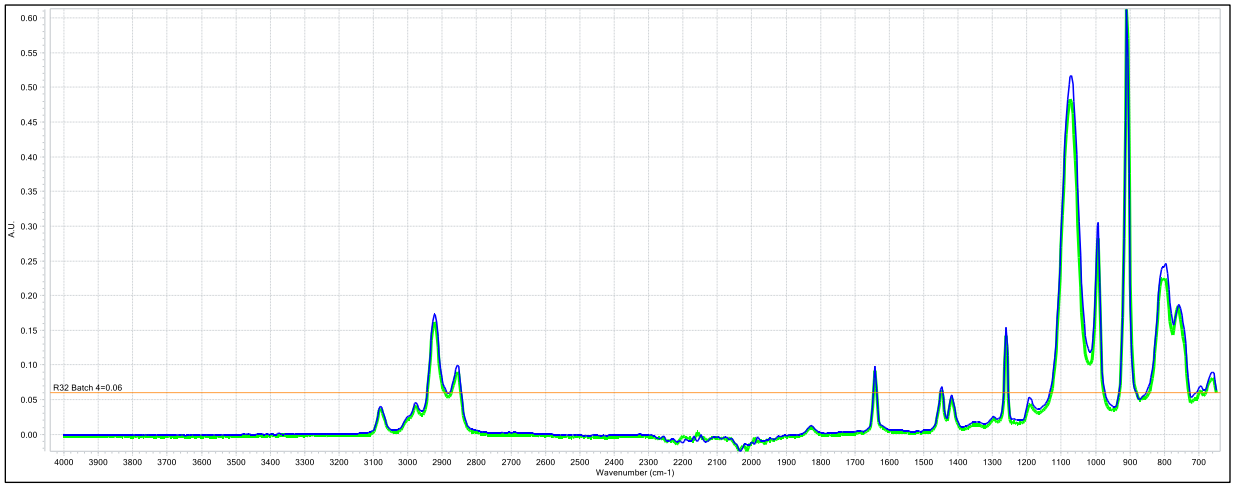



***Figure 31.*** *IR of different Batches of R32*

It can be seen that the spectra of the various batches lay nearly directly on top of each other. Any minor differences can be attributed to variation in the thickness of the sample being run. Therefore, we can rule out that the aging is affected by degradation of the intermediates themselves during storage or variations obtained during the synthesis of the intermediates. This evidence adds to our conclusion that the catalyst activity is responsible to the deactivation as a function of aging.

**Inconsistency in Reactivity of Systems.** It was discovered that several of the earlier batches of polymers, R32, vinyl functional polymer, and R44, the Si-H functional polymer, were not performing as they had in previous experiments. It was observed that the cure response, evaluated by solvent resistance, had decreased dramatically. This potentially could be attributed to the instability within each batch due to the residual catalyst. When newer batches of the materials were evaluated, the majority showed cure response. An experiment was designed to determine if the performance differences were due to batch to batch variation.

The batches of materials were numbered by the date synthesized; the lower the batch number, the older the batch. Each coating was drawn-down with 30 ppm of platinum catalyst. The systems were compared based on dry time, pot life, and cure response. The newer batches showed better crosslinking by having faster dry to touch times and better cure response at 24 hours. Also, the new batches of materials exhibited shorter pot lives than the older batches of material. The older batches had longer pot lives, and showed little to no crosslinking, and sometimes did not dry. This suggested possible catalyst degradation.

The deactivation of the catalyst can be critical to the processing of the paint formulations, their deposition operations and the subsequent performance of the coatings. Thus, either the catalyst stability must be improved, or the residual catalyst must be removed from the polymers so when a fresh catalyst is added during the paint formulation blending (just prior to the deposition operation) the curing rates and activity will be consistent.

Consequently, we have performed a series of experiments to assess techniques of either removing the catalyst via its sorbing to materials that Pt can strongly interacting with or by precise poisoning of the Pt catalyst in a way that the poisoning reagent will not attack also the freshly added Pt catalyst during the coating operation.

The following sorbing materials have been selected and tested for their capability to remove the Pt:

1) Aluminum Oxide, Basic, Powder
2) Silica gel, grade 05, 6-16 mesh
3) Kieselgel 60 GF254
4) Amberlyst 15 ion-exchange resin, strongly acidic, macroreticular resin
5) DOWEX 50WX8-400 ion exchange resin
6) DOWEX 1x8 200-400 mesh Cl –ion exchange
7) Amberlite IRA-400(OH) ion exchange resin, strongly basic gel-type resin
8) Charcoal activated

This set of experiments was not completed by the time it was decided to switch to the Si-OH curing system. Nevertheless we have been able to observe that after treating with Amberlite and Amberlyst the formulations provide extended period of pot-life, as indicated in Table 7.

***Table 7:*** *The effect of catalyst sorbents on pot-life of hydrosilylation formulations*

| Experimental Protocol | | |
|---|---|---|
| 1) Weigh out 0.5 g of each absorbent into a scintillation vial (prepare 2 sets– one set per reagent)<br>2) Dry the absorbents in the vacuum oven at 90°C overnight<br>3) Add 1.5 g of R60 to first set of absorbents<br>4) Add 1.5 g of R32 to second set of absorbents<br>5) Place each vial on rollers to mix overnight<br>6) Centrifuge each vial<br>7) Mix R60/absorbent with R32/absorbent at 1:1 equivalence<br>8) Record gelling time | | |
| **Results** | | |
| ***Sorbent*** | ***Gel time at 50 °C*** | ***at Room Temperature*** |
| Amberlite | < 1.5 hour | gelled overnight |
| Amberlyst | < 1.5 hour | gelled overnight |

**Thermal Analysis of Curing.** Formulations that were down-selected as coating compositions were also evaluated for their thermal characteristics. These characteristics can further shed light on the curability and post curing characteristics for the formulations.

The thermal analyses of formulations were performed three weeks after mixing, being placed at room temperature. The samples (duplicate specimens) were analyzed using a TA Instruments Q200 modulated differential scanning calorimeter (MDSC) with a ramp rate of 5ºC per minute and modulation parameters of 0.796º per 60 seconds. The glass transition temperatures (Tg) were measured on both the total and reversing heat flow curves and cure exotherms on both the total and non-reversing heat flow curves. These results are summarized in Table 8. A few representative scans are shown in Figure 32.

Degree of cure (at the time of measurement) was calculated on the average exotherm energies using the following relationship:

$$\text{Degree or Percent of Cure} = 100 * [(\Delta H_{Total} - \Delta H_{Residual})] / (\Delta H_{Total})$$

Where $\Delta H_{Total}$ = exotherm energy for uncured material and

$\Delta H_{Residual}$ = residual cure exotherm energy for partially cured material

The degree of the crosslinking should affect the Tg of the coating, therefore the amount of added catalyst and curing temperature should also affect the Tg. The effect of the catalyst on the Tg of the coatings is shown in Figure 33. The overall trend shows an increase in Tg values with the amount of the catalyst. The formulations cured at higher temperature are also characterized with higher Tg's evidencing towards a higher degree of crosslinking due to further completion of the hydrosilylation reaction of the multiple Si-H/ene population. Interestingly, the RT cured samples are characterized with ca. 10 degrees lower Tg values compared to the Tg's of the heated samples at a relative similar cure %.

For X36-T, two Tg values were measured at no external catalyst addition, meaning there were two distinct phase transitions. The X36 is much more sensitive to addition of catalyst which is reflected by a steeper slope of Tg vs amount of catalyst curve.

The degree of crosslinking measured for the samples via analysis of cure exotherms of the uncured and cured samples reveals a much higher cure % for X40 compared to X36. For samples with no external additional catalyst, the difference between room temperature-cured samples and samples cured at higher temperature is dramatic. Based on that, it was concluded that additional catalyst is required in order to reach the desired cure % of the formulations at RT.

***Table 8:*** *MDSC results summary for compounds X36 and X40.*

| Sample description | MDSC Results | | |
|---|---|---|---|
| | Tg, onset, ºC (reversing heat flow) | Exotherm energy, J/g (non-reversing heat flow) | Degree of cure, % |
| X36-1 (uncured) | Not Observed* | 354 J/g | |
| X36-4 (uncured) | Not Observed* | 361 J/g | |
| X40-1 (uncured) | Not Observed* | 350 J/g | |
| X40-2 (uncured) | Not Observed* | 332 J/g | |
| X40-3 (uncured) | Not Observed* | 342 J/g | |
| X36-1-R | -45ºC | 272 J/g | 23 |
| X36-1-T | -29ºC & 9.4ºC | 108 J/g | 69 |
| X36-4-R | -26ºC | 177 J/g | 51 |
| X36-4-T | 21ºC | 164 J/g | 55 |
| X40-1-R | Not Observed | 172 J/g | 51 |
| X40-1-T | -34ºC | 36 J/g | 90 |
| X40-2-R | -28ºC | 59 J/g | 82 |
| X40-2-T | -16ºC | 41 J/g | 88 |
| X40-3-R | -31ºC | 64 J/g | 81 |
| X40-3-T | -20ºC | 51 J/g | 85 |

**None observed in the temperature range utilized.*

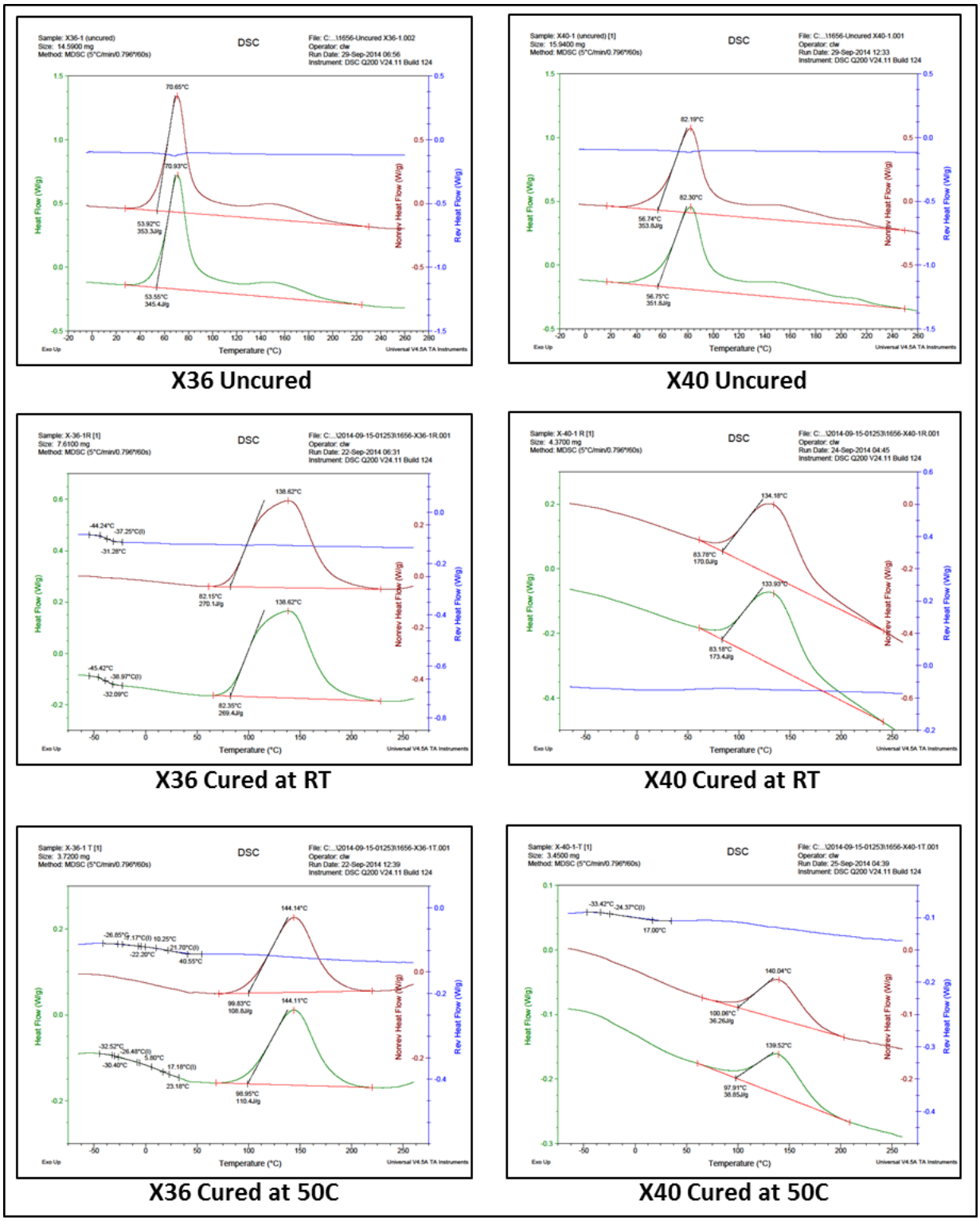



***Figure 32.*** *The DSC profiles of various formulations before and after curing*

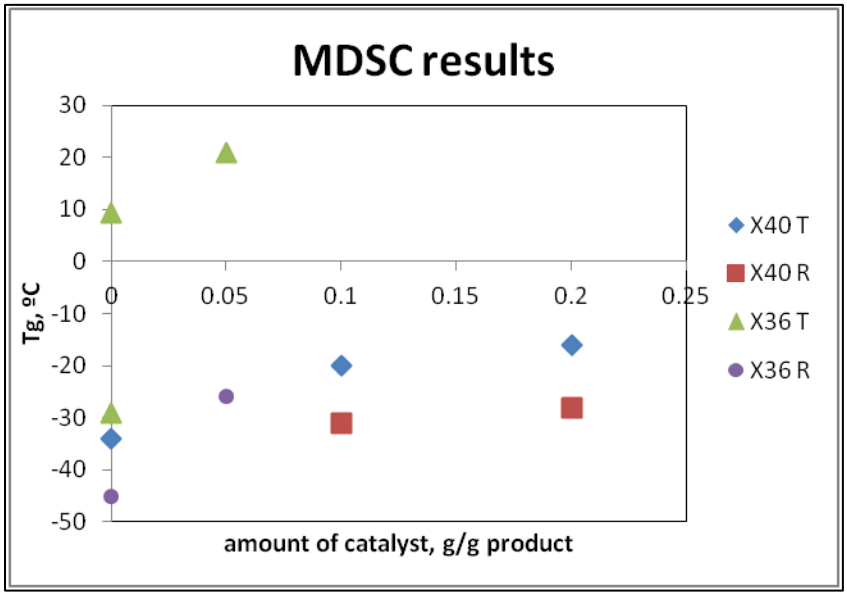



***Figure 33.*** *Change in Tg with the amount of catalyst solution (0.05% solution) added to the formulation.*

**Thermophysical Properties of Improved Formulations.** The analyses reported above were repeated with additional improved formulation at a later stage of the project. The analyzed formulations were X138 and X151, which are the reactions of R32 with R60 and R71, respectively, shown in Figure 34.

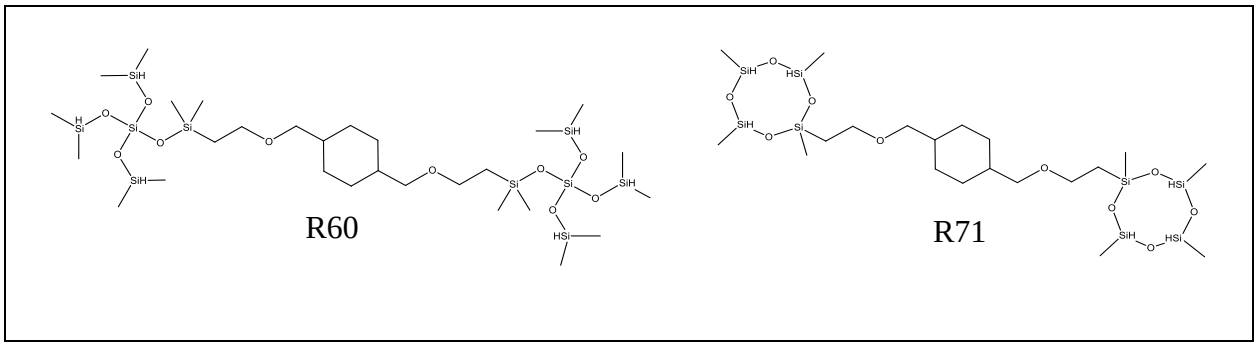



***Figure 34.*** *The molecular structures of R60 and R71.*

The procedures were similar to the ones described for X36 and X40. For comparison, the uncured samples have been mixed and placed into the calorimeter right after mixing to observe the cure exotherm and the peak curing temperature. The results are summarized in Table 9. Corresponding DSC curves are attached to the end of the report with and numbered according to Table 9.

***Table 9:*** *Summary of the DSC results for X151and X138.*

| Sample Description | MDSC Results | | |
|---|---|---|---|
| | Tg, Onset, ºC (reversing heat flow) | Exotherm (non-reversing heat flow) Energy, J/g* | Peak Temp, ºC |
| X-138 (Uncured) | Not Observed | 235 J/g | 57ºC |
| X-138-A (Uncured) | Not Observed | 282 J/g | 77ºC |
| X-151 (Uncured) | Not Observed | 323 J/g | 58ºC |
| X-151-A (Uncured) | Not Observed | 284 J/g | 55ºC |
| X151 | -31ºC** | 65 J/g (80%) | 107ºC |
| X151-T | -31ºC** | 40 J/g (88%) | 133ºC |
| X151-A | -34ºC** | 75 J/g (74%) | 126ºC |
| X151-A-T | -26ºC** | 53 J/g (81%) | 140ºC |
| X138 | -8.3ºC | 93 J/g (60%) | 139ºC |
| X138-T | 5.0ºC | 59 J/g (75%) | 140ºC |

The striking difference is the Tg of the new formulations. The Tg of X151 and X151-A is in the range of -30ºC while for X138 it is much higher (~ 0ºC). As expected, the samples that were cured at 50ºC have a higher degree of cure compared to those cured only at room temperature. Addition of VTMS to X138 (formulation X138-A) shifts the cure exotherm maximum from 57ºC to 77ºC, and leads to an increase of the heat of reaction from 235 J/g to 282 J/g. Effect of VTMS on X151 formulation (X151 vs X151-A that has no VTMS) is not dramatic. Addition of 5% wt of VTMS to X151 formulation increases the reaction exotherm from 284 to 323 J/g by affecting the offset temperature, but increases the peak temperature by only 5 degrees. These results explain why VTMS increases the pot-life of the formulations.

**(B) Hydrosilylation-Dehydrocoupling System**

The curing of this system is based on the condensation reaction of Si-OH into Si-O-Si. Similarly, we can expect reactions between the Si-OH and M-OH groups found at the surface of metallic substrates. This is particularly correct for Iron and Al based materials. The condensation reaction can be advanced thermally by heating the relevant materials to >100C or by various catalytic approaches including bases, acids, and organometallic compounds.

Overall, the condensation reactions of various Si-OH have been extensively studies in the field of sol gel, polysiloxanes, and alkoxysilane based surface modifiers and coupling agents. The generic reactivity trend is that the less steric hindrance or the higher number of Si-OH groups on the same silicon the higher the condensation rates. Hence, it is very difficult to maintain the stability of alkoxysilanes that possess 3 or 4 alkoxy groups after their hydrolysis into $–Si(OH)_{3or4}$ even in dilute solution. In contrast, polysiloxanes with the terminal sites of $-(CH_3)_2Si-OH$ are stable as neat liquids even in the case of low molecular weights (i.e., high Si-OH concentration). Such systems require both catalyst and thermal condition for achieving high condensation rates.

Base catalysts are most effective for the condensation reactions due to the $S_N2$ reaction mechanism of the condensation, while acid catalysts are much more effective in the case of hydrolysis of alkoxy-silanes (Si-OR) into the Si-OH but less effective in the condensation steps.

SRI has already developed polymers that consist of high concentration of Si-OH bonds but can be stable for long periods in relatively concentrated solutions (<35wt% in alcohol/water solutions). In particular, it is the situation for PHMS-OH in which more than 60% of the silicon atoms possess Si-OH group. The remaining Si atoms are "crosslinked" with Si-O-Si groups, but this situation does not lead to gelation, if the polymer is kept in solution under neutral conditions. Yet, it is crosslinked and gelled in the absence of solvent and the presence of a base catalyst (in the form of coatings). Such coatings can demonstrate significant hardness even after 1 hour at room temperature. The hardness and the adhesion are further improved during the first week of deposition.

In the modified system we attempted to use the knowledge gained with the PHMS-OH system and combine it with the synthesis effort performed in this project based on hydrosilylation reactions.

Table 10 compares the curability of the synthesized intermediates. For this evaluation we have used a single curing catalyst, pentamethyldiethylenetriamine (PMDTA), shown in Figure 35 as an effective catalyst for condensation, based on previous experience with the PHMS-OH system. The past experience indicates that 1 to 2 wt% of the amine relative to the solid intermediate amount, is sufficient for achieving full curing and relatively fast dry time. This catalyst was a replacement for Desmorapid PV, a catalyst sold by Bayer for commercial polyurethane curing and was discontinued about 10 years ago.

***Table 10:*** *Curability of Si-OH intermediates in the presence of PMDTA catalyst*

| Component A | Component B | A:B | % catalyst | Coating thickness | Hardness | Adhesion |
|---|---|---|---|---|---|---|
| **R60-OH** | PHMS-OH | 1:0 | 1 | 6 MIL | NC* | NC |
| | | 1:1 | 1 | 6 MIL | NC | NC |
| | | 1:3 | 1 | 6 MIL | <H | 4B |
| **R71-OH** | PHMS-OH | 1:0 | 1 | 6 MIL | 5H | 5B |
| | | 1:1 | 1 | 6 MIL | 5H | 5B |
| | | 1:3 | 1 | 6 MIL | 4H | 5B |
| **Butoxy R71-OH** | PHMS-OH | 1:0 | 1 | 6 MIL | 4H | 5B |
| | | 1:1 | 1 | 6 MIL | 4-5H | 5B |
| | | 1:3 | 1 | 6 MIL | 4H | 5B |
| **R74-OH** | PHMS-OH | 1:0 | 1 | 6 MIL | NC | NC |
| | | 1:1 | 1 | 6 MIL | NC | NC |
| | | 1:3 | 1 | 6 MIL | <H | 4B |
| **R83-OH** | PHMS-OH | 1:1 | 1 | 6 MIL | NC | NC |

Experimental Condition: 50°C for 4 hours; Room temperature study for R71-OH (24 hour) showed similar results (4H/5B for all three ratios);

* NC = not cured

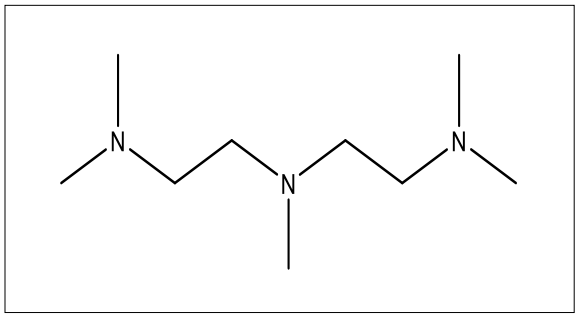


***Figure 35.*** *The structure of the PMDTA catalyst*

The relative reactivity of the Si-OH reagents synthesized thus far is as follows:

Linear [-MeSi(OH)-] > Cyclic [-MeSi(OH)-] > terminal [-Si(OH)$_3$ > terminal [-Me$_2$Si-OH]

The linear structure may be more reactive due to either the higher concentration of the Si-OH in the resin composition (considering that the cyclic compound is attached to a higher organic content. Compared with literature reports, R71-OH is more effective than –Si(OH)$_3$ in some research and commercial products, most likely because of steric hindrance and being hidden in the organic surrounding. This is also the proposed reason for the sluggish curing of R83-OH vs R71-OH, although both have the same cyclomeric reactive unit.

Other well-known condensation catalysts have been assessed for curing R71-OH. A list and results are reported in Table 11, including organo tin and titanium compounds. None of the additional catalysts worked as good as PMDTA. However, there are many other reported amine catalysts that were not assessed yet, and can be excellent candidates for the same reaction. It is recommended to assess such catalysts in the future.

R71-OH can be also cured efficiently or even better, when mixed with PHMS-OH. As discussed later, we have looked at various mixtures of PHMS-OH/R71-OH in order to identify a sweet spot between a very hard coating but brittle (PHMS-OH) vs one that is softer but can be stretched during mandrel bending tests. We did not evaluate systems in which P71-OH is the efficient crosslinkable component and other intermediates possessing less Si-OH groups per molecule are added. These combinations can further increase the flexibility of the derived coatings. It is highly recommended to assess such formulations in future activities. More information about formulations consisting of R71-OH with additional components including PHMS-OH are discussed in Tasks 3 and 4.

***Table 11:*** *Results of curing R71-OH with various condensation catalysts*

| Sample Name | | | 006A | 006B | 006C | 006D | 006E | 006F |
|---|---|---|---|---|---|---|---|---|
| **Description** | | | Batch 1 | Batch 1 | Batch 1 | Batch 1 | Batch 1 | Batch 1 |
| **Catalyst** | | | Penta methyl diethylene triamine | Dibutyltin Diacetate | Dibutyltin Dilaurate | Tyzor Tetra-n-butyl titanate | Tetrakis (2-ethylhexyl) | Triethanol amine |
| **Catalyst level based on RS** | | | 2% | 2% | 2% | 2% | 2% | 2% |
| **Dry to touch** | | | 25 minutes | 35 minutes | 20 minutes | 30 minutes | 25 minutes | 20 minutes |
| **Potlife** | | | Overnight | Overnight | Overnight | Overnight | > 24 hours | > 24 hours |
| **Dry Film Thickness (DFT) (mils) Topcoat** | | | | | | | | |
| **Solvent Resistance** | No breakage of coating | 24 hours | F 65 | F 14 | F 2, Swell | F 2 | F 5 | F 2 |
| | | 7 days | P | F 12 | F 10, S | F 5 | F 2 | F 2 |
| | | 30 days | | | | | | |
| **Konig Hardness (seconds)** | --- | 24 hours | 15 | --- | --- | --- | --- | --- |
| | | 7 days | 158 | --- | --- | --- | --- | --- |
| **Fischer Micro Indenter ($N/mm^2$)** | --- | 24 hours | 84.1 | --- | --- | --- | --- | --- |
| | | 7 days | 92.7 | --- | --- | --- | --- | --- |
| **Sample Name** | | | **005A** | **005B** | **005C** | **005D** | **005E** | **005F** |
| **Description** | | | Batch 2 | Batch 2 | Batch 2 | Batch 2 | Batch 2 | Batch 2 |
| **Catalyst** | | | Penta methyl diethylene triamine | Dibutyltin Diacetate | Dibutyltin Dilaurate | Tyzor Tetra-n-butyl titanate | Tetrakis (2-ethylhexyl) | Triethanol amine |
| **Catalyst level based on RS** | | | 1% | 1% | 1% | 1% | 1% | 1% |
| **Dry to touch** | | | 20 minutes | 20 minutes | 15 minutes | 15 minutes | 20 minutes | 20 minutes |

| Sample Name | | | 006A | 006B | 006C | 006D | 006E | 006F |
|---|---|---|---|---|---|---|---|---|
| **Pot life** | | | Overnight | Overnight | Overnight | >24 hours | >24 hours | > 24 hours |
| **DFT(mils) Topcoat** | | | 1.03 | | | | | |
| **Property** | **Spec** | **Duration** | | | | | | |
| **Solvent Resistance** | No breakage of coating | 24 hours | F 45 S | F 5 | F 5 | F 2 | F 2 | F 10 |
| | | 7 days | P | F 5 | F 3 | F 5 | F 10 | F 2 |
| | | 30 days | P | F 4 | F 2 | F 2 | F 10 | F 2 |
| **Konig Hardness (seconds)** | --- | 24 hours | 117 | --- | --- | --- | --- | --- |
| | | 7 days | 156 | --- | --- | --- | --- | --- |
| | | 30 days | 185 | --- | --- | --- | --- | --- |
| **Fischer Micro Indenter ($N/mm^2$)** | --- | 24 hours | 90.9 | --- | --- | --- | --- | --- |
| | | 7 days | 95.2 | --- | --- | --- | --- | --- |
| | | 30 days | 102.45 | --- | --- | --- | --- | --- |
| **Pencil Hardness** | | 24 hours | 3H | --- | --- | --- | --- | --- |
| | | 7 days | 5H | --- | --- | --- | --- | --- |
| | | 30 days | 4H | --- | --- | --- | --- | --- |

## TASK 3. TOPCOAT FORMULATIONS & SCREENING

### Overall Analysis and Observations

This task had the following purposes:

a) Performing rapid screening and feedback to Task 1 for further synthesis of intermediates in an iterative process.
b) Assessing curability (partial replacement of Task 2) in actual coating environment.
c) Assessing pot life of formulations.
d) Selecting preferred intermediates based on basic coating characteristics
   i) Hardness (as a function of full curing),
   ii) Solvent (MEK) resistance (also a measure of curing), and
   iii) Adhesion to substrate.
e) Providing insights for further work in Tasks 4 and 5, based on the results of purpose (d) above.

This task started soon after the initial hydrosilylation intermediates were evaluated for their reactivity and found to be adequate for curability at room temperature. The task then progressed with improved and down-selected intermediates, and more additives, such as fillers and pot-life extenders, were added to the formulations. It was then repeated for the down-selected Si-OH intermediates once we realized the need to move away from curing by hydrosilylation. The studies performed with the two different curing approaches are discussed separately below.

### (A) Formulations Based on Hydrosilylation Curing

Hundreds of formulations were screened since the chemical behavior of this system was entirely unknown. The screening formulations consisted of the following elements:

1) Various Si-H and vinyl intermediate combinations (“Part A” and “Part B”)
2) Various ratios of mol equivalents of Si-H:vinyl (beyond 1:1 mol ratio)
3) Formulations where Part A or Part B consisted of more than 1 intermediate (minor effort)
4) Different levels of catalyst
5) Addition of solvent as necessary for viscosity and derived deposition control
6) Addition of solvents and additives to increase pot life
7) Addition of coupling agents to improve adhesion to substrates

A summary of the formulations and critical observations associated with these formulations are tabularized in Appendix A.2, which highlights the best-performing formulations.

Once we selected intermediates for further formulation-performance studies, we performed additional screening of tens of formulations for testing in Task 4. The screening activities in this task were performed at SRI while PPG focused on formulations with the down-selected intermediates.

#### *Coating Deposition and Evaluation Procedures*

The coatings tested at SRI were deposited on a typical aircraft aluminum alloy (2024) that had a standard chromate surface treatment. Clear formulations were deposited by simple blading techniques with an approximate thickness of 75 microns (3 mils). Coatings that are cured at RT were checked in intervals of 1 to 4 weeks. The dry-to-touch time was checked in intervals of 1h. If RT curing was not achieved within 4h, most cases they were not curable over a longer period, either (>24h). Coatings cured at 50°C were put in a pre-heated oven after 1 hour and kept in the oven for periods of 1 to 4h.

The cured coatings were screened by pencil hardness and adhesion tests. The pencil hardness test was performed according to the ASTM D3363-74 "Pencil Test" protocol, which consists of a scale of 17 stages of pencil tip hardness from 6B to 9H, with 9H having the highest hardness on the scale and 6B the softest. The adhesion tests were performed using the ASTM D3359-02 "Adhesion Tape Test" protocol in which a grid of 10x10 deep scratches are made 1 mm apart, and then a standard adhesion tape is applied with pressure contact over the scratched area and pulled quickly away at a 45˚ angle. The level of removal of the 1x1 mm “pixels” is scored by a scale of 6 stages from 0B to 5B, where 5B is the best (indicating no pill-off of pixels), while 0B means that the entire scratched area is removed and remained glued to the pilled adhesive tape.

The curing degree and hardness/adhesion tests provided adequate indication for further iterations with variable adjustments according to the guideline set above. While some of the formulations remained uncured even when additional fresh catalyst was added, others were soft (elastomeric in their nature), and a few exhibited significant hardness. The experimental table in Appendix A.2 and reported experiments from PPG’s and Boeing’s studies indicate that certain formulations achieved combinations of hardness >4H and adhesion 4B-5B (max) when cured at 50°C. Some can also be cured to the same mechanical values at room temperature. The pot life of the formulation showed an opposite pattern, i.e., the more effective the curability, the shorter the pot life.

The screening tests led to the initial selection of three intermediates, one with multiple vinyl (R32) and two with multiple Si-H groups (R21 and R44), for scale-up. The structures of these intermediates are illustrated in Figure 36. These intermediates were sent to PPG and Boeing for self-evaluation and feedback. After the second iteration of intermediate synthesis, we selected two additional Si-H intermediates (R60 and R71 also shown in Figure 36) for scale-up and submission to PPG and Boeing. These intermediates exhibit higher viscosities than the R21 and R44 formulations. The intermediates R32, R60, and R71 were scaled up to 500g per batch.

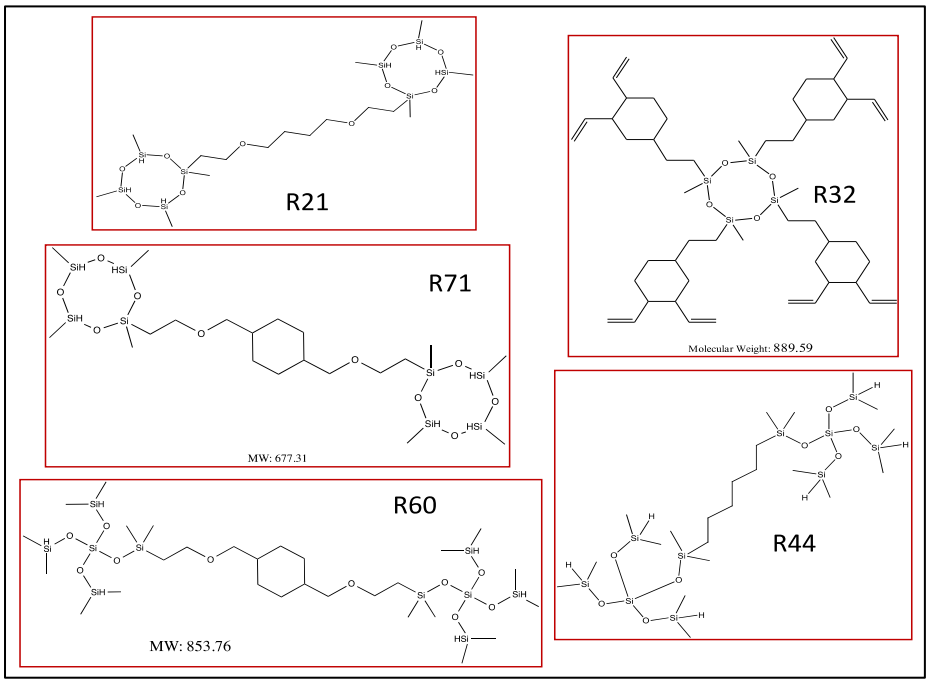



***Figure 36.*** *Intermediates selected for scale-up and evaluation at PPG and Boeing.*

We also considered extended evaluation for a third iteration of intermediates. The candidates for this iteration are illustrated in Figure 37; however, we did not proceed with this iteration due to the decision to switch to the Si-OH curing system.

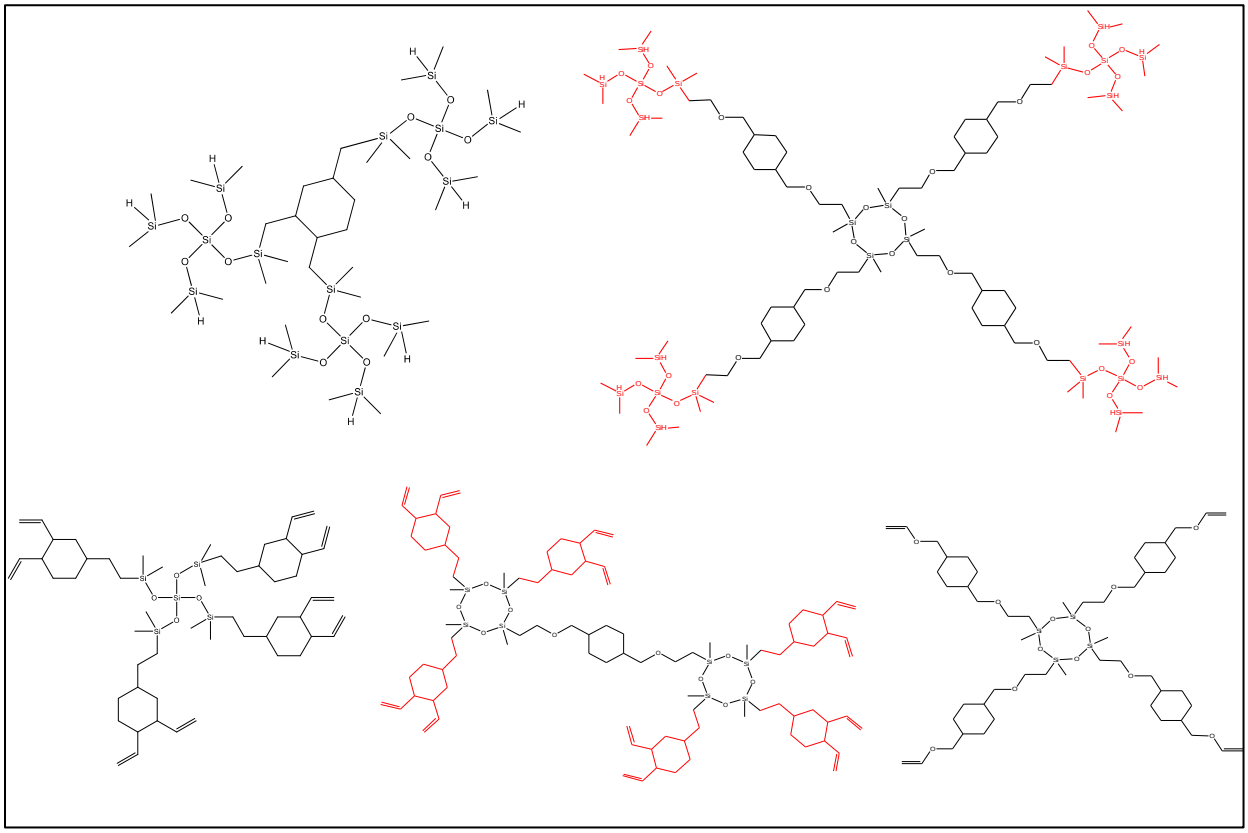


***Figure 37.*** *Other intermediate candidates currently considered for further evaluation.*

### *Additives – Formulations with Adhesion Promoters*

While the adhesion of the best formulations over a chromated-aluminum alloy were found to be adequate (in the range of 4B-5B), other formulations did not provide good adhesion. A typical approach to enhance adhesion is to deposit an adhesion promoter at the surface or to add one to the paint formulation. Many "coupling agents" are currently used by the paint industry; of them, many are based on aloxysilane compounds that have organic functional groups that can promote physical adhesion or chemical bonding to the coating's resins. The alkoxy groups of these compounds can then be hydrolyzed and adhered to the substrate, while the organic groups interact with the resin. Conventional coupling agents are ethoxy, methoxy, and acetoxy silanes that have glycidyl (epoxy) and aminoalkyl groups.

To improve the adhesion of coating formulations, we investigated a series of α-alkenyl-alkoxysilanes (alkenyl = vinyl, allyl, hexenyl; alkoxy = methoxy, ethoxy, acetoxy). These reagents chemically bond to the coating resin network via hydrosilylation, and then also bond to the substrates via hydrolysis of the alkoxy group with moisture, which is followed by bonding of the hydrolyzed Si-OH with the surface. Figure 38 represents the various coupling agents that were assessed.

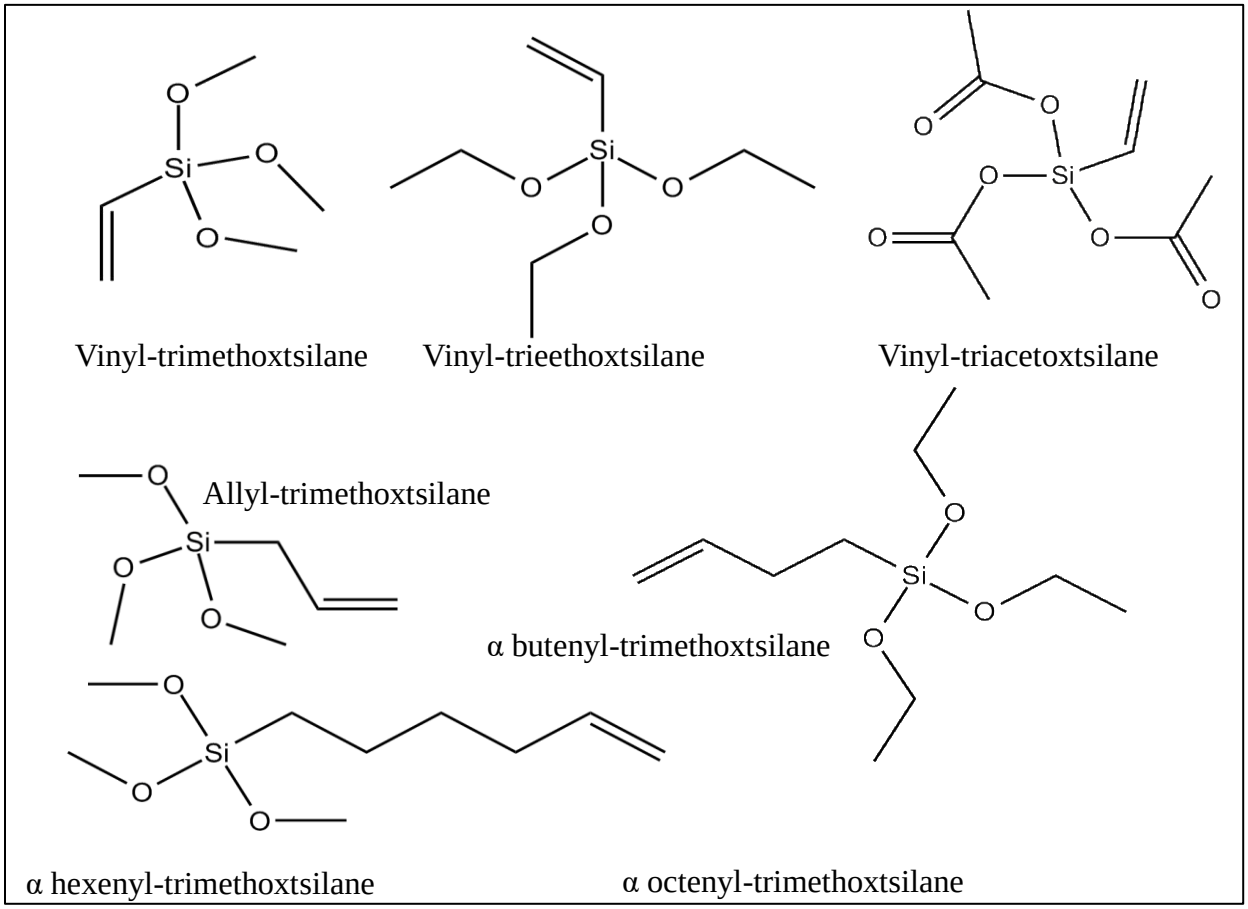



***Figure 38.*** *Various coupling agents that were assessed in formulations for coatings over metals and primers.*

By adding 5 wt% of such coupling agents, we observed improved adhesion by 1-2B, leading to a few formulations with 4B and 5B (maximum bonding). The addition of coupling agents seems to be most effective for RT curing. This work is still in progress. Thus far, there is no "universal" reagent that can be selected as "the best" and the effectiveness ranking is varied between different formulations. However, we currently use vinyltriethoxysilane as our main coupling agent.

A very intriguing observation is that while the presence of such coupling agents may increase the pot life of the formulation itself, it does not affect the overall curing much. The pot life extension can be explained by chelation of the reagent around the Pt atom. The alkene group orf the coupling agent can form a binding ligand with Pt and deactivate the catalytic activity. This observation requires further evaluation, but, if proven, it would provide an elegant solution for the contradictory effect of the Pt catalyst on pot-life duration versus adequate curing of the coatings.

### *Coatings over Primers*

After establishing good adhesion characteristics to chromated aluminum alloys, we have assessed the capability for depositing coatings over commonly used, aerospace-grade epoxy primer. PPG's CA 7502 product has been selected as the initial standard epoxy primer to be

tested as the base coat for the evolved topcoat formulations by all the participating labs (SRI, PPG, and Boeing). This effort immediately encountered a significant problem: the topcoat formulations no longer cured at all or cured into a softer coating with lack of adhesion to the primer. These observations were found for both RT and 50°C curing procedures. Our tentative conclusion was that the current Pt catalyst is poisoned by the composition of the primer. Thus, either (a) the catalyst is removed from the coating area by strong bonding to functional groups at the primer surface; (b) the catalyst reacts with traces of compounds leaching from the Primer; or (c) the catalyst is decomposed by either (a) or (b) options.

We identified this problem as the most critical issue against curing based on platinum-catalyzed hydrosilylation, and we shifted all the project attention to further defining the problem and solutions thereof. Activities for solving the problems were assessed at both SRI and PPG laboratories. We have assessed the following options:

1) Increasing the level of the current catalyst
2) Replacing the catalyst with one that is more tolerant to the reactivity with the primer
3) Adding more coupling agent to the formulation
4) Treating the primer thermally
5) Deactivating the surface of the primer by forming a passivating layer or a layer that interacts with poisoning groups at the surface

We have noticed that curing was achievable once the amount of fresh catalyst added to the formulation reached threefold that of the original catalyst level; however, this approach did not improve the poor adhesion to the surface, in-spite of achieving hardness of >4H.

Curing and improved adhesion were achieved when the surface was first coated with a neat or 10 wt% vinyltriacetylsilane solution followed by the deposition of formulations with the excessive level of catalyst. In this case, coatings cured at 50°C achieved hardness values >4H and adhesion of up to 3B.

The PPG team tried a similar surface pretreatment of the epoxy primer by depositing a conventional coupling agent, which is practiced with other paint systems over epoxy primers. This coupling agent is an epoxy-trialkoxysilane that can react with amino sites at the surface of the primer. This approach did not provide cured coatings. Similarly, baking of the primer prior to deposition of formulations was also unsuccessful.

### *Additional Formulations Analysis at PPG*

The objectives of formulation experiments at PPG had two main purposes. The first was to assess the cure response and structure-property relationships of the SRI-synthesized polymers to determine the feasibility of this chemistry as a replacement for isocyanate crosslinked urethanes. The evaluation included stability of the raw materials, compatibility with other coating layers, application (including dry and pot life), and physical properties.

The second objective was to develop and test a fully formulated topcoat based on the chemistry provided by SRI. This work included the selection of pigmentation, including both coloring and flatting, and of additives for improvement of other properties as needed. Such additives typically include surfactants, grind aids, flow and leveling additives, UV absorbers, adhesion promoters, and the like.

A considerable effort was performed on selected couples of Si-H and vinyl functional intermediates that were provided by SRI. Much of the experimentation aimed at verification of the results from preliminary testing completed by SRI. The work included crosslinking of multi-vinyl functional polymers with both cyclic and tetrakis Si-H polymers in the presence of platinum catalyst. Variations of formulations included higher and lower molecular weights of the selected intermediates, additional functionality, and varied catalyst levels.

The completed experiments clearly showed the ability to crosslink vinyl functional polymers with platinum catalyst, both at room temperature and at nominal bakes (60°C; 140°F). Many of the cured films exhibited good hardness, and some had excellent resistance to solvent. Polymers of higher molecular weight produced by SRI exhibited higher viscosity, often providing improved application and better substrate wetting.

There were issues that evolved during this set of experiments. In particular, it was noted that the cyclic Si-H polymers gave poorer cure response than the tetrakis-based Si-H polymers. It was noted that, in general, systems cured significantly faster in the bulk than they did in the form of coatings, and this issue was exacerbated as the volume of reactants increased. Another issue that arose was the apparent instability of the platinum catalyst that is inherent in the polymers from their synthesis. This creates a variable total catalyst level that causes inconsistent rates of crosslinking in the coatings.

The coating formulations were prepared based on stoichiometry and total platinum catalyst concentration. The stoichiometry and catalyst level for each experiment is noted in the data tables. “Total platinum concentration” includes the residual platinum reported to be in each of the intermediates from their synthesis plus the catalyst added.

**Procedures:** Procedures for making experimental samples and evaluating them are listed below. Other tests are described in the appropriate sections.

*Making Paint:* Between 7-15 grams of paint were made for each reaction.

1) Weighed out desired amount of part B (ene) into a scintillation vial
2) Slowly added drops of catalyst solution into the vial with part B
3) Stirred with wooden stick after catalyst had been added
4) Weighed out part A (Si-H), added it to the scintillation vial, and stirred

*Application:* The drawdowns were done with a 5-mil square drawn-down bar over unpolished 4 x 12 cold rolled steel with a zinc phosphate and zirconium pretreatment.

1) After each paint was prepared, the draw-down bar was placed on top of the substrate (5-mil section coming into contact with substrate)
2) Two transfer pipettes full of paint were placed inside of the square draw-down bar
3) Once paint was on the substrate inside the square, the bar was pulled to the end of the substrate

*Gel Time:* Each paint was mixed in a scintillation vial.

1) After each paint was drawn-down, the remaining paint in the scintillation vial was checked every 5 minutes
2) Observations were made and recorded at each time interval
3) This was done until the paint in the vial had gelled, and the time it gelled was recorded

*Dry-to-Touch Time:* The draw down panel was evaluated every 30 minutes.

1) After paint was drawn-down, the thin film was checked every 30 minutes for dryness
2) Using a Q-tip, the panel was checked for tackiness and dryness
3) Observations were recorded at each time interval until the Q-tip no longer stuck to the coating

*Solvent Resistance:* STM-0591

1) A Kimberly Clark Professional Wypall X80 towel was saturated with MEK
2) A soaked towel was rubbed on the panel with hard pressure for 100 double rubs (down and up is 1 double rub, so down and up 100 times)
3) Passing is 100 double rubs without coating breakage to the substrate

*Cross-Hatch Adhesion:* ASTM-D3359

1) A tempered steel cutting ruler graduated in 0.5 mm increments for individual cuts was placed on the designated area of the substrate
2) A sharp cutting tool was used to cut through the substrate in between the small openings of the steel lattice template
3) Once cuts had been made, the ruler was moved and placed on top of the newly cut lines, but going the opposite direction to make a lattice
4) After the lattice structure was cut through the coating to the substrate, a piece of 25-mm wide semitransparent, pressure-sensitive tape was placed on top of the lattice with about 2 inches of free tape left hanging off the panel
5) A tongue depressor was rubbed over the tape with pressure, ensuring that it was sticking to the lattice
6) Once tape was secured, it was pulled back in the opposite direction with the free end of the tape (being sure not to pull the tape straight up)
7) If the coating stuck to the tape, the process was repeated until there was no coating sticking to the tape
8) The percentage of the coating left on the panel was recorded (reported in percentages for graphical data purposes)

*Pencil Hardness:* STM-0742

1) A hardness pencil was placed on the thin film at about a 45° angle
2) Pressure was applied to the pencil, and it was pushed upward to draw a straight line
3) If the pencil cut through the substrate, pencil hardness was decreased until the pencil did not cut through to the substrate
4) If the pencil did not cut through to the substrate, then pencil hardness was increased until the pencil cut through
5) The hardest pencil that did not cut through to the substrate was recorded as the hardness measurement

*Micro-Hardness:* ISO 14577-1 and ASTM E 2546

Nanoindentation Testing in the Micrometer Range FISCHERSCOPE® HM2000 S

1) Panel was placed coating-side down on the indenter
2) Three runs were completed
3) Results were averaged

*Koenig Hardness:* ISO 1522, ASTM 4366, DIN 53157, and BS 3900: E8

Koenig & Persoz Hardness Rocker

1) Coated substrate was placed on the stage
2) Rocker was lowered onto the coating
3) Pendulum was pulled back, zeroed, and let go
4) Results were recorded when the electronic counter stopped increasing in oscillations

***Results***

Initial experiments utilized intermediates received from SRI that included R32 vinyl functional polymer and R21 and R44 Si-H polymers.

These intermediates were mixed together at a 1:1 Si-H/ene mol ratio with platinum catalyst added. The level of catalyst is indicated in the data tables below. The reactions of the cyclic Si-H polymer (R21) with the multi-vinyl polymer (R32) and the initial test data is in Table 12.

***Table 12:*** *Reactions of R32 and R21 (Reaction X36)*

| Property Description | X36 | X36 | X36 | X36 | X36 |
|---|---|---|---|---|---|
| **Catalyst added (g)/(ppm)** | 0.0003g/ 20ppm | 0.0001g/ 7.7ppm | 0.00015g/ 10.2ppm | 0.00001g/ 1ppm | 0ppm |
| **Total amount of catalyst (g)/(ppm)** | 0.000446g/ 31ppm | 0.000234g/ 17.1ppm | 0.0003g/ 20ppm | 0.0001564g/ 10.82ppm | 0.0000102g/ 10.2ppm |
| **Drawdown** | Could not draw | smooth | smooth | smooth | smooth |
| **Gel time (in jar)** | < 1 min | 5 min | < 1 min | 3 hr | 3 ½ hr |
| **DTT hard** | - | 4 hr | 3 hr | Not cured | Not cured |
| **24-hr X-hatch adhesion** | Not tested | 99 (Tape did not stick) | 0 | 90% | Not tested |
| **7-day X-hatch adhesion** | Not tested | 100 | 0 | 50 | 90 |
| **24-hr 100 MEK rub** | Not tested | Fail, 20 | Fail, 40 | Fail, 6 | Fail, 2 |
| **7-day 100 MEK rub** | Not tested | Fail, 30 | Fail, 50 | Fail, 30 | Fail, 2 |
| **Koenig hardness (oscillations)** | Not tested | 31 | 28 | 53 | ------ |

The X36 reactions did not cure as expected. This was generally true regardless of the catalyst level. While some of the drawdowns did dry, none of the reactions exhibited solvent resistance.

The reactions of the tetrakis Si-H polymer (R44) with the multi-vinyl polymer (R32) and the test data is reported in Table 13.

***Table 13:*** *Reactions of R32 and R44 (reaction X40)*

| | Formulation | | | | | | |
|---|---|---|---|---|---|---|---|
| **Description** | **X40** | **X40** | **X40** | **X40** | **X40** | **X40** | **X40** |
| **Catalyst added (g)/(ppm)** | 0.0001g/ 6.91ppm | 0.0005g/ 38.61ppm | 0.000935g/ 73.3ppm | 0.0003g/ 23.5ppm | 0 | 0.00004g/ 0.41ppm | 0.0001g/ 6.33ppm |
| **Total amount of Catalyst (g)/(ppm)** | 0.000112g/ 20ppm | 0.000512g/ 51.3ppm | 0.000947g/ 85.5ppm | 0.0003012g/ 35.7ppm | 0.000204g/ 15.3 ppm | 0.000244g/ 18.3ppm | 0.00030g/ 22.8 ppm |
| **Drawdown** | Wet away at edges | Wet away at edges | Wet away at edges | Wet away at edges | Smooth | Smooth | Wet away at edges |
| **Gel time (in jar)** | > 5 min | 5 min | 2 min | 3 ½ hr | 1 hr | 1 hr | 1 hr |
| **DT hard** | 4 hr | 4 hr | 3 hr | 5 hr | 3 ½ hr | 2 ½ hr | 3 hr |
| **24-hr X-hatch adhesion** | 100 (Tape did not stick) | 95 | 0 | ---- | 90% | 0 | 0 |
| **7-day X-hatch adhesion** | 100 | 100 | 99 | 90 | 90 | 0 | 0 |
| **24 hr 100 MEK rub** | Fail, 6 | Fail, 10 | Fail, 10 | Fail, 3 | Fail, 2 | Fail, 50 | Fail, 90 |
| **7-day 100 MEK rub** | Fail, 9 | Fail, 10 | Fail, 20 | Fail, 3 | Fail, 90 | Pass | Pass |
| **Koenig hardness (oscillations)** | 52 | 25 | 58 | 72 | 92 | 68 | 52 |

The X40 reactions generally did better than those utilizing the cyclic Si-H. In particular, hardness was better. The curing degree, as measured by solvent resistance, was marginal after 24 hours but continued to improve over time. Also, the adhesion to bare substrate improved significantly after 7 days.

A significant effect was noted in the rate of curing reaction as a function of the catalyst level. After investigation, it was found that the method for calculating catalyst level was incorrect, and many of the early experiments were over-catalyzed. Another series of experiments was performed to verify the rate of reaction based on catalyst level. This series is described in Table 14.

***Table 14:*** *Effect of catalyst level in X36- and X44-type reactions*

| Property | Formulation | | | | | |
|---|---|---|---|---|---|---|
| **Description** | **X36** | **X36** | **X36** | **X40** | **X40** | **X40** |
| **Catalyst added (g)/(ppm)** | 0.0000264g/ 2 ppm | 0.0000698g/ 4.83ppm | 0.0000987g/ 6.83ppm | 0.0000663g/ 4.98ppm | 0.000133g/ 9.98ppm | 0.0001997g/1 4.98 ppm |
| **Total amount of catalyst (g)/(ppm)** | 0.000173g/ 12ppm | 0.0002166g/ 15ppm | 0.0002455g/ 17ppm | 0.000266g/ 20ppm | 0.0000332g/2 5ppm | 0.000399g/ 30 ppm |
| **DFT (mils)** | 1.3 | 0.61 | 0.6 | 0.63 | 0.6 | 1.5 |
| **Drawdown** | Smooth | Smooth | Smooth | Smooth | Smooth | Smooth |
| **Gel time (in jar)** | 2 hr | 10 min | <1 min | 2 ½ hr | 1 hr | 30 min |
| **DTT hard** | 3 hr | 3 hr | 3 hr | 3 hr | 90 min | 90 min |
| **24-hr X-hatch adhesion** | 0 | 100 | 100 | 1 | 100 | 0 |
| **7-day X-hatch adhesion** | 95 | 100 | 100 | 100 | 100 | 0 |
| **30-day X-hatch adhesion** | 100 | 100 | 100 | 85 | 100 | 0 |
| **24-hr 100 MEK rub** | Fail, 10 | Fail, 3 | Fail, 7 | Fail, 5 | Fail, 20 | Pass |
| **7-day 100 MEK rub** | Fail, 7 | Fail, 10 | Fail, 10 | Fail, 10 | Fail, 6 | Pass |
| **30-day MEK rub** | Fail, 15 | Fail, 20 | Fail, 20 | Fail, 15 | Fail, 30 | Pass |
| **1-wk Koenig hardness (oscillations)** | 73 | 78 | 83 | 69 | 97 | 51 |
| **30-day Fischer hardness ($N/mm^2$)** | 3.17 | 45.30 | 67.67 | 4.53 | 4.90 | 5.57 |
| **30-day Fischer hardness range** | 2.9-3.6 | 25.3-34.2 | 1.5-119 | 3.7-5 | 4.8-5 | 5.2-6 |
| **30-day pencil hardness** | 2B | 4H | 2H | B | 2H | H |

Figure 39 illustrates the effect of selected levels of catalyst on the pot life, curability, and adhesion values of X36 and X40 stoichiometric formulations.

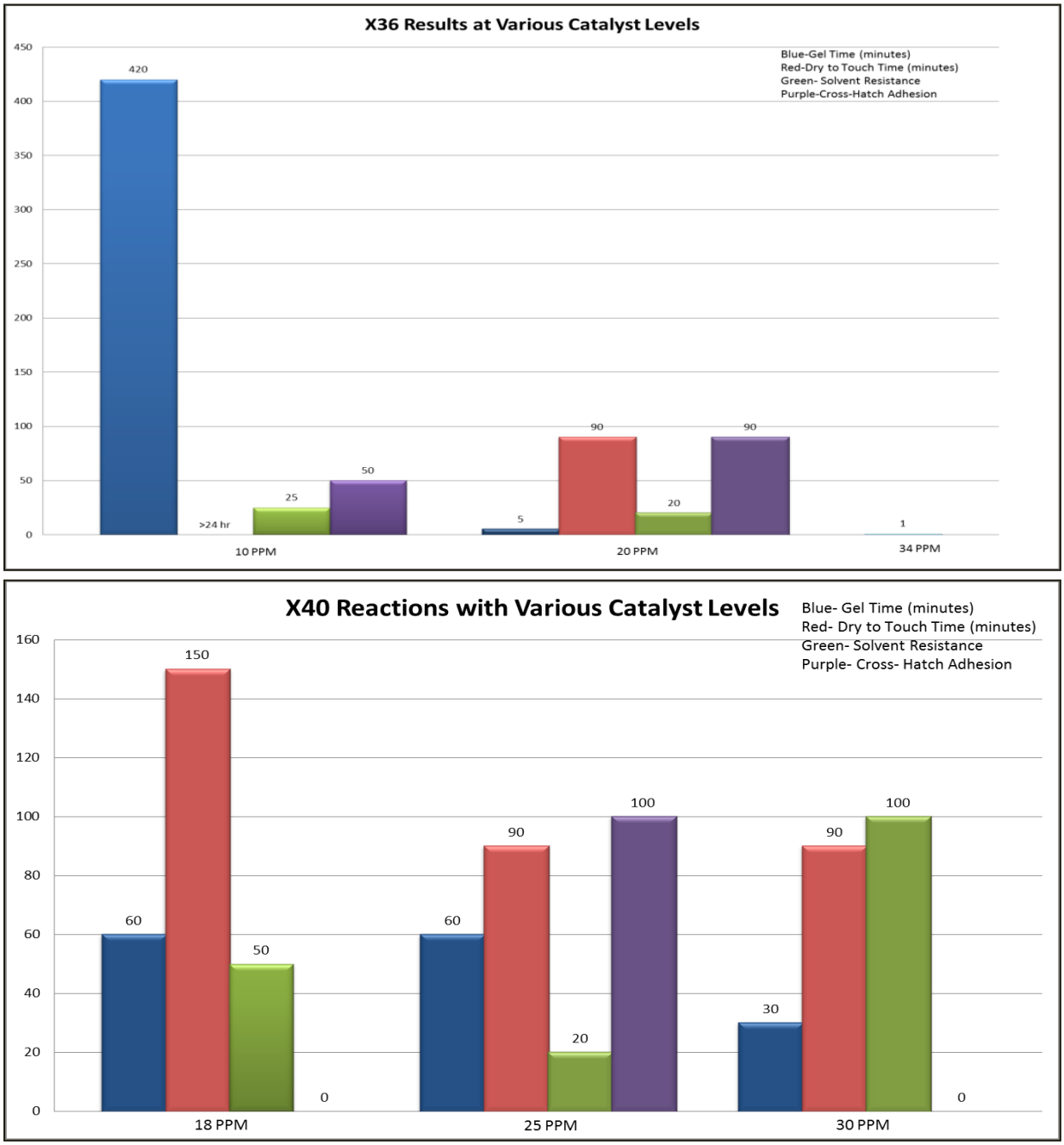



***Figure 39.*** *Curability and adhesion characteristics of X36 and X40 as a function of catalyst content.*

This set of experiments demonstrated again that the X36-type reaction (R32+R21) provided adequate crosslinking. While adhesion was good, it was likely due to poor crosslinking. On the other hand, the X40-type reactions (R32+ R44) showed improved crosslinking with additional catalyst, as indicated by better solvent resistance. The negative-to-higher catalyst level showed a

decrease in adhesion, likely due to internal stresses caused by greater crosslinking. It was interesting to note that an intermediate level of catalyst provided the hardest film in the X40 reactions.

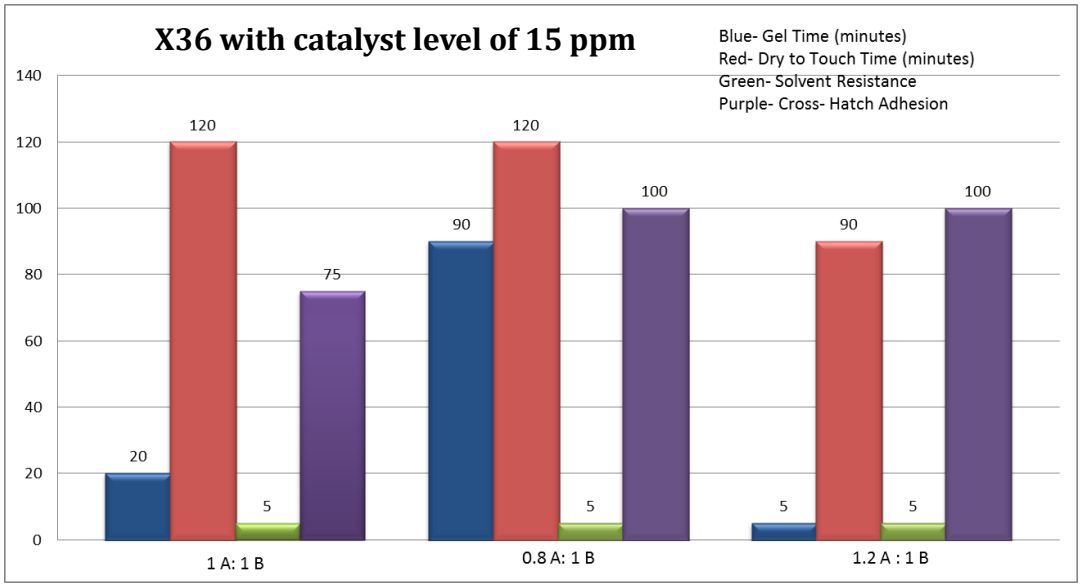
A series of formulations was designed to examine the effect of stoichiometry on the X36 and X40 reactions. The results of this experiment are included in Table 15.

***Table 15:*** *Effect of stoichiometry on Si-H/-ene reactions*

| Property Description | Formulation | | | | | |
|---|---|---|---|---|---|---|
| | X36 1:1 | X36 0.8:1 | X36 1.2:1 | X40 1:1 | X40 0.8:1 | X40 1.2:1 |
| **Catalyst added (g)/(ppm)** | 0.000723g/ 5 ppm | 0.000612g/ 5ppm | 0.000723g/ 5 ppm | 0.0001997g/ 15ppm | 0.0001997g/ 15ppm | 0.0002447g/ 15ppm |
| **Total catalyst (g)/(ppm)** | 0.0002195g/ 15ppm | 0.0001924g/1 5ppm | 0.0002442g/ 15ppm | 0.0003994g/ 30 ppm | 0.0003979g/ 30ppm | 0.0004893g/ 30ppm |
| **Draw-down** | Cratering | Cratering | Cratering | Cratering | Cratering | Cratering |
| **Gel time (in jar)** | 20 min, hard | 90 min, rubbery | 5 min, yellow tint, hard | 10 min, yellow, hard | 20 min, yellow tint, hard | <1 min, yellow, hard |
| **DT hard** | 120 min | 120 min | 90 min | 90 min | 90 min | Not tested |
| **24-hr adhesion** | 75 | 100 | 100 | 0 | 0 | Not tested |
| **7-day adhesion** | 100 | 100 | 100 | 0 | 0 | Not tested |
| **30-day adhesion** | 100 | 100 | 100 | 75 | 50 | Not tested |
| **24-hr 100 MEK rub** | Fail, 5 | Fail, 5 | Fail, 5 | Pass | Fail, 25 | Not tested |
| **7-day 100 MEK rub** | Fail, 5 | Fail, 5 | Fail, 5 | Pass | Pass | Not tested |
| **30-day 100 MEK rub** | Fail, 2 | Fail, 50 | Fail, 20 | Pass | Pass | Not tested |
| **7-day pencil hardness** | 4B | 2H | 4H | HB | 2B | Not tested |
| **7-day Fischer hardness** | 21.00 | 5.80 | 21.63 | 3.67 | 2.45 | Not tested |
| **7-day Koenig (oscillations)** | 52 | 53 | 48 | 38 | 64 | Not tested |
| **30-day Koenig (oscillations)** | 48 | 21 | 32 | 24 | 20 | Not tested |
| **30-day pencil hardness** | HB | HB | HB | HB | HB | Not tested |
| **30-day Fischer hardness** | 10.00 | 7.00 | 4.57 | 50.83 | 3.20 | Not tested |

This series showed poor cure response as determined by solvent resistance for the X36-type reactions. The X40 reactions indicated a preferred stoichiometry of 1:1 (Si-H/ene). At a lower Si-H level, the system did not have early solvent resistance, and the film was much softer. At the higher Si-H level, the system gelled almost instantly, not allowing the coating to be drawn down and tested.

Figure 40 represents results of a few different molar ratios of the intermediates and their effects on various curing and adhesion characteristics.



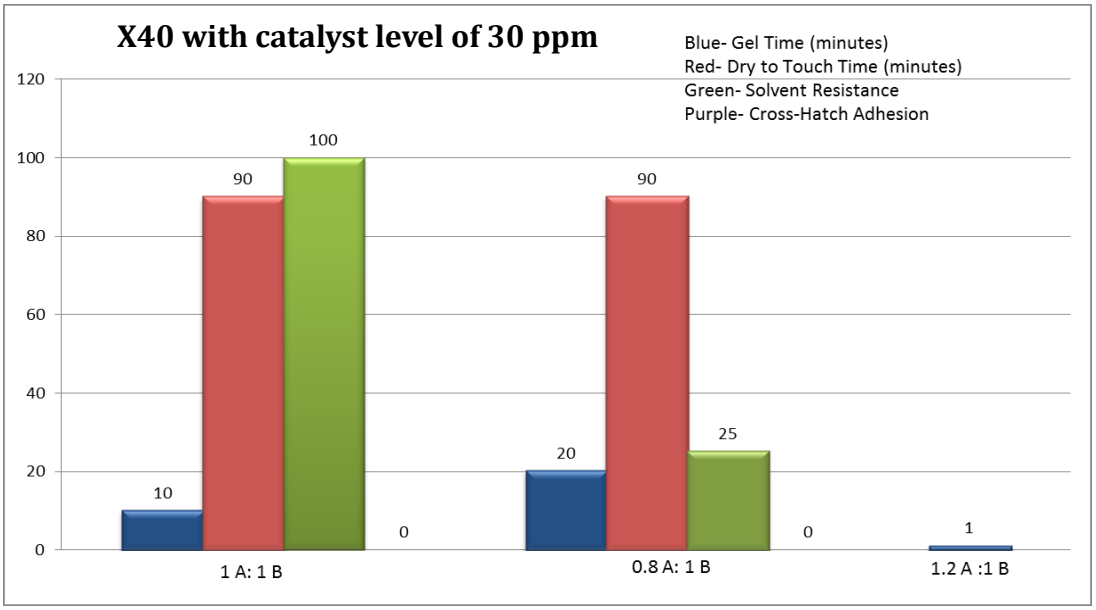




***Figure 40.*** *Curability and adhesion characteristics of X36 and X40 as a function of various molar ratios of the Si-H/Si-vinyl intermediates.*

It should be noted that, even at extremely low levels of catalyst, stoichiometric volumes of the intermediates gelled after relatively short time when placed in a container, even small ones as illustrated in Figure 41. The gelation is accelerated due to the heat generated by the exothermic hydrosilylation reaction.

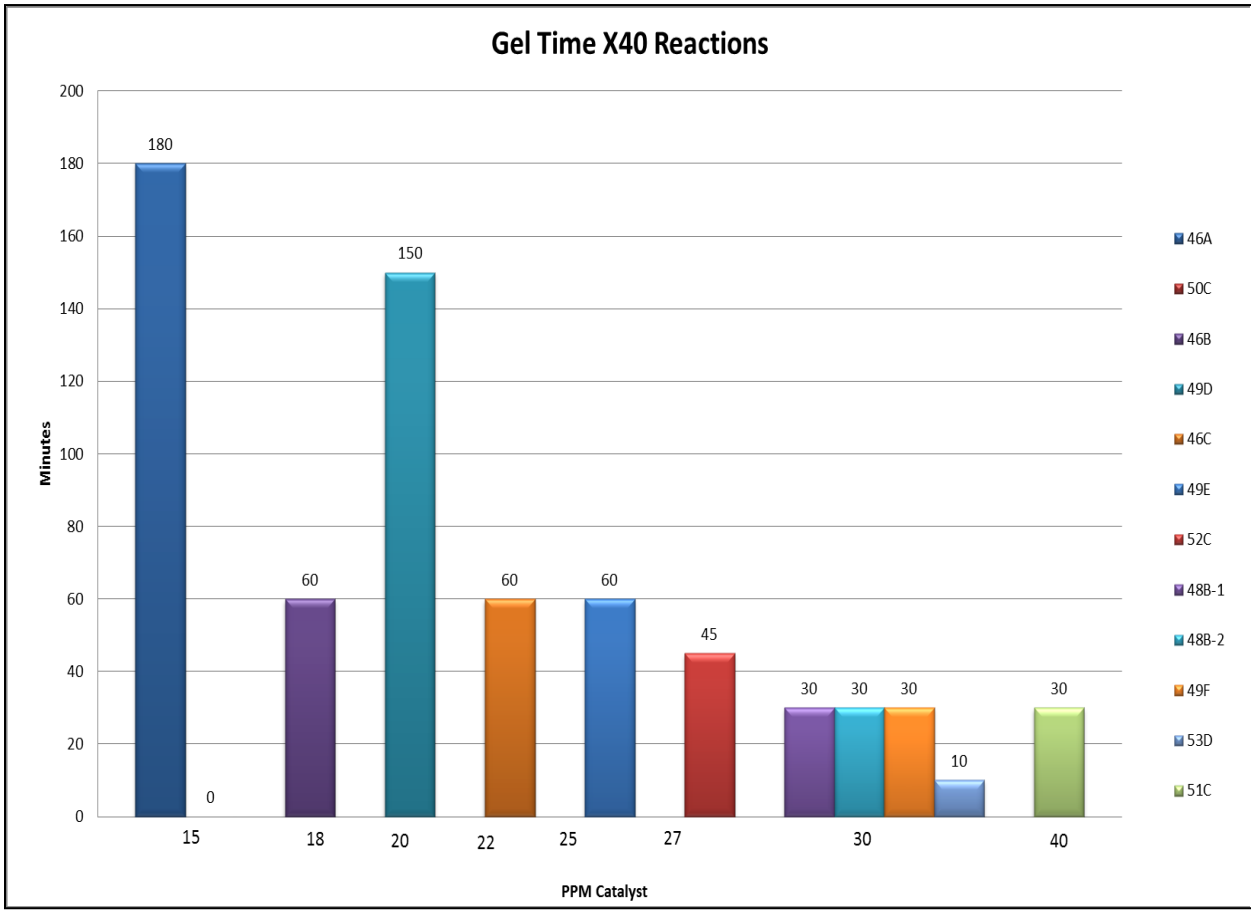



***Figure 41.*** *Rapid gelation time is observed with very small levels of Pt catalyst.*

Table 16 summarizes the gelation and coating curing characteristics of reaction X36 as a function of the level of catalyst. In this series no solvent was added, and, in spite of the very low catalyst levels, gelation was detected with any addition of catalyst at the level of more than 10ppm after a very short time. Also, the coatings in this set were cured only at RT, which was generally much less effective in the hydrosilylation system.

***Table 16:*** *Initial X36 reactions with varied levels of catalyst*

| Sample Name | | | 35A | 35A-2 | 42A | 46D | 45A |
|---|---|---|---|---|---|---|---|
| **Description** | | | X36 | X36 | X36 | X36 | X36 |
| **Catalyst Added (ppm)** | | | 20 | 7.7 | 10.2 | 1 | 0 |
| **Total Catalyst (ppm)** | | | 31 | 17.1 | 20 | 10.82 | 10.2 |
| **Appearance** | | | Not drawn-down | Smooth | Smooth | Smooth | Smooth |
| **Dry-to-Touch** | | | --- | 4 h | 3 h | > 24 h | > 24 h |
| **Pot Life** | | | < 1 min | 5 min | < 1 min | 3 h | 3.5 h |
| **Property** | **Spec** | **Duration** | | | | | |
| **Solvent Resistance** | No Breakage | 24 hours | NT | F 20 | F 40 | F 6 | F 2 |
| | | 7 days | NT | F 30 | F 50 | F 30 | F 2 |
| **Adhesion** | > 4B | 24 hours | NT | 5B | 0B | 4B | NT |
| | | 7 days | NT | 5B | 0B | 2B | 4B |
| **Koenig Hardness** | oscillations | 7 days | NT | 31 | 28 | 53 | --- |

The films with a higher catalyst level were dry within a few hours, indicating a certain degree of curing. However, at the lower catalyst levels, the films did not dry within 24 hours. Gelation occurred within 5 minutes, which also suggested crosslinking to some degree. None of the coatings exhibited solvent resistance at 24 hours or 7 days, indicating little to no crosslinking occurred without heating. Three of the reactions in this experiment had extremely short pot lives of only a few minutes.

Table 17 summarizes a similar set of tests with formulations of X36 and X40, in which the branched Si-H intermediate was used (R44). The branched Si-H functional polymer reactions were generally better than those with the cyclic Si-H intermediate. In particular, hardness was better. The reactions with higher catalyst levels tended to have shorter pot lives, gelling within a few minutes. All of the dry-to-touch times were within 4 hours. Cure, as measured by solvent resistance, was marginal after 24 hours but continued to improve over time even at RT.

***Table 17:*** *X36 and X40 reactions with varied catalyst levels (R44+R32)*

| Sample Name | | | 49A | 49B | 49C | 49D | 49E | 49F |
|---|---|---|---|---|---|---|---|---|
| **Description** | | | X36 | X36 | X36 | X40 | X40 | X40 |
| **Vinyl Polymer** | | | R32 | R32 | R32 | R32 | R32 | R32 |
| **Si-H Polymer** | | | R21 | R21 | R21 | R44 | R44 | R44 |
| **Stoichiometry** | | | 1:1 | 1:1 | 1:1 | 1:1 | 1:1 | 1:1 |
| **Catalyst Added (ppm)** | | | 2 | 5 | 7 | 5 | 10 | 15 |
| **Total Catalyst (ppm)** | | | 12 | 15 | 17 | 20 | 25 | 30 |
| **Appearance** | | | Smooth | Smooth | Smooth | Smooth | Smooth | Smooth |
| **Dry-to-Touch** | | | 3 h | 3 h | 3 h | 3 h | 1.5 h | 1.5 h |
| **Pot Life** | | | 2 h | 10 min. | < 1 min. | 2.5 h | 1 hour | 30 min. |
| **Property** | **Spec** | **Duration** | | | | | | |
| **Solvent Resistance** | No Breakage | 24 hours | F 10 | F 3 | F 7 | F 5 | F 20 | P |
| | | 7 days | F7 | F10 | F 10 | F 10 | F 6 | P |
| | | 30 days | F 15 | F 20 | F 20 | F 15 | F 30 | P |
| **Adhesion** | > 4B | 24 hours | 0B | 5B | 5B | 1B | 5B | 0B |
| | | 7 days | 4B | 5B | 5B | 5B | 5B | 0B |
| | | 30 days | 5B | 5B | 5B | 3B | 5B | 0B |
| **Koenig Hardness** | oscillations | 7 days | 73 | 78 | 83 | 69 | 97 | 51 |
| **Fischer Micro-Hardness** | (N/mm2) | 7 days | 3.17 | 45.3 | 67.67 | 4.53 | 4.9 | 5.57 |

In this experimental set, the catalyst level of the X36 and X40 reactions was varied. Generally, the higher the catalyst level present, the faster gelation occurred. The X36 reaction required much lower catalyst levels compared to the X40 reaction due to the gelation occurring more quickly. As expected, the X36 reaction still did not crosslink, but at the higher catalyst level an improvement in solvent resistance was noted, and hardness also increased, as demonstrated by the Koenig pendulum rocker and the Fischer micro-indenter. At the higher catalyst level, the X40 reaction did cure within 24 hours, as measured by solvent resistance; however, there was a loss in adhesion, likely due to internal stress caused by the increased crosslinking. At higher catalyst levels, the pot lives were shorter, but slightly more cure was achievable, as measured by both solvent resistance and hardness.

Another experimental set was designed for assessing the hydrosilylation reaction at different stoichiometries of the vinyl Si-H functional groups to show differences in cure, dry time, and pot life. The purpose was to optimize the pot life while achieving solvent resistance and hardness at 24 hours. The series is summarized in Table 18.

***Table 18:*** *Effect of stoichiometry on cure of the X36 and X40 reactions*

| Sample Name | | | 53A | 53B | 53C | 53D | 53E | 53F |
|---|---|---|---|---|---|---|---|---|
| **Description** | | | X36 | X36 | X36 | X40 | X40 | X40 |
| **Vinyl Polymer** | | | R32 | R32 | R32 | R32 | R32 | R32 |
| **Si-H Polymer** | | | R21 | R21 | R21 | R44 | R44 | R44 |
| **Stoichiometry** | | | 1:1 | 0.8:1 | 1.2:1 | 1:1 | 0.8:1 | 1.2:1 |
| **Catalyst Added (ppm)** | | | 5 | 5 | 5 | 15 | 15 | 15 |
| **Total Catalyst (ppm)** | | | 15 | 15 | 15 | 30 | 30 | 30 |
| **Appearance** | | | Crater | Crater | Crater | Crater | Crater | Crater |
| **Dry-to-Touch** | | | 2 h | 2 h | 1.5 h | 1.5 h | 1.5 h | NA |
| **Pot life** | | | 20 min. | 1.5 h | 5 min. | 10 min. | 20 min. | <1 min. |
| **Property** | **Spec** | **Duration** | | | | | | |
| **Solvent Resistance** | No Breakage | 24 hours | F 5 | F 5 | F 5 | P | F 25 | --- |
| | | 7 days | F 5 | F 5 | F 5 | P | P | --- |
| | | 30 days | F 2 | F 50 | F 20 | P | P | --- |
| **Adhesion** | > 4B | 24 hours | 3B | 5B | 5B | 0B | 0B | --- |
| | | 7 days | 5B | 5B | 5B | 0B | 0B | --- |
| | | 30 days | 5B | 5B | 5B | 3B | 2B | --- |
| **Koenig Hardness** | oscillations | 7 days | 52 | 53 | 48 | 38 | 64 | --- |
| | | 30 day | 48 | 21 | 32 | 24 | 20 | |
| **Fischer Micro-Hardness** | (N/mm2) | 7 days | 21 | 5.8 | 21.63 | 3.67 | 2.45 | --- |
| | | 30 days | 10 | 7 | 4.57 | 50.83 | 3.2 | |

The X36 reaction was completed with only 15 ppm of catalyst because at higher levels of platinum the pot life was too short, and film application could not be completed. The X36 reactions decreased in pot life and slightly in dry-to-touch time as the level of the vinyl polymer increased. However, solvent resistance at 24 hours was not achieved.

Unlike the X36 reactions, the X40 reaction at 1:1 stoichiometry had solvent resistance at 24 hours. The reaction with a 0.8:1 stoichiometry did not have solvent resistance at 24 hours, but it was cured within 7 days. The 1.2:1 ratio was not able to be drawn-down because the pot life was extremely short. It is clear that at higher levels of the vinyl functional polymer, R32, the dry time and pot life are decreased, and 24h cure is easier to achieve.

Although, the X40 reactions have longer pot lives than X36, the pot lives were still too short. The X40 reactions demonstrated better solvent resistance than the X36 reactions, which did not achieve solvent resistance even after 30 days. However, the cure is inconsistent, and some films

show solvent resistance in 24 hours and some do not. Some of the X40 films showed an increase in hardness over time, while some showed no change throughout 30 days.

### Incorporation of Acrylate Functional Resins Supplied by PPG

Investigation into the potential use of commercially available intermediates was also performed at PPG. These intermediates were designated to replace either the Si-H polymer, the vinyl polymer, or both polymers. Initially, the methacrylate functional urethane polymers used in the UV-curable coating formulations supplied by PPG were tested. The two polymers, XRR, an IPDI (isophorone diisocyanate)-based urethane acrylate, and RR-94, a HDMI (hexamethylene diisocyanate)-based urethane, were crosslinked with the R44 polymer. The formulations were evaluated with varied stoichiometries and catalyst levels. Selected results are summarized in Table 19 and Table 20. Figure 42 and Figure 43 indicate the inadequate appearance of the derived coatings.

***Table 19:*** *Acrylate functional resin, XRR, reacted with R44*

| Property | 55A | 55B | 55C |
|---|---|---|---|
| **Stoichiometry** | 0.8:1 | 1:1 | 1.2:1 |
| **Raw Materials** | XRR + R44 | XRR + R44 | XRR + R44 |
| **Catalyst Added (ppm)** | 26 | 25 | 25 |
| **Total Catalyst (ppm)** | 30 | 26 | 25 |
| **Appearance** | Orange peel, Dewetting | Orange peel, Dewetting | Orange peel, Dewetting |
| **Pot Life** | > 24 hours | > 24 hours | > 24 hours |
| **Dry-to-Touch** | Did not dry | Did not dry | Did not dry |

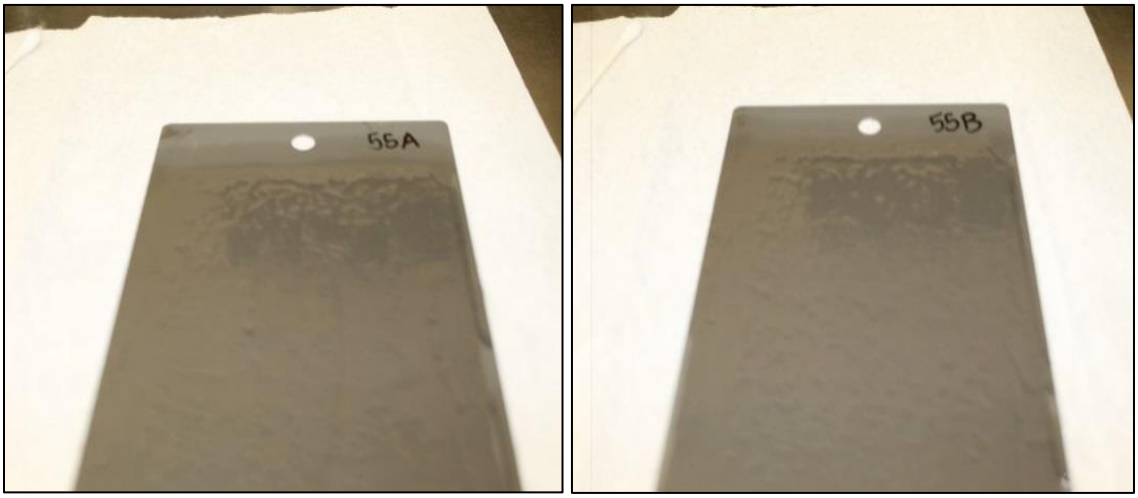



***Figure 42.*** *Appearance of XRR + R44*

***Table 20:*** *Acrylate functional resin, RR-94, reacted with R44*

| 12 | 56A | 56B | 56C |
|---|---|---|---|
| **Stoichiometry** | 0.8:1 | 1:1 | 1.2:1 |
| **Raw Materials** | RR-94 + R44 | RR-94 + R44 | RR-94 + R44 |
| **Catalyst Added (ppm)** | 27 | 27 | 26 |
| **Total Catalyst (ppm)** | 30 | 30 | 30 |
| **Appearance** | Dewetting/wavy | Dewetting/wavy | Dewetting/wavy |
| **Pot Life** | > 24 h | > 24 h | > 24 h |
| **Dry-to-Touch** | Did not dry | Did not dry | Did not dry |

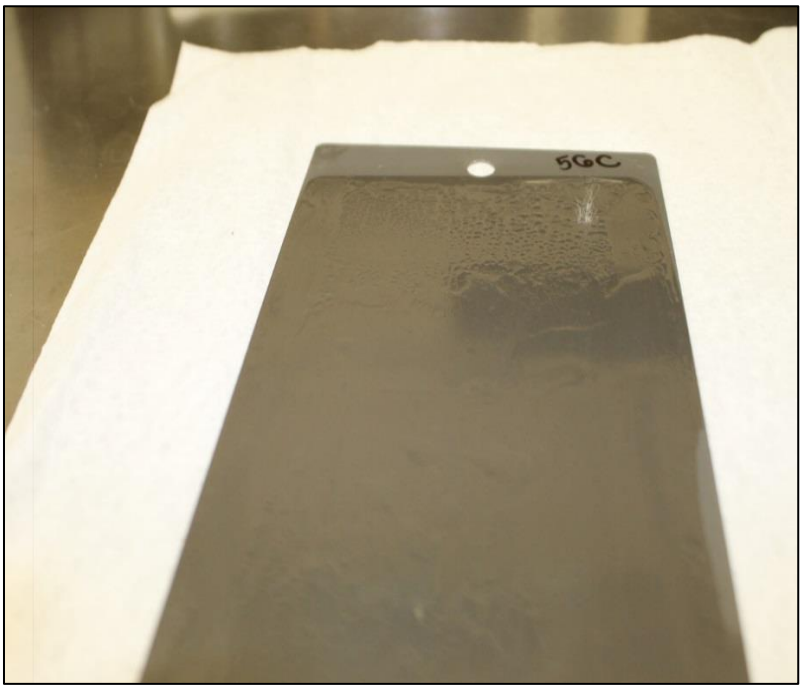


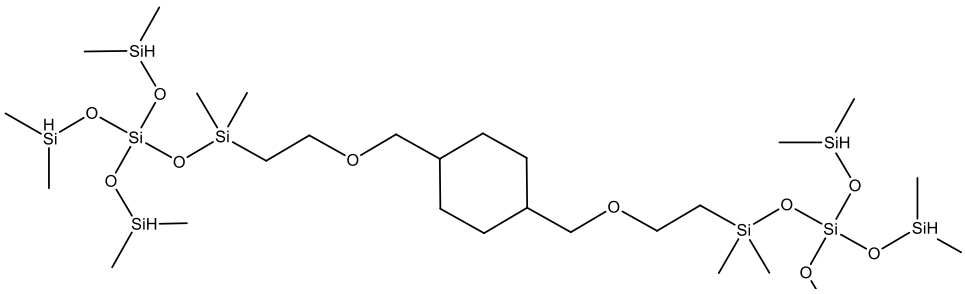

***Figure 43.*** *Appearance of coating consisting of RR-94 + R44*

It was suggested the methacrylate functionality is not reactive enough to crosslink the Si-H functional polymers even in the presence of platinum catalyst due to catalyst inhibition by the strong bonding of the acrylate functional groups to the Pt.

Several vinyl functional silicone resins that are commercially available from Gelest were also evaluated. Each polymer varied in its molecular weight: DMS-V03 (MW-500), DMS-V22 (MW=9,400), and DMS-V31 (MW=28,000). The lowest molecular weight version, DMS-V03, dried after 15 minutes; however, the coating did not have solvent resistance at 24 hours, and was very soft. The higher molecular weight versions gelled almost instantly at 30 ppm and 10 ppm platinum catalyst. The systems were studied at lower catalyst levels and without catalyst, but they did not dry. The DMS-V03 may have been too low in molecular

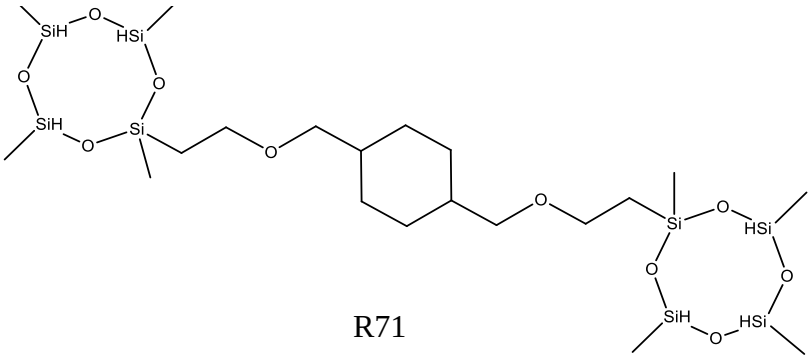
weight and did not provide enough functionality for the Si-H polymers to react. DMS-V22 and DMS-V31 were too high in their molecular weight and functionality, which would suggest why the instantaneous gelation occurred.

Due to the inconsistent cure mechanism and the inability to fully crosslink the vinyl intermediate R32, two new, higher molecular weight, Si-H functional polymers were prepared at SRI and further evaluated at PPG. The purpose of higher molecular weight polymers was to increase the curability and crosslinking for improved coating property evaluation. Another reason was to increase the formulation viscosity to a convenient level for coating operation. The polymers R71 and R60, shown in Figure 44, include a cyclohexane group for improved viscosity and better compatibility with other polymers.



R60

Molecular Wt = 677.31g; Equivalents = 6; Equivalent Wt = 112.89g



R71

Molecular Wt = 853.76g; Equivalents = 6; Equivalent Wt = 142.29g

***Figure 44.*** *Higher molecular weight Si-H functional polymers*

The polymers were reacted with R32, the tetrakis vinyl functional intermediate that was also used with for the X36 and X40 formulations. Based on a recommendation from SRI, the polymers were also evaluated with the addition of 5% vinyltrimethoxysilane based on resin solids. The silane was added in order to improve the adhesion of the system. The reactions with R71 and R60 are assigned as X138 and X151 respectively, a nomenclature also used at SRI and Boeing testing. Table 21 summarizes the results.

***Table 21:*** *Higher molecular weight Si-H polymers, R60 & R71, reacted with the vinyl functional polymer R32*

| Property | Formulation | | | |
|---|---|---|---|---|
| | 15A | 15B | 15c | 15D |
| **Description** | X138 1:1 | X138 1:1 | X151 1:1 | X151 1:1 |
| **Raw materials** | R71+R32 | R71+R32 | R60+R32 | R60+R32 |
| **Vinyl silane** | 0 | 5% VTMS | 0 | 5% VTMS |
| **Catalyst added (g)/(ppm)** | 18ppm | 18ppm | 29ppm | 28ppm |
| **Total Catalyst (ppm)** | 15ppm | 15ppm | 36ppm | 35 ppm |
| **Gel time (in jar)** | 2 min | Liquid after 4 hr | 6 min | 40 min |
| **DT hard** | 3 hr | Did not dry | 90 min | 60 min |
| **24-hr adhesion** | 5B | 0B | 3B | 0B |
| **7-day adhesion** | 5B | 0B | 2B | 5B |
| **30-day adhesion** | 5B | 2B | 5B | 0B |
| **24-hr 100 MEK rub** | Fail, 60 | Fail, 15 | Pass | Pass |
| **7-day 100 MEK rub** | Pass, marred | Pass | Pass | Pass |
| **30-day 100 MEK rub** | Pass | Pass | Pass | Pass |
| **7-day pencil hardness** | HB | Figure 44, 2H | 2H | 2H |
| **30-day pencil hardness** | 2H | 2H | 2H | H |
| **7-day Fischer hardness** | 1.3 | 2.9 | 4.3 | 4.5 |
| **30-day Fischer hardness** | 10.1 | 5.8 | 6.1 | 7.2 |
| **7-day Koenig (oscillations)** | 20 | 20 | 32 | 38 |
| **30-day Koenig (oscillations)** | 33 | 27 | 36 | 35 |

All of the reactions were formulated with a 1:1 ene: Si-H stoichiometry with additional platinum catalyst. Like the previous polymers, R60 and R71 were synthesized with residual catalyst. In the data table, the catalyst added value is the additional amount of catalyst added into the reaction, and the total catalyst is the total amount of catalyst including the residual and the quantity added. The R71 coatings had poor 24-hour solvent resistance, indicating the film was not cured at that point. However, cure at 7 days was improved as indicated by the improved solvent resistance, but resulted in a loss of adhesion. The branched polymer R60 showed better cure response after

24 hours, but resulted in an adhesion loss. The hardness of the coating was measured by the Koenig pendulum rocker and the Fischer micro-indenter. Both forms of measurement indicated that the solvent-resistant films were soft. These results indicate improvement in curing and adhesion after aging at room temperature. However, the hardness of the coatings was not as good as that observed at SRI and Boeing.

The vinyltrimethoxysilane (VTMS) did not improve adhesion in either system. The VTMS was added as a 5% additive based on resin solids. This translates to a relatively large portion of available vinyl functionality. The overall stoichiometry for the reactions were 0.9:1 and 0.93:1 Si-H: Ene, respectively. The results are summarized in Table 22.

***Table 22:*** *Vinyltrimethoxy silane modifications & varying catalyst levels*

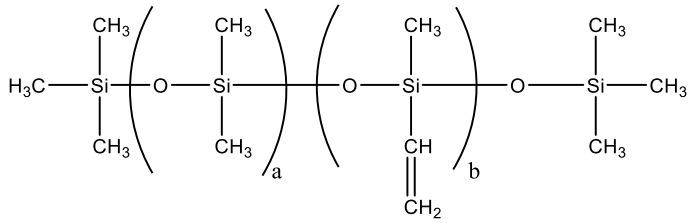
| Property | Formulation | | | | | |
|---|---|---|---|---|---|---|
| | 26A | 26B | 26c | 26D | 26E | 26F |
| **Description** | X138 | X138 | X138 | X151 1:1 | X151 | X151 |
| **Raw materials** | R71+R32 | R71+R32 | R71+R32 | R60+R32 | R60+R32 | R60+R32 |
| **Vinyl silane** | 0 | 0 | 50% equiv. | 0 | 0 | 50% equiv. |
| **Catalyst added (ppm)** | 19ppm | 32ppm | 22 ppm | 29ppm | 33ppm | 32ppm |
| **Total catalyst (ppm)** | 27ppm | 40ppm | 27ppm | 36ppm | 40ppm | 36ppm |
| **Gel time (in jar)** | 5 min | seconds | | 10 min | 2 min | 1 hr |
| **DT hard** | 90 min | 90 min | 24 hr | 60 min | 60 min | 60 min |
| **24 hr adhesion** | 0B | 0B | 0B | 0B | 0B | 0B |
| **7 day adhesion** | 0B | 0B | 0B | 0B | 0B | 0B |
| **24 hr 100 MEK rub** | Fail, 15 | Fail, 10 | Fail, 10 | Pass | Fail, 80 | Pass |
| **7 day 100 MEK rub** | Fail, 20 | Fail, 10 | Fail, 5 | Pass | Fail, 80 | Pass |
| **7 day Pencil Hardness** | 2H | 2H | 2H | 3H | 2H | 2H |
| **7 day Fischer hardness** | 2.4 | 2.9 | 1.9 | 3.8 | 3.2 | 5.4 |
| **7 day Koenig (oscillations)** | 31 | 20 | 21 | 4 | 40 | 56 |

Again, the cyclic Si-H functional polymer did not show cure within 24 hours, and the VTMS did not improve adhesion. Two of the X151 reactions cured within 24 hours. However, both the X151 reaction and X138 exhibited soft films, as measured by Koenig and Fischer micro-indenter. Like the X138 reaction, the VTMS did not improve adhesion in the X151 reactions, but did extend the pot life. Importantly, the use of the vinyltrimethoxysilane could be used as a method to extend pot life without sacrificing dry-to-touch time.

### Formulation Modifiers

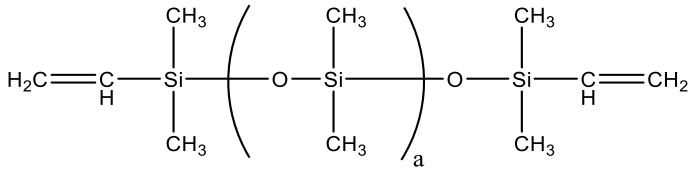
Several vinyl silicone polymers from Siltech were evaluated as modifiers for the X138 and X151 systems. The polymers received were Silmer VIN J10, and Silmer VIN C50. VIN J10 was a multi-functional, high molecular weight, silicone pre-polymer with vinyl functional groups (Figure 45). The VIN C50 was a tri-functional, high molecular weight, silicone pre-polymer with reactive vinyl groups. These materials were added as 50% and 100% replacements for the vinyl functionality in R32 based on equivalence.

**Multi-functional**



Siltech Polymer: Silmer J10 (Eq. Wt. = 846)

**Linear-functional**



Siltech Polymer: Silmer C50 (Eq. Wt = 3851) Tri-functional
Gelest Polymers: DMS-V03 (MW = 500; Equivalence = ~2; Eq. Wt. = 250)
DMS-V22 (MW = 9400; Equivalence = ~2; Eq. Wt. = 4700)

***Figure 45.*** *Commercially available vinyl terminated polymers*

As shown in Table 23, the Silmer J10 material was used either in conjunction with the Si-H polymers or as a partial replacement for the SRI vinyl functional polymer, and was formulated with a 1:1 stoichiometry. It did not dry as a thin film. No further work was done with the Silmer J10 due to poor crosslinking with the SRI reagents.

***Table 23:*** *Silmer VIN J10 reacted with Si-H polymers*

| | 19A | 20A | 27B | 27E |
|---|---|---|---|---|
| **Description** | R44 + Silmer J10 | R44 + Silmer J10 | R71 + Silmer J10 + R32 | R60 + Silmer J10 + R32 |
| **Total Catalyst (ppm)** | 5 | 30 | 10 | 10 |
| **Dry-to-Touch Time** | Did not dry | 3 hours | did not dry | Did not dry |
| **Pot Life** | Did not gel | 1.5 hours | > 24 hours | Did not gel |
| **24 hours Solvent Resistance** | Not tested | F 10 | Not tested | Not tested |

Table 24 represents reactions where Silmer C50 was added. Similarly to Silmer VIN J10, the Silmer VIN C50 did not exhibit promising results. The Silmer VIN C50 was reacted at a 1:1 stoichiometry with the SRI Si-H functional polymers and was used as a partial or full replacement of the R32. Again, the majority of the films did not dry, and if the film did dry, it showed no solvent resistance in 24 hours.

***Table 24:*** *Silmer VIN C50 reacted with Si-H polymers*

| | 19B | 20B | 27C | 27F |
|---|---|---|---|---|
| **Description** | R44 + C50 | R44 + C50 | R71 + C50 | R60 + C50 + R32 |
| **Total Catalyst (ppm)** | 5 | 30 | 10 | 10 |
| **Dry-to-Touch Time** | Did not dry | 3 hours | Did not dry | Did not dry |
| **Pot Life** | Did not gel | 1 hour | > 24 hours | > 24 hours |
| **24 hours Solvent Resistance** | Not tested | F 3 | Not tested | Not tested |

### Additional Formulation Analysis at Boeing

The Boeing team has also assessed the down-selected formulations using scaled up batches provided by SRI. Various formulations of X36 and X40, based on combinations of R32 reacting with either R21 or R44 and additional Pt-catalyst, were assessed for pot life, appearance, hardness, cure time and temperatures. The *ene* part, R32, was mixed with the corresponding Si-H reagent, R21 or R44 to maintain 1:1 molar equivalent ratios. The various amounts used for the evaluated formulations are listed in Table 25. The Pt-catalyst was added to the *ene*-component prior to mixing with the siloxane. The effect of the catalyst on the cure time and temperature was assessed by adding various amounts of catalyst to the reaction mixtures.

***Table 25:*** *Summary of reagent ratios and resulting compounds (Theoretical amounts are shown as plain text, and real quantities are included in parentheses.)*

| Specimen | Catalyst (g of 0.05 % xylene sol) | Reagents (g) | |
|---|---|---|---|
| **X40-1** | 0.0 | R32 (1.111) | R44 (1.239) |
| **X40-2** | 0.2 (0.2035) | R32 (1.122) | R44 (1.234) |
| **X40-3** | 0.1 (0.106) | R32 (1.128) | R44 (1.240) |
| **X36-1** | 0.0 | R32 (1.127) | R21 (1.040) |
| **X36-2** | 0.2 (0.205) | R32 (1.128) | R21 (1.046) |
| **X36-3** | 0.1 (0.106) | R32 (1.126) | R21 (1.052) |
| **X36-4** | 0.05 (0.054) | R32 (1.129) | R21 (1.048) |

The *ene* (R32) was first measured into a scintillation vial (while cold) followed by dropwise catalyst addition. The mixture was then stirred with a magnetic stirrer for approximately one minute. The (cold) Si-H component was then weighed into the vial and mixed again with the magnetic stirrer. After mixing, the mixture was drawn onto the Al 2024 panels with the bar and air dried at ambient temperature (samples marked as **R**). A duplicate panel for each formulation was placed in the oven (samples marked as **T**) and held at 50ºC for about 18 hours, and then removed from the oven and kept at room temperature. Observations on the properties of the compounds are reported in Table 26.

***Table 26:*** *Summary of the cure conditions and properties of thecompounds X-40 and X-36 after Mixing*

| Specimen | Cure temp, ºC | Pot life | Comments |
|---|---|---|---|
| **X40-1 R** | 20 | 4hr | Clear liquid; still flows 4 hrs after coating on the Al panel |
| **X40-1 T** | 50 | | |
| **X40-2 R** | 20 | <10 min | Clear liquid; gelled in the vial in less than 10 minutes |
| **X40-2 T** | 50 | | |
| **X40-3 R** | 20 | c.15 min | Clear liquid; gelled in about 15 minutes |
| **X40-3 T** | 50 | | |
| **X36-1 R** | 20 | > 4 hrs | Clear liquid; the material at room temp did not completely cure on the Al panel for at least 10 days |
| **X36-1 T** | 50 | | Material was hard to touch after several hours |
| **X36-2** | 20 | < 2 sec | Rapid exothermic reaction followed by gelation within 10 sec |
| **X36-3** | 20 | <10 sec | Rapid exothermic reaction followed by gelation within c. 20 sec |
| **X36-4 R** | 20 | 1 hr | Clear liquid |

*Pencil hardness tests.* Samples were tested for hardness buildup after 4h (for those kept in the oven) and 24 hours after mixing (all formulations) using the standard procedure pencil hardness test (ASTM D3363). The results of the pencil hardness tests are summarized in Table 27. The most promising mixtures were X40-1, X36-1, and X36-4, all of which cured at 50ºC. Overall, the force-dried formulations (cured at 50ºC) had a better hardness performance. In summary, both the X36 and X40 formulations provide combinations that demonstrate sufficient curing and adhesion after 24h (Figure 46). The combinations are based on stoichiometric variations, additives, and levels of catalyst.

The study of X36 and X40 was stopped once improved intermediates, R60 and R71 were identified. Work with the improved intermediates is described below.

***Table 27:*** *Pencil hardness test results for the compounds X36 and X40 cured at room temperature (R) and held in the oven for 18 hours (at 50°C) (T)*

| Sample | Pencil hardness* | | | | | |
|---|---|---|---|---|---|---|
| | 3B | 2B | 1B | HB | F | H |
| **X40-1 R** | F | F (brittle) | | | | |
| **X40-1 T** | Pass/Pass | Fail/Pass | NA/Pass | NA/Pass | NA/Pass | NA/Fail |
| **X40-2 R** | Pass | Pass | Pass | Fail | | |
| **X40-2 T** | Pass/Pass | Pass/Pass | Fail/Pass | NA/Pass | NA/Pass | NA/Fail |
| **X40-3 R** | Pass | Fail | | | | |
| **X40-3 T** | Pass/Pass | Pass/Pass | Fail/Pass | NA/Fail | | |
| **X36-1 R** | Still wet @ 24 h | | | | | |
| **X36-1 T** | Fail/Pass | Fail/Pass | Fail/Pass | NA/Pass | NA/Pass | NA/Fail |
| **X36-4 R** | Fail (brittle) | Fail | | | | |
| **X36-4 T** | Pass/Pass | Pass/Pass | Fail/Pass | Fail/Pass | NA/Pass | NA/Fail |

** For the compounds held at the room temperature, the hardness test has been done 24 hours after mixing; for the heat-treated samples, the tests were done 4 hours and 24 hours after mixing (hence two numbers reported).*

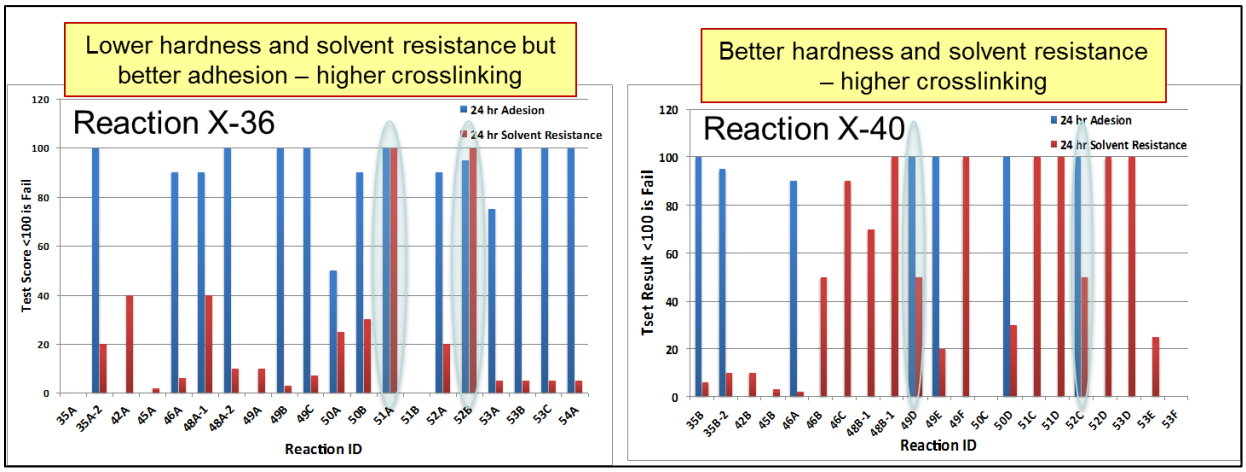



***Figure 46.*** *Hardness and adhesion values for formulations X36 and X40 after 24-hour curing at 50 °C.*

## Testing of Further Down-Selected Formulations (X151 and X138)

*Synthesis and appearance of the formulations*

Improved multi Si-H intermediates developed at SRI were further studied as formulations with R32. The intermediates R60 and R71 are illustrated in Figure 44. Formulations X138 (with R71) and X151 (with R60) were prepared according to the quantities shown in Table 28 and hand-drawn onto bare Al 2024 (T3) substrates that had previously been washed with isopropyl

alcohol. Vinyltrimethoxysilane (VTMS) was added to a few of the formulations to advance adhesion to the Al alloy. For each formulation, one panel was left to dry at ambient conditions and a duplicate panel was placed into convection oven for approximately 16 hours (overnight). After drying, all panels were inspected and kept at the room temperature.

***Table 28:*** *Amounts of reagents in synthesis of formulations X-138, X-151 and X-151-A.*

| Formulation | | Reagents | | | |
|---|---|---|---|---|---|
| **1** | **X151** | **R32 -B3** | **R60** | **Pt-cat** | **VTMS** |
| | | 0.67g | 0.85g | 0.1g | 0.08g |
| **2** | **X151-A** | **R32 -B3** | **R60** | **Pt-cat** | **VTMS** |
| | | 0.67 | 0.85 | 0.1 | 0 |
| **3** | **X138** | **R32 - B3** | **R71** | **Pt-cat** | |
| | | 0.75g | 0.76g | 0.06g | |
| **4** | **X138-B** | **R32 - B3** | **R71** | **Pt-cat** | |
| | | 0.75g | 0.76g | 0.03g | |
| **5** | **X138-A** | **R32-B3** | **R71** | **Pt-cat** | **VTMS** |
| | | 0.75g | 0.76g | 0.03g | 0.08g |

After mixing, all formulations remained liquid in the jar and wet-to-touch for at least 30 minutes, with X151 remaining liquid and wet-to-touch for at least 1 hour. The X151 formulations provided a much better coating that was uniform and with no obvious defects. X138 was more viscous and behaved as slightly gelled when hand-drawn, which resulted in an uneven coating with several defects (Figure 47).

To test the effect of the coupling agent on the film quality, the formulation X151-A was generated without VTMS (Figure 47, left). X151-A gelled faster in the vial compared to X151, and resulted in a less uniform coating with several defects (fish eyes). One of the causes for the different coating quality may be the difference in viscosity of the formulations; X151-A was much less viscous than X151-A and X138. Another potential reason for the faster gelation in the absence of VTMS is

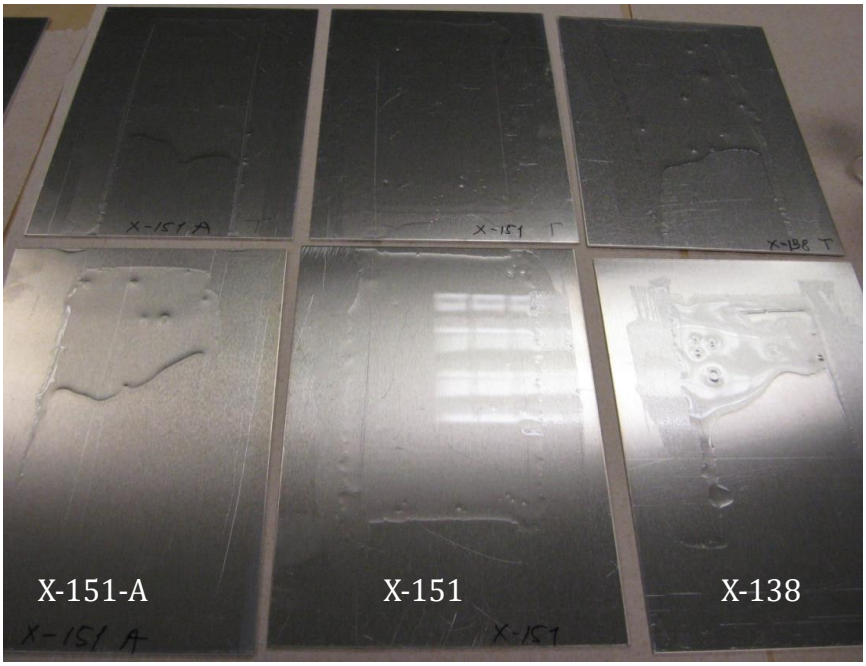



***Figure 47.*** *Assessment of the appearance of X151, X151-A and X138.*

the inhibiting effect of VTMS that was identified in other experimental sets during the attempts to advance adhesion over primers.

To improve the quality of the X138 coating, the X138-A formulation was prepared by adding VTMS to the X138 formulation and reducing the catalyst amount to half of what was added into X138. A control sample, X-138-B, was prepared with the reduced amount of catalyst but no VTMS. Both modifications resulted in a better film quality, with the VTMS being more efficient (Figure 48).

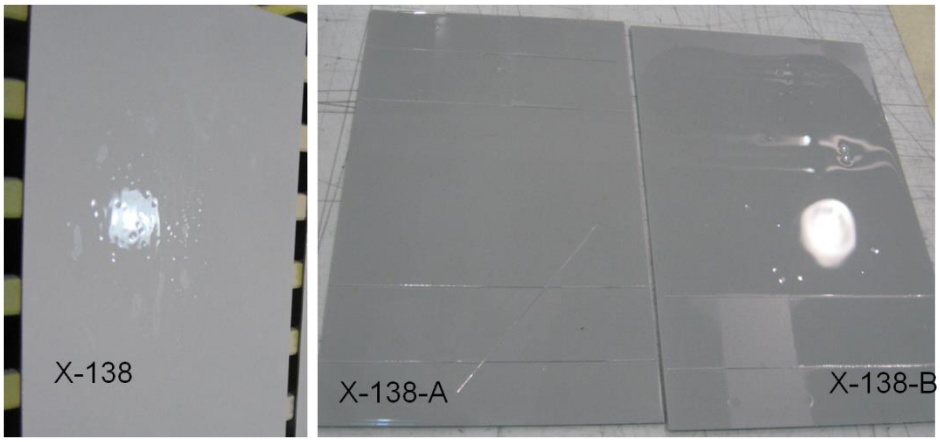



***Figure 48.*** *Images of X138, X138-A and X138-B drawn on the primed substrate.*

Attention should be paid to the fact that, when amounts of the reagents were scaled up to 10 times more than the quantities in Table 28, X151 and X138 formulations gelled in the vial within several minutes and released high levels of heat. This did not happen when smaller amounts of the reagents were mixed, which shows that in large volumes the heat of the coupling reaction accumulates and acts as additional catalyst (Figure 49).

***Figure 49.*** *X138 mixed in a smaller quantity (right), and scaled up to 15 ml (left), which gelled very quickly.*

Reaction X151 between R60 and R32 was also assessed for its reactivity as a function of Pt catalyst. Reactions of 7g-formulations placeed in a glass vial were monitored with a thermometer to assess the rapid heat generated due to the exothermic hydrosilylation reaction. Indeed, there is a rapid elevation of temperature once the reaction starts, which is followed by rapid gelation. The thermal profiles of X151 in the presence of various levels of Pt catalyst are illustrated in Figure 50. The temperature can increase by about 140°C in one minute.

### Compatibility with Different Primers

Once the lack of curing of coatings deposited over primers was realized, additional studies were performed by each of the teams to assess the problem. The tests at Boeing were different than those performed at SRI and PPG in that Boeing ensured the primers were fully cured by either aging the primer coatings for 7 days at RT or by force-curing at 50°C for at least 16h. In contrast,

a similar evaluation at SRI was based on epoxy primer that was cured at RT for a few hours or a day before depositing the topcoat formulation.

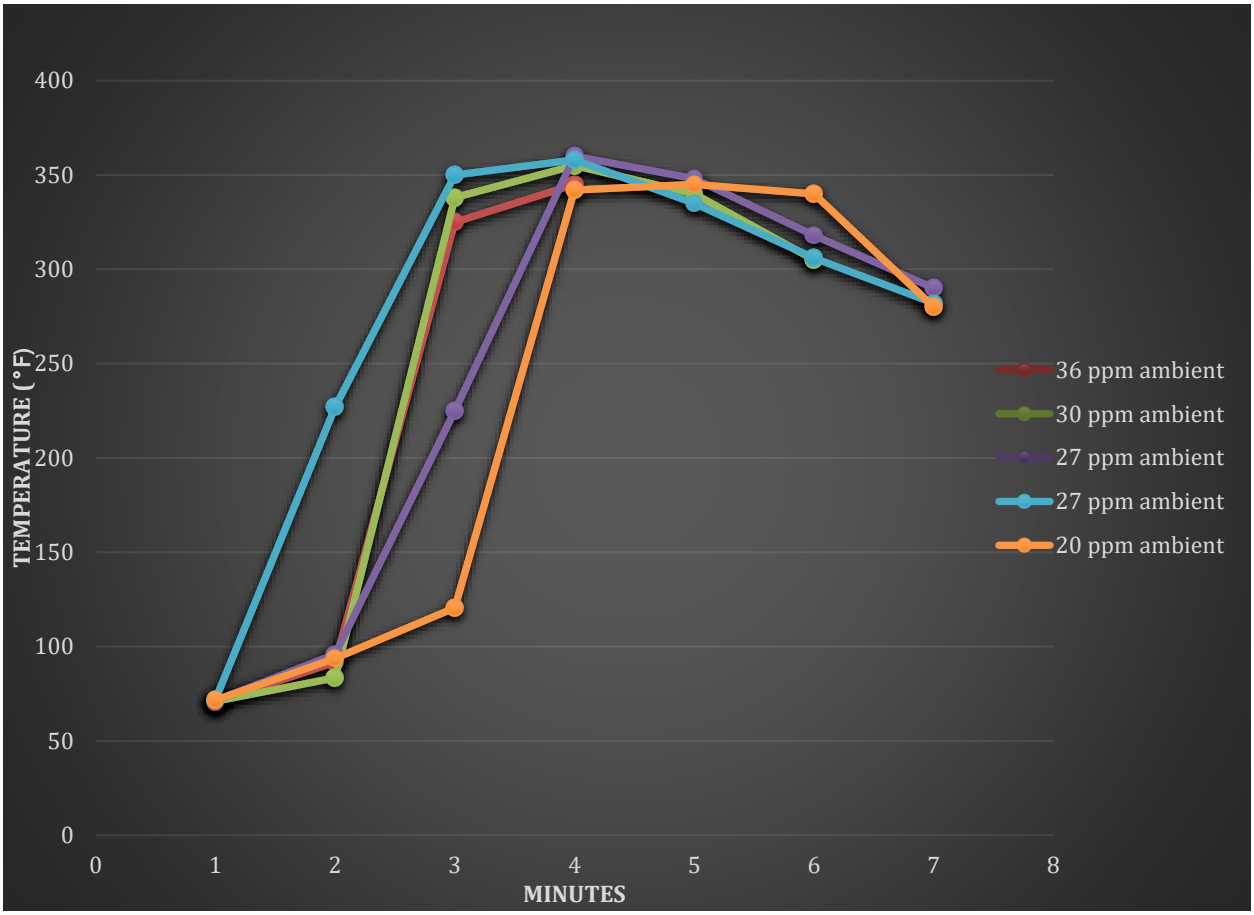



***Figure 50.*** *The thermal profiles of X151 formulations with varied levels of Pt catalysts.*

*PPG Study*

Several of the formulations were tested over a PPG commercial aerospace epoxy primer, CA7502. This primer is used over treated aluminum in many aerospace applications. It was noted by SRI that the coating, which uses R32 as the vinyl functional component and R71 or R60 as the Si-H functional component, did not cure when applied over the CA7502. An experiment was designed to replicate the problem and evaluate several potential solutions to the issue. The systems were prepared as followed:

Substrate preparation:

Use 3- 12x12x0.02" 2024 T3 bare; Alcoa lot number: 331858

1. Solvent wipe with MEK
2. Scuff with Scotchbrite
3. Prime with CA7502
4. Use 4:1 mix ratio by volume as per the product data sheet
5. Film build: 0.8-1 mil

Substrates used:

A. Epoxy-primed electro-coated steel
B. 2024 T3 bare aluminum, primed, and dried at room temperature for 2 hours
C. 2024 T3 bare aluminum, primed, and sprayed with an A-187 solution
D. 2024 T3 bare aluminum, primed and dried for 1 hour at ambient temperature, and then baked in oven for 30 minutes at 60°C
E. Polished bare aluminum Q panel

The topcoat used in this experiment was a 1:1 stoichiometry of the R32 vinyl polymer: R60 Si-H polymer. Platinum catalyst was added at 35 ppm. After the coating was mixed, it was applied by using a 5 mil square draw down bar. The results are summarized in Table 29.

***Table 29:*** *SRI topcoat over epoxy primer CA7502*

| | 33A | 33B | 33C | 33D | 33E |
|---|---|---|---|---|---|
| **Dry Condition** | Ecoat, RT | 2 hour RT temp | 1 hour RT, A-187 tie coat | 1 hour RT, 30 minute bake | Aluminum Q panel, RT |
| **Dry-to-Touch Time** | 1.5 hours | Did not dry | Did not dry | Did not dry | 1.5 hours |
| **Pot Life** | 1 hour | 1 hour | 1 hour | 1 hour | 1 hour |
| **24 Hour Solvent Resistance** | F 30 | Not tested | Not tested | Not tested | F 50 |

As observed by SRI, the coating did not cure over the epoxy primer. It was thought that the amine in the epoxy primer was poisoning the platinum catalyst in the SRI topcoat, so a 30-minute bake at 140°F was done to accelerate cure of the primer; this did not improve cure of the topcoat over the primer. The spray of the A-187 epoxy functional silane was used as a tie-coat to react the residual amine from the primer to the epoxy of the A-187 and eliminate the catalyst poisoning; however, this did not improve the dryness of the topcoat. Although the SRI topcoat did not achieve solvent resistance within 24 hours over the electro-coated sample or the aluminum Q panel, the films did dry over the substrate. This experiment replicated the initial results seen by SRI, the topcoat did not dry over the CA7502.

*Boeing Study*

Two primers were selected at Boeing for the preliminary screening of their compatibility with the coatings: CA 7502 (PPG, non-chrome, epoxy; also used by the SRI and PPG teams) and JetFlex (polyurethane primer produced by Sherwin Williams). The later selection also satisfied a request by the program review committee to evaluate the newly developed coating system for its compatibility with pre-deposited polyurethane coatings.

A full preparation of the test panels is required to test primer compatibility. Therefore, the Al 2024 clad (T3) panels were solvent-cleaned, deoxidized (abraded and alodined) and sol-gel treated prior to priming according to procedures developed at Boeing. The pre-treated Al panels were masked so that only half of the panel would be covered with the primer and the other half would stay unprimed. After the primer was spray-coated, the panels were left to cure for 7 days before the coatings were applied.

The formulations were prepared and hand-drawn onto the primed panels several minutes after mixing the reagents. A draw bar of 2.5 mil (~ 60 µm) film thickness was used. After coating, one of the panels was left to cure at ambient conditions, and a duplicate panel was force-cured at 50°C overnight (except for the X138 samples). Table 30 summarizes the formulation matrix used in the study.

All coatings (force-cured at 50°C and air-cured) except X138 were dry-to-touch and hard when examined ~16 hours after deposition (Figure 51). No visual differences were observed for the formulations coated on primed vs the unprimed parts of the panels. The panels were left at room temperature for 7 days and then examined for tape adhesion according to BSS7225.

***Table 30:*** *Test matrix for primer compatibility of the X40, X138 and X151 formulations*

| Formulation | Reagents (g) | | | | Observations | Substrate | Cure conditions |
|---|---|---|---|---|---|---|---|
| | R32 (b2) | R44 (b2) | Pt-cat | VTMS | | | |
| **X40-3-N** | 1.112 | 1.233 | 0.1 | | | | |
| | 7.784 | 8.631 | 0.7 | | | PU, Epoxy, no-primer | RT, 50°C |
| | R32 (b2) | R71 | Pt-cat | VTMS | | | |
| **X138** | 0.75 | 0.76 | 0.06 | | | | |
| | 7.5 | 7.6 | 0.6 | | Gelled in the vial | | |
| | 3.75 | 3.8 | 0.3 | | | PU, Epoxy, no-primer | RT |
| **X138-A** | 3.75 | 3.8 | 0.15 | 0.3 | | Epoxy | RT |
| **X-138-B** | 3.75 | 3.8 | 0.15 | | | Epoxy | RT |
| | R32 (b2) | R60 | Pt-cat | VTMS | | | |
| **X-151** | 0.67 | 0.85 | 0.1 | 0.08 | | | |
| | 6.7 | 8.5 | 1 | 0.8 | Gelled in the vial | | |
| | 3.35 | 4.25 | 0.5 | 0.4 | | PU, Epoxy, no-primer | RT, 50°C |
| **X-151-A** | 0.67 | 0.85 | 0.1 | | | | |
| | 6.7 | 8.5 | 1.0 | | | PU, Epoxy, no-primer | RT, 50°C |

All formulations passed class I dry tape adhesion tests (no scribes), including RT cured X138 and its derivatives. The results of the class II and class III (when applicable) tape adhesion tests are summarized in Table 31 and are graphically represented in Figure 52. With the lack of statistics, it is hard to say that there is a big difference in adhesion of the coatings to any kind of primers. The adhesion on the primed surfaces is also quite similar to that of the sol-gel treated surfaces with no primers. However, formulations of X138 without the coupling agent resulted in

a very poor adhesion to any of the tested substrates. Addition of VTMS to the above formulations improves the quality of the coating and its adhesion. The X40 formulations (even without any additional coupling agent) exhibited the best adhesion among three formulations that were tested. Another noticeable trend is that coatings cured at 50$^{o}$C have a better adhesion to the substrate.

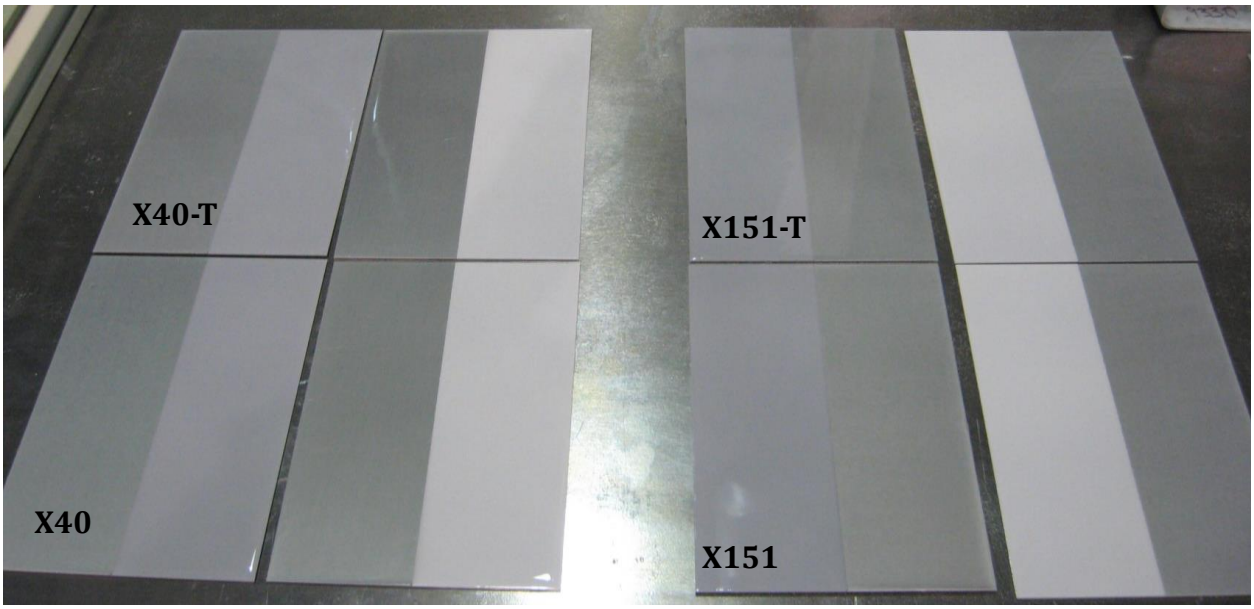



***Figure 51.*** *X-40 and X-151 coated on the masked panels with different primers.*

Overall, topcoats over completely cured primers with topcoat formulations that were cured overnight on both polyurethane and epoxy primers provided adequate adhesion both at ambient conditions and when heated in the oven. This is in contrast to coatings that were deposited on primers that have not been fully cured. These observations reinforce the assumption that the Pt catalyst is poisoned by components in the uncured primers, most likely the amine components that can leach to the topcoat if they still have mobility.

The inability to deposit the formulations before full curing of the primers makes formulations based on hydrosilylation curing much less desirable; in most operations, it is impractical and uneconomical to wait such a long period or to use heat for curing. This was one of the main reasons for making the decision to move to the Si-OH curing system.

***Table 31:*** *Results for the dry tape adhesion tests*

| | Class II | | | | | Class III | | |
|---|---|---|---|---|---|---|---|---|
| **Formulation** | Cure | Primer | Value | No Primer Value | | Primer | Value | No Primer Value |
| **X-151** | air | PU | 2 | 2 | fail | | | |
| | | | 2 | 2 | | | | |
| **X-151** | forced | PU | 4 | 3 | | | | |
| | | | 5 | 6 | | | | |
| **X-151** | air | epoxy | 3 | 2 | | | | |
| **X-151** | forced | epoxy | 2 | 3 | | | | |
| | | | 2 | 6 | | | | |
| **X-40** | air | PU | 3<br>2 | 5<br>2 | fail | | | |
| **X-40** | forced | PU | 8 | 8 | pass | PU | 6 | 5 |
| | | | 5 | 6 | | | | |
| **X-40** | air | epoxy | 5<br>3 | 3<br>7 | | | | |
| **X-40** | forced | epoxy | 8 | 5 | | epoxy | 4 | 4 |
| **X-138** | Air | PU | 1 | | | | | |
| **X-138-A** | Air | Epoxy | 8 | | | Epoxy | 2 | |
| **X-138-B** | Air | Epoxy | 1 | | | | | |

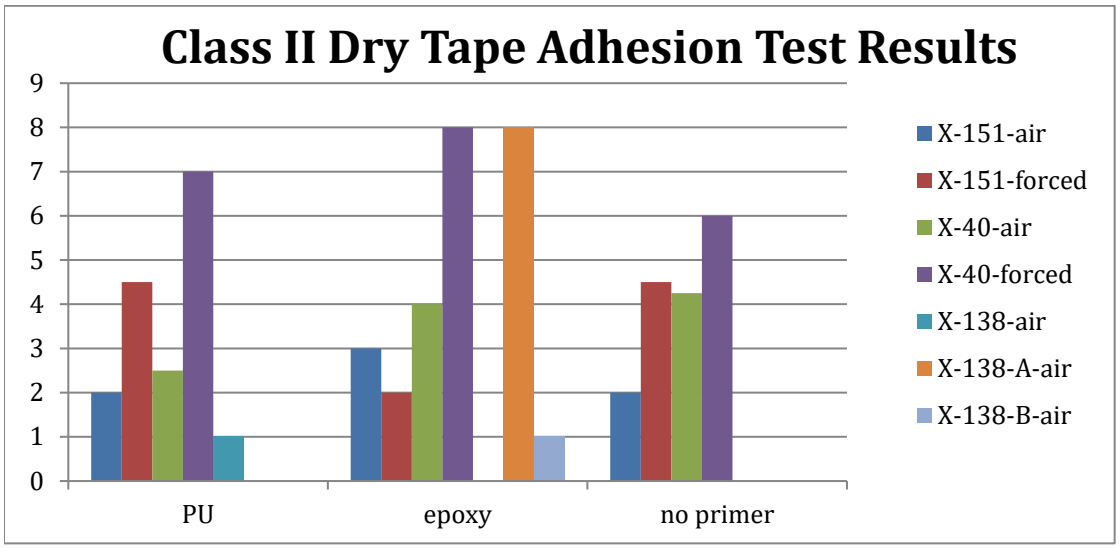



***Figure 52.*** *Results of the class II dry tape adhesion tests for the formulations deposited onto different primers.*

**(B) Formulations Based on Condensation Curing**

As indicated by the coating-over-primer tests and many other factors, the efficiency of a platform based on hydrosilylation reaction *at ambient temperature* was found to be very problematic. It requires special pretreatment of the primer surface, an extra level of catalyst (resulting in higher costs and very short pot-life), or development of a completely new catalytic system. In contrast, SRI has already developed another coating platform based on the use of Si-H containing siloxanes that are converted by a dehydrocoupling reaction to Si-OH that is then cured by efficient Si-OH condensation reactions.

In the third year of the project, we have assessed a few intermediates that consist of multiple Si-OH but also have significant linear nonaromatic content. We utilized intermediates consisting of multiple Si-H that were found advantageous in our hydrosilylation concept assessment and converted their Si-H to primarily Si-OH with some mild condensation to Si-O-Si units.

The curing work at SRI with the Si-OH modified intermediates focused mainly on formulations to be coated over Al and primers for further testing at Boeing and NAVAIR. Many formulations of R71-OH and mixtures of R71-OH with PHMS-OH both with and without additional pigments were found suitable for curing at RT, providing hardness values exceeding 4H and adhesion in the range of 4B and 5B. They were also found to be solvent-resistant by Boeing's own testing procedures. This information is discussed in Task 4.

Parallel studies at PPG were less conclusive (discussed below). The variation between the tests at the different locations is unclear.

***Evaluation of Si-OH Functional Polymers at PPG***

Several silanol functional polymers prepared by SRI were evaluated:

1) R71-OH was generated by dehydrocoupling of the R71 intermediate as a pre-polymer.
2) R71-OH/Butoxy was prepared as above by letting the R71 react first with the butanol solvent before adding water to the dehydrocoupling reaction. The dehydrocoupling reaction also occurs efficiently with alcohol; however, in the presence of water, the reaction is overwhelmingly favored with the water. If all the Si-H sites are replaced with the alcohol, the intermediate is defined as R71-butoxy (as shown in Figure 53). In all cases where an alkoxy group is added to the intermediate, the group needs to be hydrolyzed during the curing step. Thus, the curing catalyst should do both hydrolysis and condensation.
3) PHMS-OH was prepared by a synthesis established and scaled-up at SRI using commercially available polyhydromethylsiloxane (PHMS). Both polymers were kept as solutions in large quantities of alcohol for stability, and each polymer supplied was low (approximately 20-30%) in solid resin content.

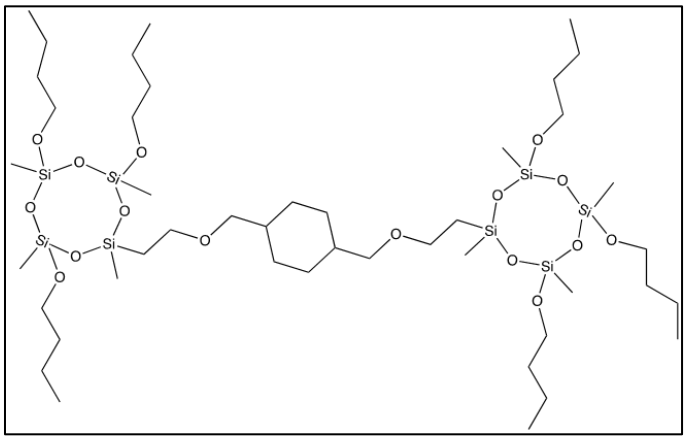


***Figure 53.*** *R71-Butoxy molecular structure*

Initially, the experiments were designed to prepare a coating using both R71-OH and PHMS-OH with the aid of the triamine catalyst, pentmethyldiethylene triamine. However, since the reagents crosslinked individually, experiments were designed using each polymer and catalyst separately. R71-Butoxy was crosslinked individually, with the assistance of triamine catalyst.

The intermediates of R71-OH, PHMS-OH, and R71-Butoxy, were tested with several different catalysts, including triamines, tin complexes, and Titanates, as well as dipodal silanes to aid in increasing crosslink density and hardness. Pigmented coatings utilizing each reagent were also explored. Table 32 summarizes the curing of formulations consisting of 1:1 weight ratio of R71-OH with PHMS-OH

***Table 32:*** *RT Curing of mixtures of R71-OH and PHMS-OH in the presence of 1% triamine.*

| **Sample Name** | | | **133A** | **133B** |
|---|---|---|---|---|
| **Description** | | | 1:1 R71-OH: PHMS-OH | 1:1 R71-OH: PHMS-OH |
| **Catalyst Added** | | | 1% | 1% |
| **Dry-to-Touch** | | | 1.5 hours | 1.5 hours |
| **Pot Life** | | | 5 hours | 5 hours |
| **Property** | **Spec** | **Duration** | | |
| **Solvent Resistance** | No Breakage | 24 hours | F 2 | F 10 |
| | | 7 days | F 12 | F 30 |
| | | 30 days | F 5 | P |
| **Pencil Hardness** | | 24 hours | 4H | H |
| | | 7 days | 4H | 4H |
| | | 30 days | --- | 4H |
| **Koenig Hardness** | Seconds | 24 hours | 180 | 155 |
| | | 7 days | 170 | 169 |
| **Fischer Micro-Hardness** | ($N/mm^2$) | 24 hours | 97.77 | 61.73 |
| | | 7 days | 93.9 | 92.03 |

In this experimental set, the R71-OH and PHMS-OH were reacted at a 1:1 stoichiometry based on resin solids, along with 1% Pentamethyldiethylene Triamine. The films dried to touch within 1.5 hours. The pot life was longer (5 hours) than for the previous Si-H polymers used. Although the coatings were hard according to the Fischer micro-indenter, Koenig pendulum rocker, and pencil hardness test, the films did not pass 24-hour solvent resistance. The low solvent-resistance performance in this series at PPG contradicts other cured-coating tests performed at SRI and Boeing, indicating improved solvent resistance as a function of time for various R71-OH/PHMS-OH formulations.

### Additional Testing of R71-OH and R71-Butoxy

After the gelation of several containers of the R71-OH reagent, SRI synthesized a new batch of R71-OH, which was evaluated for coating properties. A batch of R71-butoxy was also received and evaluated. Table 33 summarizes results from several formulations consisting of the new batch of R71-OH. This time, the results indicated much better curing performance, especially after a duration of 30 days.

***Table 33:*** *Evaluation of a "new" R71-OH + dipodal silane*

| Sample Name | | | 30A | 30B | 30C |
|---|---|---|---|---|---|
| **Description** | | | R71-OH Ctrl | R71-OH + SIB 1820.0 | R71-OH + SIB 1820.0 |
| **Catalyst Added** | | | 1% | 1% | 1% |
| **Dipodal Silane Added** | | | | 2% | 5% |
| **Pot Life** | | | Overnight | Overnight | Overnight |
| **Property** | **Spec** | **Duration** | | | |
| **Solvent Resistance** | No Breakage | 24 hours | F 20 | F 22 | F 25 |
| | | 7 days | F 50 | F 23 | F 42 |
| | | 30 days | P | P | P |
| **Pencil Hardness** | | 24 hours | 4H | 4H | 4H |
| | | 7 days | 4H | 4H | 4H |
| | | 30 days | 4H | 4H | 4H |
| **Koenig Hardness** | Seconds | 24 hours | 37 | 32 | 29 |
| | | 7 days | 83 | 93 | 94 |
| | | 30 days | 117 | 127 | 126 |
| **Fischer Micro-Hardness** | (N/mm2) | 24 hours | 50.35 | 27.03 | 30.77 |
| | | 7 days | 61.4 | 63.9 | 55.65 |
| | | **30 days** | 67.6 | 67.75 | 63.2 |

R71-OH was crosslinked with 1% catalyst and 2% or 5% of bis(triethoxysilyl)octane, the dipodal silane shown in figure 54. The experiment was designed to test if the dipodal silane would assist in the cure process and increase crosslink density since the R71-OH was unable to cure within 24 hours with catalyst. The dipodal silane did not aid in accelerating the cure process within 24 hours, and the coatings did not achieve solvent resistance until 30 days. Each coating showed increased hardness from 24 hours to 30 days, as suggested by Koenig, Fischer micro, and pencil hardness. However, the R71-OH films were not as hard as the PHMS-OH films, and they took longer to produce solvent resistance than the PHMS-OH coatings. The PHMS-OH films did not achieve solvent resistance within 24 hours, but were solvent-resistant by 7 days.

The R71-butoxy polymer is similar to an alkoxy silane (as in Figure 54), which are generally more stable than silanols. Alkoxy silanes are also stable at 100% solids, as opposed to silanols. However, the R71-butoxy was stored at 24% resin solids in alcohol. Silanes are better for crosslinking because the materials are more stable without the presence of solvent and are

compatible with a wider variety of polymers. The objective was to utilize R71-butoxy in a coating formulation to achieve solvent-resistance while maintaining hardness. The results are shown in Table 34.

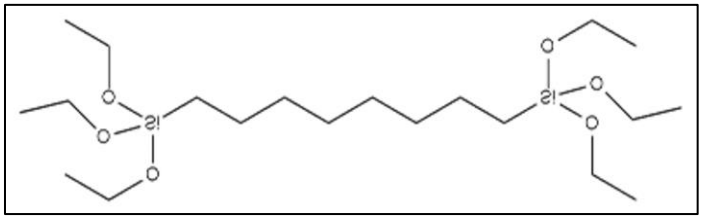


***Figure 54.*** *Dipodal Silane, bis(triethoxysilyl)octane*

***Table 34:*** *R71-butoxy + dipodal silane for increased crosslink density*

| Sample Name | | | 31A | 31B | 31C |
|---|---|---|---|---|---|
| **Description** | | | R71-Butoxy | 2% SIB 1820.0 | 5% SIB 1820.0 |
| **Catalyst Added** | | | 1% | 1% | 1% |
| **Pot Life** | | | Overnight | Overnight | Overnight |
| **Property** | **Spec** | **Duration** | | | |
| **Solvent Resistance** | No Breakage | 24 hours | F 5 | F 6 | P |
| | | 7 days | P | P | P |
| | | 30 days | P | P | P |
| **Pencil Hardness** | | 24 hours | 2H | 2H | H |
| | | 7 days | 6H | 6H | 6H |
| | | 30 days | 4H | 4H | 4H |
| **Koenig Hardness** | Seconds | 24 hours | 26 | 26 | 25 |
| | | 7 days | 89 | 73 | 104 |
| | | 30 days | 118 | 116 | 115 |
| **Fischer Micro-Hardness** | ($N/mm^2$) | 24 hours | 37.00 | 20.13 | 3.03 |
| | | 7 days | 64.3 | 56.6 | 58.4 |
| | | **30 days** | 17.25 | 16.15 | 18.25 |

The R71-butoxy reagent was evaluated with and without the dipodal silane, SIB1820.0, to assist in curing and increase crosslink density. R71-butoxy and 1% pentamethyldiethylene triamine did not cure within 24 hours; however, the film did cure by 7 days. SIB1820.0 was added at 2% and 5% on solid resin content. The coating containing 2% SIB1820.0 did not achieve solvent resistance at 24 hours; however, it was solvent resistant in 7 days. The coating containing 5% SIB1820.0 did pass solvent resistance at 24 hours, indicating the film is cured. The Koenig hardness increased from 24 hours to 30 days, which was an indication of increasing crosslink density; conversely, according to pencil hardness and Fischer micro-hardness, the hardness decreased from 7 to 30 days.

These measurements could be potentially within the margin error of the measurement as there was no change in the Koenig Hardness test. However, it might be that over-curing causes stress in the coatings that later on influence the mechanical integrity of the coatings. Nevertheless, the satisfactory curing results with the all-alkoxy system need to be revisited in any future activities with this system, as it demonstrated performance that is not inferior to the curing of the R71-OH formulations. Unfortunately, by the time of obtaining these results, we had already selected R71-OH as the intermediate for evaluation in the final testing cycles for Tasks 4 and 5.

### Pigmented Formulations

SRI has a lot of very positive experience of using PHMS-OH with a broad range of inorganic oxide pigments and aluminum flakes. For example, in Task 4, we successfully evaluated $TiO_2$, black $Fe_3O_4$, Al flakes, and $Al_2O_3$ particles as pigments.

In addition, the three Si-OH intermediates PPG has evaluated were all also formulated with Chromaflo Plasticolor CF pigment, which is designed for the polysiloxane system. These results are shown in Table 35.

***Table 35:*** *Pigmented PHMS-OH, R71-OH, and R71-butoxy*

| Sample Name | | | 38A | 37B | 38C | 38D | 38E | 38F |
|---|---|---|---|---|---|---|---|---|
| **Description** | | | R71-OH Ctrl | R71-OH 5% 1284.0 | R71-Butoxy Ctrl | R71-Butoxy 5% 1824.0 | PHMS-OH Ctrl | PHMS-OH 5% 1824.0 |
| **Appearance** | | | Wavy | Wavy | Wavy | Wavy | Wrinkled | Wrinkled |
| **DTT** | | | 2 hours | 2 hours | 2 hours | 2 hours | 2 hours | 2hours |
| **Pot Life** | | | Overnight | Overnight | Overnight | Overnight | 5 hours | 5 hours |
| **Notes** | | | All coatings are pigmented with Chromaflo; no 24-hour tests were performed due to not curing in 24 hours | | | | | |
| **Property** | **Spec** | **Time** | | | | | | |
| **Solvent Resistance** | No breakage of coating | 24 h | F 6 | F 2 | F 10 S | P | F 7 | F 22 |
| | | 7 d | F 15 | F 38 | P | P | F 35 | P |
| **Koenig Hardness (seconds)** | --- | 24 h | --- | --- | --- | 21 | --- | --- |
| | | 7 d | 114 | 81 | 112 | 86 | 104 | 75 |
| **Fischer Micro-Indenter ($N/mm^2$)** | --- | 24 | --- | --- | --- | 4.93 | --- | --- |
| | | 7 d | 45.8 | 40.15 | 52.7 | 35.77 | 86.45 | 92.2 |
| **Pencil Hardness** | | 24 h | --- | --- | --- | <4B | --- | --- |
| | | 7 d | B | 2H | HB | 3H | 2B | < 4B |

The experiments discussed above were implemented in clear coats, and this set of tests was designed to investigate the performance of pigmented formulations. Each Si-OH reagent formulation included 1% catalyst and 15% pigment, which was a pigment to binder ratio of approximately 0.55-0.6. Also, there was an offset to each control with 5% SIB1820.0 because earlier work done with the Si-H reagents suggested various pigments will poison the catalyst. However, in this platform, there is no more dependence in the efficacy of the Pt catalyst.

Due to the small volumes of reagents available, composite grinds of pigments were not possible. Based on previous work done at PPG, pigment dispersions prepared by Chromaflo were found to be compatible with silane functional coating systems. For these reasons, the Chromaflo dispersions were used to pigment the silanol and butoxy formulations.

R71-butoxy, with the aid of 5% SIB1820.0, cured within 24 hours; however, the other coatings did not. The R71-butoxy control and PHMS-OH with 5% dipodal silane established solvent resistance by 7 days, indicating cure. Each coating was tested for hardness by Koenig, pencil, and Fischer micro-indenter, and all indicated the films were soft. The pigment did not improve or hinder cure as solvent-resistance results were similar to those for the clear coats. Conversely, the pigments did hinder hardness because their dispersant medium is a polyester, which is apparently incompatible with the Si-OH intermediates.

## TASK 4. SCREENING & DEVELOPMENT OF CANDIDATE FORMULATIONS

### Hydrosilylation System

#### *Work at PPG*

The initial experimentation effort at PPG primarily consisted of testing intermediates, additives, and the catalyst provided by SRI. Each of the raw materials was shipped to PPG overnight in cooled packaging to avoid any possibility of overheating. Once the materials were received, they were blanketed with nitrogen and moved to a chemical storage refrigerator. The materials were brought out as needed, and allowed to come to room temperature before experimentation began.

Each of the coating compositions were prepared based on the stoichiometry of the active sites of the intermediates and total platinum catalyst concentration. The stoichiometry and catalyst level for each experiment is noted in the data tables. “Total platinum concentration” includes the residual platinum reported to be in each of the intermediates from their synthesis plus the catalyst added.

**Procedures.** Procedures for making experimental samples and evaluating them are listed below. Other tests are as described in appropriate sections.

*Making Paint.* Between 7-15 grams of paint were made for each reaction according to the following procedure:

1) The desired amount of part B (ene) was weighed out into a scintillation vial
2) Drops of catalyst solution were slowly added into the vial with part B
3) A wooden stick was used to stir with after catalyst had been added
4) Part A, (Si-H) was weighed out, added to the scintillation vial, and stirred

*Application.* The drawdowns were done with a 5-mil square drawn-down bar over an unpolished 4 x 12 CRS with a zinc phosphate and zirconium pretreatment. The following steps were used:

1) After each paint was prepared, the draw-down bar was placed on top of the substrate
2) 5-mil section came into contact with substrate
3) Two transfer pipettes full of paint were placed on the inside of the square draw-down bar
4) Once paint was on the substrate, inside the square, the bar was pulled to the end of the substrate

*Gel Time.* Each paint was mixed in a scintillation vial, and the observation procedures were as follows:

1) After each paint was drawn down, the remaining paint in the scintillation vial was checked every 5 minutes
2) Observations were made and recorded at each time interval
3) This was done until the paint in the vial had gelled, and the time it gelled was recorded

*Dry to Touch Time.* Draw-down panel was evaluated every 30 minutes.

1) After paint was drawn down, the thin film was checked every 30 minutes for dry time
2) Using a Q-tip, the panel was checked for tackiness and dryness
3) Observations were recorded at each time interval until the Q-tip no longer stuck to the coating

*Solvent Resistance:* STM-0591

1) A Kimberly Clark Professional Wypall X80 towel was saturated with MEK.
2) A soaked towel was rubbed on the panel using hard pressure 100 times for 100 double rubs (down and up is 1 double rub, so down and up 100 times). The passing score was 100 double rubs without coating breakage to the substrate

*Cross-Hatch Adhesion:* ASTM-D3359

1) A cutting ruler of tempered steel with 0.5-mm gradations for individual cuts was placed on the designated area of substrate
2) A sharp cutting tool was used to cut through the substrate in between the small openings of the steel lattice template
3) Once cuts were made, the ruler was moved and placed on top of the newly cut lines and additional cuts were made in the opposite direction to make a lattice
4) After the lattice structure was cut through the coating to the substrate, a piece of 25-mm wide, semitransparent pressure-sensitive tape was placed on top of the lattice
5) About 2 inches of free tape were left hanging off the panel
6) A tongue depressor was rubbed over the tape with pressure, ensuring that the tape was stuck to the lattice
7) Once the tape was secured, the free end was pulled back in the opposite direction (taking care not to pull the tape straight up)
8) If coating stuck to the tape, the process was repeated until no coating was stuck to the tape
9) The percentage of the coating left on the panel was recorded, and the graphical data results were reported in percentages

*Pencil Hardness:* STM-0742

1) A hardness pencil was placed on the thin film at about a 45° angle
2) Pressure was applied to the pencil, and it was pushed upward to draw a straight line
3) If the pencil cut through substrate, a softer pencil that did not cut through to the substrate was used
4) If the pencil did **not** cut through to the substrate, pencil hardness was increased so the first pencil that did not cut through to the substrate was the designated hardness measurement

*Micro Hardness:* ISO 14577-1 and ASTM E 2546

*Nanoindentation Testing* in the Micrometer Range FISCHERSCOPE® HM2000 S

1) The panel was placed coating down on the indenter
2) Three runs were completed
3) Results were averaged

*Koenig Hardness:* ISO 1522, ASTM 4366, DIN 53157, and BS 3900: E8; Koenig & Persoz Hardness Rocker

1) The coated substrate was placed on the stage
2) The rocker was lowered onto the coating
3) The pendulum was pulled back, zeroed, and let go
4) The results were recorded when the oscillations on the electronic counter stopped increasing

Overall, the trends observed at PPG were similar to the ones seen at SRI and Boeing. The work focused on RT curing and systematic study of the coating characteristics as a function of time (measured from 1 to 30 days). Many of the formulations showed an expected trend of improved curing, adhesion, and hardness over 30 days that was similar to what has been found for many low-temperature thermoset systems.

As for the developed hardness, there was not always a correlation between the different techniques; this can be explained by the different modes of damage associated with each of the techniques. PPG's attempts to find an adequate solution for the non-curability of coating over the selected primer have not been successful.

The work at PPG also assessed additional multivinyl compounds including a few in-house synthesized acrylates and polysiloxanes. Several vinyl functional silicone polymers from Siltech® were evaluated as modifiers for the newer higher-molecular-weight polymers. They included Silmer VIN J10 and Silmer VIN C50. The VIN J10 is a multi-functional, high-molecular weight, silicone pre-polymer with reactive vinyl groups. The VIN C50 is a tri-functional, high-molecular weight, silicone pre-polymer with reactive vinyl groups. These materials were added as 50% and 100% of the equivalence of the vinyl functionality. However, these additives have not improved the pot-life stability, curability, or the adhesion of the coatings thus far.

PPG also identified curability issues associated with the aging of R32. Old batches lose their reactivity and require addition of fresh Pt catalyst. This phenomenon has been explained; the residual catalyst is deactivated by the synthesis of the intermediate.

**Performance over Epoxy Primer.** Some tests for depositing formulations over epoxy primers were performed at PPG, using a PPG commercial aerospace epoxy primer, CA 7502. This primer is used over treated aluminum in many aerospace applications. It was noted by SRI that coating formulations utilizing R32 as the vinyl functional component and R71 or R60 as the Si-H

component did not cure when applied over that particular epoxy primer. An experiment was designed to replicate the problem and to evaluate several potential solutions to the problem. The procedure was as follows.

*Substrate preparation:*

- 3 12 x 12 2024 T3 Bare 0.02" x 12" x 12"
- Alcoa lot number: 331858
- Solvent wipe with MEK
- Scuff with Scotch Brite
- Prime with CA7502 40:40:10 by volume as per Product Data Sheet

*Substrates:*

- Electrocoat steel
- 2024 T3 bare aluminum, primed dried at room temperature for 2 hours
- 2024 T3 bare aluminum, primed, sprayed with A-187 solution
- 2024 T3 bare aluminum, primed flash 1 hour at ambient temperature, then baked in oven for 30 minutes at 140°F
- Aluminum Q panel

The topcoat formulation consisted of 1:1, R32 vinyl polymer: R60 Si-H polymer with 35 PPM platinum catalyst.

Coating was mixed, then drawn down with a 5-mil bar. Results are included in Table 36.

***Table 36:*** *Topcoats over epoxy primer.*

| Code | Description | | SiH:Ene | Total Catalyst (ppm) | Drawn-down | Dry to touch time | Gel time | 24-hr Solvent Resistance |
|---|---|---|---|---|---|---|---|---|
| **033A** | R60/R32 | E-coat | 1:1 | 35 | ✓ | 90 min | 1 hr | 30 DR |
| **033B** | R60/R32 | RT dry primer | 1:1 | 35 | ✓ | Did not dry | 1 hr | DNT |
| **033C** | R60/R32 | A-187 spray | 1:1 | 35 | ✓ | Did not dry | 1 hr | DNT |
| **033D** | R60/R32 | 140°F bake | 1:1 | 35 | ✓ | Did not dry | 1 hr | DNT |
| **033E** | R60/R32 | Alum. Q panel | 1:1 | 35 | ✓ | 90 min | 1 hr | 50 DR |

As observed by SRI, the coating did not cure at all over the epoxy primer. In fact, it did not dry at all. We assessed various approaches to prevent the poisoning of the catalyst as summarized below.

1) *Baking the primer prior to topcoat deposition.* No improvement has been observed. Complete curing of the primer actually reduces the adhesion.
2) *Adding more catalyst.* This helped some but significantly reduced the pot life.
3) *Treating the primer surface with a "monolayer" of coupling agents (alkoxysilanes) containing vinyl groups.* We observed promising results, but this added another coating step, which is undesired by the industry (although it is a feasible approach).

4) *Incorporating alternative catalysts in the formulations.* The screening assessment of formulations containing other hydrosilylation catalysts did not yield improved results and was abandoned.
5) *Treating the primer surface with amine blocking compounds.* No assessment was performed with this approach.

***Work at Boeing***

Parallel evaluation was performed at Boeing with the same selected intermediates synthesized at SRI. Boeing evaluated both RT "air curing" and 120°F "forced curing". Boeing specification BSS7225 for adhesion testing was used, which is a variation of the ASTM method used by SRI and PPG. The results were consistent with the observations at SRI and PPG.

Boeing also extended the testing of the compatibility of formulations over primers and polyurethanes. Two primers were selected for the preliminary screening of the compatibility with these coatings: CA 7502 (PPG, non-chrome, epoxy) and JetFlex polyurethane primer from Sherwin Williams. A third chromated primer (BMS10-11 IB) will be assessed in the near future. After a primer was spray-coated, the panels were left to cure for 7 days before the coatings were applied. The draw bar of 2.5-mil (~ 50-µm) film thickness was used. After coating, one panel was left to cure at ambient conditions, and a duplicate panel was force-cured at 50ºC overnight. Early results indicate that the adhesion can be varied based on the formulations and curing conditions. The addition of VTMS increases the adhesion values. More work is currently being performed.

The work at Boeing also includes thermal assessment of the pre- and post-cured formulations using TGA and DSC analyses. The latter provides important information about formulations, processing, and the post-curing glass temperature point. The peak temperature of the hydrosilylation products is analyzed to assess at what temperature the catalytic activity is maximal. This study shows there is an increase of crosslinking reactivity of about 20°C in the catalytic reactivity once a 5-wt% coupling agent is added to formulations. Such a maximum is a shift from ~ 60 to ~ 80°C. The threshold reactivity for the catalytic curing is around RT, indicating curing at this temperature is significantly slow. This technique can guide us in future activities regarding how to balance between the prolonged pot life and adequate curing at low temperature by controlling additives and concentrations of the active catalysts.

**Formulation Studies with Intermediates based on Dehydrocoupling.** Most of the work in Task 4 has already been performed with the dehydrocoupling intermediates, particularly R71-OH and PHMS-OH. Since one of the main drawbacks of the hydrosilylation curing was its lack of adequate adhesion to aircraft primers, the initial work with Si-OH resins attempted to assess the adhesion of such paints over epoxy primers. To allow a quick assessment, we used PHMS-OH as developed at SRI. This system had already demonstrated advantages over the hydrosilylation cured system, yielding adequate pot-life, room temperature curability, and significant hardness after curing was complete; however, it was clear that PHMS-OH by itself was not flexible enough for aircraft topcoat applications.

We have successfully screened a few formulations of PHMS-OH for their characteristics. Table 37 summarizes the results of various PHMS-OH formulations with different fillers that were

***Table 37:*** *Results of coating formulations consisting of PHMS-OH on primed and unprimed substrates*

| Formulations | Compositions | Primed | | Not primed | | Notes |
|---|---|---|---|---|---|---|
| | | 50°C | Room Temp. (days) | 50°C | Room Temp. | |
| **No pigments Thin coat** | PHMS-OH and 0.5% PMDETA | RT overnight + 50°C/4hr: 6H/5B?* | | | | *Thin clear coat – difficult to see on tape for adhesion test |
| **No pigments Thick coat** | PHMS-OH and 0.5% PMDETA | RT overnight + 50°C/4hr: 4H/1B | | | | |
| **Black paint w/ iron oxide 0.5% PMDETA** | 1 kg of 30wt% PHMS-OH in 85% ethanol/15% water (300g solids in 700 ml solvent) + 300 g iron oxide & 0.5% PMDETA | 50°C/3hr: 5H/4-5B | 3 days 6H/4-5B | 50°C/3hr: 5H/4-5B | 3d: 6H/4-5B | |
| **White paint w/ titanium oxide 0.5% PHDETA** | Same ratio as black paint - replaced iron oxide with titanium oxide & 0.5% PMDETA | 50°C/4hr + 19d RT: 6H/1-2B | 19 days 6H/1B | 50°C/4hr + 19d RT: 7H/4-5B | 19d: 2-3H/0B | |
| **White paint w/ titanium oxide 1% PHDETA 1 Coat** | Same ratio as black paint - replaced iron oxide with titanium oxide & 1% PMDETA | 50°C/4hr + 13d RT: 7H (bumpy area 5H)/4-5B | 7H/2B | 50°C/4hr + 13d RT: 7H/4-5B | 7H/4-5B | Gelled quickly Uneven coat |
| **White paint w/ titanium oxide 1% PMDETA 2 Coats** | Same ratio as black paint - replaced iron oxide with titanium oxide & 1% PMDETA | 50°C/4hr + 13d RT: 7H/2-3B | 6H/0-1B | 50°C/4hr + 13d RT: 7H/5B | 6H/4-5B | Gelled quickly. Uneven coat |

| Formulations | Compositions | Primed | | Not primed | | Notes |
|---|---|---|---|---|---|---|
| | | 50°C | Room Temp. (days) | 50°C | Room Temp. | |
| **White paint w/ titanium oxide 0.5% PMDETA Pre-treatment: 1% PMDETA** | Same ratio as black paint - replaced iron oxide with titanium oxide & 0.5% PMDETA | RT overnight + 50°C /4hr: 6H/5B | 1 day 5H/4-5B | RT overnight + 50°C /4hr: 6H/5B | 1d: 5H/5B | Pre-treat plates by spraying 1% PHDETA – wait 2 h before spraying white paint |
| **Metallic gray paint w/aluminum/ alumina (3:1:1) 0.5% PMDETA** | 30 g of 30 wt% PHMS-OH in ethanol (9 g PHMS-OH), 3 g Al flake, 3 g $Al_2O_3$ & 0.5% PMDETA | 50°C/4hr + 3d RT: 6H/5B + 5d RT: 6H/5B | 3 days 2H/5B 5d: 5H/5B | 50°C/4hr + 3d RT: 2H/5B + 5d RT: 2H/5B | 3d: 2H/0B 5d: 2H/0B | |
| **Metallic gray paint w/aluminum/ alumina (1:1:1) 0.5% PMDETA** | 16.67 g of 30 wt% PHMS-OH in ethanol (5 g PHMS-OH), 5 g Al flake, 5 g $Al_2O_3$ & 0.5% PMDETA | 50°C/4hr + 2d RT: 6H/5B | 2 days <H/0B | 50°C/4hr + 3d RT: 6H/5B | 2d: <H/0B | Gritty texture |

deposited on top of PPG's cured primer. The coatings were cured at 50°C. They demonstrated excellent adhesion and hardness values exceeding 5H (some are 7H and above). Adequate fillers include $Fe_3O_4$, $TiO_2$, $Al_2O_3$, Al flakes, and carbon black. An amount of 0.5 to 1.0 wt% of multiamine compound, pentamethyldieethylenetriamine (PMDETA), served as an efficient condensation catalyst that allows curing at room temperature and 50°C.

The white formulations in Table 37 shows topcoats consisting of PHMS-OH pigmented with conventional silica-coated $TiO_2$ (shown in Figure 55) that demonstrated good bonding to the epoxy primer and high hardness. The adhesion to the primer is improved as a function of time (days) when the curing is performed at RT. We noticed that the adhesion was improved if the cured primer was sprayed first with a solution of 1 wt% PMDETA before depositing the PHMS-OH white formulation. The improvement may be due to acceleration of the curing at the surface first or an overall higher curing catalyst during the curing of the topcoat.

There was not much difference between coatings deposited over Alodine aluminum plates or epoxy primer and no significant differences between curing at RT or 50°C. Full adhesion of up to 5B has been seen with PHMS-OH formulations over the epoxy primers. However, in certain cases we obtained unexpectedly low adhesion. We later realized that the deposition of Si-OH-based topcoats were much better adhered and cured if the primer was not completely cured.

***Figure 55.*** *Titania-filled PHMS-OH coatings over chromated Al alloy*

Hardness values up to 6-7H were seen with various formulations. It should be noted that the adhesion and hardness values were related to the formulation of the PHMS-OH, and some of the formulations were found to be inadequate. However, the performance of the coatings over bare metal or a primed surfaces was very similar for each of the formulations and at the same curing conditions. Curing at RT can be adequate even when 0.5% PMDETA is added as the condensation curing catalyst. In other studies (as well as in additional experiments in this project), we have added up to 2 wt% of the condensation catalyst and, in most cases, ("standard") 1 wt% to accelerate and maximize the curability.

***Formulations of R71-OH with SRI's PHMS-OH.*** Soon after the down-selection of R71-OH as the prime Si-OH intermediate, a series of formulations was evaluated in which R71-OH was formulated with and without pigments and was also mixed in various ratios with PHMS-OH. It was initially assumed that R71-OH by itself would be sluggish in its dry time and in full curing. Eventually, it was found that all formulations can be cured at RT very efficiently in the presence of an amine catalyst. The condensation catalyst used in this series was PMDETA, and it was added as 1 wt% compared to the combined resin solid content.

All the initial assessments for formulations containing R71-OH over primers were performed over fully cured primers—until we realized that the performance was much improved if the topcoat was deposited before the primer was highly cured. Coatings over partially cured primers are advantageous for practical reasons because they allow the deposition of the topcoat soon after the deposition of the primer, hence shortening the overall painting duration and allowing the primer and the topcoat to cure together.

Before we realized it was advantageous to coat over semi-cured primer, we tried treating the surface of the primer in order to improve the adhesion of the R71-OH-containing formulations to primed substrates. The deposition of thin films of PMDETA, tetraethoxysilane (TEOS, a precursor to silica), and PHMS-OH did not improve the adhesion. However, a thin film of aminopropyltriethoxysilane (APTES), deposited as 1-wt% solution over the cured primer, has improved the adhesion of the topcoats to the primer. We assume the amine functional group bonds to residual epoxy or carboxylic groups of the primer, and then the hydrolyzed Si-OH groups derived from APTES can interact with the Si-OH of the topcoat formulation. A similar attempt to bond another coupling agent to the primer by depositing an epoxy containing alkoxysilane (glycidoxypropyl trimethylsiloxane, GPTMS) did not provide good results. It took a long time to dry the GPTMS, and it did not dry evenly; sticky/concentrated spots formed on the substrates after a few hours.

This effort was stopped once we realized the Si-OH formulations adhere and cure much better when the primer is not fully cured. We obtained good topcoat adhesion results with primers that were aged for 1 to 6h at room temperature. Aging primers for 2 to 4h before topcoat deposition became the standard technique for any further evaluation.

Table 38 provides a comparison between (a) the original hydrosilylation system, (b) the revised hydrosilylation/dehydrocoupling approach, and (c) use of PHMS-OH by itself. The analysis indicates a very promising approach. Instantaneously, we solved the issues of short pot-life, catalyst poisoning, curability at RT (after adding an amine condensation catalyst), adhesion to substrate and primer coatings, and the inadequate flexibility associated with the hydrosilylation-only approach.

The formulations in the comparative screening consisted of the following R71-OH:PHMS-OH ratios: 1:0, 1:1, 1:3, and 0:1. Cured PHMS-OH itself is highly crosslinked and therefore brittle and may not provide coatings with adequate stretchability and flexibility (associated with bending capability) as required by aircraft topcoat specifications. In addition, the thickness of coatings derived from PHMS-OH by itself is limited due to the stresses generated because of its high crosslinking during curing. However, when PHMS-OH was mixed with the less cross-linkable R71-OH, we enhanced the coating flexibility to levels meeting the MIL specs and achieved thicker coatings to meet aircraft industry practices (while still maintaining adequate hardness and adhesion).

By using R71-OH itself and mixtures of 1:1 and 1:3 weight ratio with PHMS-OH, we have obtained coatings that passed the mandrel bend test performed at Boeing per Boeing's internal specs. The mixture blend allows build-up of coatings thicker than 50 µm per layer. With PHMS-OH itself, we were limited to about 25-µm thick layers due to stress build-up during the curing.

***Table 38:*** *Comparative results of coatings consisting of R71-OH compared with R32/R71 (best hydrosilylation formulation) and PHMS-OH (currently tested for robust automotive coatings).*

| Characteristics | *(R32/R71)* Hydrosilylation | PHMS-OH* Dehydro-coupling/ Condensation | R71-OH/PHMS-OH 1:3 Dehydro-coupling/ Condensation | R71-OH/PHMS-OH 1:1 Dehydro-coupling/ Condensation | R71-OH only Dehydro-coupling/ Condensation |
|---|---|---|---|---|---|
| **Pot Life (h)** | | | | | |
| **Without inhibitor** | 0.1-0.2 | > 4h | > 4h | >> 4h | >> 4h |
| **With inhibitor (h)** | > 4h<br>(leads to sluggish curing at RT and low hardness) | Not needed | Not needed | Not needed | Not needed |
| **Curing** | | | | | |
| **Over chromated aluminum** | Good @RT<br>Very good @50°C | Excellent | Excellent | Excellent | Excellent |
| **Over primer @RT** | Inadequate | N/A | Excellent<br>over uncured primer | Excellent<br>over uncured primer | Excellent<br>over uncured primer |
| **Over primer @50°C** | Low hardness<br>Improved with surface pretreatment and aging of primer | | Excellent<br>over uncured primer | Excellent<br>over uncured primer | Excellent<br>over uncured primer |
| **Hardness (H scale 1-9)** | | | | | |
| **Over chromated Al @RT** | 2-4 | ≥ 7 (least bendable) | 4 (after 24 h)<br>6 (after 1 mo.) | 4 (after 24 h)<br>6 (after 1 mo.) | 4 (after 24 h)<br>6 (after 1 mo.) |
| **Over cured primer** | ≤ 3 @ 50°C<br>≤ 2 @ RT | @ 50°C<br>Thin coat (10-20 µm) – 6H<br>Thick coat (30-40 µm) – 4H | N/A; *Better not to cure primer!* | N/A; *Better not to cure primer!* | N/A; *Better not to cure primer!* |
| **Over uncured primer** | Uncured @RT<br>Sluggish @50°C | N/A | 6 | 5 | 4-5 |

| Characteristics | *(R32/R71)* Hydrosilylation | PHMS-OH* Dehydro-coupling/ Condensation | R71-OH/PHMS-OH 1:3 Dehydro-coupling/ Condensation | R71-OH/PHMS-OH 1:1 Dehydro-coupling/ Condensation | R71-OH only Dehydro-coupling/ Condensation |
|---|---|---|---|---|---|
| **Adhesion (B scale 0-5)** | | | | | |
| **Over chromated Al** | 3-4 | 5 | 5 | 5 | 5 |
| **Over cured primer** | 1-2 | Thin coat (10-20 µm) – 5 Thick coat (30-40 µm) – 1; too much stress | N/A; *Better not to cure primer!* | N/A; *Better not to cure primer!* | N/A; *Better not to cure primer!* |
| **Over cured primer + surface treatment** | 2-3 | 5 | N/A; *Better not to cure primer!* | N/A; *Better not to cure primer!* | N/A; *Better not to cure primer!* |
| **Over uncured primer** | 0-2 | 5 | 5 | 5 | 5 |
| **Mandrel Bending (Boeing test)** | | | | | |
| **Over Al; 10-20 µm** | Very good | Low (too much cross-linking) | Good | Good | Excellent |
| **Skydrol Soaking (Boeing test)** | | | | | |
| **1 month** | Not tested | Not tested | Pass | Pass | Pass |
| **Water Soaking (Boeing test)** | | | | | |
| **1 month** | Not tested | Not tested | Pass | Pass | Pass |

The coatings passed an MEK rubbing test (solvent resistance), and the results of the mandrel bending test indicated higher flexibility of the coatings with R71-OH relative to PHMS-OH alone. All samples passed a 1-month soaking in water without any visual or hardness change. Furthermore, selected coatings passed a 1-month soaking in hydraulic fluid (Skydrol) according to Boeing's internal testing procedures. No visual changes have been detected, and the hardness remained the same or slightly reduced, which is still acceptable by Boeing standards. Skydrol is considered by the Boeing team as the most aggressive solvent-resistance test in the operating environment. Many tested coatings fail to pass this test. It should be noted that the terminal sites of R71-OH are cyclomers with Si-OH on three or four different Si atoms. Since R71-OH is adequately cured at room temperature and yet is stable in solution, this terminal site formation may be useful as curing elements for other organic-siloxane systems. Other commercial products that are based on hydrolysis-condensation curing of alkoxysilanes are reported to be very sluggish to cure at RT.

All the coatings with R71-OH cured well at RT in the presence of 1% organic base catalyst (the only amine-based coating evaluated thus far). Coatings were dry to touch in less than 2h and significant hardness was achieved within 12h. Hardness values > 4H were developed within 24h. Hardness measurements after a few weeks were in the range of 6H to > 8H. Table 39 summarizes the hardness obtained for various mixtures of 1:1 R71-OH with PHMS-OH, deposited by various techniques and coated over primer or bare metal and then cured at RT for one month. Notice that both 0.5- and 1-wt% base catalyst are sufficient for achieving hardness of 6 to 8H.

***Table 39:*** *Pencil hardness values of various coatings containing R71-OH*

| R71-OH:PHMS-OH (ratio) | % Catalyst | Primed? (Y or N) | Method | Pencil Hardness* |
|---|---|---|---|---|
| **1:1** | 0.5% | N | Hand drawn (6 Mils) | 7H |
| **1:1** | 1% | y | Air-sprayed (multiple coats) | 7H |
| **1:1** | 1% | N | Air-sprayed (multiple coats) | 6H |
| **1:3** | 0.5% | N | Hand drawn (6 Mils) | 6H |
| **1:3** | 1% | Y | Air-sprayed (multiple coats) | 8H** |
| **1:0** | 0.5% | N | Hand drawn (6 Mils) | 7H |
| **1:0** | 1% | Y | Air-sprayed (multiple coats) | 8H |
| **1:0** | 1% | N | Air-sprayed (multiple coats) | 7H |

The bonding of the coatings was excellent for both chromated Al and primer epoxy paint, provided that the primer was not fully cured when the new formulations were deposited as topcoats. This observation adds another positive attribute to the new approach, as it is highly desirable to coat “wet” on “wet” (i.e., to deposit the topcoat over the primer without waiting for the curing of the bottom primer layer). This approach dramatically reduces the time the aircraft must occupy the painting space.

## TASK 5. ADAPTATION TO SPECIFIC AIRCRAFT NEEDS & PRACTICES

Boeing's team objectives were to identify application-based performance metrics with respect to topcoat performance specific to the aircraft industry practices within and beyond MIL-PRF-85285. A series of screening tests has been outlined in order to evaluate performance of the resins based on the reagents developed by SRI, in particular R71-OH and combination of R71-OH and PHMS-OH. As agreed between Boeing and SRI, rain erosion tests were not performed because the current formulations are still in the early stages of development and have yet to be optimized.

We conducted three series of tests: the first series was performed according to the Boeing standards, and the last two sets were more systematic and performed per MIL-PRF-85285E or in close proximity to the procedures therein. The following tests have been chosen for the preliminary screening of the resin performance:

6) *Thermo-physical analysis* of the reagents and their combinations (not in specifications).
7) *Flexibility* (impact and low-temperature bend) – this test was chosen because polysiloxanes are well known for their hardness and stability, but are also known to be brittle, which may be a concern.
8) *Fluids resistance* (lubricating oil, hydraulic fluid and jet-fuel) – the fluids-resistance test provides an idea about chemical stability of the paint to the common fluids. Military specification requires shorter test duration at elevated temperature, while Boeing standards require longer exposures at RT.
9) *Pencil hardness and cross-hatch adhesion* are the common tests that allow assessment of the paint hardness and its adhesion to the primer or substrate. Those tests are often required in order to evaluate performance of the paint in the fluids-resistance tests.
10) *Weathering* – Since polysiloxanes are known for their good weathering and UV resistance, we wanted to evaluate resin performance in this test and compare it with the conventional coatings. The weathering test was performed per ASTM D7869. We note the materials assessed in the current tests were the raw reagents, with no (or minimal amount of) fillers/UV-blockers. etc.
11) *Condensing humidity* – this complements the weathering test and allowed us to assess resin potential to withstand moisture.

The objective of testing was to allow a better understanding of paint formulation and/or chemistry modification of the intermediates. Since the project is now completed, the conclusions and the recommendations regarding how to continue the development of this revised system will be executed in another development effort.

### Test Descriptions and Results

#### *Thermophysical Evaluation of R71-OH and R71-OH:PHMS-OH Mixtures*

Three samples were analyzed by DSC and TGA. Samples were scribed from the cured panels provided by SRI, and are described in Table 40. The samples (duplicate specimens) were analyzed using a TA Instruments Q200 MDSC, with a ramp rate of 5ºC per minute and modulation parameters of 0.796º per 60 seconds. The glass transition temperatures (Tgs) calculated on the reversing heat flow curves are summarized in Table 40.

The samples (duplicate specimens) were also analyzed using a TA Instruments Hi Res Q500 TGA, with a ramp rate of 20ºC per minute and high-resolution parameters of 2.0 sensitivity and 4.0º resolution. Weight losses were calculated as a percent by weight of the initial sample weight and degradation temperatures were the peak temperatures observed in the derivative weight loss (%/ºC) curves. Selected results have been summarized in Table 40.

***Table 40:*** *Results of thermophysical analyses of R71-OH and its combinations with PHMS-OH.*

| | MDSC Results | TGA Results |
|---|---|---|
| **Sample Description** | Tg, Onset, ºC (Reversing Heat Flow) | Weight Loss, % to 200C |
| **R71-OH:PHMS-OH ratio = 1:1** | 68.22, 75.28 | 2.337, 2.451 |
| | Average: 72ºC* | Average: 2.4% |
| **R71-OH:PHMS-OH ratio = 1:0** | 55.24, 61.06 | 1.528, 1.874 |
| | Average: 58ºC* | Average: 1.7% |
| **R71-OH:butoxy-PHMS-OH ratio = 1:3** | 55.42, 56.93 | 2.134, 2.432 |
| | Average: 56ºC* | Average: 2.3% |

**Very broad and indistinct Tg without well-defined onset or midpoint temperatures.*

All three samples showed relatively high thermal stability (about 2% weight loss at 200°C and up to 10% weight loss at 425°C), and high Tg values (on the order of 60°C). While mixing PHMS-OH to R71-OH had almost no effect on thermal stability, the Tg of the material increased when PHMS-OH was added to pure R71-OH (Tg jumps from 58°C (sample 4) to 72°C for sample 1). Interestingly, for sample 10 (1:3 ratio of butoxy R71-OH to PHMS-OH), the Tg dropped down to 56°C.

The Tg values for the exterior topcoats that are currently used in commercial airplanes vary from ~ 0°C to ~30°C, with some clearcoats exhibiting higher Tg values (on the order of 40 – 50°C). The high Tg values of the reagents may yield a good hardness; their tendency to form brittle coatings with reduced flexibility at lower temperatures may be mitigated by addition of plasticizers.

***Preliminary tests on R71-OH and R71-OH:PHMS-OH mixtures (per Boeing internal standards)***

Two sets of the samples with varying ratios of PHMS-OH and R71-OH on primed and unprimed surfaces have been initially received by Boeing from SRI. Panels were sprayed on primed and unprimed aluminum 2024 substrates and dried at ambient conditions for at least 14 days. Panels have been tested with a conical mandrel bending test (ASTM D522), pencil hardness (BSS7263) and cross-hatch adhesion (BSS7552, class 5) tests, and have been placed into water for a 7-day wet cross-hatch adhesion test; panels were also placed in hydraulic fluid (Skydrol) for a 30-day fluid-resistance test. Test results are summarized in Table 41.

***Table 41:*** *Results of the preliminary tests on R71-OH and R71-OH:PHMS-OH mixtures (per Boeing internal standards)*

| Panel # | R71-OH:PHMS-OH ratio | % catalyst | Primed? (Y or N) | Method | Pencil hardness | Dry tape adhesion BSS7225, Class 5 | Wet tape adhesion | Skydrol soak Skydrol LD4 | Mandrel bending (per ASTM D522) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1:1 | 1% | N | Air-sprayed (multiple coats) | 2H | 10 | 10 | 2B | FAIL (cracks throughout the panel) |
| 2 | 1:1 | 1% | Y | Air-sprayed (multiple coats) | 7H | 9 | 9 | 4H | FAIL (paint peel off all the way, failure on the interface between primer and metal) |
| 3 | 1:1 | 1% | N | Hand-drawn ("free") | 2H | 10 | 10 | 2H (thick end) 2B (thin end) | |
| 4 | 1:0 | 1% | N | Hand-drawn ("free") | | | | | PASS (no cracks, but seems “soft”) |
| 5 | 1:3 | 1% | N | Hand-drawn (8 mils) | 2H | 10 | 10 | B | |
| 6-1 (thick) | 1:1 with $TiO_2$ | 1% | N | Air-sprayed (multiple coats) | 3H | 8 | 8 | 2B | FAIL |
| 6-2 (Thin) | 1:1 with $TiO_2$ | 1% | N | Air-sprayed (two coats) | | | | | PASS |
| 7 | 1:1 (with $TiO_2$) | 1% | Y | Air-sprayed (multiple coats) | 7H | 9 | 9 | 7H | PASS (small cracks, hard to see) |
| 8 | 1:0 | 1% | N | Hand-drawn (6 mils) | | | | | |
| 9 | 1:1 | 1% | N | Hand-drawn (6 mils) | | | | | |
| 10 | 1:3 (butoxy R71-OH) | 1% | N | Hand-drawn (6 mils) | | | | | PASS (no cracks), but soft |

According to the Boeing exterior decorative finish specification (BMS10-72), acceptable performance in the mandrel bending test is when the applied material shows no cracking, flaking, or loss of adhesion beyond 0.5 in from the 0.125-in diameter end of a conical mandrel. Out of all received samples, samples 4, 6-2, 7, and 10 passed and showed no cracking when bent. Samples 4 and 10 had lower Tg values compared to sample 1, which might explain the more brittle nature of sample 1. The important conclusion is that pure R71-OH seems to be more flexible compared to the mixtures with PHMS-OH. Also, addition of titanium dioxide acts as a plasticizer and improves coating flexibility.

A side note for the conical mandrel bend tests described above is that the primer is not supposed to be applied underneath the topcoat for the standard flexibility test, and the substrate temper should be T0 instead of the T3 we used. Therefore, the mandrel bend test results should only be used for a relative comparison between different combinations.

Overall, samples show a good cross-hatch adhesion performance and high pencil hardness. We have noticed the 1:1 (R-71-OH:PHMS-OH) samples on primer show exceptionally high pencil hardness of 6H – 7H. Wet cross-hatch adhesion results were encouraging, showing no loss of adhesion after the 7-day water soak.

Samples show moderate Skydrol (LD-4) resistance. For the panels on which topcoat was applied over CA 7502 primer, insignificant softening was observed; the unprimed panels, however, showed a more significant softening. No other damage was observed after the 30-day hydraulic fluid test. Even for the panels that showed softening, the final pencil hardness values were within the standard requirements for the conventional polyurethane topcoats.

Preliminary screening tests per Boeing's internal standards showed that the raw resin had a high thermal stability and hardness, good adhesion, and moderate-to-high Skydrol resistance. Such qualities suggest the newly developed reagents have the potential for further development into a topcoat that can be used on commercial aircraft. Since requirements are different for commercial and military applications, the next section will discuss additional testing per military standards.

The set of Figures 56-61 below illustrates the physical performance of the various formulations discussed above.

***Figure 56.*** *Sample #1 after conical mandrel bend. R71-OH:PHMS-OH = 1:1. No primer. Air sprayed – multiple coats.*

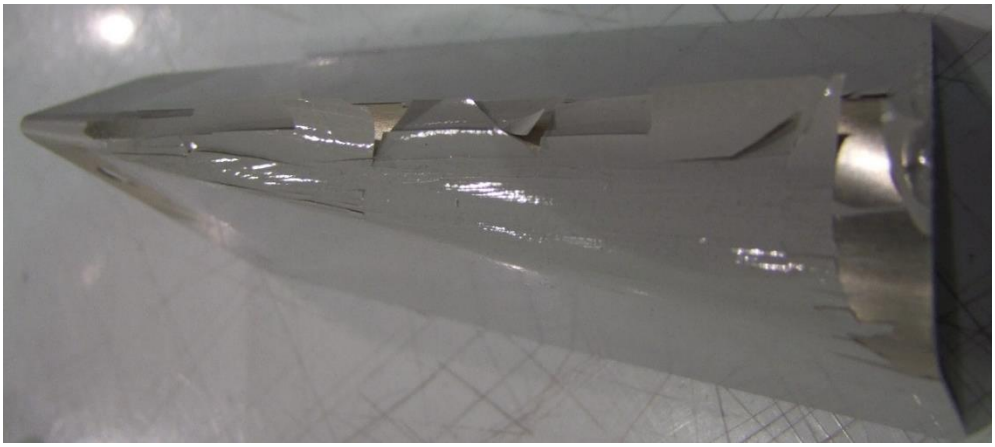


***Figure 57.*** *Sample #2 after conical mandrel bend. R71-OH:PHMS-OH = 1:1 on CA 7502 primer. Air sprayed – multiple coats.*

***Figure 58.*** *Sample #4. R71-OH, no primer. Hand-drawn (free film).*

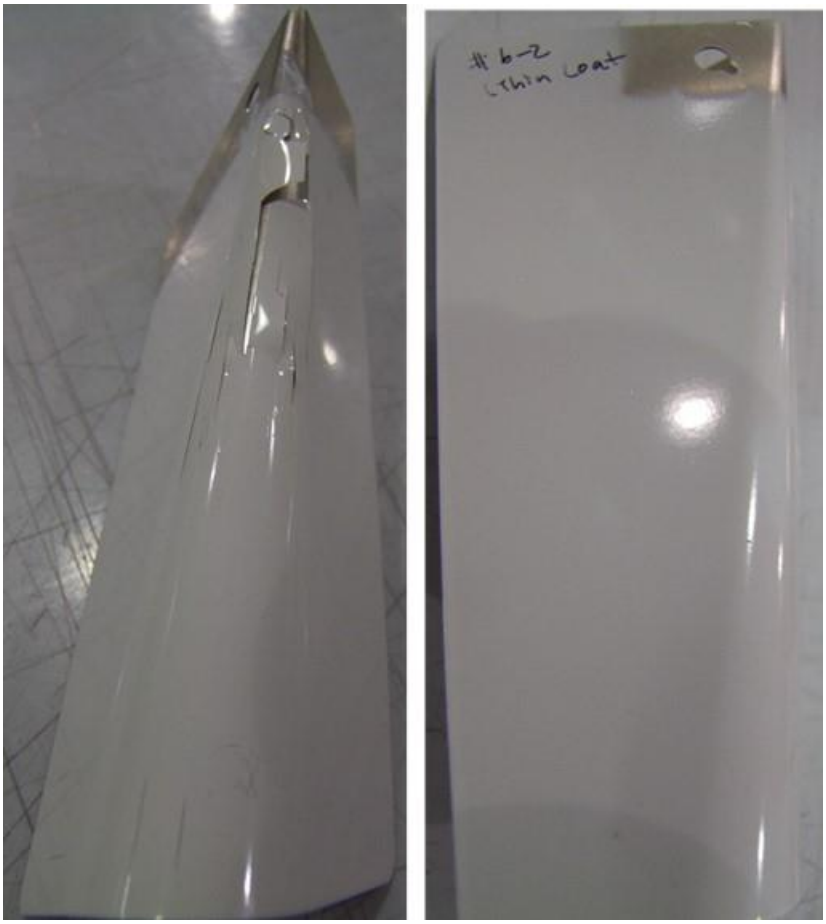



***Figure 59.*** *Sample #6-1 (thick) – left, and #6-2 (thin) – right, after conical mandrel bend. R71-OH:PHMS-OH = 1:1. No primer. Air sprayed.*

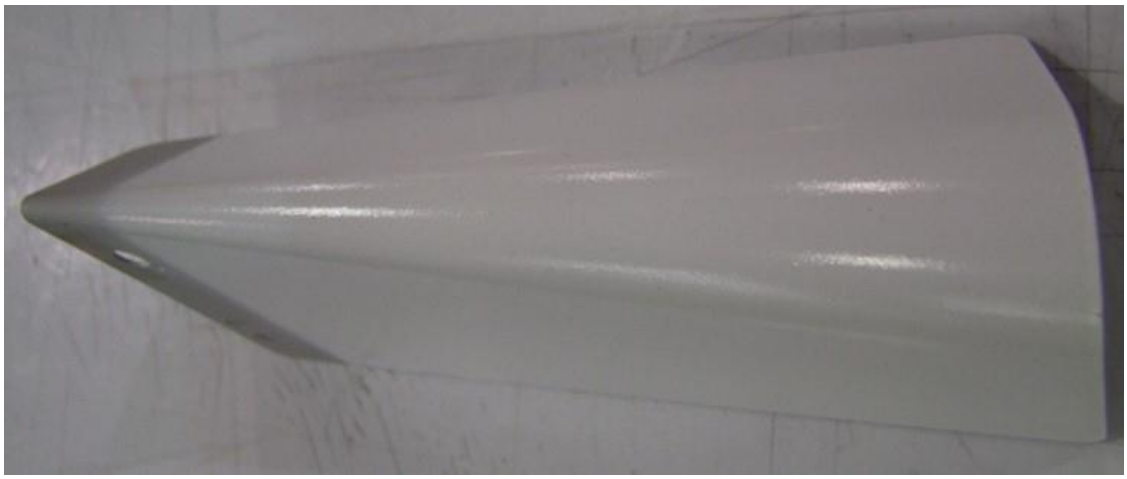


***Figure 60.*** *Sample #7 after conical mandrel bend. R71-OH:PHMS-OH = 1:1, with $TiO_2$. On CA7502 primer. Air sprayed (multiple coats).*

***Figure 61.*** *Sample #10 after conical mandrel bend. R71-OH:PHMS-OH = 3:1. No primer. Hand drawn.*

**Weathering**

Overall, two tests were performed: ASTM D7869 and ASTM G155. ASTM G155 is required by MIL-PRF-85285 and is slightly less intense. The initial assessment with formulations that did not contain a UV blocker and light stabilizer was performed using only ASTM D7869.

The second set of panels, which included a UV blocker and light stabilizer, went into both chambers (ASTM D7869 and ASTM G155). The results from ASTM G155 looked good at 500 hours of exposure, showing no blisters and only slight color change.

Unfortunately, the ASTM D7869 chamber broke several days after the panels were placed in the chamber, and the test could be continued only after the chamber was fixed. The panels stayed in

the chamber with no exposure to anything for an additional 2 weeks. The total exposure to weathering for those panels was 500 kJ (normally achieved in 2 weeks).

The topcoat on the panel with no pigment blistered up and popped out; the primer is not the problem as it remained intact. The reason for this panel's inferior performance is not clear, but it may be associated with bad adhesion between CA 7502 and the topcoat. The white panel (pigmented with $TiO_2$) looked better, but it still had significant color loss compared to the panels in the previous test set (on a yellowish primer).

Overall, it looks like either UV protectors do not improve weathering performance, or something is not working right between CA 7502 and the modified formulation. It is highly possible that the selected UV blocker and/or the light stabilizer are not appropriate for this system.

More details about the weathering tests are provided below.

***Screening tests of R71-OH and R71-OH:PHMS-OH mixtures according to military standards***

In this series of tests, more attention was paid to standard test panel preparation process. Panels were prepared according to the MIL-PRF-85285E specification and treated with the required conversion coating (alodine or anodize) at Boeing and sent to SRI for spray-outs. At SRI, panels were primed and top-coated with either pure R71-OH or mixture of R71-OH and PHMS-OH. A MIL-PRF-23377 Ty 1, Cl N (nonCr) solvent-reducible primer was chosen for testing as CA 7502 is not currently on MIL-PRF-85285 QPL. Duplicate samples were run for each condition. The abbreviations are defined as follows: AR stands for R71-OH; ART stands for R71-OH with addition of titanium dioxide; and AMT stands for the R71-OH:PHMS-OH 1:1 mix with titanium dioxide; R stands for R71-OH on a primed panel; RT stands for R71-OH with addition of titanium dioxide on a primed panel; M stands for R71-OH:PHMS-OH 1:1 mix; and MT stands for R71-OH:PHMS-OH 1:1 mix with titanium dioxide on a primed panel.

Panels were prepared according to the following plan.

Flexibility tests:

- Substrate: Al 2024 bare T0, 4 x 6 x 0.02-in panels, chromic acid anodize
- No primer
- Topcoat was sprayed at SRI; average thickness ranged between ~ 1 mil and 2 mil. A couple panels were sprayed with much thicker coverage (~ 6 mil)
- Required topcoat thickness was 1.7 – 2.3 mil
- Topcoat was allowed to dry for more than 14 days (ambient temperature)

All other tests:

- Substrate: Al 2024 bare T3; alodined with alodine 600, 4 x 6 x 0.04-in panels
- Some additional panels were tested at SRI.
- Primed at SRI (MIL-PRF-23377 Ty 1, CL C2 (SrCrO4) solvent-reducible primer)
- Topcoat sprayed at SRI the next day (some problems with overcoat over primer were observed)
- Target primer thickness was 0.6 – 0.9 mil, topcoat target thickness was 1.7 – 2.3 mil.
- Panels were allowed to cure for more than 14 days (ambient temperature).

The test results are described below.

**1. Impact flexibility test (ASTM D6905)**
An impact flexibility test was performed per ASTM D6905. The impactor was dropped on the panel through the impactor guide, ensuring that the impression of the entire rim of the impactor was made in the panel (Figure 62). The percent elongation corresponding to the largest spherical impression at which no cracking occurs was recorded in Table 42. Microscopy images of the spherical impression for some samples are shown in Figure 63.

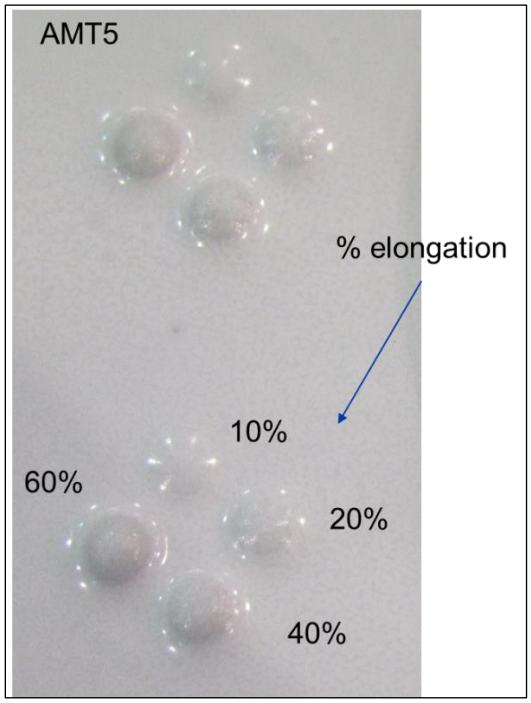



***Figure 62.*** *AMT5 sample after impact flexibility test.*

***Table 42:*** *Results of impact flexibility test*

| Panel number | DFT, mil | Std Deviation, mil | % Elongation, trial 1 | % Elongation, trial 2 | Comments |
|---|---|---|---|---|---|
| AR4 | 5.36 | 0.66 | <10 | <10 | All fail, very brittle |
| AR3 | 2.15 | 0.25 | 10 | 10 | < 10 (if examined at higher magnification) |
| ART1 | 1.15 | 0.19 | 10 | 10 | Looks better than AMT |
| ART2 | 0.93 | 0.18 | 10 | 10 | |
| AMT4 | 1.17 | 0.43 | <10 | <10 | Small cracks at 10% |
| AMT5 | 1.15 | 0.12 | <10 | <10 | |

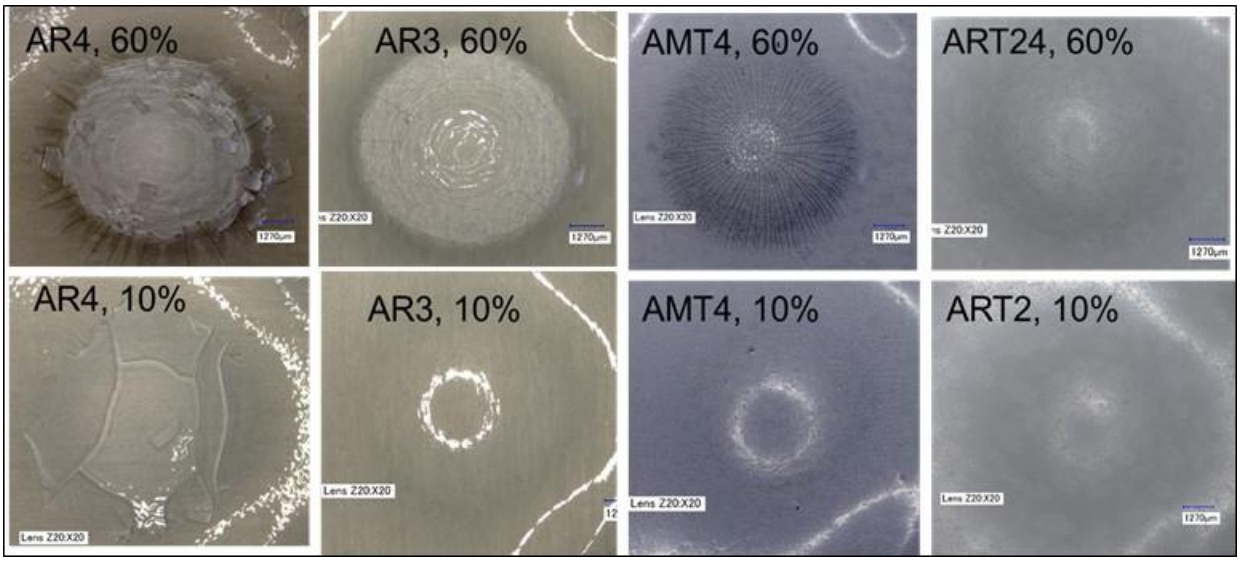



***Figure 63.*** *Microscopy images of 10 and 60% elongation impressions for AR4, AR3, AMT4, and ART2 samples.*

Impact flexibility tests show that pure R71-OH materials were more flexible compared to the mixture of R71-OH and PHMS-OH. Similar to the conclusion from the conical mandrel bend test, these test showed that the addition of titanium dioxide pigment acted as a plasticizer and led to slightly better flexibility. The best test performance of ART (R71-OH with $TiO_2$) was 10% elongation, which was considerably lower than the specification requirement of 40%.

### 2. Low-temperature flexibility (per ASTM D522)

Unlike the commercial specification, military specification requires a mandrel bend at low temperature [1.0-in cylindrical mandrel bend at a temperature of -51 ±3 °C (-60 ±5 °F)]. The test was performed according to the ASTM D522 standard. The mandrel and panels were conditioned for at least 24 h before the bend. Test results are summarized in Table 43 and shown in Figure 64.

***Table 43:*** *Results of cylindrical mandrel bend test.*

| Panel # | DFT, mil | Std | Pencil hardness | Pass / Fail |
|---|---|---|---|---|
| AR5 | 1.83 | 0.22 | 4H | Pass |
| AR2 | 6.31 | 0.58 | 6H | Tested the wrong side of this panel, cracked |
| AR1 | 2.1 | 0.3 | 4H | Pass |
| ART3 | 0.99 | 0.15 | 4H | Pass |
| ART4 | 0.9 | 0.17 | 4H | Pass |
| AMT2 | 0.91 | 0.11 | 6H | Very slight cracking |
| AMT3 | 1.16 | 0.07 | 4H | Very slight cracking |

***Figure 64.*** *Images of panels after cylindrical mandrel bend test.*

### 3. Fluids resistance

Fluids resistance testing was performed by immersing panels in lubricating oil conforming to MIL-PRF-23699, hydraulic fluid conforming to MIL-PRF-83282, and JP-4 fuel. The coating was checked for blistering, softening, or other coating defects (slight staining of the coating is acceptable per specification requirements, and no softening is allowed). Immersion into the turbine fuel for 7 days at room temperature was performed. Lubricating oil immersion was for 24 h at 250°F, and hydraulic fluid immersion was for 24 h at 150°F.

Results of the tests are summarized in Table 44. Most of the samples passed jet fuel soaks, and following hydraulic and oil immersion, there was no substantial softening. However, in all immersion tests at elevated temperatures, severe cracking was observed (Figure 65). This cracking is believed to be the result of inconsistency between primer and topcoat that may be a consequence of incorrect primer application or primer-topcoat interactions that led to fast curing of the topcoat on the interface and stress accumulation. Additional panels were placed in the oven at 120°F for 2 h; after heat exposure, similar cracking was observed. Discoloration of the primer in the oil panels may have been caused by excess amines in the primer, which is also indicative of an error in primer mixing or application.

***Table 44:*** *Fluid immersion test results.*

| Panel | DFT, mil | Std | Pencil Hardness (before fluid immersion) | Pencil hardness (after immersion) | Pass / Fail | Test |
|---|---|---|---|---|---|---|
| RT3 | 4.81 | 0.7 | 2H | 2H | Failed due to cracking *Less cracking of panels | Hydraulic fluid |
| RT12 | 4.79 | 1.01 | 2H | 2H | Failed due to cracking *Less cracking of panels | Hydraulic fluid |
| MT3 | 3.25 | 0.35 | 6H | 4H | Failed due to cracking and softening | Hydraulic fluid |
| MT11 | 4.66 | 0.86 | 2H | 2H | Failed due to cracking | Hydraulic fluid |

| Panel | DFT, mil | Std | Pencil Hardness (before fluid immersion) | Pencil hardness (after immersion) | Pass / Fail | Test |
|---|---|---|---|---|---|---|
| R6 | 3.91 | 0.78 | 2H | 2H | Failed due to cracking | Hydraulic fluid |
| R7 | 4.16 | 1.06 | HB | HB | Failed due to cracking | Hydraulic fluid |
| M5 | 3.36 | 0.41 | 2H | 2H | Failed due to cracking and pitting | Hydraulic fluid |
| M6 | 3.1 | 0.33 | 2H | 2H | Failed due to cracking | Hydraulic fluid |
| R4 | 4.29 | 0.75 | 4H | HB | Failed due to softening | Jet fuel |
| R5 | 3.48 | 0.57 | 4H | 4H | Pass | Jet fuel |
| M3 | 4.15 | 0.45 | 2H | 2H | Pass | Jet fuel |
| M4 | 3.26 | 0.43 | 2H | 2H | Pass | Jet fuel |
| RT4 | 4.3 | 0.9 | 4H | 4H | Pass | Jet fuel |
| RT10 | 4.46 | 0.67 | 4H | 2H | Failed due to softening | Jet fuel |
| MT6 | 4.17 | 0.82 | 4H | 4H | Pass | Jet fuel |
| MT12 | 5.86 | 0.87 | 4H | 4H | Pass | Jet fuel |
| RT1 | 5.69 | 0.8 | 2H | 2H | Failed due to cracking | Lubricating oil |
| RT5 | 3.75 | 0.72 | 2H | 2H | Pass | Lubricating oil |
| MT1 | 4.05 | 0.54 | 4H | 4H | Failed due to cracking | Lubricating oil |
| MT7 | 4 | 0.65 | 8H | 4H | Failed due to cracking and softening | Lubricating oil |
| R2 | 3.66 | 0.46 | HB | HB | Failed due to cracking and staining discoloration | Lubricating oil |
| R3 | 4.34 | 0.55 | HB | HB | Failed due to cracking and staining discoloration | Lubricating oil |
| M1 | 4.59 | 0.4 | 2H | 2H | Failed due to cracking and staining discoloration | Lubricating oil |
| M2 | 3.13 | 0.57 | 2H | 2H | Failed due to cracking and staining discoloration | Lubricating oil |

***Figure 65.*** *Panels after 24 h exposure to lubricating oil.*

### 4. Weathering (ASTM D7869) and condensing humidity tests

Panels were placed into the weathering chamber and exposed according to the scheme described in ASTM D7869. Weathering cycles included a small rise and drop in temperature and cycling between wet and dry cycles and UV-exposure. Within the first two weeks of exposure, the panels showed significant cracking. We believe this was also due to primer/topcoat incompatibility that may have resulted from improper primer processing. Panels that had clear coating over the primer showed significant primer discoloration due to primer decomposition after UV exposure. Panels that had titanium dioxide pigment showed some color change (Table 45) and cracking, but to a lesser extent than clear coats. RT panels showed fewer cracks compared to MT panels (Figure 66).

***Table 45:*** *Results of weathering test (14-d exposure).*

| Panel Number | DFT, mil | 14 days, ΔE | 2 weeks (500 kJ) |
|---|---|---|---|
| MT5 | 3.7 | 1.11 | Cracked all over |
| MT8 | 3.31 | 0.94 | Cracked all over |
| RT2 | 4.01 | 1.13 | Slightly cracked |
| RT6 | 2.9 | 1.13 | Slightly cracked |

In addition, a panel that was prepared for flexibility testing (anodized, no primer, thin clear topcoat) was also placed in the weatherometer. Its appearance was observed for three 2-week cycles during which it reached 1500 kJ of exposure. No cracking or defects were observed at 500 kJ or 1000 kJ, but at 1500 kJ the topcoat blistered and delaminated (Figure 67).

Humidity resistance testing was performed in a condensing humidity cabinet maintained at 49 ±2 °C (120 ±3 °F) and 100 percent relative humidity (RH). After 30 days of exposure, panels showed slight discoloration and cracking similar to that observed in weathered panels.

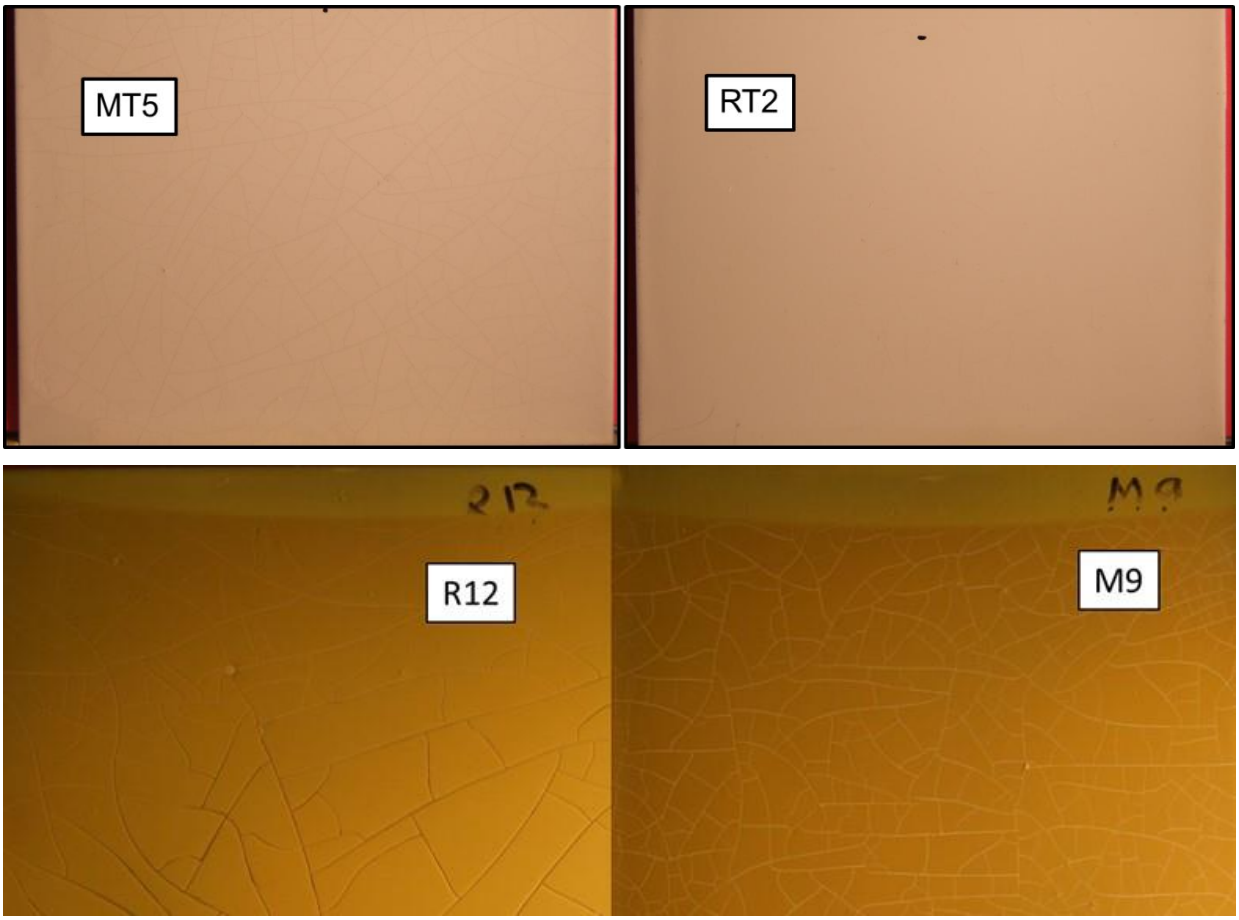



***Figure 66.*** *Panels after 14 days of weathering*

***Figure 67.*** *AR6 panel (R71-OH with 1% catalyst, no primer, anodized panel) after 1500 kJ (6 weeks) exposure*

**5. Adhesion**
Dry cross-hatch adhesion was tested on the panels according to ASTM D3359, method A. Most of the panels showed passing adhesion results except one panel (shown in Figure 68). Cracking of the panels after heating did not affect paint performance in cross-hatch adhesion test.

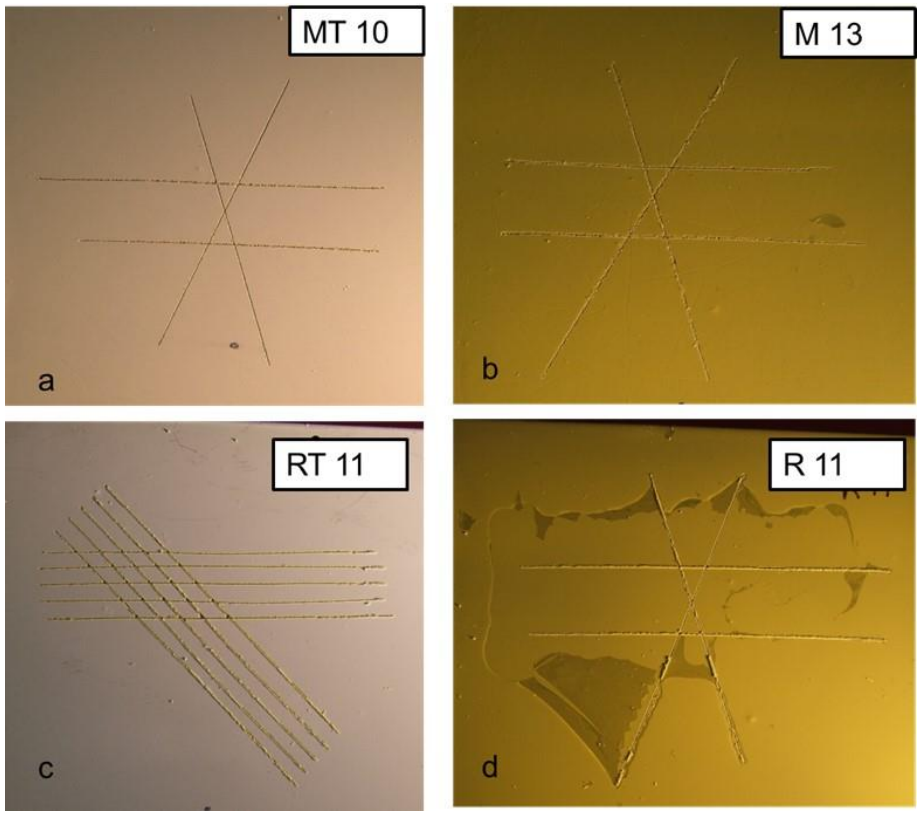



***Figure 68.*** *Cross-hatch adhesion of the pigmented and clear R71-OH and R71-OH:PHMS-OH (1:1) coatings*

**6. Conclusions for the above set of coatings**
As was already established in the previous tests, flexibility of the system might be a challenge. While some R71-OH panels did pass the mandrel bend at low temperature, no samples passed impact flexibility tests. The fact that pigment leads to improvement of flexibility is encouraging because flexibility might be improved by addition of plasticizers. Following the fluids immersion testing, many of the test panels did not exhibit softening or blistering, but some showed incompatibility between the topcoat and applied primer, which led to cracking; these results preclude us from drawing solid conclusions about the testing. Weathering of the transparent coating over primer led to a fast degradation of the primer underneath the topcoat; this may be mitigated in the future by adding pigments and UV blockers to the formulation.

***Screening tests of R71-OH with UV-blockers added to the formulation, over CA 7502 primer***

The next series of tests included fluids sensitivity and weathering of the R71-OH formulated with pigment ($TiO_2$) and UV-stabilizing agents. The paint was applied on the Al2024 T3 bare alodined panels (treated with Alodine 600) over CA 7502 primer (PPG). Panels were alodined at Boeing and sent to SRI overnight for spraying with primer and topcoat. CA 7502 primer is not currently on the MIL-PRF-85285 QPL but is used as a baseline in the commercial airplane production. It has been known to behave well under R71-OH in previous trials at SRI. After spraying, panels were cured for at least 14 days and sent back to Boeing for testing.

### 1. Fluids resistance

Fluids soaks were performed according to the procedures described in MIL-PRF-85285E and in the previous section. Results of the fluids resistance tests are summarized in Table 46. The panels denoted as R71-OH-UV-X (with X representing the panel number) are clear coating over CA 7502 primer (which is grey) while the panels with the letter T in the name (R71-OH-UV-T-X) are the ones with titanium dioxide added to the formulation.

***Table 46:*** *Results of the fluids resistance tests.*

| Panel | Color | DFT, mil | TEST | Pencil hardness before fluid immersion | Pencil hardness after immersion | Comments |
|---|---|---|---|---|---|---|
| R71-OH-UV-1 | Gray | 2.12 | OIL | 4H | 2H | Fail - discoloration and softening |
| R71-OH-UV-10 | Gray | 1.76 | OIL | 4H | HB | Fail - discoloration and softening |
| R71-OH-UV-9 | Gray | 2.61 | OIL | 8H | 4H | Fail - discoloration and softening |
| R71-OH-UV-7 | Gray | 1.9 | JP-4 | 2H | 2B | Fail - softening |
| R71-OH-UV-11 | Gray | 2.19 | JP-4 | 4H | HB | Fail - softening |
| R71-OH-UV-12 | Gray | 2.58 | JP-4 | 2H | 6B | Fail - softening |
| R71-OH-UV-2 | Gray | 2.14 | HYDRAULIC | 4H | 4H | Pass |
| R71-OH-UV-18 | Gray | 1.79 | HYDRAULIC | 4H | 2H | Fail - softening |
| R71-OH-UV-16 | Gray | 2.13 | HYDRAULIC | 8H | 2H | Fail - softening |
| R71-OH-UV-T-1 | White | 1.91 | OIL | 4H | 2H | Fail - softening |
| R71-OH-UV-T-3 | White | 1.84 | OIL | 4H | 2H | Fail - softening |
| R71-OH-UV-T-4 | White | 1.87 | OIL | 4H | HB | Fail - softening |
| R71-OH-UV-T-5 | White | 2.02 | JP-4 | 4H | HB | Fail - softening |
| R71-OH-UV-T-6 | White | 1.95 | JP-4 | 4H | HB | Fail - softening |
| R71-OH-UV-T-7 | White | 2.04 | JP-4 | 4H | HB | Fail - softening |
| R71-OH-UV-T-8 | White | 2.04 | HYDRAULIC | 4H | 4H | Pass |
| R71-OH-UV-T-9 | White | 1.61 | HYDRAULIC | 4H | 4H | Pass |
| R71-OH-UV-T-11 | White | 1.9 | HYDRAULIC | 4H | 4H | Pass |

Unlike the previous set of panels, the panels with CA 7502 primer did not show cracking when heated or soaked in fuels at elevated temperatures. The initial pencil hardness of the finishes ranged from 2H to 8H, which was comparable to the results observed in the previous tests. However, all panels exhibited considerable softening after immersion into jet fuel and lubricating oil. Pigment ($TiO_2$) had a stabilizing action: all pigmented panels passed hydraulic fluid immersion test, while two out of three unpigmented panels showed softening. In other fluids, pigmented panels showed more consistent readings and less significant softening compared to the clear coating. Panels that had no pigment turned pink after 24 h in lubricating oil. The panels with the white pigment stayed white (tinted with pink) after oil immersion, but showed pink primer underneath the coating around the pencil scribe (Figure 69); this may indicate that oil was heavily absorbed by CA 7502 primer.

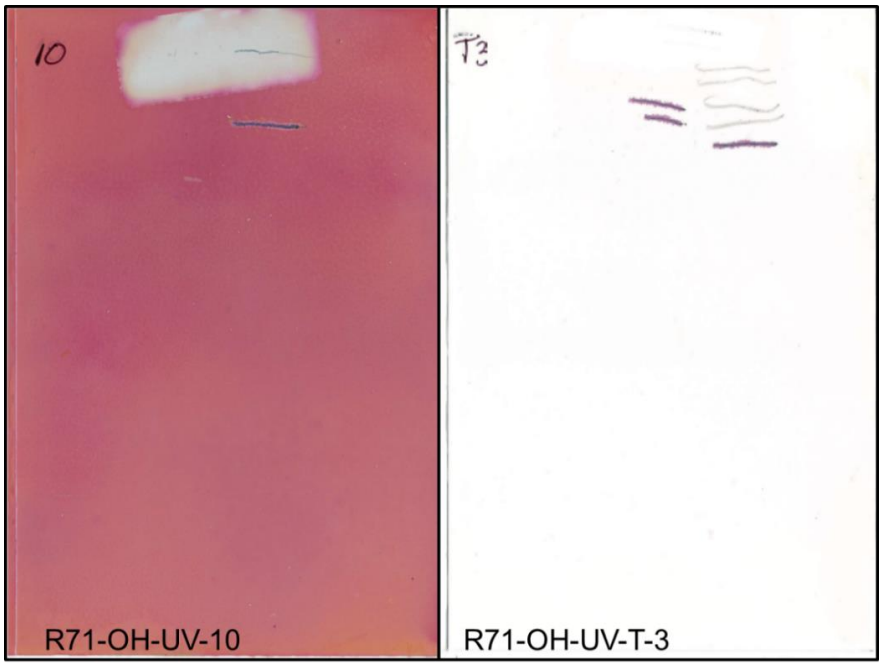



***Figure 69.*** *Scanned Images of the test panels after 24hrs immersion in lubricating oil.*

**2. Adhesion**

Dry cross-hatch adhesion tests performed on the panels showed poor adhesion between primer and topcoat (Figure 70a). Adhesion testing performed after oil immersion testing showed substantial loss of adhesion (Figure 70b), possibly due to swelling of the primer or topcoat. Additional analysis would be desirable to find the cause of adhesion failure in this series of tests and specifically in the oil immersion testing. Overall, the poor adhesion

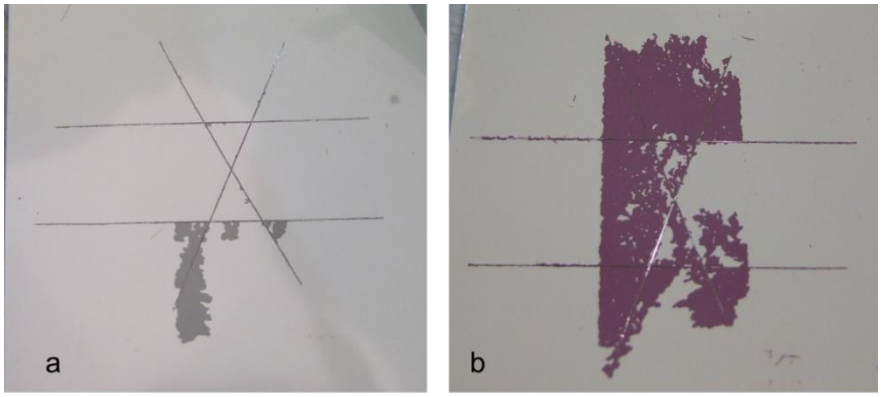



***Figure 70.*** *Tape adhesion test for (a) a pigmented panel before immersion, (b) pigmented panel after immersion into oil.*

of the paint to primer may be caused by incorrect processing (a long overcoat time between primer and topcoat).

### 3. Mandrel bend

The low-temperature mandrel bend test was performed on the primed, alodined panels; this was not per the specified procedure but was supposed to provide a quick control check of flexibility for the last series of reagents. All panels (both pigmented and clear) showed drastic failures that may be the result of interaction between the CA 7502 primer and topcoat that showed some stress during curing. Results of low-temperature mandrel bend are shown in Figure 71. As a result of bending, paint flaked off from the surface, partially with the primer and with alodine, which resulted in a very unique, brush-like appearance. Such behavior was very different from mandrel bend test results performed with no primer but was similar to the severe paint peeling and cracking observed in the conical mandrel bend test for R71-OH and R71-OH:PHMS-OH mixtures when coated on CA 7502 primer. It is most likely that the inferior performance of the coatings in this case is due to the incorporation of the UV blocker or the light stabilizer. We suggest repeating the testing using the same materials with no primer and on anodized substrates and assessing other blockers and stabilizers if work with this system continues.

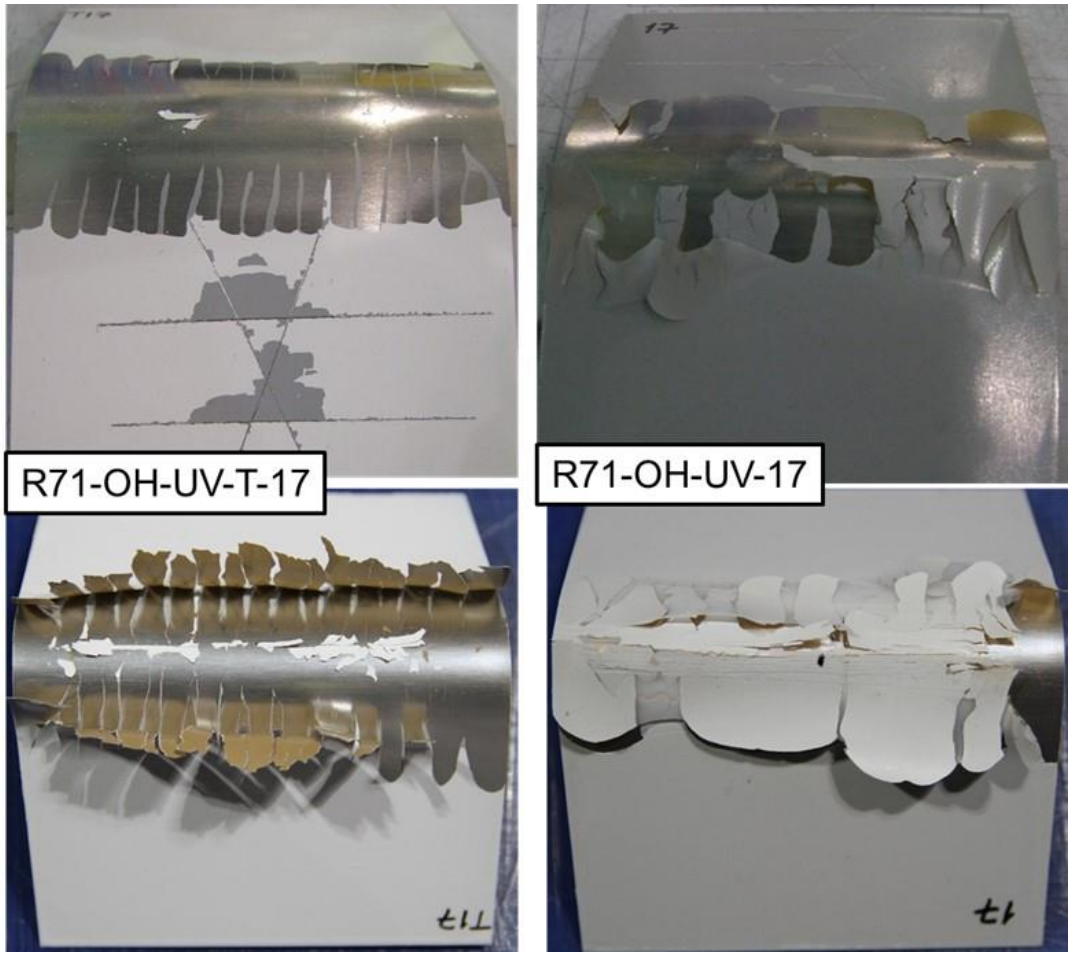



***Figure 71.*** *R71-OH-UV-T-17 and R71-OH-UV-17 panels after low-temperature mandrel bend.*

**4. Weathering**

Panels were placed into a xenon-arc weatherometer and exposed for 500 h according to ASTM G155 standard. After the 500-h exposure, panels were examined for color, gloss, and general appearance. Panels showed no cracking or blistering but exhibited color changes as shown in Figure 72. Panels with the clear coat on top of CA7502 primer showed primer discoloration, which is reflected in higher ΔE values. Pigmented panels have much smaller ΔE values compared to the panels with colorless coating. The weathering test in the current test set was performed according to ASTM G155, while in the previous test set, weathering exposure was performed per ASTM D7869. The 500 h ΔE values of the pigmented panels used in the current test set are comparable to those of the previously tested panels and are slightly above 1, which is not a passing value according to the MIL-PRF-85285E requirements, but is very close to the passing value of ΔE <= 1. The 60º gloss measured for the unpigmented and pigmented panels was about 40 specular units and did not change with weathering exposure. Compared to the first test series, the second set (with UV blockers) had better gloss readings (40 gloss units vs 20-25 gloss units for the first test set). Gloss seemed to be less affected by weathering in the second test set.

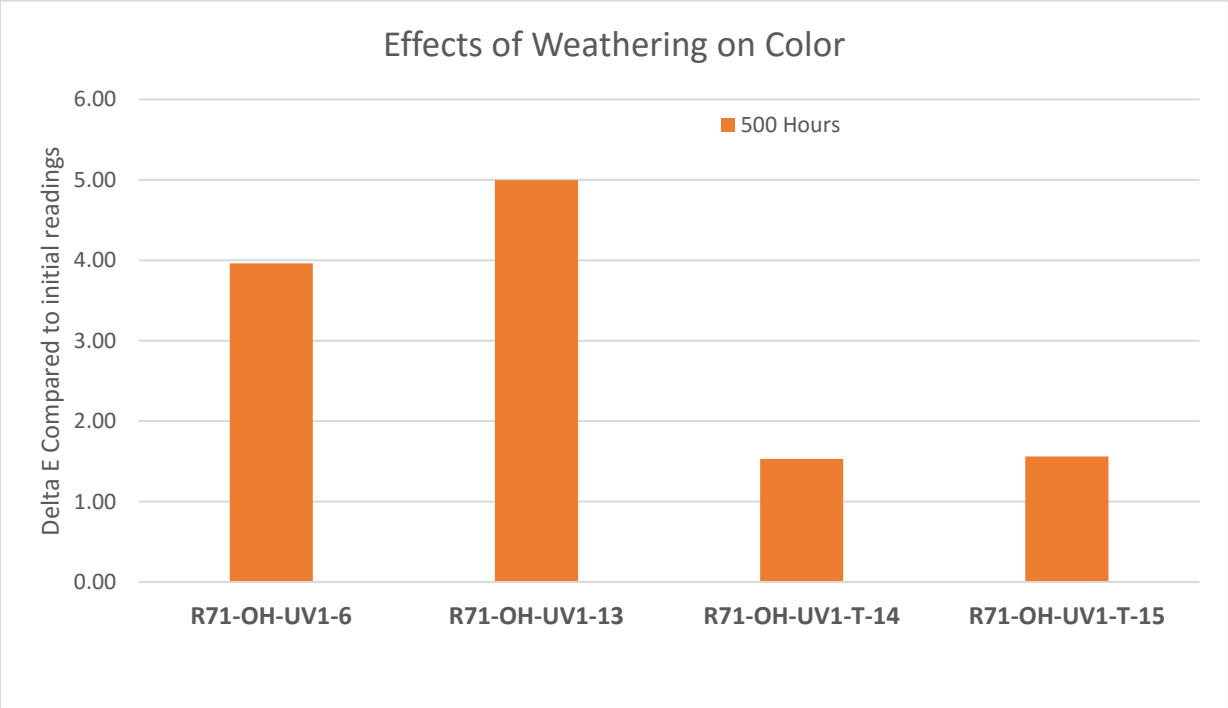



***Figure 72.*** *Effect of weathering on color. ΔE values of the panels exposed to weathering for 500 h per ASTM G155. ΔE values are calculated as a difference between 500-h values and initial average color values measured before weathering exposure.*

### 5. Humidity resistance

Panels were exposed to condensing humidity at 120 °F and 100% RH for 31 days. Two out of three gray panels (R71-OH-UV-15 and R71-OH-UV-8) showed cracking (Figure 73). The pigmented panels showed no cracking or other visual defects.

***Figure 73.*** *Panel R71-OH-UV-15 after 21 days in condensing humidity chamber.*

### 6. Conclusions

Several series of tests were performed in order to evaluate properties of R71-OH-based systems with different additives (PHMS-OH and UV blockers, with and without pigment and on different primers). Tests were performed according to Boeing internal standards and according to MIL-PRF-85285E. Some tests were performed as a check of properties and not per standard practices (e.g., the mandrel bend when paint was applied over the alodined panel and over the primer).

Despite of the addition of UV blockers, the results from this test series were unfortunately inferior to those of the previous series. In fact, it seems that the UV blockers were responsible for inferior coating characteristics and may have been reacted with the cured formulation. The peeling and the pink color (not observed before) are evidence for chemical reactivities with the UV blocker and light absorber. In future studies, other UV reagents should be identified and assessed as weathering aids.

R71-OH-based coatings have high thermal stabilities and hardness and are fairly resistant to jet-fuel and hydraulic fluid. However, without specific additives, the preliminary systems are brittle in nature and show a tendency to crack because of low flexibility (specifically impact flexibility). Interaction of the R71-OH based materials with the standard epoxy primers should be investigated in more details, as some tests indicate there are stresses on the interface between the primer and topcoat that may lead to thermal cracking. Loss of adhesion was occasionally observed between primer and topcoat. Formulations with pigment added to the base material showed better fluids resistance, flexibility, and weathering resistance compared to the clear coatings. More work should be done to find functional additives that will help mitigate current problems in the performance of the materials.

## TASK 6. TECHNOLOGY TRANSFER PLANNING

Although we have reached the end of the project, we do not yet have formulations ready for technology transfer. There are many other intermediate options that were not explored once the project shifted to studying the Si-OH curing system. We studied one intermediate extensively, and it has passed many of the required military and Boeing specifications. It was practical to formulate and use in topcoat operations and is suitable for ambient temperature curing. Its main shortcomings are in bending, impact, and weathering stability; however, it showed significant improvements in overall performance and these specific issues should be improved as a result of the organic and siloxane chains connecting the two Si-OH containing rings. Adequate UV inhibitors and light stabilizers have not been researched in-depth at this point.

Additional development will be required before large-scale field tests can be conducted by the military and the technology can be transferred to a potential paint producer. We will try to continue the work via other government or commercial funding. Similarly, we plan to assess the hybrid formulations developed by the original approach of hydrosilylation curing as an intriguing approach for making membranes for efficient chemical separations at industrial scale. This may result in efficient and energy-saving techniques for separating petrochemicals, especially those used for mass production of plastics.

Another potential market for the chemistry developed with the Si-OH curing is the use of the evolved functional Si-OH cyclomer groups in the fields of coupling and surface modifications. The unique multi Si-OH cyclomeric group, utilized for R71-OH curing and adhesion, is different than the traditional R-Si(alkoxy)$_3$ reagents that dominate these markets. Traditionally, all the Si-OH groups are on the same silicon atom, making it harder to react beyond the first Si-OH. After the condensation reaction of the first Si-OH in the Si(alkoxy)$_3$ unit, the steric hindrance increases significantly. In contrast, the new group possesses single Si-OH groups only, each on a separate silicon atom. We plan to explore the opportunities for the new coupling group.

We have surveyed the availability and potential cost of all the reagents involved in the formation of R-71-OH as an intermediate representative that can be scaled up. Some of the gathered cost numbers require additional assumptions for large-scale pricing as they are rarely used at present and are therefore expensive. We estimate their cost is at least an order of magnitude higher than if produced at the significantly larger quantity that would be required for a commercial scale of the evolved topcoat system.

Table 47 summarizes the early-stage assessment for the cost of producing R71-OH as a representative intermediate for the developed Si-OH system. The table takes into account the following:

(1) Current prices of the reagents as found in lab research catalogs (like Sigma-Aldrich or Gelest);

(2) Identified sources for current bulk productions of the reagents (most of the lowest prices are from China);

**(3)** The assumption that even current “bulk” production of the main reagents, tetramethyl-cyclotetrasiloxane and bisvinyloxy-cyclohexane, is very expensive due to lack of market and very small demand. As such, we have made some assumptions based on analog products.

***Table 47: Price estimates for R71-OH***

| Reaction Compound *[CAS #]* | Lab Supplier | Price ($/Kg) | Bulk Supplier | Price ($/Kg) | Equivalent compound sold in bulk *[CAS #]* | Bulk Supplier | Price ($/Kg) | Estimated bulk Price per Kg of R71-OH ($/) *[% in product]* |
|---|---|---|---|---|---|---|---|---|
| **Methylhydro cyclosiloxanes (n=3-5; mostly 4)** *[68037-53-6]* | Gelest | 336 | Gelest | 48.5 | Poly methyhydrosiloxane *[63148-57-2]* | Gelest | 8.75 | 6.56 (75 wt%) |
| **1,4, divinyl cyclohexane-dimethanol, ether** *[17351-75-6]* | Aldrich | 700 | BASF (solely?) | No response | 1,3-Bis (isocyanatomethyl) cyclohexane *[10347-54-3]* | Career Henan Chemical | 4.30 | 1.08 (25 wt%) |
| **Pt divinyl tetramethyl-disiloxane (2% solution)** *[68478-92-2]* | Gelest | 5600/L | J&H Chemical Co., LTD | 1350 | NA | NA | NA | 1.4* |
| **Triruthenium dodeca-carbonyl** *[15243-33-1]* | Aldrich | 50,000 | Alfa Aesar | 8,750 | NA | NA | NA | 0.9* |

**Can be recovered by sorbing techniques.*

Based on this table the reagents that constitute 1 kg of solid intermediates such as R71-OH will cost ~ $10. The cost of solid polymer (after synthesis) will be in the range of $15-20/kg, and we assume 1 to 2 kg of solid polymer are needed for 1 gallon of topcoat paint. Current aircraft urethane-based topcoats retail for $200-300 per gallon. Hence, the overall cost of the new platform compositions is well in the range of currently available commercial topcoats for aircraft applications.

## TASK 7. MANAGEMENT AND REPORTING

This was a 3-year project with each year constituting a development phase as discussed below. Table 48 illustrates the 3-year project divided by phases (years) and quarters. Milestones included submission of selected formulations and duration of testing, as well as all reporting requirements according to SERDP's practices.

***Table 48:*** *Project schedule and milestones*

| Tasks | GFY 13 (Phase I) | | | | GFY 14 (Phase II) | | | | GFY 15 (Phase III) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 |
| 1. Synthesis and Modification of Building Blocks and Intermediates. | | | | | | | | | | | | |
| 2. Curing and Structure-to-Property Assessment. | | | | | | | | | | | | |
| 3. Initial Topcoat Formulations and Screening. | | | | | | | | | | | | |
| 4. Screening and Development of Candidate Formulations. | | | | | | | | | | | | |
| 5. Adaptation to Specific Aircraft Needs and Practices. | | | | | | | | | | | | |
| 6. Technology Transfer Planning. | | | | | | | | | | | | |
| 7. Management and Reporting | | | | | | | | | | | | |
| • Fact Sheet | | | | ✱ | | | | ✱ | | | | ✱ |
| • Execution Plan | | | | ✱ | | | | ✱ | | | | |
| • Quarterly Progress Report | | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | |
| • Monthly Financial Report | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | ✱ | |
| • Final Technical Report | | | | | | | | | | | | ✱ |
| • SERDP Limited Scope Report | | | | | | | | | | | | ✱ |
| • In-Progress Review | | | | ✱ | | | | ✱ | | | | |
| • End-of-Project Briefing | | | | | | | | | | | | ✱ |

***Phase I.*** The first year focused on the chemical aspects of the developed platform. Chemical reactivities and curability of the hydrosilylation reactions at ambient and mildly elevated temperatures were analyzed. The basic catalyst system for synthesizing intermediates was developed. A few iterations of formulations have already been performed, and critical issues concerning the new paint platform and it potential practicing have been identified.

***Phase II.*** In the second year we developed and assessed improved clear formulations. In this phase, we altered the formulation and catalyst system to meet processing and MIL specifications. We began long-term bench testing, accelerated testing of the advanced formulations, and assessed the effects of pigment and additional additives on topcoat performance. Due to potential shortcomings, we began to assess a revised platform based on a curing Si-OH condensation reaction to replace the originally proposed hydrosilylation curing.

***Phase III.*** We completely shifted focus to the revised Si-OH condensation platform, which demonstrated superior characteristics and performance over the original curing concepts. We overcame all the shortcomings associated with hydrosilylation curing. We could not optimize the formulations since we had only a very short time to evaluate many potential intermediates before down-selecting and shifting the emphasis toward scale-up, formulation, and testing of coatings on the down-selected intermediate. The coatings passed many of the MIL specification tests, but there is plenty of room for improvements in the future.

# CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH/IMPLEMENTATION

## CONCLUSIONS

The original approach of making a new platform for aircraft topcoats via hydrosilylation reactions was not entirely successful. Although synthesis of tens of appropriate intermediates was simple and extremely effective (and hundreds of more candidates are feasible), the use of the hydrosilylation reaction during paint formulations and curing was problematic, especially for ambient temperature curing. We discuss the shortcomings below.

We encountered numerous challenges once we formulated intermediate couples in paint formulations and attempted to bond and cure them on various surfaces. When the paint formulations contained amine-based components or were deposited over amine-containing primer coatings, e.g., epoxy or polyurethane, the catalysts became super-reactive once we mixed "Part A" and "Part B" and were readily "poisoned," which stopped the hydrosilylation reaction and resulted in a number of challenges:

- Very short pot life of hydrosilylation after mixing Part A with Part B (pot life from 1 min to 1 h, but > 4 h duration is desired);
- Thermal take-off of Part A + Part B formulations once we increased their volume (due to the exothermic and very rapid hydrosilylation combined with slow release of the heat);
- Full curing at room temperature was sluggish, and it was necessary to raise the temperature to 50°C for most formulations;
- Adhesion of the formulation to substrates coated with primers was less than adequate unless a surface pretreatment was applied (adding an extra painting step);
- Adhesion to aluminum alloy was adequate for the best formulations but did not reach the maximum values according to the ASTM.

Although we found partial solutions for these problems, they were not very elegant and required additional steps and expense. Also, the hardness and the adhesion of this system were at the low end of what is acceptable for topcoat applications.

Nevertheless, intermediates synthesized by the hydrosilylation reactions were good candidates for the synthesis of selective membranes, considering the various functional groups that can be incorporated to provide selective affinity to organic chemicals. Some of the Si-H intermediates were also good candidates for synthesis of the Si-OH intermediates via dehydrocoupling reactions. We would like to assess these intermediates further, because we believe they are excellent candidates for gas separation of organic compounds when tailored-affinity membranes are used.

The switch in the third year of the project toward a modified platform based on hydrosilylation-dehydrocoupling reactions was found to be much more attractive; however, more development is needed to achieve optimal formulations. The hydrosilylation-deydrocoupling intermediates are good candidates for further R&D activities focusing on topcoats for aircraft and non-aircraft applications. Indeed, all the problems mentioned above and, in addition, adhesion and hardness have been improved. We demonstrated topcoat formulations with the maximum level of

adhesion (ASTM methods) and pencil hardness of 5H to 6H. This was 2 or 3 hardness units above those of the best hydrosilylation-only coatings. These higher values can be achieved even when the curing is performed at ambient temperature.

The benefits of the proposed hydrosilylation-dehydrocoupling system are its versatile intermediate synthesis capabilities, the chemical stability of the derived coatings, and the fact that there are many commercially available reagents that are suitable candidates for intermediate synthesis via this route.

Given the very low levels of transition-metal catalysts, the overall cost of the formulations will be similar or lower than the currently produced polyurethanes used as aircraft topcoats.

## IMPLICATIONS AND IMPLEMENTATION

The improved platform was studied only in the last year of the project. A very limited number of intermediates were synthesized and tested. Only one down-selected intermediate was deemed appropriate for a complete set of testing according to the military specifications defined in MIL-PRF-85285E. This intermediate has passed many of the requirements of the MIL specs but still lacks adequate bending and impact resistance (though it is close to meeting the standards). Appropriate weathering additives and fillers will still require a developmental phase of research.

It should be noted that the terminal sites of R71-OH are cyclomers with Si-OH on three or four different Si atoms. Since R71-OH is adequately cured at room temperature and yet is stable in solution, it may be useful in curing elements for other organic-siloxane systems. Other commercial products that are based on hydrolysis-condensation curing of alkoxysilanes are reported to perform very sluggishly at RT. The Si-OH ring strategy can be also used for forming surface modifiers that bond strongly to substrates. Hence, they may be used instead of R'-Si-$OR_3$ reagents, and we would anticipate better bonding to metals, glasses, and ceramics.

## RECOMMENDATIONS

In order to optimize the intermediates, formulations, and coating processes, this coating system will require one or two more years of development before it reaches a technology transfer stage. The additional R&D will further optimize the intermediates and their formulations and allow technology transfer at a pilot stage so that long-term field testing can be completed.

Such effort should include an intensive effort of synthesizing and screening other novel intermediates before down-selection of the best two to three candidates for testing according to the MIL specs and other vigorous tests such as rain-erosion evaluations, which can be performed at Boeing facilities. We estimate the synthesis of up to 10 additional intermediates (Task 1) based on hydrosilylation procedures established in this project and dehydrocoupling procedures established in other programs at SRI. The additional synthesis/screening activity will further ensure the transfer of optimized formulations for military applications.

We recommend a systematic curing study with a range of optional catalysts (Task 2).

We also recommend severaliterations of formulation screening (Task 3) with each of the additional intermediates.

We recommend an extension of Task 4 from limited evaluation of R71-OH to a full evaluation of three down-selected intermediates (including R71-OH). Modifications of intermediates such as R71-OH by exchanging some of the Si-OH groups with Si-OR (alkoxy groups) should also be assessed. This will extend the shelf-life of the final formulations (prior to adding the curing catalyst) even in field conditions and allow us to reduce the solvent content. In this task, we would also evaluate the capability of the down-selected formulations to adhere and cure well over a series of commercial primers and polyurethanes. The coatings over polyurethanes will repair damage to existing coatings that contain polyurethane as the original topcoat.

We recommend extension of Task 5 using the three most successful formulations and down-select the final formulation. In this effort, we would also assess the issue of reducing solvents (alcohols) or replacing VOC solvents with ones exempted from the VOC list. Hence, we would make sure that the coatings meet current and future environmental and hazard regulations.

Finally, we recommend that one of the formulations be selected for scale-up and technology-transfer activities and documentation (Task 6). We would assess elements for cost reduction, if necessary, based on cost analysis of the final formulation candidate.

Overall, this recommended extended effort would result in an optimized topcoat system that is fully evaluated, and it would extend the technology beyond use in aircraft topcoats and provide solutions for other military applications. It may also yield information about the use of the system as a primer, which could result in a combined primer-topcoat coating system.

The chemistry developed in this project will be transferable for use in other commercial paint systems cured by hydrolysis-condensation of alkoxysilane sites and may improve sluggish curability at RT.

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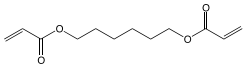
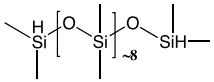
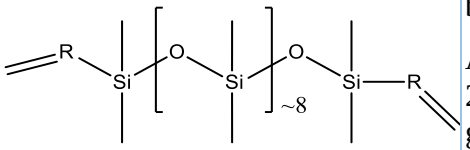
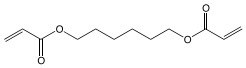
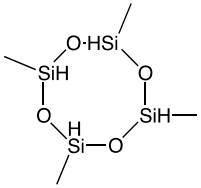
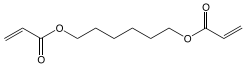
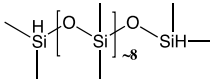
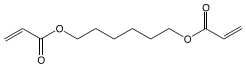
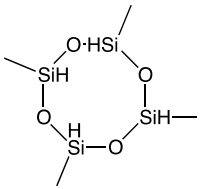
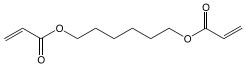
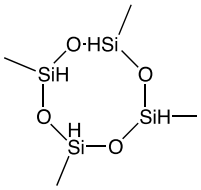
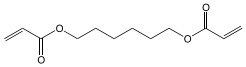
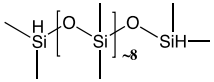
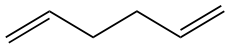
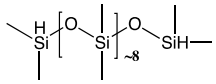
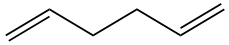
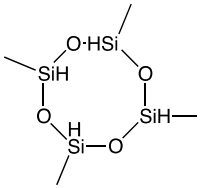
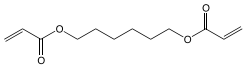
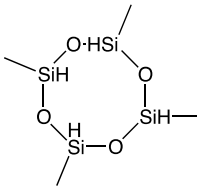
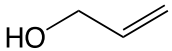
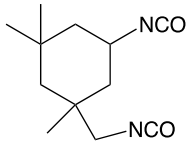
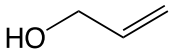
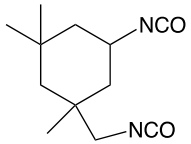
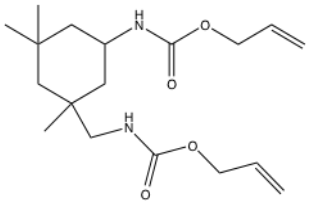
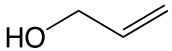
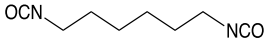
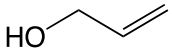
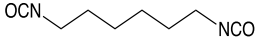
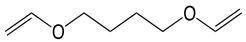
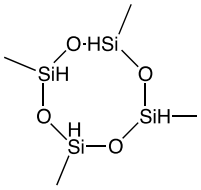
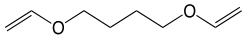
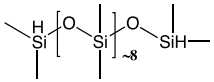
# APPENDIX A: SUPPORTING DATA

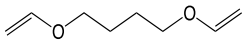
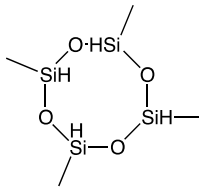
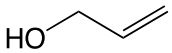
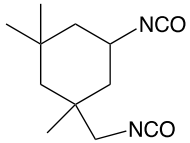
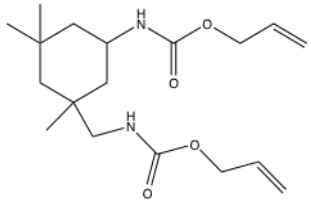
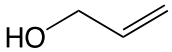
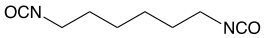
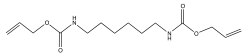
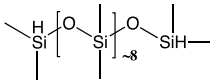
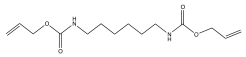
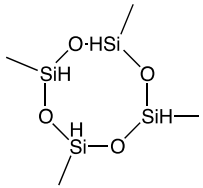
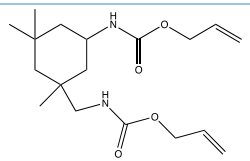
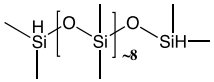
## A.1 SYNTHESIS OF INTERMEDIATES VIA HYDROSILYLATION REACTIONS

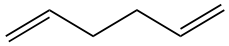
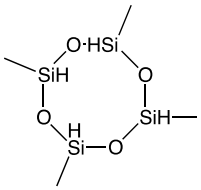
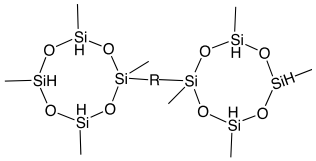
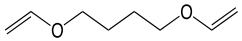
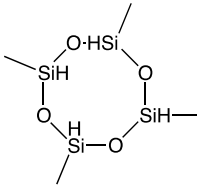
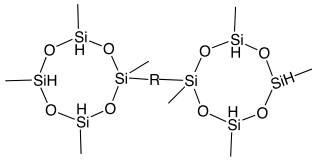
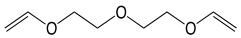
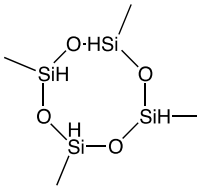
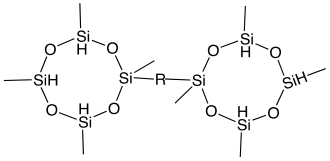
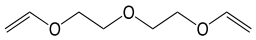
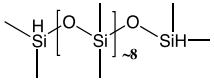
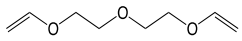
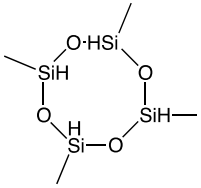
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R1 |  R<br>MW:226.3 |  MW:400-500 | 1:1 ene: SiH<br>30°C Neat<br>50ppm Pt Cat<br>@ 21.5 hrs 50ppm Pt Cat added |  | FTIR @ 21 hrs indicates new band in carbonyl @ 1685 $cm^{-1}$.<br>Added another 50ppm Cat @ 21.5 hrs and 15 min later gelled.<br>FTIR of Gel indicates Si-H visible and ene is not. |
| R2 |  |  | 1:1 ene: SiH<br>30°C Neat<br>50ppm Pt Cat | POLYMER | FTIR at 21.5 hrs indicates NO reaction, another 50ppm added, flask broken and reaction lost. |
| R3 |  |  | 1:1 ene: SiH<br>30°C Neat<br>75ppm | POLYMER | FTIR: @3hrs 1685 $cm^{-1}$. Observed<br>reaction gelled @ 3.5 hrs.<br>Gel FTIR similar to rxn 2, BUT more Si-H observed, no ene observed. |

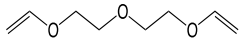
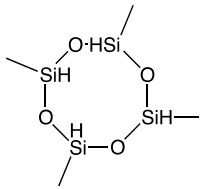
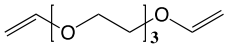
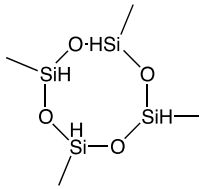
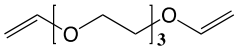
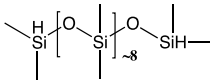
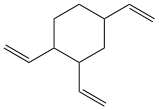
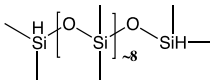
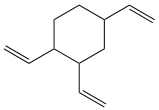
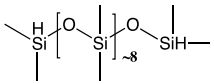
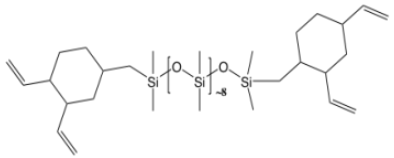
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R4 |  |  | 1:1 ene: SiH<br>30°C Neat<br>100ppm Pt Cat | POLYMER | @ 21 hrs additional 50ppm Pt Cat<br>@ 44 hrs additional 50ppm Pt Cat gelled ? minutes later<br>FTIR: No Rxn @ 20 hrs, @ 45 hrs 1685 $cm^{-1}$ is significant.<br>FTIR of Gel indicates Si-H and ene still present. |
| R5 |  |  | 1:1 ene: SiH<br>30°C Neat<br>100ppm Pt Cat<br>100ul Acetic Acid | POLYMER | FTIR indicated at 3 days reaction was proceeding.<br>Glass stopper stuck, reaction lost. |
| R6 |  |  | 1:1 ene: SiH<br>30°C Neat<br>50ppm Pt Cat<br>100ul Acetic Acid | POLYMER | FTIR @ 9 and 24 hrs indicates new and increasing intensity band in carbonyl @ 1685 $cm^{-1}$.<br>Reaction continued. |

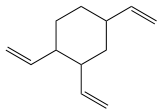
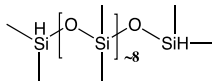
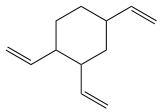
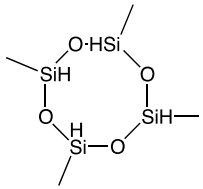
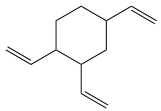
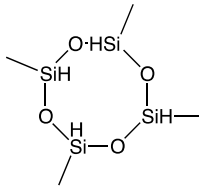
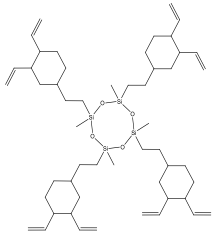
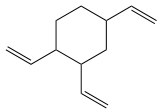
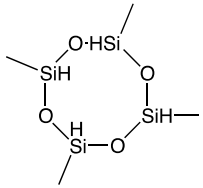
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R7 |  |  | 1:1 ene: SiH<br>30°C Neat<br>50ppm Pt Cat | POLYMER | Exotherm generated immediately after addition of Pt Cat<br>FTIR indicates Si-H has been 100% reacted.<br>NMR obtained, under review. |
| R8 |  |  | 1:1 ene: SiH<br>30°C Neat<br>50ppm Pt Cat | POLYMER | Heated and gelled immediately upon catalyst addition (actually half, 25ppm, was added). |
| R9 |  |  | 1:1 ene: SiH<br>30°C Neat<br>100ppm Pt Cat<br>200ul Acetic Acid | POLYMER | Inadequate reaction |
| 10 |  |  | 2:1<br>1M in Acetonitrile<br>No Catalyst | NO REACTION | In acetonitrile at 1M diisocyanate<br>Medium viscosity liquid after solvent removal<br>FTIR: under review<br>NMR: NO REACTION |

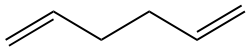
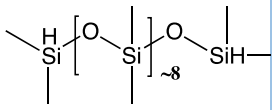
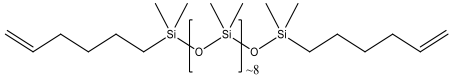
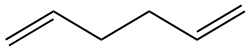
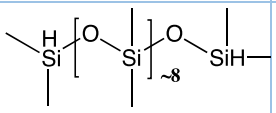
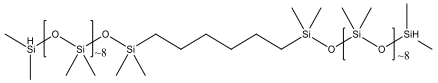
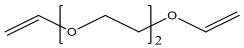
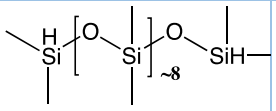
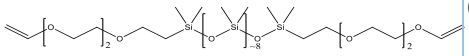
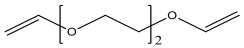
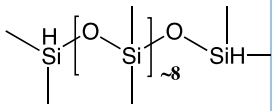
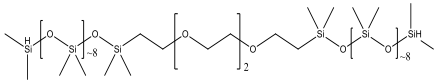
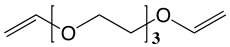
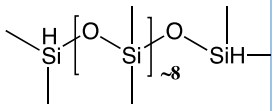
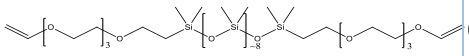
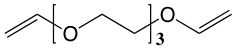
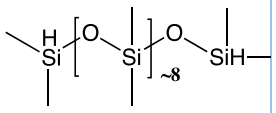
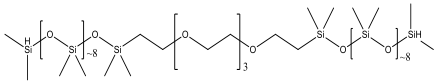
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| 10nd |  |  | 2:1 Neat<br>20ul Tin Catalyst |  | Very high viscosity liquid<br>FTIR: under review<br>NMR: Indicates incomplete |
| R11 |  |  | 2:1<br>1M in Acetonitrile 60ul Tin Cat | | In acetonitrile at 1M diisocyanate, solid obtained after removing solvent.<br>FTIR: under review<br>NMR: Consistent with predicted |
| R11nd |  |  | 2:1 Neat<br>20ul Tin Cat | | Solid obtained<br>NMR: Consistent with predicted |
| R12 |  |  | 1:1 ene: SiH<br>30°C Neat<br>100ppm Pt Cat | POLYMER | Gelled and over heated, try again with 1/10th cat |
| R13 |  |  | 1:1 ene: SiH<br>30°C Neat<br>100ppm Pt Cat | POLYMER | Liquid<br>No gelation |

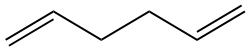
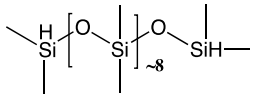
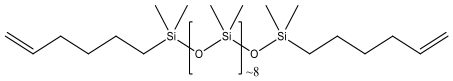
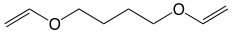
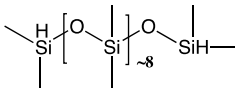
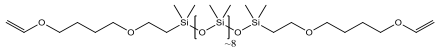
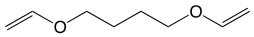
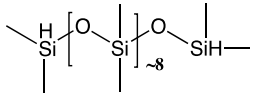
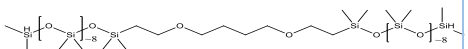
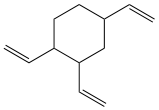
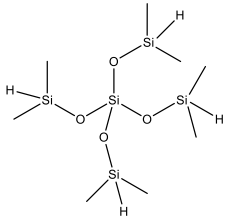
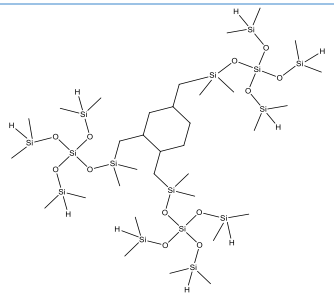
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R14 |  |  | 1:1 ene: SiH<br>30°C Neat<br>10ppm Pt Cat | POLYMER | Gelled |
| R15 |  |  | 2:1 ene:cyanate |  | Synthesis of a divinyl reagent |
| R16 |  |  | 2:1 ene:cyanate | | Synthesis of a divinyl reagent |
| R17 |  |  | 1:1 ene: SiH<br>30°C Acetone<br>10ppm Pt Cat | NO REACTION | Starting material is product from reactions 11 and 16 |
| R18 |  |  | 1:1 ene: SiH<br>30°C Acetone<br>10ppm Pt Cat | NO REACTION | Starting material is product from reactions 11 and 16 |
| R19 |  |  | 1:1 ene: SiH<br>30°C Acetone<br>50ppm Pt Cat | NO REACTION | |

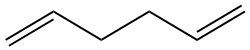
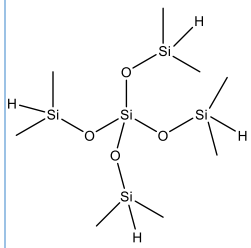
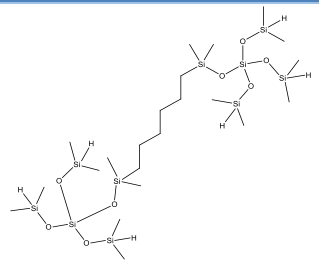
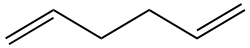
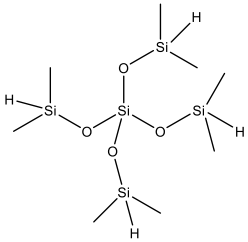
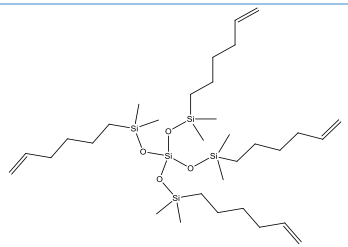
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R20 |  R MW:82.14 |  MW:240.51 | 1:4 ene: SiH 30°C Neat 5ppm Cat |  MW:563.16 | Confirmed by FTIR NMR |
| R21 |  R MW:142.2 |  MW:240.51 | 1:4 ene: SiH 30°C Neat 5ppm Pt Cat |  MW:623.22 | Confirmed by FTIR NMR |
| R22 |  R MW:158.19 |  MW:240.51 | 1:4 ene: SiH 30°C Neat 5ppm Pt Cat |  MW:639.22 | Confirmed by FTIR NMR |
| R23 |  |  | 1:1 ene: SiH 30°C Neat 50ppm Pt Cat | POLYMER | Viscous liquid |
| R24 |  |  | 1:1 ene: SiH 30°C Neat 10ppm Pt Cat | POLYMER | |

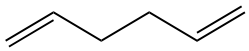
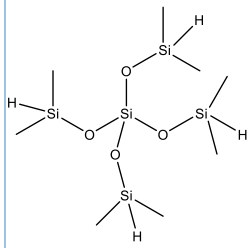
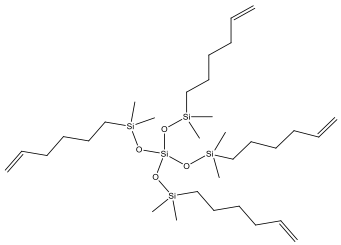
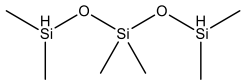
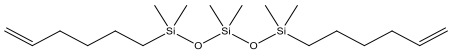
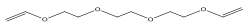
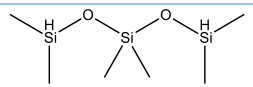
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R25 |  |  | 1:1 ene: SiH<br>30°C Neat<br>25ppm Pt Cat | POLYMER | Gelled in 20 min |
| R26 |  |  | 1:1 ene: SiH<br>30°C Neat<br>20ppm Pt Cat | POLYMER | Gelled |
| R27 |  |  | 1:1 ene: SiH<br>30°C Neat<br>50ppm Pt Cat | POLYMER | Linear; liquid |
| R28 |  |  | 1:1 ene: SiH<br>30°C Neat<br>25ppm Pt Cat | POLYMER | Gelled |
| R29 |  <br>R<br>MW:162.27 |  | 3:1 ene: SiH<br>30°C Neat<br>25ppm Pt Cat |  | Confirmed by FTIR |

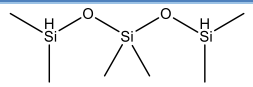
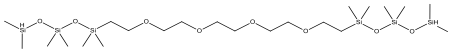
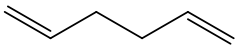
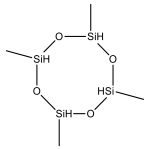
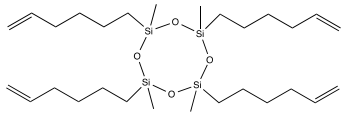
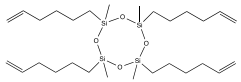
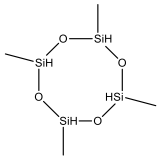
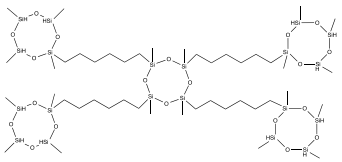
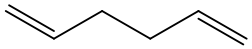
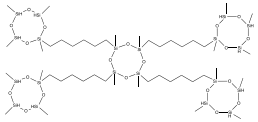
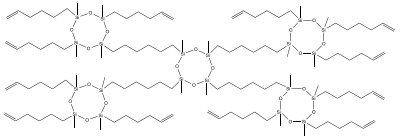
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R30 |  |  | 1:2 ene: SiH<br>30°C Neat<br>25ppm Pt Cat | POLYMER | 30-1) 25ppm Cat added, gelled-exotherm<br>30-2) 10ppm Cat added, gelled-exotherm<br>30-3) 5ppm Cat mixed in H-PDMS, Gelled<br>30-4) 2ppm Cat mixed in H-PDMS, resin obtained |
| R31 |  |  | 1:1 ene: SiH<br>30°C Neat<br>ppm Pt Cat | POLYMER | Gelled at 15ppm (3 aliquots of 5ppm) catalyst |
| R32 |  <br>R<br>MW:162.27 |  <br>MW:240.51 | 3:1 ene: SiH<br>30°C Neat<br>ppm Pt Cat |  <br>MW: 889.61 | Confirmed by FTIR<br>NMR: |
| R33 |  |  | 1:4 ene: SiH<br>30°C Neat<br>ppm Pt Cat | | Confirmed by FTIR<br>NMR |

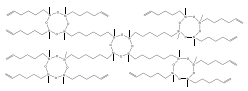
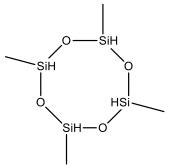
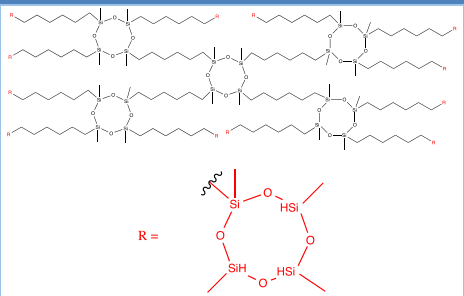
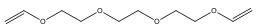
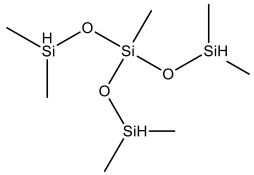
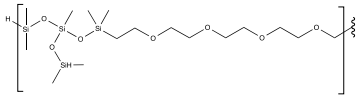
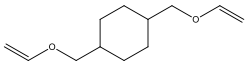
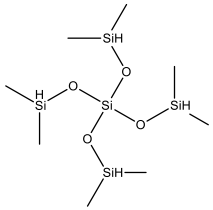
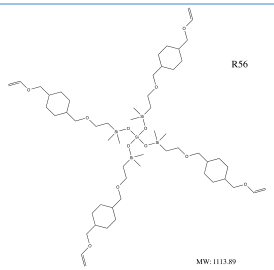
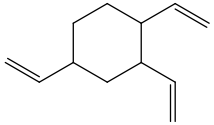
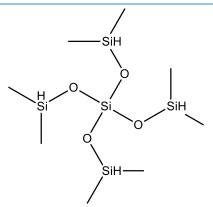
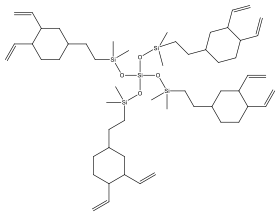
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R34 |  |  | 2:1 ene: SiH<br>50ppm RT |  | Confirmed by FTIR |
| R35 |  |  | 1:2 ene: SiH<br>50ppm RT |  | Confirmed by FTIR |
| R36 |  |  | 2:1 ene: SiH<br>25 ppm RT |  | Confirmed by FTIR |
| R37 |  |  | 1:2 ene: SiH<br>25ppm RT |  | Confirmed by FTIR |
| R38 |  |  | 2:1 ene: SiH<br>25 ppm RT |  | Confirmed by FTIR |
| R39 |  |  | 1:2 ene: SiH<br>25ppm RT |  | Confirmed by FTIR |

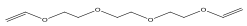
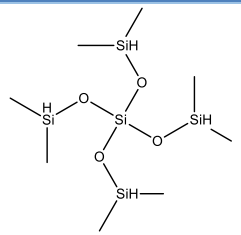
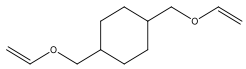
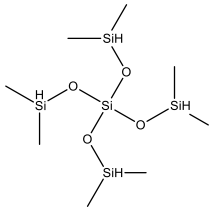
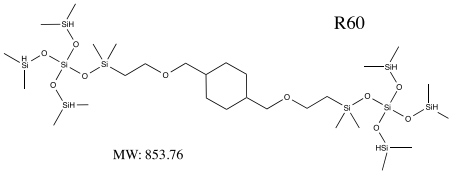
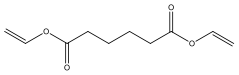
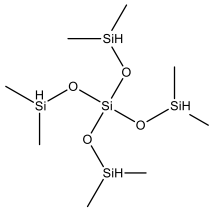
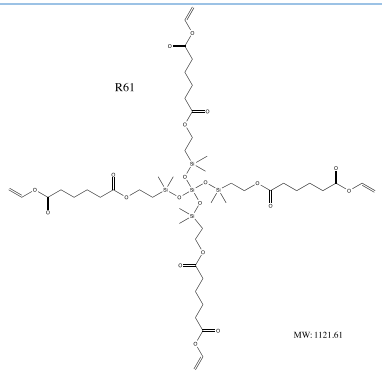
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R40 |  |  | 2:1 ene: SiH<br>10ppm RT |  | Repeat of 34 less catalyst<br>Confirmed by FTIR. |
| R41 |  |  | 2:1 ene: SiH<br>25ppm RT |  | Confirmed by FTIR |
| R42 |  |  | 1:2 ene: SiH<br>25ppm RT |  | Confirmed by FTIR |
| R43 |  <br>1<br>R<br>MW:162.27 |  <br>3<br>MW:328.73 | 3 Si-H molecules:1 ene molecule (4 Si-H: 1ene)<br>Pt: 15 ppm for Si-H molecule; 3.6 mol ppm Pt vs ene |  <br>MW:1106.39 | Reaction at 30°C overnight. Completed according to NMR. |

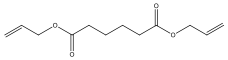
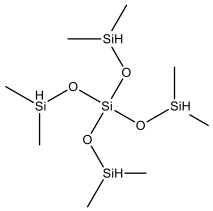
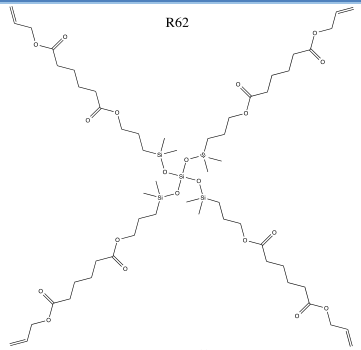
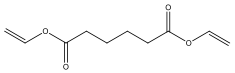
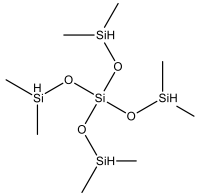
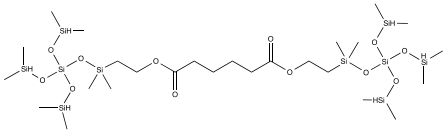
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R44 |  <br>1<br>R<br>MW:82.14 |  <br>2<br>MW:328.73 | 2 Si-H molecules:1 ene molecule (4 Si-H: 1ene)<br>Pt: 15 ppm for Si-H molecule; 3.6 mol ppm Pt vs ene |  <br>MW:739.61 | Reaction at RT overnight. Got warmed by the exothermic reaction. Completed according to NMR. |
| R45 |  <br>4 (excess to prevent gelation due to lack of hexanediene via volatilization |  <br>1 | 1 Si-H molecules: 4 ene molecule (1 Si-H: 2 ene)<br>Pt: 15 ppm for Si-H molecule; 3.6 mol ppm Pt vs ene |  <br>MW:657.31 | Reaction at RT. Gelled after 3h due to lack of diene because of its evaporation. |

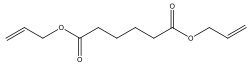
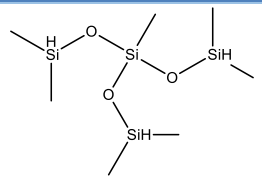
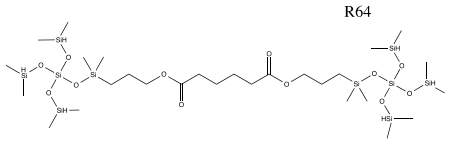
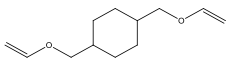
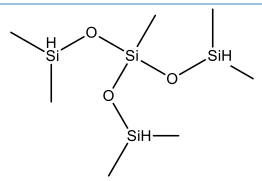
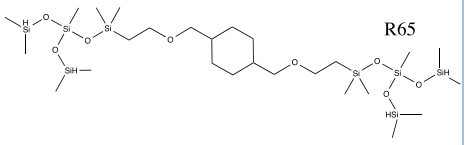
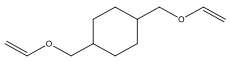
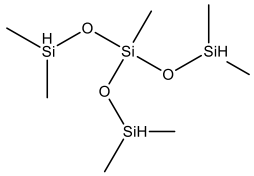
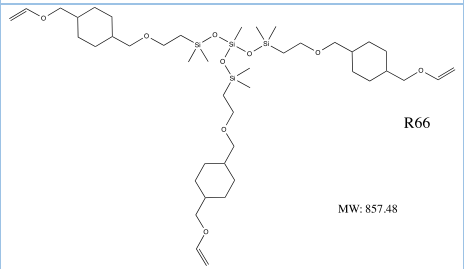
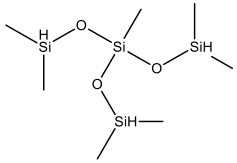
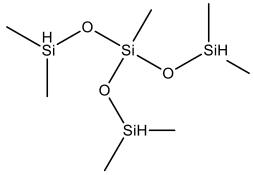
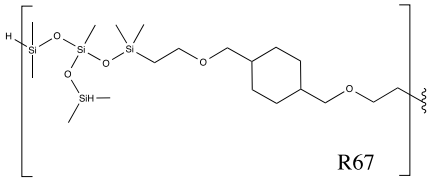
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R46 |  <br>8<br>MW:82.14<br>(excess of diene to prevent agglomeration) |  <br>1<br>MW:328.73 | 1 Si-H molecules: 4 ene molecule (1 Si-H: 2 ene)<br>Pt: 15 ppm for Si-H molecule; 3.6 mol ppm Pt vs ene |  <br>MW:657.31 | Reaction at RT overnight. Reaction completed and excess of hexadiene was evaporated. |
| R47 | <br>4<br>(excess of diene to prevent agglomeration) |  <br>1<br>MW:208.48 | 1 Si-H molecules: 2 ene molecule<br>Pt: 15 ppm |  <br>MW:372.77 | Reaction at RT overnight. Reaction completed and excess of hexadiene was evaporated. |
| R48 |  <br>M.W:202.25 |  <br>MW:208.48 | Ene: Si-H<br>2:1 (mol) | <br>M.W:612.97 | |

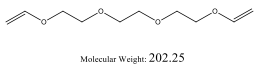
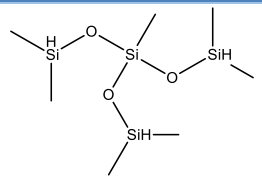
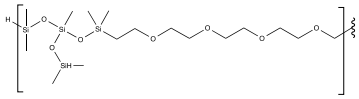
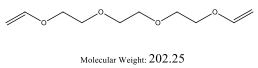
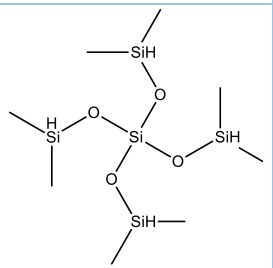
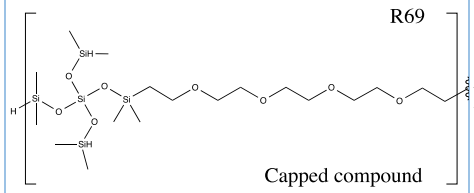
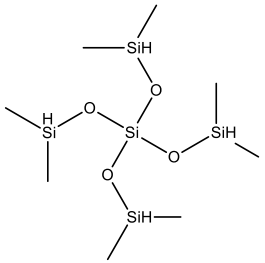
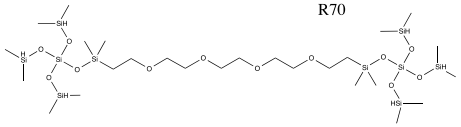
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R49 | M.W:202.25 |  MW:208.48 | Ene: Si-H<br>1:2 (mol) |  | |
| R51 |  MW: 82.15 |  MW: 240.51 | Ene: Si-H<br>6:1 (mol)<br>Excess hexadiene<br>Pt Cat: 7 ppm |  | Low viscosity |
| R52 |  |  MW: 240.51 | Ene: Si-H<br>1:6 (mol)<br>Excess TMHCS<br>Pt Cat: 16 ppm |  | High viscosity<br>Stable |
| R53 |  MW: 82.15 |  | Ene: Si-H<br>18:1 (mol)<br>Excess hexadiene<br>Pt Cat: 19 ppm |  | High viscosity<br>Gelled after a storing period |

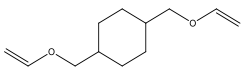
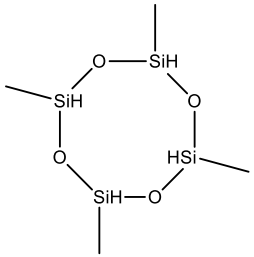
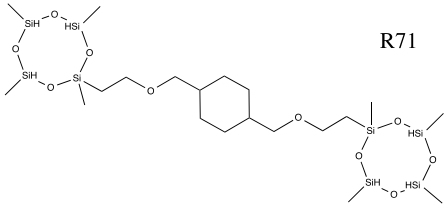
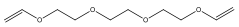
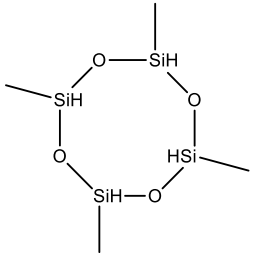
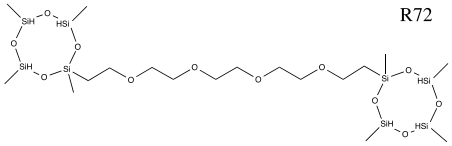
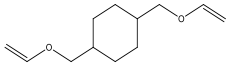
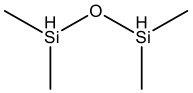
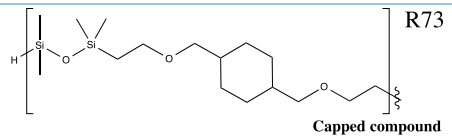
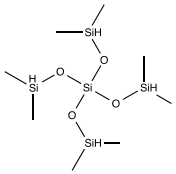
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R54 |  |  MW: 240.51 | Ene: Si-H<br>: (mol)<br>Pt Cat: 46 ppm |  | Very high viscosity<br>Rapidly gelled |
| R55 |  Molecular Weight: 202.25 |  Molecular Weight: 268.61 | Ene: Si-H<br>0.8:1 (mol)<br>Pt Cat: 11 ppm |  Capped compound<br>R68 = R55 | Gelled after heating at 65°C |
| R56 |  Molecular Weight: 196.29 |  Molecular Weight: 328.73 | Ene: Si-H<br>4:1 (mol)<br>Pt Cat: 4 ppm |  R56<br>MW: 1113.89 | |
| R57 |  M.W:162.27 |  Molecular Weight: 328.73 | Ene: Si-H<br>4:1 (mol)<br>Pt Cat: 10 ppm |  | |

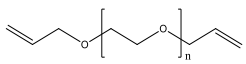
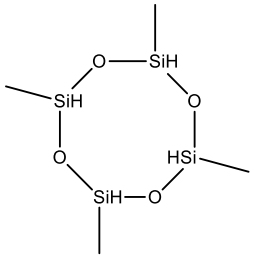
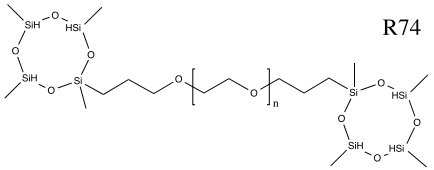
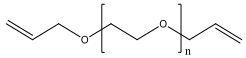
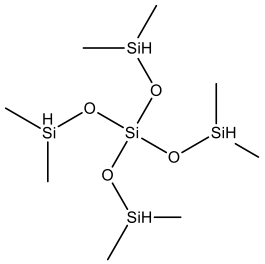
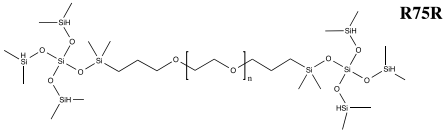
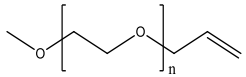
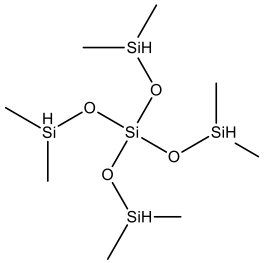
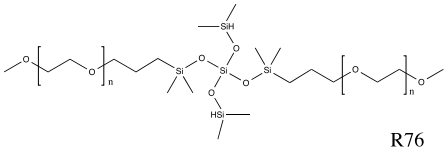
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R58 |  |  Molecular Weight: 328.73 | Ene: Si-H<br>4:1 (mol)<br>Pt Cat: 10 ppm | | |
| R60 |  MW: 196.29 |  Molecular Weight: 328.73 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 3 ppm |  R60 MW: 853.76 | |
| R61 |  Molecular Weight: 198.22 |  Molecular Weight: 328.73 | Ene: Si-H<br>6:1 (mol)<br>Pt Cat: 15 ppm |  R61 MW: 1121.61 | |

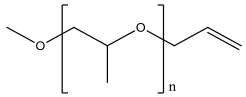
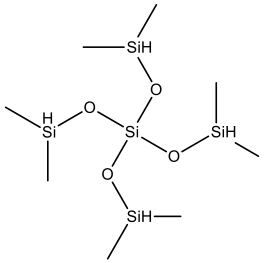
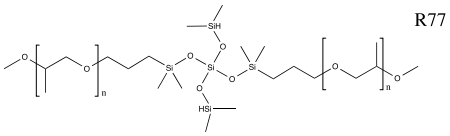
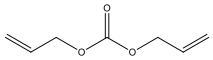
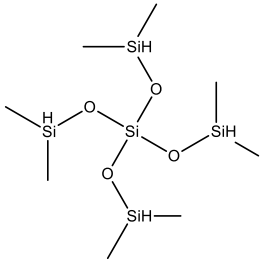
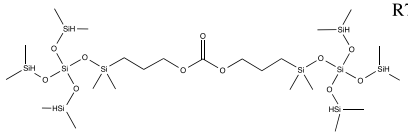
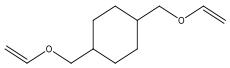
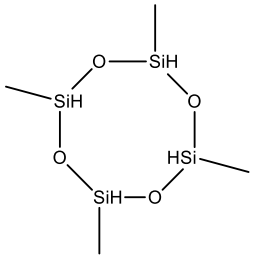
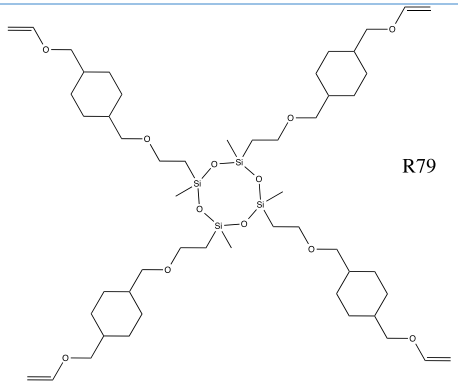
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R62 |  Molecular Weight: 226.27 |  Molecular Weight: 328.73 | Ene: Si-H<br>6:1 (mol)<br>Pt Cat: 3 ppm |  R62 MW: 1233.82 | |
| R63 |  Molecular Weight: 198.22 |  Molecular Weight: 328.73 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 4 ppm |  MW: 855.68 R63 | Incomplete NMR<br>(Solid) |

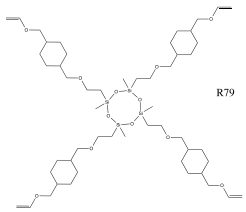
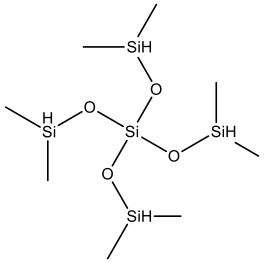
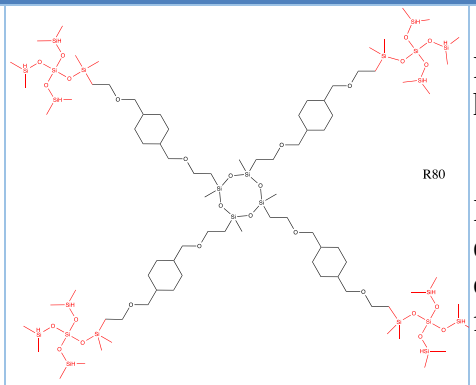
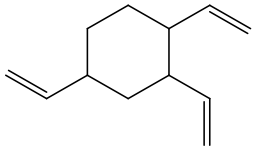
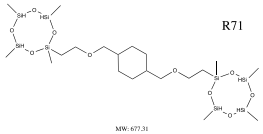
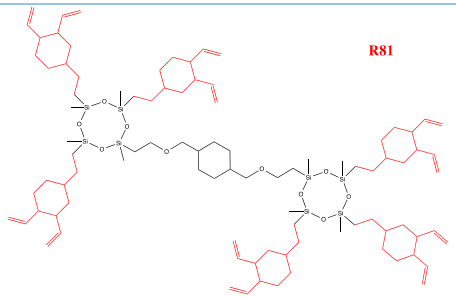
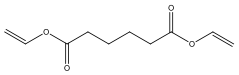
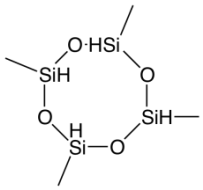
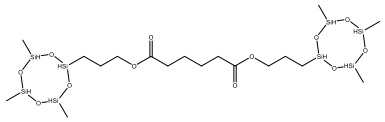
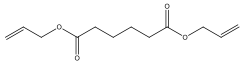
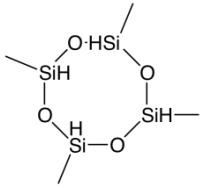
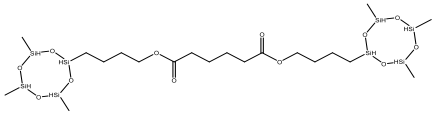
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R64 |  Molecular Weight: 226.27 |  Molecular Weight: 268.61 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 3 ppm |  R64 MW: 883.74 | |
| R65 |  MW: 196.29 |  Molecular Weight: 268.61 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 3 ppm |  R65 MW: 733.50 | |
| R66 |  MW: 196.29 |  Molecular Weight: 268.61 | Ene: Si-H<br>3:1 (mol)<br>Pt Cat: 18 ppm |  R66 MW: 857.48 | |
| R67 |  Molecular Weight: 268.61 |  Molecular Weight: 268.61 | Ene: Si-H<br>1:1 (mol)<br>Pt Cat: 9 ppm |  R67 Capped compound | Gelled<br>Repeat (lower amount of catalyst)- Gelled |

| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R68 |  Molecular Weight: 202.25 |  Molecular Weight: 268.61 | Ene: Si-H<br>1:1 (mol)<br>Pt Cat: 9 ppm |  R68 = R55<br>Capped compound | Applied heat - 70°C for 6 hr |
| R69 |  Molecular Weight: 202.25 |  Molecular Weight: 328.73 | Ene: Si-H<br>1:1 (mol)<br>Pt Cat: 7 ppm |  R69<br>Capped compound | Reacted at 70°C for 6 hr |
| R70 | Molecular Weight: 202.25 |  Molecular Weight: 328.73 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 5 ppm |  R70 | Reacted at 70°C for 1 hr |

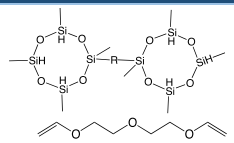
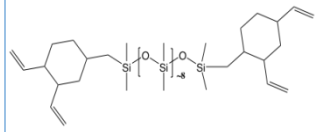
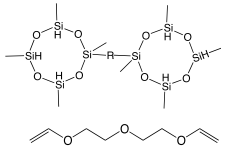
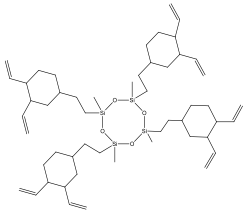
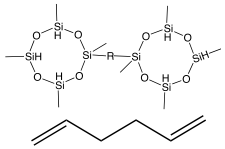
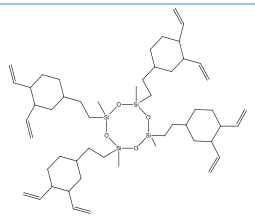
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R71 |  MW: 196.29 |  MW: 240.51 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 4 ppm |  R71 MW: 677.31 | Reacted at 70°C |
| R72 |  Molecular Weight: 202.25 |  MW: 240.51 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 9 ppm |  R72 MW: 683.27 | Reacted at 70°C<br>Clear liquid |
| R73 |  MW: 196.29 |  Molecular Weight: 134.32 | Ene: Si-H<br>1:1.5 (mol)<br>Pt Cat: 29 ppm |  R73 Capped compound<br>  + MW: 328.73 | Rxn heated at 100°C<br>Clear light green viscous liquid |

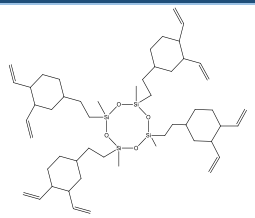
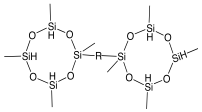
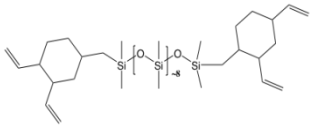
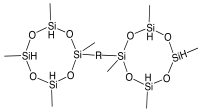
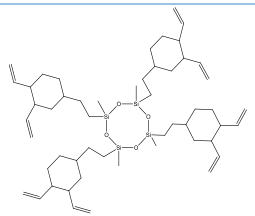
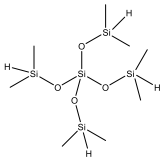
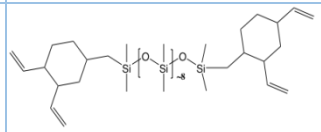
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R74 |  MW: 1000 |  MW: 240.51 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 13 ppm |  R74 MW: 1481.02 | Diene was dissolved in THF before added to cyclic-SiH<br>(solid) |
| R75R |  MW: 1000 |  Molecular Weight: 328.73 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 15 ppm |  R75R MW: 1328.73 | Diene was dissolved in THF then added to tetrakis<br>Rxn mixture was stirred at 70°C |
| R76 |  MW: 1500 - 2000 |  Molecular Weight: 328.73 | Dissolve diene in toluene/THF<br>Pt Cat: 15 ppm |  R76 MW: 3328.73 - 4328.73 | Mixture was stirred at 70°C<br>NMR indicated no reaction<br>(at larger scale the diene appears to be insoluble in both toluene and THF) |

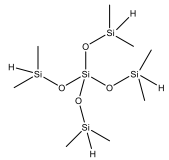
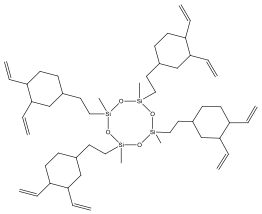
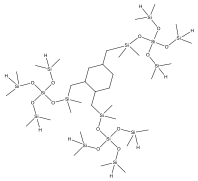
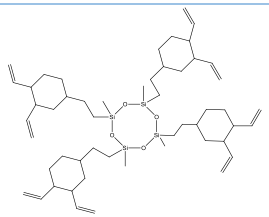
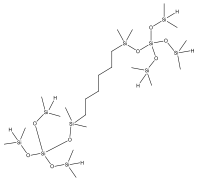
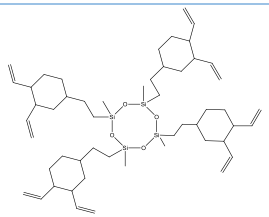
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R77 |  MW: 1500 |  Molecular Weight: 328.73 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 15 ppm |  R77 MW: 3328.73 | Miscible in THF & toluene;<br>Added 20m ml toluene to diene<br>NMR was used to determine rxn progress as IR did not show significant difference |
| R78 |  Molecular Weight: 142.15 |  Molecular Weight: 328.73 | Ene: Si-H<br>1:2 (mol)<br>Pt Cat: 5 ppm |  R78 MW: 799.62 | Rxn was stirred at RT for ~ 40-45 hrs<br>IR & NMR indicate the complete formation of R78 |
| R79 |  MW: 196.29 |  MW: 240.51 | Ene: Si-H<br>4.1:1 (mol)<br>Pt Cat: 5 ppm |  R79 | Rxn was stirred at RT for ~ 17 hrs<br>IR & NMR indicate trace amounts of cyclic Si-H still present in the mixture.<br>Clear viscous liquid |

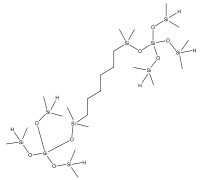
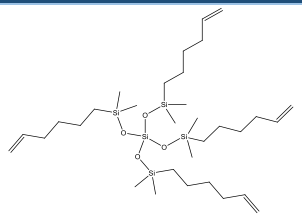
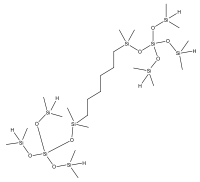
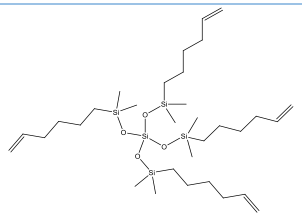
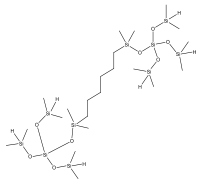
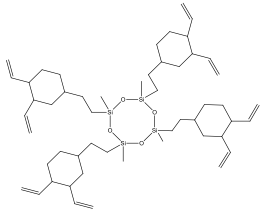
| Rxn # | Part A | Part B | Conditions | Product | Notes |
|---|---|---|---|---|---|
| R80 |  |  Molecular Weight: 328.73 | Pt Cat: 4 ppm |  | Rxn was stirred at RT for ~ 17 hrs<br><br>It appears that subsequent effort to push the rxn to completion resulted in gel formation. |
| R81 |  |  | Ene: Si-H<br>1:1 (mol)<br>Pt Cat: 3 ppm |  | Clear viscous liquid |
| R82 |  Molecular Weight: 198.22 |  | Ene: Si-H<br>2:1<br>Pt Cat: 15 ppm |  | |
| R83 |  Molecular Weight: 226.27 |  | Ene: Si-H<br>2:1<br>Pt Cat: 15 ppm |  | |

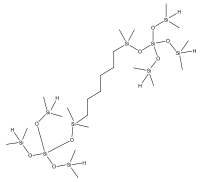
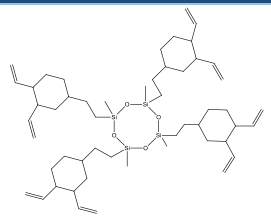
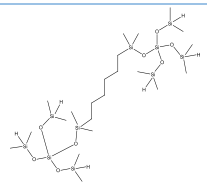
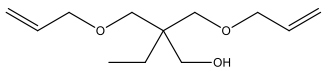
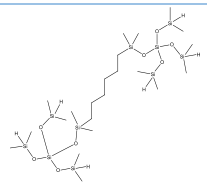
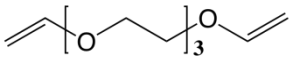
## A.2 FORMULATIONS WITH HYDROSILYLATION INTERMEDIATES

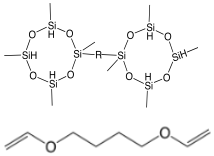
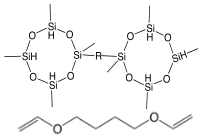
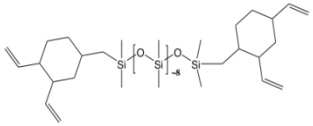
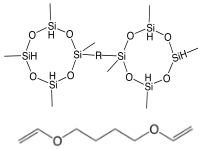
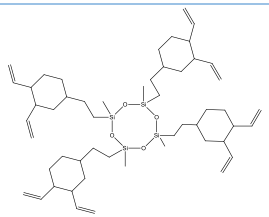
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X31 |  R22 |  R29 (1:1) | 20 | 50/4h | 2H | 5B | Pass |
| X32 |  R22 |  R32 (1:1) | 20 | 50/4h | 4H | 5B | Tearing ++ |
| X33 |  R20 |  R32 (1:1) | 20 | 50/4h | 4H | 5B | Pass |

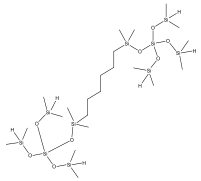
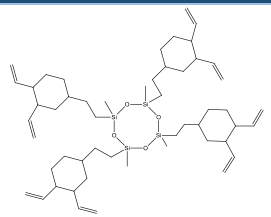
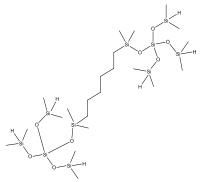
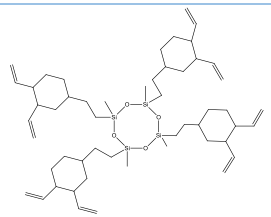
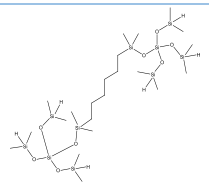
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X34 | R20 |  R32 (1:1) | 20 | 50/4h | 4H | 5B | Pass |
| X35 |  R21 |  R29 (1:1) | 20 | 50/4h<br>RT | 5H<br>Not cured | 5B | Pass |
| X36 |  R21 |  MW=889.59<br>R32 (1:1) | 20 | 50/4h<br>RT | 5H<br>Not cured | 5B | Pass |
| X37 |  |  R29 (1:1) | 20 | 50/4h<br>RT | 4H<br>Not cured | 5B | Teared + |

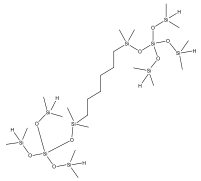
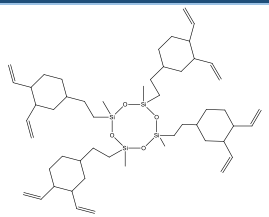
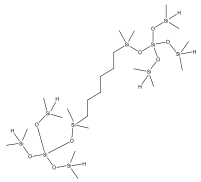
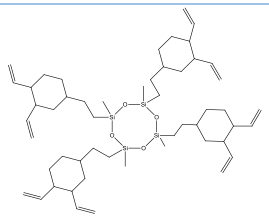
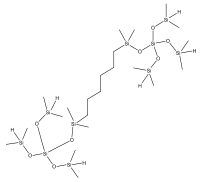
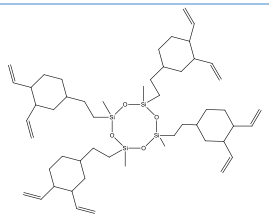
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X38 |  |  <br>MW=889.59<br>R32 | 20 | 50/4h<br>RT | 4H<br>Not cured | 5B | Teared + |
| X39 |  <br>R43 |  <br>MW=889.59<br>R32 (1:1) | 75 | 50/1h<br>50/4h<br>RT/1h<br>RT/1d<br>RT/14d | 4H<br>4H<br>1H<br>2H<br>4H | 5B | Pass |
| X40 |  <br>MW=739.61<br>R44 |  <br>MW=889.59<br>R32 (0.75:1) | 75 | 50/1h<br>50/4h<br>RT/1h<br>RT/1d<br>RT/14d | 4H<br>4H<br><1H<br>2H<br>4H | 5B | Pass |

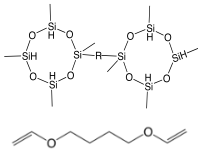
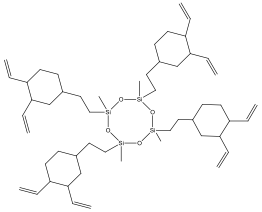
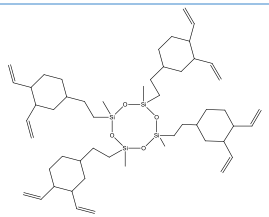
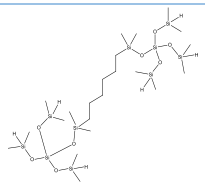
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X41 |  MW=739.61 R44 |  MW=657.31 R46 (1:1.5) | 20 | 50/1h<br>50/4h<br>RT/1d | <1H<br><1H<br><1H | 0B | |
| X42 |  MW=739.61 R44 |  MW=657.31 R46 (1:1.5) | 75 | Gelled immediately | | | |
| X43 |  MW=739.61 R44 |  MW=889.59 R32 (0.75:1) | 20 | 50/1h<br>50/4h<br>RT/1d | 1H<br>1H<br>1H | 4B | |

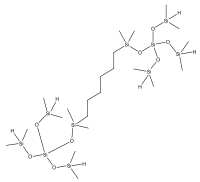
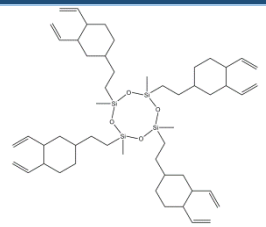
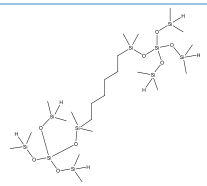
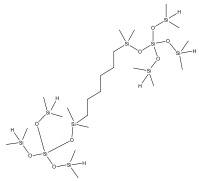
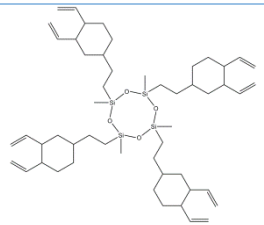
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X44 |  MW=739.61 R44 |  MW=889.59 R32 (0.75:1) | 27.5 | 50/1h<br>50/4h<br>RT/1d | 2H<br>2H<br><1H | 1B | |
| X45 |  MW=739.61 R44 |  MW=214 (1:3) | 35<br>25 | Gelled immediately<br>50/1h | Not cured | | |
| X46 |  MW=739.61 R44 |  MW=215 (1:3) | 35 | 50/1h | Not cured | | |

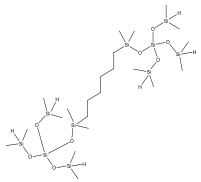
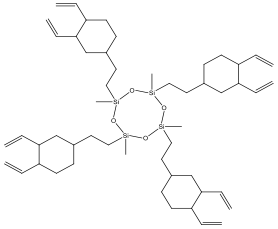
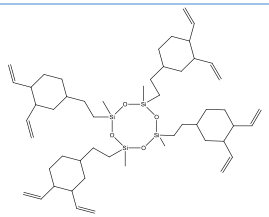
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X48 | <br>R48 |  <br>R21 (3:1) | 15<br>5 | Gelled in <5min<br>50/4h | <H | | |
| X49 |  <br>R21 |  <br>R29 (1:1) | 15<br>5 | Gelled immediately<br>50/4h | 4H | 1-2B | Repeat of X35 with additional catalyst |
| X50 |  <br>R21 |  <br>MW=889.59<br>R32 (1:1) | 45<br>25 | Gelled in <5min<br>50/4h | 5H | 2-3B | Repeat of X36 with additional catalyst |

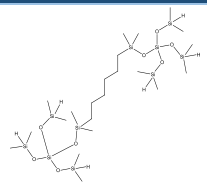
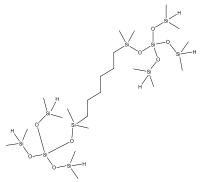
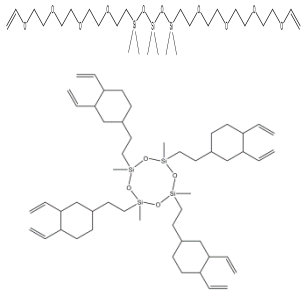
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X52 |  MW=739.61 R44 |  MW=889.59 R32 (0.75:1) | 45 | 50/1h<br>50/4h | 3H<br>4H | 3-4B | |
| X53 |  MW=739.61 R44 |  MW=889.59 R32 (1:1) | 45 | 50/1h<br>50/4h | 3H<br>4H | 3-4B | |
| X54 |  MW=739.61 R44 | R48 (1:3) | 45 | 50/1h<br>50/4h | | | Not cured |

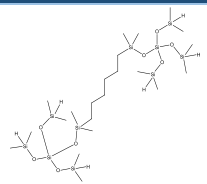
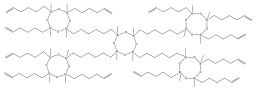
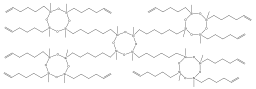
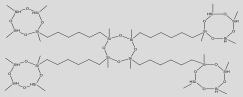
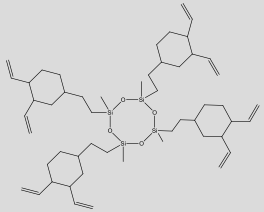
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X57 |  MW=739.61 R44 |  MW=889.59 R32 (0.75:1) | 45 | Dried unevenly/separated @50C/4h: H | | *Repeat of X52 with bulk R32 | Heated Bulk R32 and tried again – @ 50°C/4h: 4H/2-3B |
| X58 |  MW=739.61 R44 |  MW=889.59 R32 (1:1) | 45 | Dried unevenly/separated @50C/4h: H | | *Repeat of X53 with bulk R32 | Heated Bulk R32 and tried again – @ 50°C/4h: 4H/2-3B |
| X60 |  MW=739.61 R44 |  MW=889.59 R32 (1:0.75) | 45 | 50/4h | 2H | | Vial content gelled in <5min |

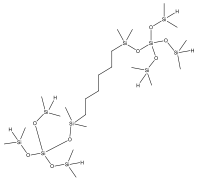
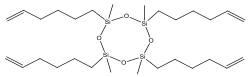
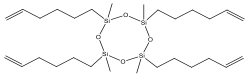
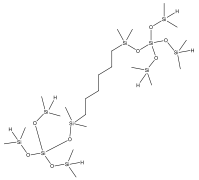
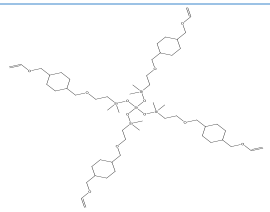
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X61 |  R21 |  MW=889.59 R32 (1:1.2) | 0 | 50/4h | 4H | 4B | |
| X62 | R21 |  MW=889.59 R32 (1.2:1) | 0 | 50/4h | 4H | 4B | |
| X63 |  MW=739.61 R44 | R48 (1:2) | 45 | Gelled in < 6min | | | Initially opaque – became clear after catalyst was added |

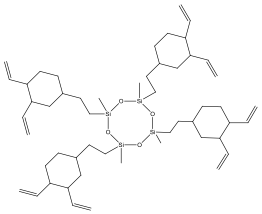
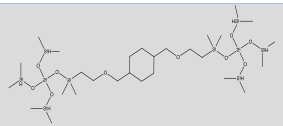
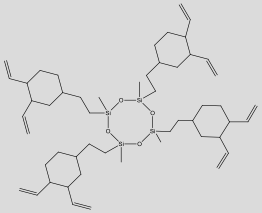
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X64 |  MW=739.61 R44 |  R48 & R32 (1:1:0.5) | 45 | Gelled in < 2min | | | |
| X65 |  MW=739.61 R44 | R48 (1:2) | 30 | 50C/4h | Not Cured | | |
| X66 |  MW=739.61 R44 |  R48 & R32 (1:1:0.5) | 24 | Gelled in < 5min RT 30days | <1H | | Initially opaque – became clear after catalyst was added |

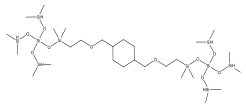
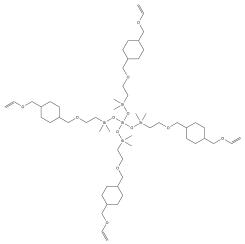
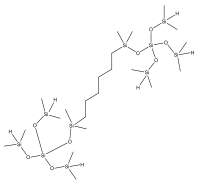
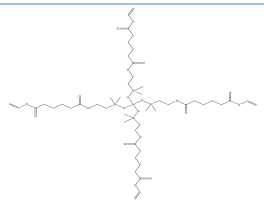
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X67 | SIT7278.0 | R48 (1:1.2) | 24 | 50C/4h<br>RT | Not cured<br>Not cured | | |
| X68 |  <br>MW=739.61<br>R44<br>& SIT7278.0 |  <br>MW=889.59<br>R32 (0.5:0.5:1) | 0<br>0<br>45 | 50C/4h<br>RT/no Pt-Cat-10days<br>RT/0.1g Pt-Cat- 10days | 4-5H<br><H<br>4H | 3B<br>2B | |
| X69 | <br>R49 |  <br>MW=889.59<br>R32 (1:1) | 0 | 50C/4h | <H | | |

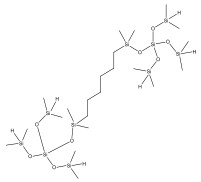
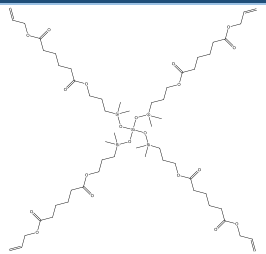
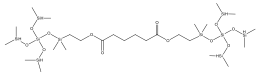
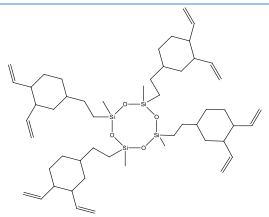
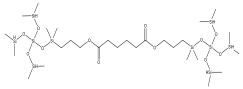
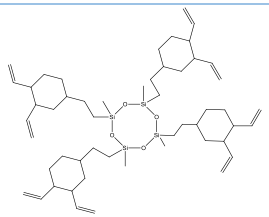
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X70 |  MW=739.61 R44 | R48 (1:2) | 45 | 50C/4h | <H | | Initially opaque – became clear after catalyst was added |
| X71 |  MW=739.61 R44 |  R48& R32 (1:1:0.5) | 45 | Gelled in < 2min | (extremely brittle) | | Initially opaque – became clear after catalyst was added |

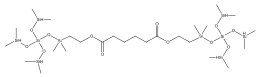
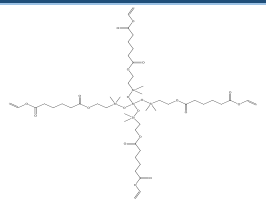
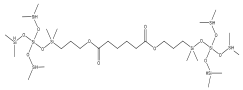
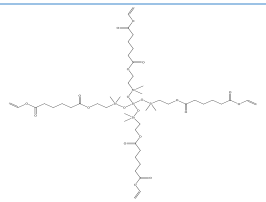
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X72 |  MW=739.61 R44 |  R53 (1:0.5) | 20 | Opaque mixture | Gelled unevenly | | Phase separation? |
| X73 | R21 |  R53 (1:0.5) | 0 | 50C/4h | 2H | | |
| X74 |  R52 |  MW=889.59 R32 (0.5.:1) | 15 | 50C/4h<br>RT/1mo+ | 5H<br>5H | 3B<br>3B | *To do: Repeat with less catalyst (see X110, S111) |

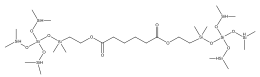
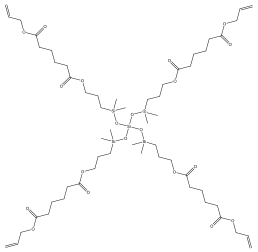
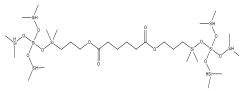
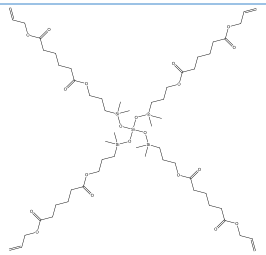
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X75 |  MW=739.61 R44 |  R51 (1:1) | 1 drop<br>0 | Gelled immediately<br>50C/4h | H | | |
| X76 | R21 |  R51 (1:1) | 0 | 50C/4h | 2H | | |
| X77 |  MW=739.61 R44 |  R56+THF(1:1:1) | 24 | 50C/4h | <H | | Content in vial gelled in <5min<br>Opaque mixture |

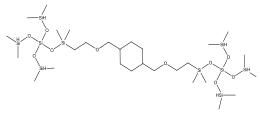
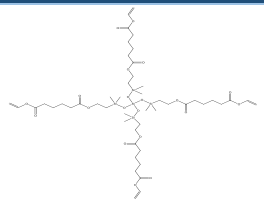
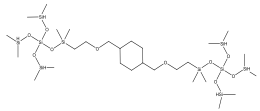
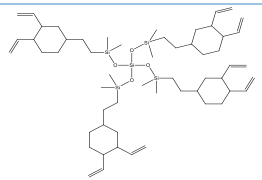
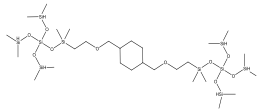
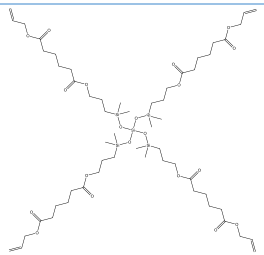
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X78 | R21 | MW=889.59<br>  <br>R32+R44<br>(0.5:0.5:1) | 40<br>15 | Gelled immediately<br>50C/4h<br>RT 30d | 4-5H<br>2H | 2B | Not a clear mixture – appeared to have insoluble bits |
| X79 |  <br>MW=853.76<br>R60 |  <br>MW=889.59<br>R32 (1:1) | 0<br>45 | 50C/4h<br>RT 30d<br>50C/4h<br>RT 30d | 5H<br><H<br>4H<br>4-5H | 3B<br>2-3B<br>4B | Note: runny consistency |

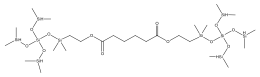
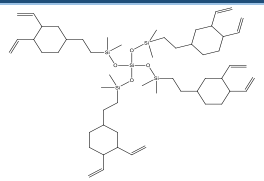
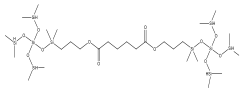
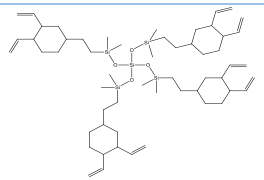
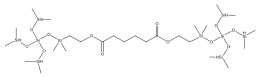
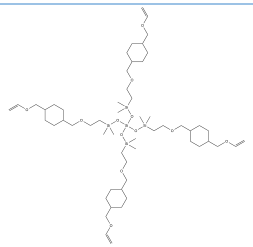
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X80 |  MW=853.76 R60 |  MW:1113.89 R56 (1:1) | 15 | 50C/4h | <1H | | Dried unevenly *To do: Add more catalyst and solvent (THF) (see X144) |
| X81 |  MW=739.61 R44 |  R61 MW=1121.61 (1:1) | 30 | 50C/4h | Not cured | | Note: runny mixture Initially opaque – became clear after catalyst was added |

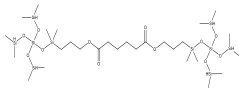
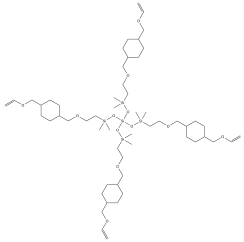
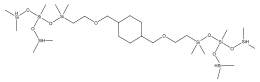
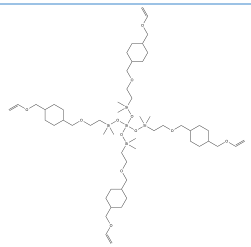
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X82 |  MW=739.61 R44 |  R62 MW=1233.82 (1:1) | 45 | 50C/4h | Not cured | | Opaque mixture |
| X83 |  MW=855.68 R63 |  MW=889.59 R32 (1:1) | 45 | 50C/4h | Not cured | | Runny/clear |
| X84 |  MW=883.74 R64 |  MW=889.59 R32 (1:1) | 45<br>25 | 50C/4h<br>50C/4h | 4H<br>2H | | Runny/clear<br>Uneven coat-needs to be repeated |

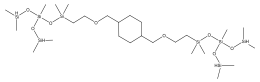
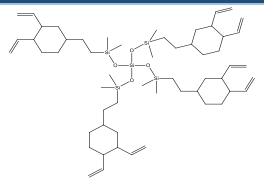
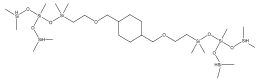
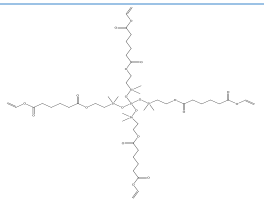
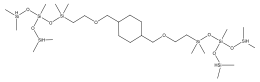
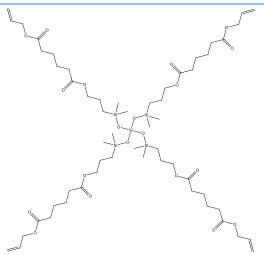
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X85 |  MW=855.68 R63 |  R61 MW=1121.61 (1:1) | 45 | 50C/4h | Not cured | | Runny/clear |
| X86 |  MW=883.74 R64 |  R61 MW=1121.6 (1:1) | 45 | 50C/4h | Not cured | | Runny/clear |

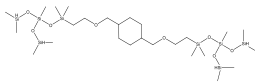
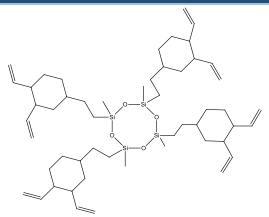
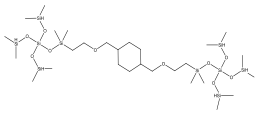
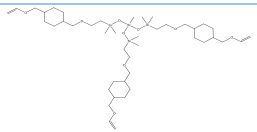
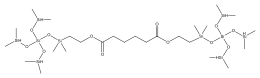
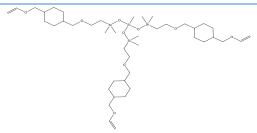
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X87 |  MW=855.68 R63 |  R62 MW=1233.82 (1:1) | 45 | 50C/4h | Not cured | | Initially opaque – became clear after catalyst was added |
| X88 |  MW=883.74 R64 |  R62 MW=1233.82 (1:1) | 45<br>15 | Gelled in <5 min (started smoking)<br>50C/4h | Not cured | | |

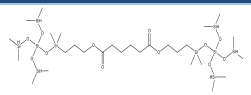
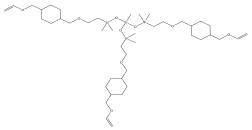
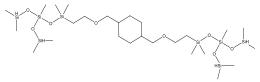
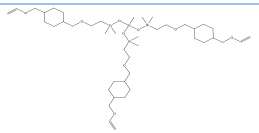
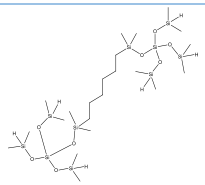
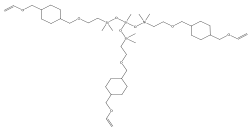
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X89 |  MW=853.76 R60 |  R61 MW=1121.6 (1:1) | 50 | 50C/4h | Not Cured | | Runny mixture – observed small particles |
| X90 |  MW=853.76 R60 |  MW=977.82 R57 (1:1) | 15 | 50C/4h | 2H | | Viscous mixture<br><br>To Do: add more catalyst |
| X91 |  MW=853.76 R60 |  R62 MW=1233.82 (1:1) | 45 | 50C/4h | Not Cured | | Opaque mixture- became clear after catalyst was added |

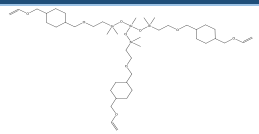
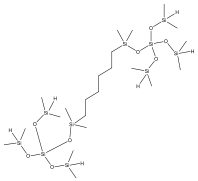
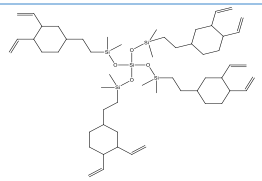
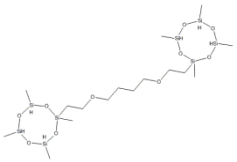
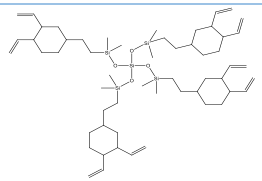
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X92 |  MW=855.68 R63 |  MW=977.82 R57 (1:1) | 45 | 50C/4h | Not Cured | | Runny mixture |
| X93 |  MW=883.74 R64 |  MW=977.82 R57 (1:1) | 45<br>0 | 50C/4h (vial content gelled in <5min)<br>50C/4h | <H<br>Not cured | | Runny mixture |
| X94 |  MW=855.68 R63 |  MW:1113.89 R56 (1:1) | 45 | 50C/4h | Not Cured | | Runny mixture |

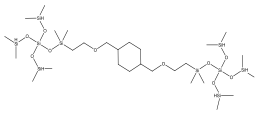
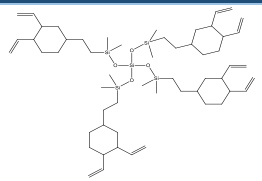
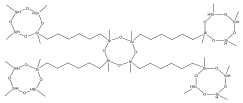
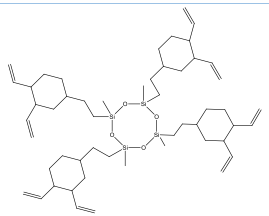
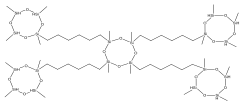
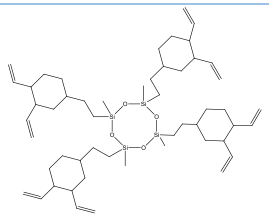
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X95 |  <br>MW=883.74<br>R64 |  <br>MW:1113.89<br>R56 (1:1) | 50<br><br>15 | 50C/4h<br>(vial content gelled in <5min)<br><br>50/4h<br>(vial content gelled in <2h) | <H<br><br><H | | |
| X96 |  <br>MW:733.5<br>R65 |  <br>MW:1113.89<br>R56 (1:1) | 20 | 50C/4h | <H | | |

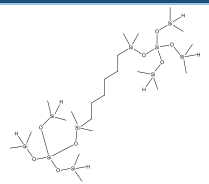
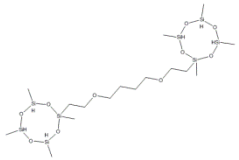
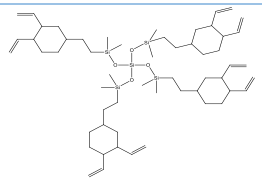
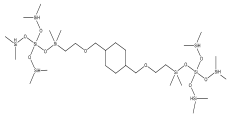
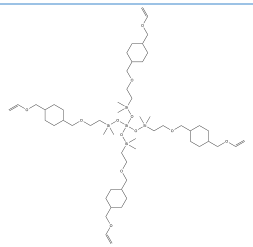
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X97 |  MW:733.5 R65 |  MW=977.82 R57 (1:1) | 30 | 50C/4h | <H | | Vial content gelled <2hr |
| X98 |  MW:733.5 R65 |  R61 MW=1121.61 (1:1) | 45 | 50C/4h | Not cured | | Runny mixture |
| X99 |  MW:733.5 R65 |  R62 MW=1233.82 (1:1) | 45 | 50C/4h | Not cured | | Opaque mixture Vial content gelled <5min |

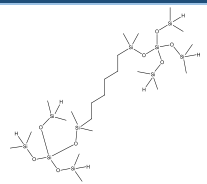
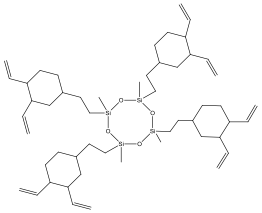
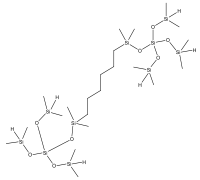
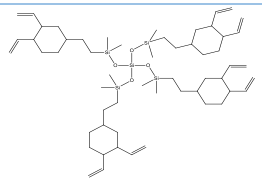
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X100 |  MW:733.5 R65 |  MW=889.59 R32 (1:1) | 25 | 50C/4h | 2H | | Vial content gelled <2hr |
| X101 |  MW=853.76 R60 |  MW:857.48 R66 | 20 0 | 50C/4h | Gelled immediately H | | Note: observed solids in R60 |
| X102 |  MW=855.68 R63 |  MW:857.48 R66 | 45 | 50C/4h | Not cured | | |

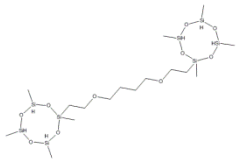
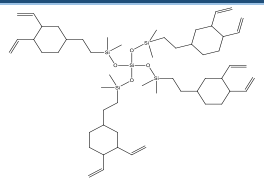
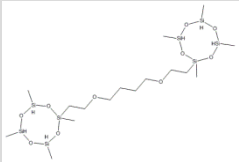
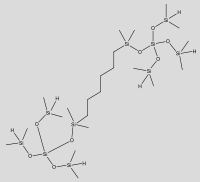
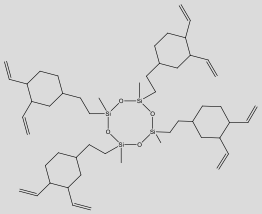
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X103 |  MW=883.74 R64 |  MW:857.48 R66 | 30 | 50C/4h | Not cured | | |
| X104 |  MW:733.5 R65 |  MW:857.48 R66 | 0 | 50C/4h | <H | | Viscous mixture |
| X105 |  MW=739.61 R44 |  MW:857.48 R66 | 0 | 50C/4h | <H | | Opaque, viscous mixture |

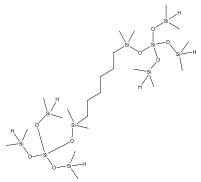
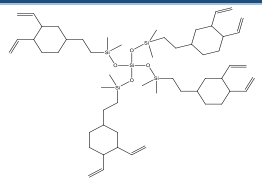
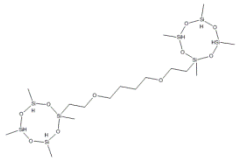
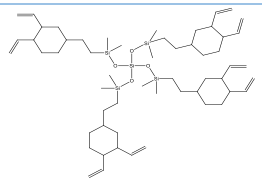
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X106 | R21 |  MW:857.48 R66 | 0 | 50C/4h | 2H | | Clear, viscous mixture |
| X107 |  MW=739.61 R44 |  MW=977.82 R57 (1:1) | 40 | 50C/4h<br>RT/1mo+ | 5H<br>5H | 0/1B<br>0/1B | Slightly opaque mixture |
| X108 |  R21 |  MW=977.82 R57 (1:1) | 0 | 50C/4h<br>RT/1mo+ | 5H<br><H | 0/1B | Slightly opaque mixture/viscous (see X113, X114) |

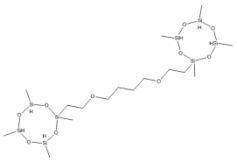
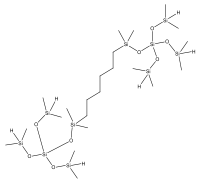
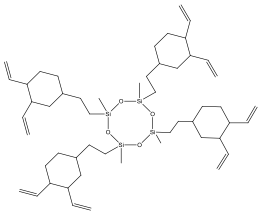
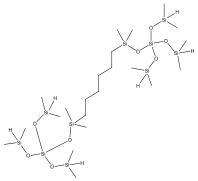
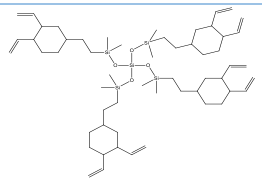
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X109 |  MW=853.76 R60 |  MW=977.82 R57 (1:1) | 30 | 50C/4h | Gelled in <1min (gelled turned yellow) | | |
| X110 |  R52 |  MW=889.59 R32 (0.5:1) | 0 | 50C/4h RT/2mo | 2H 5H | 5B | Runny mixture |
| X111 |  R52 |  MW=889.59 R32 (1:1) | 0 | 50C/4h | 2H | | Runny mixture |

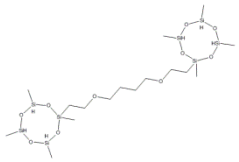
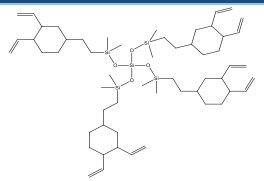
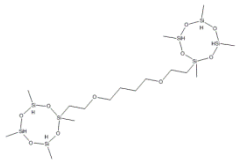
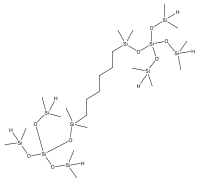
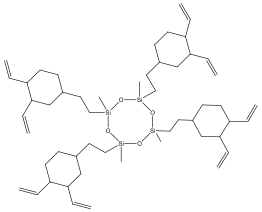
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X112 |  MW=739.61 R44 | R48 (1:1) | 45 | 50C/4h | Not cured | | Opaque mixture/runny Uneven coat/partially evaporated |
| X113 |  R21 |  MW=977.82 R57 (1:1) | 13 | 50C/4h | Gelled after adding 0.04g of Pt-Cat | | Slightly opaque (see X108, X117) |
| X114 |  R60 |  MW:1113.89 R56 (1:1) & 10% THF | 35 | 50C/4h | Gelled in <5min | | |

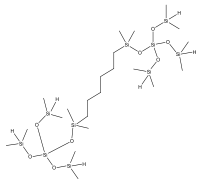
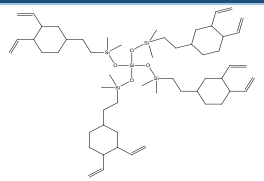
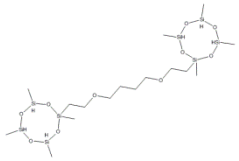
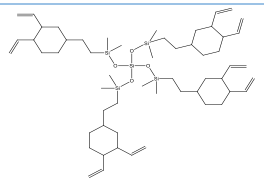
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X115 |  <br>MW=739.61<br>R44<br> <br>R48 |  <br>MW=889.59<br>R32 (1:1:0.5) | 15 | 50C/4h | <H | | |
| X116 |  <br>MW=739.61<br>R44 |  <br>MW=977.82<br>R57 (1:1)<br>& 19% VTMS | 30 | 50C/4h<br>RT/1mo+ | 5H<br>2H | 2B<br>0/1B | Clear/runny mixture |

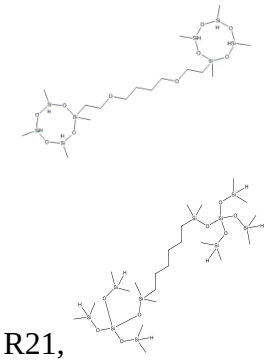
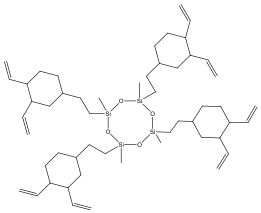
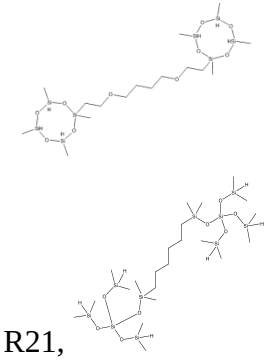
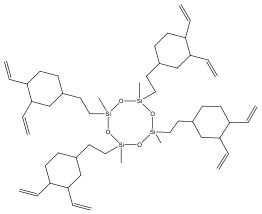
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X117 |  <br>R21 |  <br>MW=977.82<br>R57 (1:1)<br>& 19% VTMS | 30 | 50C/4h | 4-5H | 0-1B | Opaque mixture<br>Cured unevenly-slight separation<br>(see X108, X113, X123) |
| X118 |  <br>R21<br>  <br>R44 |  <br>R32 (1:1:1)<br>& 20% VTMS | 30 | 50C/4h<br>RT/1mo+ | 5H<br>5H | 3-4B<br>2B | Clear runny mixture |

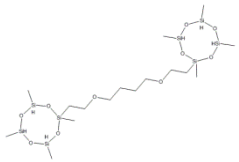
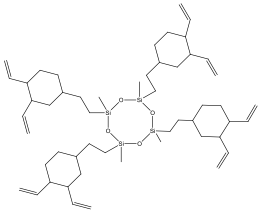
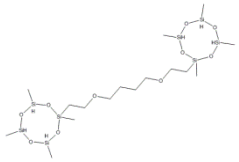
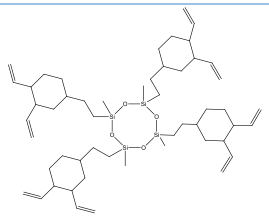
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X119 |  MW=739.61 R44 |  MW=977.82 R57 (1:1) & ATMS | | 50C/4h | | | (Spilled) |
| X120 |  R21 |  MW=977.82 R57 (1:1) 0.6g in 1.5g ATMS | 30 | 50C/4h | 5H | 2B | RT/1mo+: cured unevenly (separated) |

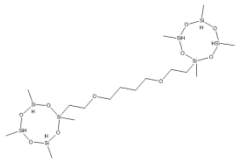
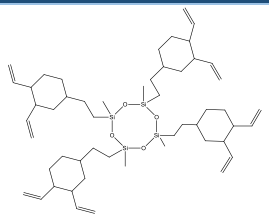
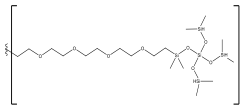
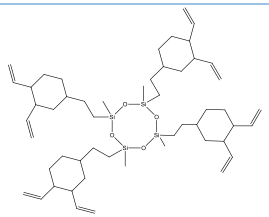
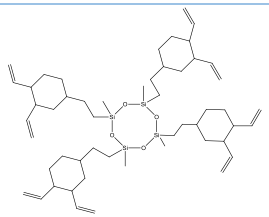
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X121 |  R21,  R21<br>MW=739.61<br>R44 |  <br>MW=889.59<br>R32, ATMS | 15 | 50C/4h<br>RT/1mo+ | 3-4H<br>5H | 4B<br>4B | Cured unevenly |
| X122 |  <br>MW=739.61<br>R44 |  <br>MW=977.82<br>R57 (1:1)<br>& 10% ATMS | 30 | 50C/4h | Gelled <5min | | Slightly opaque |

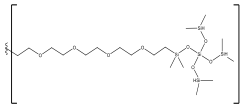
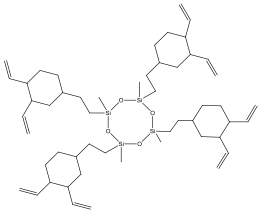
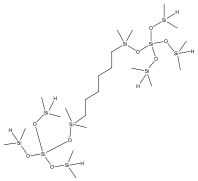
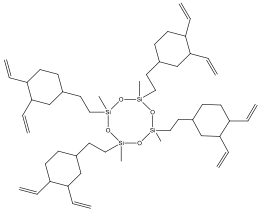
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X123 |  <br>R21 |  <br>MW=977.82<br>R57 (1:1)<br>10% ATMS | 30 | 50C/4h<br>RT/1mo+ | (Gelled <1min ) 5H<br>4H | 4-5B<br>4B | Slightly opaque<br>RT cured unevenly<br>(see X117) |
| X124 |  <br>  <br>R21,<br>MW=739.61<br>R44 |  <br>MW=889.59<br>R32 (1:1:1)<br>10% ATMS | 15 | 50C/4h<br>RT/1mo+ | 2-3H<br>4/5H? | 2B | Cured unevenly |

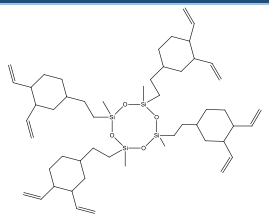
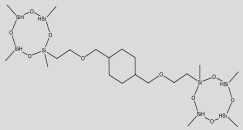
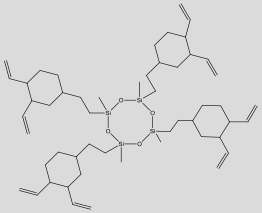
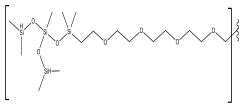
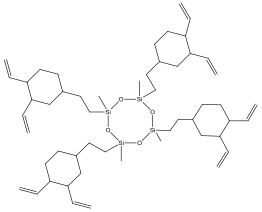
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X125 |  MW=739.61 R44 |  MW=977.82 R57 (1:1) 10% VTMS | 15 | 50C/4h RT/1mo+ | 5H H | 2-3B | Clear mixture |
| X126 |  R21 |  MW=977.82 R57 (1:1) 10% VTMS | 15 | 50C/4h RT/1mo+ | 5H 5H | 2B 4B | Opaque mixture |

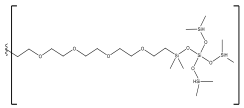
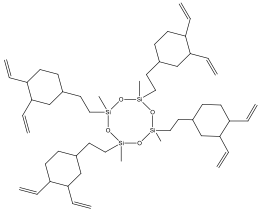
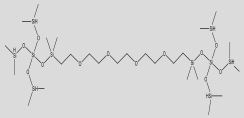
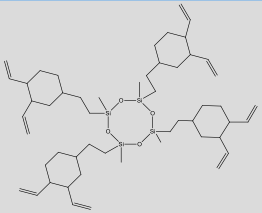
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X127 |  R21, MW=739.61 R44 |  MW=889.59 R32 (1:1:1) 10% ATMS 0.3g MEK | 25 | 50C/4h | (w/o MEK: gelled <5min) | | w/ MEK: observed separation – spread unevenly |
| X128 |  R21, MW=739.61 R44 |  MW=889.59 R32 (1:1:1) 10% ATMS 0.3g acetylacetone | 25 | 50C/4h | | | w/ acetylacetone: observed separation – spread unevenly |

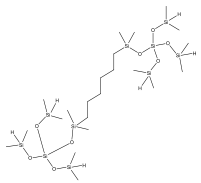
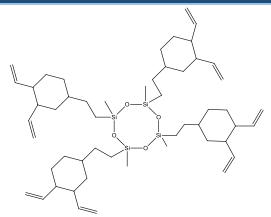
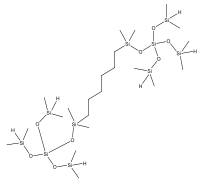
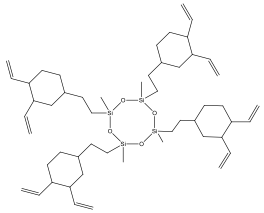
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X129 |  <br>R21 |  <br>MW=889.59<br>R32 (1:1) | 25 | 50C/3h<br>50C/3h+5d RT<br>RT/3h<br>RT/5d<br>RT/1 mo+ | 4H<br>5H<br>1H<br>5H<br>5H | 4B<br>2-3B<br>4B | Gelled in <10min |
| X130 |  <br>R21 |  <br>MW=889.59<br>R32 (1:1)<br>MEK | 25 | 50/4h | | | Waited 1hr in vial before spreading onto plate<br>Gelled <1hr |

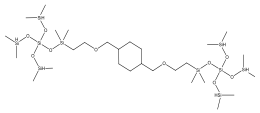
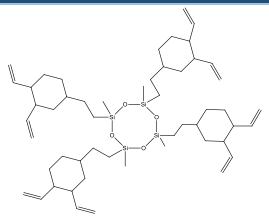
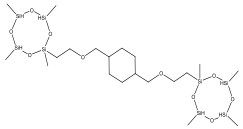
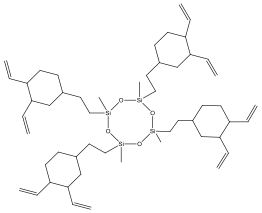
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X131 |  <br>R21 |  <br>MW=889.59<br>R32 (1:1)<br>acetylacetone | 25 | 50C/3h<br>50C/3h+5d RT<br>RT/3h<br>RT/5d<br>RT/1mo+ | 4H<br>5H<br>1H<br>5H<br>5H | 2B<br>4B<br>4B | Waited 1hr in vial before spreading onto plate |
| X132 |  <br>R69 |  <br>MW=889.59<br>R32 | 15<br>0 | Gelled<br>Observed separation/un-even coating | | | Viscous/opaque |
| X133 | <br>R70 |  <br>MW=889.59<br>R32 (1:1) | 30 | 50/4h<br>RT/1mo+ | 5H<br>5H | 1B<br>2/3B | Clear/ runny mixture<br>Spread unevenly-bubble/separation |

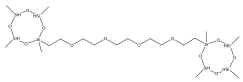
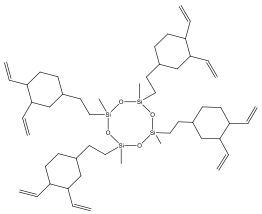
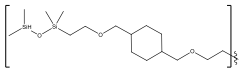
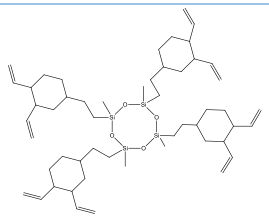
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X134 |  <br>R69 |  <br>MW=889.59<br>R32 | 24 | X134-A: (1:2) R69: cyclohexane<br>X134-B: (1:2) R69:xylene<br>X134-C: (1:2) R69:dixane<br>X134-D: (1:2) R69:THF | Uneven coating<br>Uneven coating<br>Partially separated<br>Even coating | H | X134-A: (1:2) R69:cyclohexane – soluble<br>X134-B: (1:2) R69:xylene – partially soluble<br>X134-C: (1:2) R69:dixane - partially soluble<br>X134-D: (1:2) R69:THF – soluble |
| X136 |  <br>MW=739.61<br>R44 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTMS | 30 | 50/4h<br>RT/1mo+ | 5-6H<br>6H | 1-2B<br>2B | |

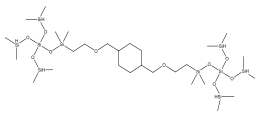
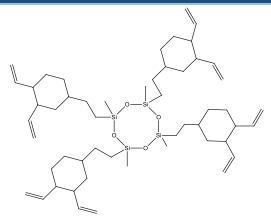
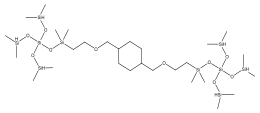
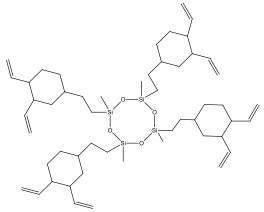
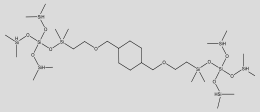
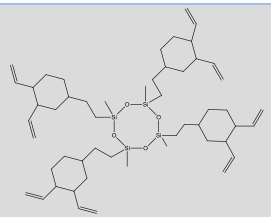
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X137 | R70 |  MW=889.59 R32 (1:1) 5% VTMS | 15 | 50/4h RT/1mo+ | 5-6H 4H | 2B 3B | Runny/clear mixture |
| X138 |  R71 |  MW=889.59 R32 (1:1) | 20 | 50/4h RT/1mo+ | 5H 5H | 3-4B 4B | Clear mixture |
| X139 |  R68 |  MW=889.59 R32 (1:1) | 30 | 50/4h RT/1mo+ | 4H? <H | | Observed separation-uneven plate |

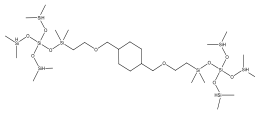
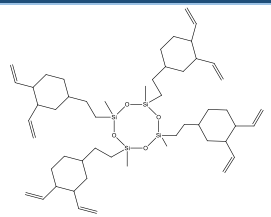
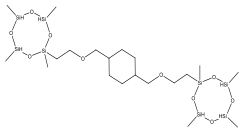
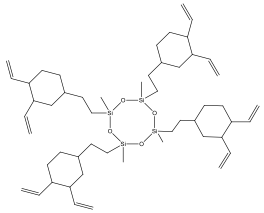
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X140 |  R69 |  MW=889.59 R32 (1:1) | 15 | 50/4h RT/1mo+ | 2H? <H | | Add (2:1) MEK to R69 before mixing w/R32 Observed separation-uneven plate |
| X141 |  R70 |  MW=889.59 R32 (1:1) 5% VTAS | 30 | 50/4h RT/1mo+ | 5H 4H | 3B 4-5B | Clear mixture (observed tiny bubbles in coating) |

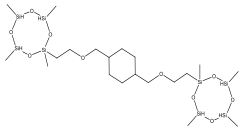
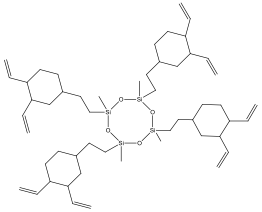
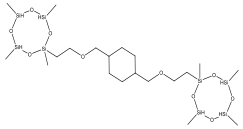
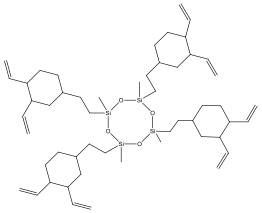
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X142 |  MW=739.61 R44 |  MW=889.59 R32 (1:1) 5%VTAS | 30 | 50/4h<br>RT/1mo+ | Not Cured<br>Not Cured | | Uneven coating - separation |
| X143 | R21,  MW=739.61 R44 |  MW=889.59 R32 (1:1) 5% VTAS | 15 | 50/4h<br>RT/1mo+ | Not Cured<br>Not Cured | | Uneven coating - separation |

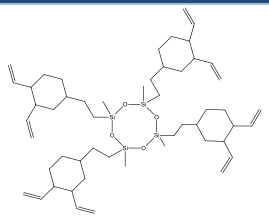
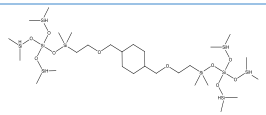
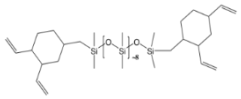
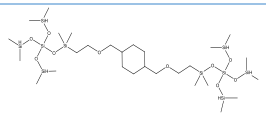
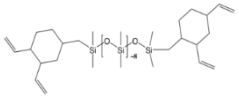
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X144 |  <br>MW=853.76<br>R60 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTAS | 30 | 50/4h<br>50/4h+RT/6d<br>RT/1mo+ | 5H<br>2H | 3-4B<br>4-5B<br>4-5B | |
| X145 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1) | 30 | 50/4h<br>RT/6d<br>RT/1mo+ | 5H<br><H<br>6H | 2-3B<br>Slightly sticky to touch<br>3B | RT (small bubbles in coating) |

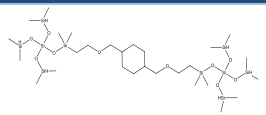
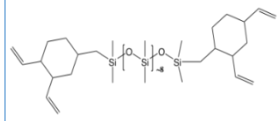
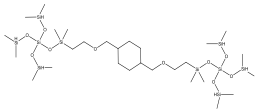
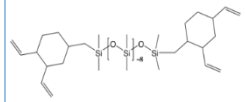
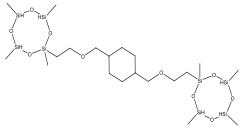
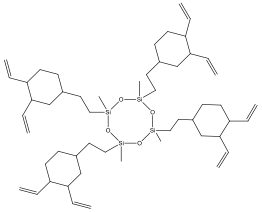
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X146 |  <br>R72 |  <br>MW=889.59<br>R32 (1:1) | 30 | 50/4h<br>RT/6d<br>RT/1mo+ | 5H?<br><H<br>5H? | Slightly sticky to touch<br>4/5B | Uneven coating - separation |
| X147 |  <br>R73 |  <br>MW=889.59<br>R32 (1:1) | 30 | 50/4h | <H | | Separated – uneven coating |
| X148 | DIALLYL | R64 | 45 | 50/4h | Not cured | | Observed smoke in <5min |

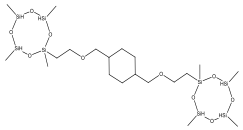
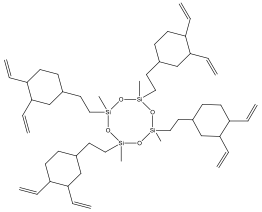
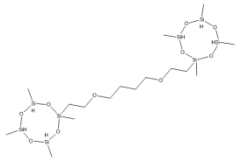
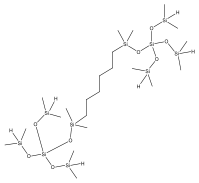
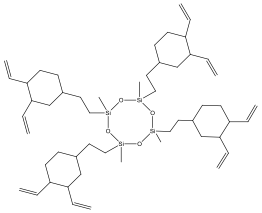
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X149 |  <br>MW=853.76<br>R60 |  <br>MW=889.59<br>R32 (0.8:1) | 30 | 50/4h<br>RT/4d<br>RT/1mo+ | 5H<br>4H<br>5H | 3B<br>2B<br>2B | |
| X150 |  <br>MW=853.76<br>R60 |  <br>MW=889.59<br>R32 (1:0.8) | 30 | 50/4h<br>RT/4d<br>RT/1mo+ | 5H<br>4H<br>6H | 2B<br>2-3B<br>2-3B | |
| X151 |  <br>MW=853.76<br>R60 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTMS | 30 | 50/4h<br>RT/4d<br>RT/1mo+ | 5H<br>4H<br>6H | 4B<br>1-2B<br>3-4B | |

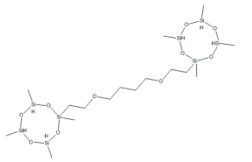
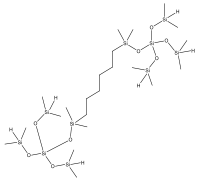
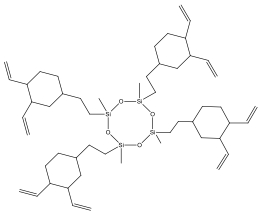
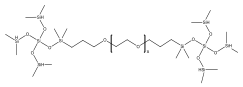
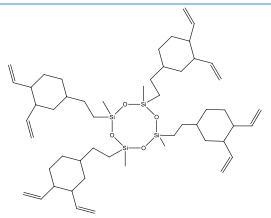
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X152 |  <br>MW=853.76<br>R60 |  <br>MW=889.59<br>R32 (1:1)<br>5% ATMS | 30 | 50/4h<br>RT/4d<br>RT/1mo+ | 4-5H<br>5H<br>5H | 1-2B<br>2B<br>4-5B | |
| X153 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTAS | 30 | 50/4h<br>RT/3d<br>RT/1mo | 5H<br>Sticky to touch<br><H | 4-5B | |

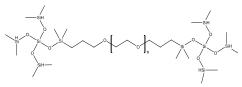
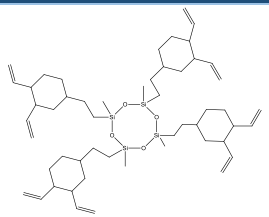
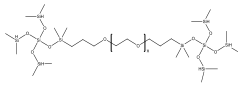
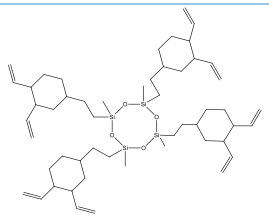
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X154 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTMS | 30 | 50/4h<br>RT/3d<br>RT/1mo | 5H<br>Slightly sticky to touch – 2H<br>5-6H | 3B<br>4-5B | |
| X155 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% ATMS | 30 | 50/4h<br>RT/3d<br>RT/1mo | 5H<br>2H<br>6H | 3B<br>4-5B | |

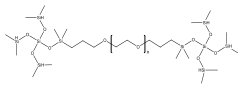
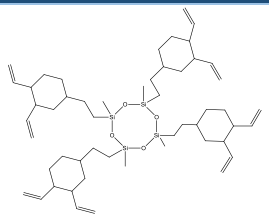
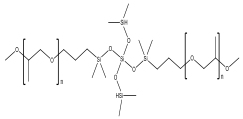
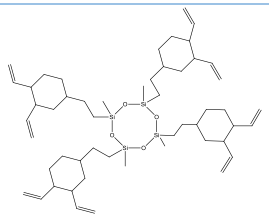
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X156 | <br>R70 |  <br>MW=889.59<br>R32 (1:1)<br>5% ATMS | 30 | 50/4h<br>RT/3d<br>RT/1mo | 2H<br>H<br>4H | 1B<br><br>1-2B | |
| X157 |  <br>MW=853.76<br>R60 |  R29 | 15 | 50/4h | <H | | |
| X158 |  <br>MW=853.76<br>R60 |  R29<br>(1:1)<br>5% VTAS | 15 | 50/4h | <H | | |

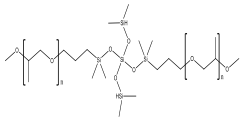
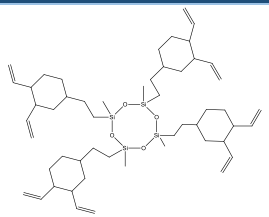
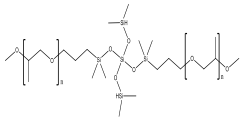
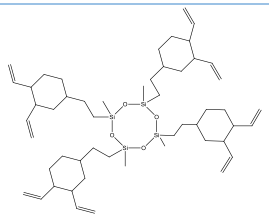
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X159 |  <br>MW=853.76<br>R60 |  <br>R29 (1:1)<br>5% ATMS | 15 | 50/4h | H | | |
| X160 |  <br>MW=853.76<br>R60 |  <br>R29 (1:1)<br>5% VTMS | 15 | 50/4h | H | | |
| X161 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1) | 15 | 50/4h<br>RT/1mo+ | 5H<br>2H | 2/3B<br>4B | (X138 repeat)<br>Uneven coat |

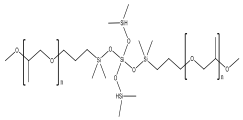
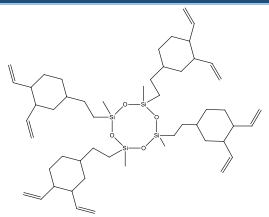
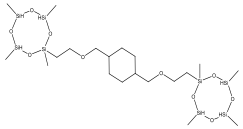
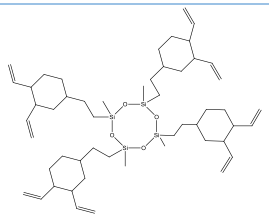
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X162 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTAS | 15 | 50/4h<br>RT/1mo+ | <H<br>Not cured | | X153 repeat |
| X163 |  <br>  <br>R21,<br>MW=739.61<br>R44 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTAS | 15 | 50/4h<br>RT/1mo+ | <H<br>Not cured | | X113Var.-ratio, coupling agent) |

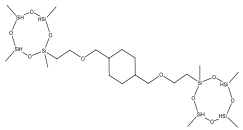
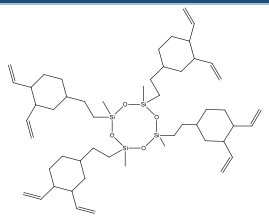
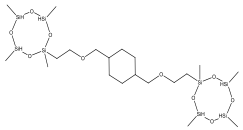
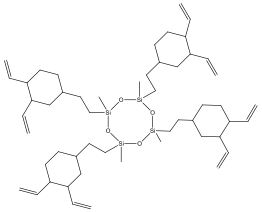
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X164 |   R21, MW=739.61 R44 |  MW=889.59 R32 (1:1) 5% VTMS | 15 | 50/4h<br>RT/1mo+ | 5H<br>5H | 4-5B<br>4B | X113Var.-ratio, coupling agent) |
| X165 |  R75R |  MW=889.59 R32 (1:1) | 30 | 50/4h<br>RT/1mo+ | <H<br>Not Cured | | |

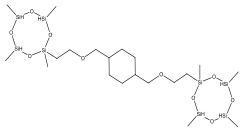
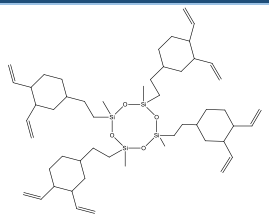
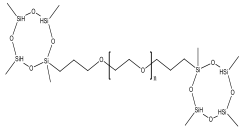
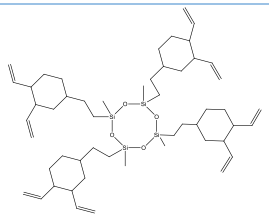
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X166 |  <br>R75R |  <br>MW=889.59<br>R32 (1:1)<br>5% VTAS | 30 | 50/4h<br>RT/1mo+ | <H<br>Not Cured | | |
| X167 |  <br>R75R |  <br>MW=889.59<br>R32 (1:1)<br>5% ATMS | 30 | 50/4h<br>RT/1mo+ | <H<br>Not Cured | | |

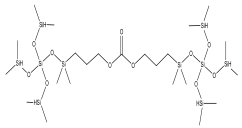
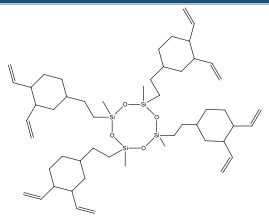
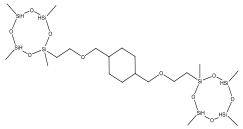
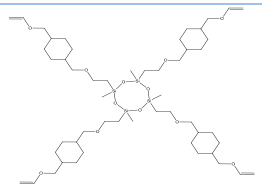
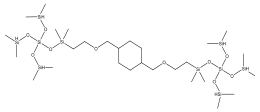
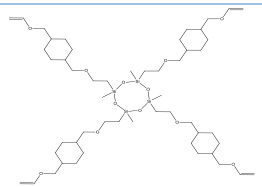
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X168 |  |  <br>MW=889.59<br>R32 (1:1)<br>5% VTMS | 30 | 50/4h<br>RT/1mo+ | <H<br>Not Cured | | |
| X169 |  <br>R77 |  <br>MW=889.59<br>R32 (1:1) | 15 | 50/4h<br>RT/1mo+ | <H<br>Not Cured | | |

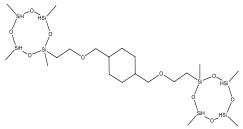
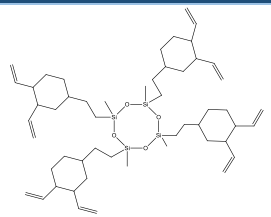
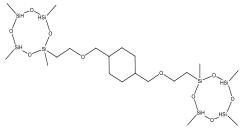
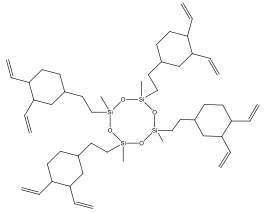
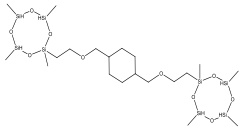
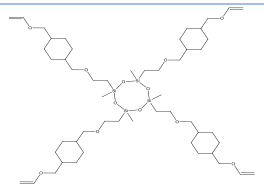
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X170 |  R77 |  MW=889.59 R32 (1:1) 5% VTAS | 15 | 50/4h RT/1mo+ | <H Not Cured | | |
| X171 |  R77 |  MW=889.59 R32 (1:1) 5% ATMS | 15 | 50/4h RT/1mo+ | <H Not Cured | | |

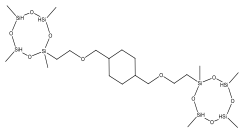
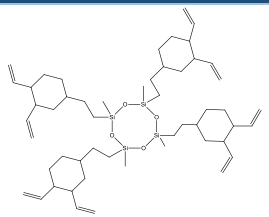
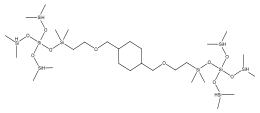
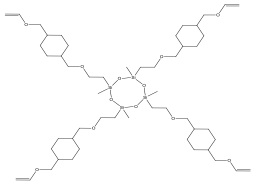
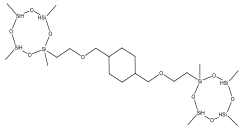
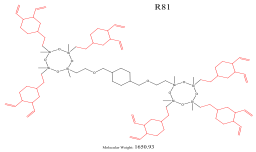
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X172 |  <br>R77 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTMS | 15 | 50/4h<br>RT/1mo+ | <H<br>Not Cured | | |
| X173 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% BTES<br>(butenyltriethoxy-silane) | 0 | 50/4h<br>RT/4d<br>RT/1mo+ | 5/6H<br>Not cured (sticky)<br>2H | 1/2B<br>5B | Pot life – did not harden even after 4 days |

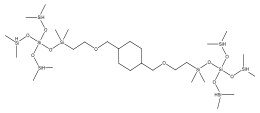
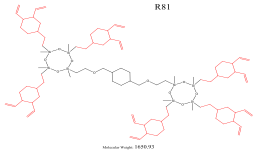
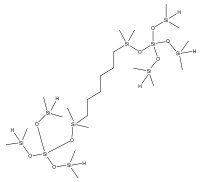
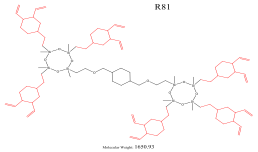
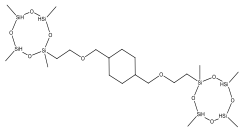
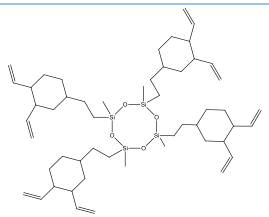
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X174 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% HTMS<br>(hexenyltrimethoxy-silane) | 0 | 50/4h<br>RT/4d<br>RT/1mo+ | 5/6H<br>Not cured (sticky)<br>H | 3B<br>2B | Pot life – did not harden even after 4 days |
| X175 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% 7-OTMS | 0 | 50/4h<br>RT/4d<br>RT/1mo+ | 5/6H<br>Not cured (sticky)<br>H | 3-4B<br>5B | Pot life – did not harden even after 4 days |

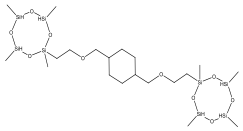
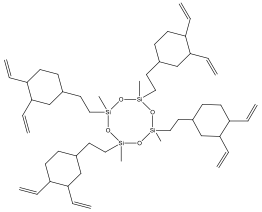
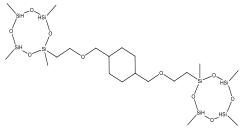
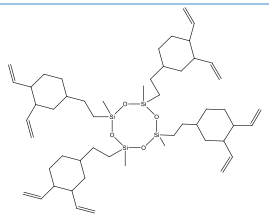
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X176 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>5% VTES<br>(vinyltrethoxysilane) | 0 | 50/4h<br>RT/4d<br>RT/1mo+ | 5/6H<br>Not cured (sticky)<br>H | 3-4B<br>4B | Pot life – did not harden even after 4 days |
| X177 |  <br>R74 |  <br>MW=889.59<br>R32 (1:1) | 30 | 50/4h<br>RT/1mo+ | Not cured<br>Not Cured | | Opaque mixture |

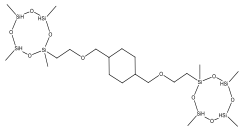
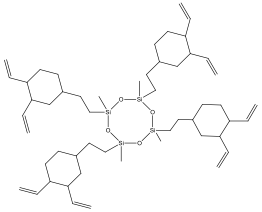
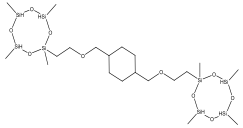
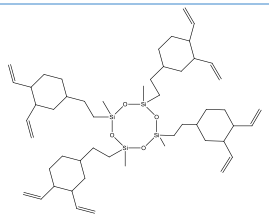
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X178 |  R78 |  MW=889.59 R32 (1:1) | 30 | 50/4h RT/1mo+ | 5H Not Cured | 2B | |
| X179 |  R71 |  R79 | 0 | 50/4h RT/1mo+ | 4-5H Not Cured | 0-1B | Uneven coat (separation) |
| X180 |  R60 |  R79 | 0 | 50/4h RT/1mo+ | 4-5H Not Cured | 0-1B | Uneven coat (separataion) |

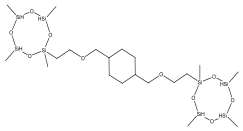
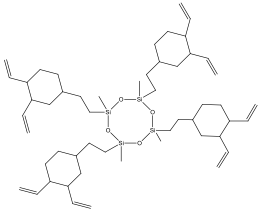
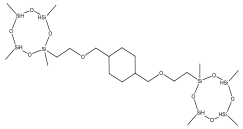
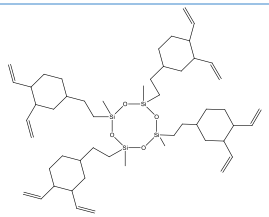
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X181 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1) | 15 | 50/4h | 6H | 1-2B | Observed bubbles/uneven coat |
| X182 |  <br>R71 |  <br>MW=889.59<br>R32 (1:1)<br>Xylene/solvent (0.3g) | 15 | 50/4h<br>RT/10d | 6H<br>6H | 2B<br>1-2B | |
| X183 |  <br>R71 |  <br>R79<br>Xylene (0.3g) | 15 | 50/4h<br>RT/10d | 6H<br>6H | 1-2B<br>0-1B | |

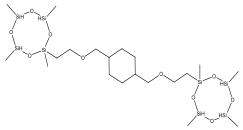
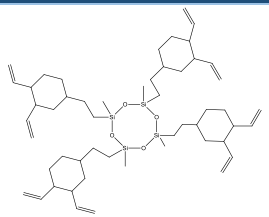
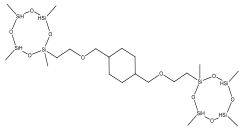
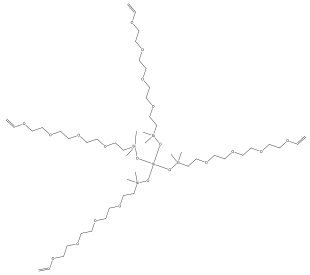
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X184 |  <br>R71 |  <br>R32 (SUB2) | 20 | 50/4h<br>RT/10d | 6H<br>6H | 1-2B<br>0-1B | |
| X185 |  <br>R60 |  <br>R79<br>Xylene (0.3g) | 30 | 50/4h<br>RT/2d<br>RT/1mo+ | 4H<br><H (slightly tacky)<br><H | 0-1B<br>0-1B | |
| X186 |  <br>R71 |  <br>R81<br>Xylene (0.2g) | 20 | 50/4h<br>RT/2d<br>RT/1mo+ | 6H<br>2H<br>2H | 4-5B<br>3-4B | Uneven coat |

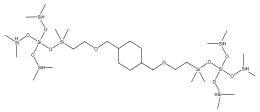
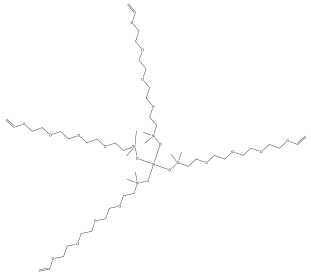
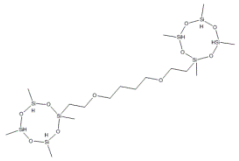
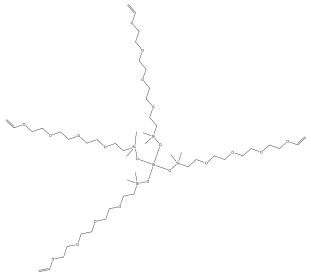
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X187 |  <br>R60 |  <br>R81<br>Xylene (0.2g) | 20 | 50/4h<br>RT/2d<br>RT/1mo+ | 5H<br>2H<br>2H | 3-4B<br>3B | Uneven coat |
| X188 |  <br>R44 |  <br>R81 | 30 | 50/4h<br>RT/2d<br>RT/1mo+ | 4H<br>2H<br>4H | 2-3B<br>2-3B | Uneven coat (separation) |
| X221 |  <br>R71 |  <br>R32<br>(1:1)<br>5%<br>Butenyltriethoxysilane | 30 | 50/4h | 2H | 2B | |

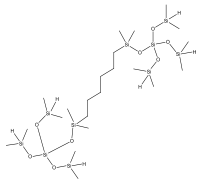
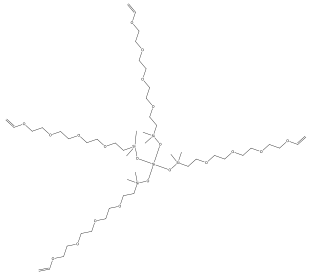
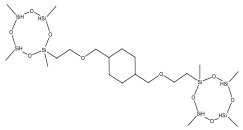
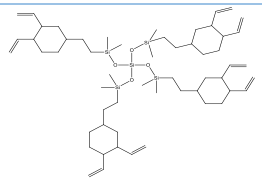
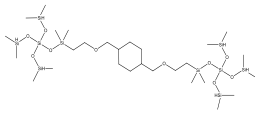
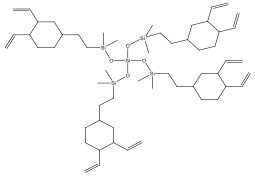
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X222 |  R71 |  R32 (1:1) 5% Hexenyltrimethoxysilane | 20 | 50/4h | 2H | 0-1B | |
| X223 |  R71 |  R32 (1:1) 5% 7-Octenyltrimethoxisilane | 20 | 50/4h | 2H | 3B | |

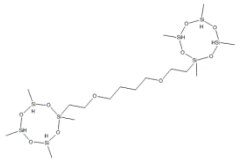
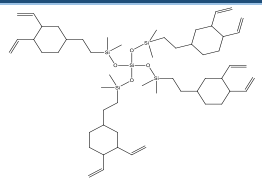
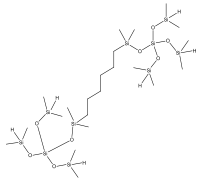
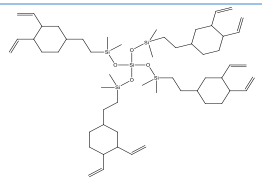
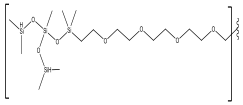
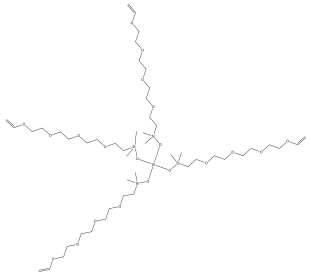
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X224 |  R71 |  R32 (1:1) 5% Vinyltriethoxysilane | 20 | 50/4h | 4H | 4B | |
| X225 |  R71 |  R32 (1:1) 5% Butenyltriethoxysilane | 15 | 50/4h | H | 0B | Tested on primed plate |

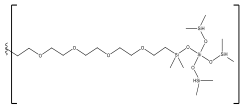
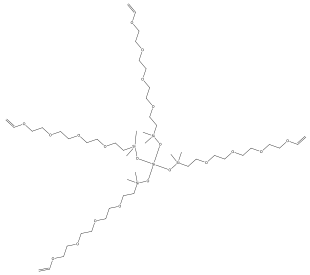
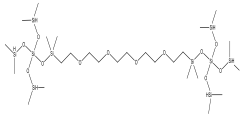
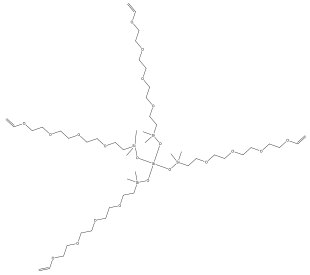
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X226 |  R71 |  R32 (1:1) 5% Hexenyltrimethoxysilane | 20 | 50/4h | H | 0B | Tested on primed plate |
| X227 |  R71 |  R32 (1:1) 5% 7-Octenyltrimethoxisilane | 20 | 50/4h | 3H | 0B | Tested on primed plate |

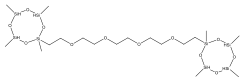
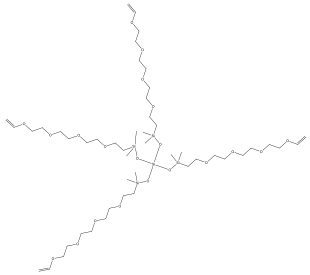
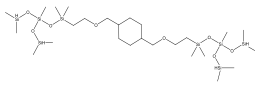
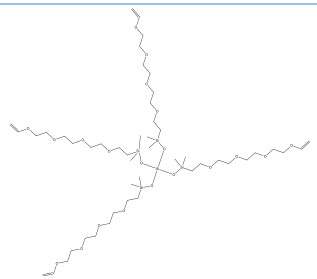
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X228 |  R71 |  R32 (1:1) 5% Vinyltriethoxysilane | 20 | 50/4h | 2H | 0B | Tested on primed plate |
| X229 |  R71 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | <H<br>Not cured | | Uneven Coating |

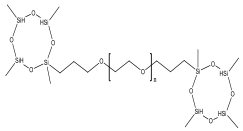
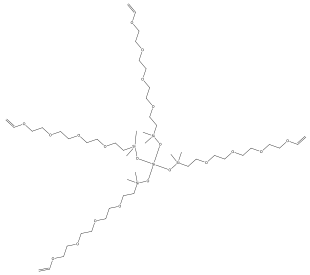
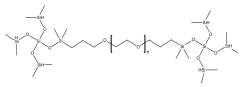
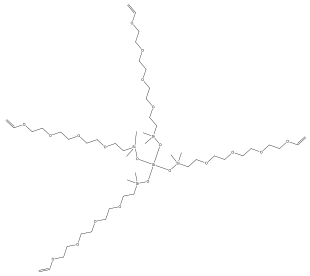
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X230 |  R60 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | <H<br>Not cured | | Uneven Coating |
| X231 |  R21 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | <H<br>Not cured | | |

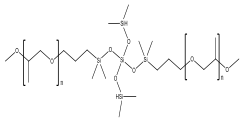
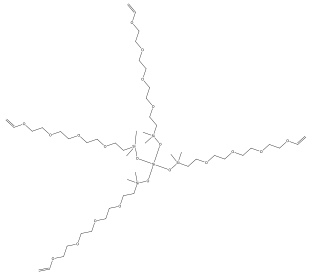
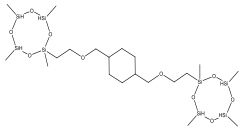
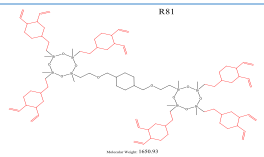
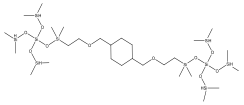
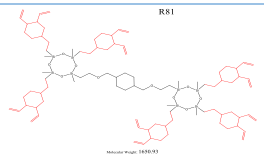
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X232 |  R44 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | <H<br>Not cured | | Uneven Coating |
| X233 |  R71 |  R57 (1:1) | 15 | 50/4h<br>RT/1 week | 5H<br><H | 0B | |
| X234 |  R60 |  R57 (1:1) | 15 | 50/4h<br>RT/1 week | 5H<br>H | 2B | |

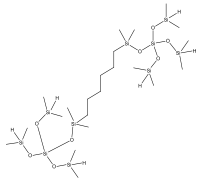
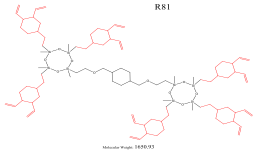
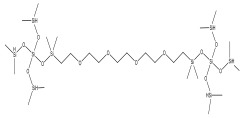
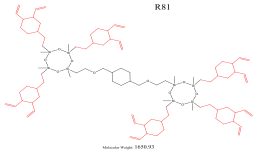
| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X235 |  R21 |  R57 (1:1) | 15 | 50/4h<br>RT/1 week | 5H<br><H | 0B | |
| X236 |  R44 |  R57 (1:1) | 15 | 50/4h<br>RT/1 week | 5H<br><H | 2B | |
| X237 |  R68 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | <H<br>Not cured | | Observed separation |

| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X238 |  R69 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | Not cured<br>Not cured | | Added xylene to thin out R69 (too viscous by itself)<br>Uneven Coating |
| X239 |  R70 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | <H<br>Not cured | | |

| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X240 |  R72 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | <H<br>Not cured | | Uneven Coating |
| X241 |  R65 |  R58 (1:1) | 30 | 50/4h<br>RT/1 week | <H<br>Not cured | | |

| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X242 |  R74 |  R58 (1:1) | 30 | 50/4h<br>RT/1 week | Not cured<br>Not cured | | |
| X243 |  R75R |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | Not cured<br>Not cured | | |

| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X244 |  R77 |  R58 (1:1) | 15 | 50/4h<br>RT/1 week | Not cured<br>Not cured | | |
| X284 |  R71 |  R81 (1:1) | 20 | 50/4h<br>RT/1d | 2H<br><H | 4B | |
| X285 |  R60 |  R81 (1:1) | 20 | 50/4h<br>RT/1d | 4H<br><H | 3-4B | |

| Form # | A = Si-H part | B = Ene Part (A:B equiv. ratio) | Pt Catalyst (ppm) | Cure Temp (°C; Room Temp) / time (hours; days) | Hardness | Adhesion | Notes |
|---|---|---|---|---|---|---|---|
| X286 |  R44 |  R81 (1:1) | 30 | 50/4h<br>RT/1d | H<br><H | 4B | |
| X287 |  R70 |  R81 (1:1) | 30 | 50/4h<br>RT/1d | 2H<br><H | 1-2B | |

*Please refer to the Catalyst Table for Formulations # 245-257.*
*Please refer to the Solvent/inhibitor Table for Formulations # 288-294.*

# APPENDIX B: SCIENTIFIC/TECHNICAL PUBLICATIONS

We plan to convert this report into two manuscripts: one that discusses the hydrosilylation-only system and one that addresses the Si-OH condensation system.