**UCT’S PETRARCH® PRODUCTS**

- **Silanes**
  \[
  Z(CH_2)_y\text{Si}X
  \]
  \[
  O
  \]
  \[
  Z = \text{NH}_2, \text{SH}, \text{C-H},
  \]
  And Other Reactive Functional Groups

- **Silicones**
  \[
  Y\text{SiO} \left[ \text{Si} - \text{O} \right] \text{Si} - Y
  \]
  \[
  O
  \]
  \[
  Y = \text{H}, \text{Vinyl}, \text{Amino}
  \]
  And Other Reactive Functional Groups

- **Platinum Catalysts**
  \[
  \text{Pt}^\circ \left[ \text{INHIBITOR} \right]_x
  \]
## PRODUCT APPLICATIONS

### Silanes
- Adhesion Promoters
- Hydrophobic Coatings
- Surface Modifying Reagents
- Lenses Monomers
- Chromatographic Stationary Phases

### Silicones
- Lubricants
- Adhesives
- Electronic Coatings
- Dental Fillings
- Fiber Optic Coatings
- Releasing Agents
- Medical Coatings
- High Performance Coatings

### Platinum Catalysts
- Hydrosilylation
- Room Temperature Silicone Curing Agent
- High Temperature Silicone Curing Agent
Platinum vinylsiloxane complexes have found extensive use as catalysts for promoting hydrosilation reactions. The bond forming chemistry proceeds according to the following equation:

\[ \equiv \text{SiH} + \text{CH}_2 = \text{CHSi} \xrightarrow{\text{Platinum Catalyst}} \equiv \text{SiCH}_2\text{CHHSi} \equiv \]

Applications include two part silicone compositions (RTV addition cure systems) utilized in dental impression compounds, prototype molding, sealants, and electronic coating applications. Cure time is reduced from hours to minutes in RTV systems due to the solubility of these catalysts in dimethylsiloxane polymers.
This article will attempt to highlight the benefits of homogeneous platinum catalysts of the Karstedt type (Ref 6) over other catalyst systems commonly used in curing polydimethylsiloxane resins. The technology is also applicable to organic synthesis where an active silyl functionality needs to be grafted onto an olefinic moiety. In order to better understand the benefits of this technology over other cure systems, some common industrial terms must be clearly understood. Table 1 is a listing of these terms with pertinent United Chemical Technologies catalysts when appropriate. In many chemical reactions the reacting groups are color coded for clarity.
Table 1 Common Terms

Basic Terminology

**Cure:** Crosslink a liquid polymer system to where it forms an elastic gel (sets up and solidifies).

**Addition Cure:** Platinum Catalyzed,
Examples: PC072, PC075, PC085

**Condensation Cure:** Tin, Zinc Catalyzed,
Examples: PC040, PC050

**Peroxide Cure:** Peroxide Catalyzed,
Example: PC010

**RTV:** Room Temperature Vulcanizable (curable) system,
Usually an addition or condensation cure resin.
Other nomenclature commonly encountered is related to the orientation of the addition of a hydrosilane to a double bond. Table 2 defines Markonikov and anti-Markonikov addition with simple color coded examples.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH=CH₂ + HX</td>
<td>X = Halogen or Silicon, R = alkyl group</td>
<td></td>
</tr>
</tbody>
</table>

**Markonikov Addition:**
Hydrogen adds to **least substituted** double bond.

- Example: RCHₓ-CH₂ H

**Anti-Markonikov Addition:**
Hydrogen adds to **most substituted** double bond.

- Example: RCHH-CH₂ X
For resin systems typically a Vinyl silicone (PS437-PS449.5) is reacted with a Hydrosilicone (PS118-PS124.5) and a homogeneous platinum catalyst PC065-PC088.3(platinum catalysts). Silicon in the hydride adds preferentially to the least substituted double bond. Some of the other isomer (~5-10%) is always present. Our platinum catalysts are primarily **zero valent** (non ionic).

\[
\text{R}_1\text{R}_2\text{R}_3\text{SiH} + \text{CH}_2=\text{CHR} \xrightarrow{\Delta \text{PC065-088.3 Catalysts}} \text{R}_1\text{R}_2\text{R}_3\text{SiCH}_2\text{CHHR}
\]
Figure 1 also illustrates the two modes of addition for a simple terminal vinyl substituted alkene when reacted with a trifunctional hydrosilane. X is typically halogen (usually chloro or bromo) or alkoxy (usually methoxy or ethoxy).
Figure 1 Stereochemistry of Hydrosilation
“Anti-Markonikov” Addition Preferred

\[
\text{R – C = CH}_2 + \text{H – Si – X}_3 \xrightarrow{\Delta} \text{R – C – CH}_2 – \text{SiX}_3
\]

“Anti-Markonikov”

\[
\text{H} \\
\text{R – C – CH}_2 – \text{SiX}_3
\]

MAJOR PRODUCT
USUALLY >90%

“Markonikov”

\[
\text{H} \\
\text{R – C – CHH}_2 \\
\text{SiX}_3
\]

MINOR PRODUCT
Table 3 summarizes electronic and steric effects observed for the hydrosilation reaction. Due to these constraints, best results are obtained with halogen or alkoxy functional hydrosilanes or hydrosilicones on reaction with a terminal double bond.
Table 3 Electronic and steric effects on the rate of hydrosilation reactions

1) Electronic Effects
   a) Electron donating groups on Silicon retard Rate, Electron withdrawing groups on silicon accelerate rate.
      Example: ClSiH > (CH3)3SiH
      Chlorine is electron withdrawing, methyl electron donating.

   b) Electron withdrawing groups conjugated (next to) to double bonds retard rate of hydrosilation.
      Electron donating groups conjugated (next to) to double bonds accelerate rate of hydrosilation.
      Example: CH2CH=CH2 >> CH2=CHCN
      Ethyl group is electron donating. Cyano group is electron withdrawing.

2) Steric Effects
   Terminal Double bonds hydrosilate much faster than internal.
   Example: RCH=CH2 >> RCH=CHR’
The composition of zero valent Karstedt (Ref 6) type catalysts is complex and consists of monomeric, dimeric and polymeric species. Small amounts of divalent platinum also are present. Figure 2 illustrates firstly the synthetic utility of the hydrosilation process in a process generating a specialty hexyl functional polydimethylsiloxane (Structure ii). Typical reaction products of chloroplatinic acid with divinyltetramethyldisiloxane (Solution A) and tetramethyltetravinylcyclo-tetrasiloxane (Structure vii) are also illustrated. Tight process control as practiced by United Chemical Technologies produces reproducible mixtures for consistent catalyst reactivities.
Figure 2

Platinum Metals Rev., 1997, 41, (2), 66-75

Reference as above
Figure 3 illustrates the structure of a discrete dimer isolated from the reaction of chloroplatinic acid with dimethyl divinyl silane (D6206.5). Also illustrated are the reaction products of a monomeric and dimeric platinum complex with the inhibitor dimethyl fumarate. The role of an inhibitor will be explained later in this article.
Fig. 1 The three dimensional structure of 3 produced by the reaction of H₂PtCl₆ with (CH₃)₃Si(CH=CH₂)₂. This dinuclear complex has two bridging chlorine atoms and a bridging (CH₃)₃Si(CH=CH₂)₂ ligand. Each platinum atom in 3 contains a η¹:η¹-(CH₃)₃Si(CH=CH₂)(CH₂CH₃) ligand (20).
The mechanism of hydrosilation is complex due to the different species initially present, but a simplified model is easily comprehended. Equations 1-3 illustrate the attack of an inhibited platinum complex by an alkene (Equation 1), followed by addition of a hyridosilane, forming a Pt-H functional intermediate (Equation 2). Intramolecular hydride transfer generates the product and a transient intermediate (Equation 3). The intermediate then loops back and continues the catalytic process by reaction with additional alkene.
Classical mechanism for hydrosilation reactions (simplified for clarity)

A molecule of inhibitor is displaced and the alkene forms a d-pi complex with the platinum. \((\text{Adduct 1})\)

\[
\text{(Eq 1) } \quad \text{Pt}(0)[\text{INHIBITOR}]_n + \text{RCH} = \text{CH}_2 = \text{Pt}(0)[\text{INHIBITOR}]_{n-1}[\text{RCH} = \text{CH}_2]
\]

(Adduct 1)

The hydrosilane or hydrosilicone then reacts with the complex above and forms a platinum hydride intermediate \((\text{Adduct 2})\).

\[
\text{(Eq 2) } \quad \text{Pt}(0)[\text{INHIBITOR}]_{n-1}[\text{RCH} = \text{CH}_2] + \text{R'}\text{R''}\text{R'''}\text{SiH} = \text{R'}\text{R''}\text{R'''}\text{SiPt}(0)\text{H}\ [\text{INHIBITOR}]_{n-1}[\text{RCH} = \text{CH}_2]
\]

(Adduct 2).
Classical mechanism for hydrosilation reactions (continued)

This intermediate (Adduct 2) then undergoes an internal hydride transfer, generating the product and a electron deficient platinum species.

\[
\text{(Eq 3) } R'R''R'''\text{SiPt}(0)\text{H [INHIBITOR]}_{n-1}[\text{RCH=CH2]} \rightarrow \text{Pt}(0) \text{ [INHIBITOR]}_{n-1} + \text{RCHH-CH2SiR'R''R'''}
\]

The adduct 3 species above then reacts with more alkene, regenerating adduct 1, and continuing the catalytic process.

The potency of the inhibitor, valence state of the platinum, and quantity of excess inhibitor all affect catalyst reactivity. Oxygen and cyclic sugars also accelerate hydrosilation rates.
The factors affecting reactivity of homogeneous platinum catalysts have been reviewed by Lewis (Ref 1). Potency of inhibitor, platinum valence state, and presence or absence of oxygen during the hydrosilation process have been shown to be significant factors. Cyclic ethers (Ref 3) also accelerate hydrosilations. Table 4 summarizes these effects.
### Table 4 Factors affecting platinum catalyst reactivity

1) **The potency of the inhibitor**
   PS925 (inhibitor for PC085) is much more potent than D6210 (inhibitor for PC072/PC075). Therefore PC085 is slower than PC072/PC075.

2) **Quantity of excess inhibitor**

3) **Valence state of the platinum**
   (Pt is most active in zero valence state)

4) **Presence/absence of oxygen (Ref 1)**
   (Oxygen accelerates hydrosilation rates)

5) **Presence/absence of cyclic sugars (Ref 3)**
   (Cyclic sugars accelerate hydrosilation rates)
The advantages of homogeneous catalysts over representative heterogeneous systems are presented in Table 5. Although homogeneous platinum catalysts remain in the cured resin, the low levels of platinum required compensate for the non-recoverability of the metal.
Our platinum catalysts are **homogeneous**, i.e. they dissolve in the reaction medium. They are preferable to **heterogeneous**, i.e. insoluble catalysts, in that homogeneous catalysts do not depend on irregular surface effects for their activity.

**Homogeneous catalysts remain in cured resins.**

### Examples

<table>
<thead>
<tr>
<th>Heterogeneous</th>
<th>Homogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt on alumina</td>
<td>Pt(0) Vinylsiloxane complex(PC072)</td>
</tr>
<tr>
<td>Pd on Carbon</td>
<td>Pt(0) Cyclovinyl complex(PC085)</td>
</tr>
<tr>
<td>Ru on CaCO3</td>
<td>Pt(+2) Octanol complex(PC088.3)</td>
</tr>
</tbody>
</table>
A wide variety of functionalities can be introduced into polymer resins or monomers via homogeneous platinum catalyzed hydrosilations. Availability of suitable terminal alkene functionalities is the only limitation. Figure 4 lists functionalities which may be introduced from common commercially available starting materials.
Figure 4 Typical Hydrosilation Reactions:

\[
\begin{align*}
\text{Si - H} & \quad \text{MONOMER OR POLYMER} \\
\text{Si - CH}_2 - \text{CH}_2 - R \quad \text{(HYDROCARBON)} & \quad \text{Si - CH}_2 - \text{CH}_2 - \text{O} - \text{CH}_2 \quad \text{(ETOXY)} \\
\text{Si - CH}_2 - \text{CH}_2 - \text{C} = \text{N} \quad \text{(NITRILE)} & \quad \text{Si - CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \quad \text{(AMINE)} \\
\text{Si - CH}_2 - \text{CH}_2 - \text{C} = \text{N} \quad \text{(NITRILE)} & \quad \text{Si - CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{C} - \text{CH}_3 \quad \text{(ESTER)}
\end{align*}
\]
The other common methods for curing silicone resins will now be reviewed. Condensation cure systems, whose cure chemistry is reviewed in Table 6, have been in use for many years. They are primarily employed in one and two part moisture cure adhesives. Peroxide catalyzed systems are most often employed in curing of high molecular weight silicone gum stock, as reviewed in Table 7.
Table 6 Condensation Cure Systems

Silanol fluid (PS340-PS349.5) + Alkoxy silane (T1807, PS9120, etc.)
+ Tin or Zinc Catalyst (PC040, PC050, PC055)

All evolve Volatile organic byproducts (underlined Ⅰ)

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACYLOXY</td>
<td>$\text{R}_3\text{SiOH} + \text{AcOSiR'}_3$</td>
<td>$\text{R}_3\text{SiOSiR'}_3 + \text{AcOH}$</td>
</tr>
<tr>
<td>ENOXY</td>
<td>$\text{R}_3\text{SiOH} + \text{CH}_2 = \text{COSiR'}_3$</td>
<td>$\text{R}_3\text{SiOSiR'}_3 + \text{CH}_3\text{CCH}_3$</td>
</tr>
<tr>
<td>OXIME</td>
<td>$\text{R}_3\text{SiOH} + \text{R}_2\text{C}=\text{N-OSiR'}_3$</td>
<td>$\text{R}_3\text{SiOSiR'}_3 + \text{R}_2\text{C}=\text{NOH}$</td>
</tr>
<tr>
<td>ALKOXY</td>
<td>$\text{R}_3\text{SiOH} + \text{MeOSiR'}_3$</td>
<td>$\text{R}_3\text{SiOSiR'}_3 + \text{MeOH}$</td>
</tr>
<tr>
<td>AMINE</td>
<td>$\text{R}_3\text{SiOH} + (\text{CH}_3)_2\text{NSiR'}_3$</td>
<td>$\text{R}_3\text{SiOSiR'}_3 + (\text{CH}_3)_2\text{NH}$</td>
</tr>
</tbody>
</table>
## Table 7 Peroxide Cure Systems

Vinyl silicones (usually with functionality >2) can be cured with peroxide catalysts (e.g. benzoyl peroxide or dichlorobenzoyl peroxide) at temperatures $\geq 100^\circ$C.

**Example:**

PS255 (vinyl functional silicone gum) +1% Dichlorobenzoyl peroxide (PC010) → 130°C → Cured Elastomer
Homogeneous platinum catalyzed resin systems have significant advantages over the other cure systems as outlined in Table 8 and Table 9. For these reasons they are utilized by major dental, fiber-optic and resin manufacturers.
Table 8 Advantages of Addition Cure (Platinum) Over Condensation Cure (Tin, Zinc) Systems:

A) No volatile byproducts.

B) Lower catalyst concentrations.
(5-30 ppm vs 100-300 ppm).

C) Less moisture sensitivity

D) Smoother reaction profiles.
Table 9 Advantages of Addition Cure (Platinum) Over Peroxide Cure Systems:

A) **Lower curing temperatures possible.**

B) **No corrosive acidic byproducts.**
   (e.g., benzoic acid from benzoyl peroxide cure).

C) **No “frothing” from oxygen byproduct of cure.**

D) **No oxidative degradation of elastomer possible.** Oxidation often gives colored byproducts.

E) **Wider range of curable silicones available.**
The original homogeneous platinum catalyst was chloroplatinic acid in alcohol, commonly known as Speiers catalyst (Ref 5). This (+ 4 valent) catalyst has been largely replaced by the zero valent Karstedt type catalysts reviewed in this article. Major advantages of the Karstedt type catalysts are summarized in Table 10.
### Table 10 Advantages of Platinum (0) Vinyl Siloxane Complexes PC065-PC086 Over Chloroplatinic Acid, H$_2$PtCl$_6$

<table>
<thead>
<tr>
<th>Advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Homogeneous</td>
</tr>
<tr>
<td>2) Higher reactivity</td>
</tr>
<tr>
<td>3) Reactivity is fine tuned by choice of solvent and inhibitor</td>
</tr>
<tr>
<td>4) No corrosive HCl or chloride byproducts.</td>
</tr>
<tr>
<td>5) Colorless catalyst solutions are available.</td>
</tr>
</tbody>
</table>
United Chemical Technologies is a major manufacturer of high quality Karstedt type catalysts, that is, homogeneous Pt(0) complexed with linear or cyclic vinyl silane retarders. Table 11 and Table 12 list the most common commercial offerings. PC065 through PC076 are of the Karstedt type. Reactivities are fine tuned by choice of inhibitor and platinum concentration. Lower reactivity variations are referred to as “Ashbey’s catalyst”, Pt (0) complexed with a cyclic vinyl retarder, and “Lamoreaux’s catalyst”, Pt (+2) in octanol/octanal. Ashbey catalysts such as PC085 are commonly used in high temperature extruded silicone systems. Lamoreaux catalysts such as PC088.3 improve the fire retardant properties of cured silicone rubbers.

In general, the chemist or formulator fine tunes his cure profile by variation of both platinum metal and inhibitor level. Starting guidelines are provided in Table 13.
Table 11 Product Line

Also see our Catalyst Brochure: 1%, 2%, 3%, 5% and 10% platinum concentrations are available.

PC074 (~2% Pt in Xylene) is optically clear and should find application where high transparency cured silicones are required. Examples include fiber optic and laser based technologies.

Relative Reactivity:

PC072 (PC074)>PC075>PC085

PC072 (and PC074) are for room temperature cures.

PC075 can be used for either room temperature or thermal cures.

PC085 is exclusively for >100°C extruded silicone or other elastomer curing systems.

Typical catalyst concentrations are 5-20ppm of platinum metal.

To convert to total catalyst needed, multiply by 50 for the above ~2% Pt concentration catalysts.
# Table 12 Homogeneous Platinum Catalysts

<table>
<thead>
<tr>
<th>Product</th>
<th>Percent Platinum (1)</th>
<th>Carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC065</td>
<td>10</td>
<td>Linear Inhibitor</td>
</tr>
<tr>
<td>PC072</td>
<td>2</td>
<td>Xylene</td>
</tr>
<tr>
<td>PC073</td>
<td>1</td>
<td>Xylene</td>
</tr>
<tr>
<td>PC074 (CLEAR)</td>
<td>2</td>
<td>Xylene</td>
</tr>
<tr>
<td>PC074.5</td>
<td>2</td>
<td>Octamethylcyclotetrasiloxane</td>
</tr>
<tr>
<td>PC075</td>
<td>2</td>
<td>Linear Silicone</td>
</tr>
<tr>
<td>PC075.3</td>
<td>3</td>
<td>Linear Silicone</td>
</tr>
<tr>
<td>PC075.5</td>
<td>5</td>
<td>Linear Silicone</td>
</tr>
<tr>
<td>PC076</td>
<td>1</td>
<td>Linear Silicone</td>
</tr>
<tr>
<td>PC085</td>
<td>2</td>
<td>Cyclic Silicone (Ashbey’s catalyst)</td>
</tr>
<tr>
<td>PC085.3</td>
<td>3</td>
<td>Cyclic Silicone (Ashbey’s catalyst)</td>
</tr>
<tr>
<td>PC086</td>
<td>1</td>
<td>Cyclic Silicone (Ashbey’s catalyst)</td>
</tr>
<tr>
<td>PC088.3</td>
<td>2.1</td>
<td>Octanol/Octanal (Lamoreaux’s catalyst)</td>
</tr>
</tbody>
</table>

For hydrosilation reactions of two part RTV systems, it is recommended that platinum catalysts be utilized at the 5-50 ppm range based on total formulation weight. The reactivity of PC065-PC086 can be modified using retarders such as UCT's products designated D6210, T2160 or PS925 to achieve optimum reactivity characteristics.

Relative catalyst reactivity rates:

- PC072 > PC075 >> PC085 (~ 2% concentrations)
- PC073 > PC076 > PC086 (~ 1% concentrations)

Variations with additional platinum concentrations, solvents and inhibitors are available. Contact us with your specialized requirements.
The chemist of formulator must be careful to avoid certain compounds or commercial materials during his monomer synthesis or curing step. Table 14 lists the most common poisons. It is prudent to avoid running both platinum cure and condensation cure systems in the same vessel, as traces of tin from a condensation cure batch could poison a subsequent batch of platinum cured product.
### Table 14: Poisons to Avoid

- Sulfur compounds
- Amines
- Phosphines
- PVC’s
- Chloride ions
- Silver salts
- Tin salts

### Avoid:
- Natural rubbers
- PVC beakers
- Amino functional adhesion promoters
- Fertilizers
- Mercaptans
- Sulfides
Considerable confusion over the terms inhibitor, retarder and poison exists in the literature. Table 15 is an attempt to define these terms specifically and also gives pertinent examples of each class.
**Table 15 Definitions**

**Moderator (Retarder):** Retards speed of a reaction by complexing with the platinum, but dissociates at higher temperatures, i.e., it reversibly binds to the platinum.

**Examples:** Divinyltetramethyldisiloxane (D6210), Dimethyl Fumarate

**Inhibitor:** Shuts down reaction permanently when present but can be volatilized off to reactivate.

**Examples:** Methyl-isobutynol or other low boiling acetylenic alcohols.

**Poison:** Irreversibly complexes with the platinum, shutting down the reaction permanently. Cannot be volatilized off.

**Examples:** Ethyl Mercaptan, Diethyl Sulfide, Hydrogen Sulfide.
Common retarders offered by United Chemical Technologies and their structures are listed in Table 16 along with application guidelines. Acetylenic alcohol and fumarate inhibitors are available from standard organic chemical suppliers.
Table 16 Typical Inhibitors (Retarders)

D6210, PS925, T2160: To retard (slow down or stop) platinum cure, add 1-2 drops per 100g of polymer. To reactivate, heat to 80-100°C.

**Common Inhibitors and Retarders:**
Vinylsiloxanes, Acetylenic alcohols, dimethyl fumarate

Divinyltetramethyldisiloxane
D6210

Vinylmethylcyclosiloxanes
PS925 N = 3-5
T2160 N = 4
Experienced formulators and compounders can startup new materials research with little guidance, but for those new to silicone formulation Tables 17-19 are convenient starting points. The crosslinker, catalyst and plasticiser levels can all be varied to achieve the formulator’s unique cure profile and physical properties requirements. Other general guidelines are:

a) For two part systems, always put the platinum catalyst in the “A” (vinyl or “base”) side to avoid slow reaction of the catalyst with the hydrosilicone.

b) Plasticiser and vinyl fluid can be partially mixed with the “B” (hydrosilicone) side to achieve a better mix ratio. Care must be taken to avoid metal contamination on the “B” side if this approach is taken.

c) Avoid exposure to the poisons listed in Table 14.
This formulation has low modulus and durometer but is useful as a molding compound. No special procedure or apparatus is required and the procedure may be modified by varying the ratios of concentration to accelerate or retard the cure rate. Alternatively, the cure rate may be retarded by addition of T2160 inhibitor.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PS443</td>
<td>(Vinyl Fluid)</td>
<td>100 parts</td>
</tr>
<tr>
<td>SS0216</td>
<td>(Filler)</td>
<td>50 parts</td>
</tr>
<tr>
<td>PS123</td>
<td>(Hydrosilicone)</td>
<td>3-4 parts</td>
</tr>
<tr>
<td>PC075</td>
<td>(Catalyst)</td>
<td>150-220 ppm</td>
</tr>
</tbody>
</table>

With a spatula or tongue depressor, stir the PS443 into the SS0216. A plastic beaker or coffee cup is a convenient disposable receptacle. After producing a uniform paste, stir in the PS123. This paste is stable at room temperature if stored. For activation add the platinum solution drop wise with eyedropper or syringe and rapidly stir with spatula. Expect a 5-10 minute work life. Let cure overnight at room temperature to optimize physical properties.
## Table 18 Typical Pt Catalyzed RTV Formulation

**PART A (Base)**

- PS443 (Vinyl Fluid) 82g
- SS0216 (Filler) 17.85g
- PC075 (Catalyst) 0.15g

**TOTAL:** 100g

**PART B (Crosslinker)**

- PS443 (Vinyl Fluid) 90g
- PS123 (Hydrosilicone) 10g

**TOTAL:** 100g

Prepare parts A and B separately.
Mix 3 parts A with one part B.
Cure at ambient conditions for four hours.

**Physical Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore A</td>
<td>20-30</td>
</tr>
<tr>
<td>Elongation</td>
<td>400-500%</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>3.5 Mpa (500psi)</td>
</tr>
<tr>
<td>Tear Strength</td>
<td>16N/mm (91ppi)</td>
</tr>
</tbody>
</table>
Table 19 Typical Pt Catalyzed Optical Coating

<table>
<thead>
<tr>
<th>PART A (Base)</th>
<th>PART B (Crosslinker)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS443 (Vinyl Fluid)</td>
<td>PS123 (Hydrosilicone)</td>
</tr>
<tr>
<td>PS496 (Q RESIN)</td>
<td></td>
</tr>
<tr>
<td>PC085 (Catalyst)</td>
<td></td>
</tr>
<tr>
<td>TOTAL:</td>
<td></td>
</tr>
</tbody>
</table>

Procedure:
Prepare parts A and B separately. Mix 10 parts A with one part B. Cure at 150°C for 20 minutes.

Physical Properties
Shore A >18
Index of Refraction (25°C) 1.4066 ± 0.0005
The basic feed stocks employed in homogeneous platinum catalyzed silicone resin systems are vinyl fluids, whose structural types are outlined in Table 20, and hydrosilicones, outlined in Table 21. Vinyl fluids are typically blended in the “base” or “Part A” side while hydrosilicones are put into the “crosslinker” or “Part B” side. The A side and B side convention is sometimes violated and inverted by major turn key formulated silicone manufacturers. Technical datasheets and MSDS sheets should be reviewed for unequivocal determination of each sides identity.

United Chemical Technologies is also a major manufacturer of these silicone resins. Table 22 and Table 23 list these materials and their most common applications.
Table 20 Vinyl Fluids

Vinyl Terminated Siloxanes (Part “A” base resins)

Vinyl Functional Copolymers (Part “A” reinforcing resins)
**Table 21 Hydrosilicones**

<table>
<thead>
<tr>
<th>Hydrosilicones</th>
<th>Organohydrosiloxane Polymers and Copolymers (Crosslinkers)</th>
<th>Hydride Terminated Polydimethylsiloxanes (Chain Extenders)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃—Si—O—CH₃</td>
<td>(H—Si—O—Si—O—Si—CH₃)ₙ</td>
<td>(H—Si—O—Si—O—Me)ₙ Si(CH₃)₂H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **CH₃—Si—O—CH₃**: Organohydrosiloxane Polymers and Copolymers (Crosslinkers)
- **(H—Si—O—Si—O—Si—CH₃)ₙ**: Hydride Terminated Polydimethylsiloxanes (Chain Extenders)
# Table 22 UCT’s Vinyl Fluids

<table>
<thead>
<tr>
<th>Description (CAS #)</th>
<th>Viscosity in centistokes</th>
<th>Weight % Vinyl</th>
<th>Specific Gravity</th>
<th>Primary Use in RTV Addition Cure Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydimethylsiloxanes, Vinyl terminated CAS No. [68951-99-5]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 4437</td>
<td>2-3</td>
<td>10-12</td>
<td>0.919</td>
<td>Modifiers or inhibitors</td>
</tr>
<tr>
<td>PS 4438</td>
<td>4-6</td>
<td>7-9</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>PS 4441</td>
<td>100</td>
<td>12.14</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>PS 441.2</td>
<td>200</td>
<td>0.01-0.02</td>
<td>1,000,000</td>
<td>Base polymers or part of Polymer blends of liquid RTV systems</td>
</tr>
<tr>
<td>PS 442</td>
<td>500</td>
<td>0.03-0.07</td>
<td>65,000</td>
<td></td>
</tr>
<tr>
<td>PS 443</td>
<td>1000</td>
<td>0.18-0.26</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>PS 446</td>
<td>5000</td>
<td>0.97</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>PS 445</td>
<td>10,000</td>
<td>0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 447.5</td>
<td>65,000</td>
<td>0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 446</td>
<td>100,000</td>
<td>0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 446.5</td>
<td>165,000</td>
<td>0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 446.5</td>
<td>600,000</td>
<td>0.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 446.5</td>
<td>1,000,000</td>
<td>0.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polydimethylsiloxane, Mononovinyl, Monon-Butylmethyl Terminated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 491</td>
<td>10,000</td>
<td>0.05-0.1</td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>

**Description and CAS Number:**

- **Polydimethylsiloxanes, Vinyl terminated**: CAS No. [68951-99-5]
- **Polydimethylsiloxane, Mononovinyl, Monon-Butylmethyl Terminated**: [Additional information not provided]
<table>
<thead>
<tr>
<th>Description (CAS #)</th>
<th>Viscosity in centistokes</th>
<th>Weight % Vinyl</th>
<th>Specific Gravity</th>
<th>Primary Use in RTV Addition Cure Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vinylidimethyl, Dimethylsiloxane Copolymers, Trimethylsiloxy Terminated CAS No. [67762-94-1]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS422</td>
<td>1000</td>
<td>5-7</td>
<td>1.02</td>
<td>Peroxide or Plasms</td>
</tr>
<tr>
<td>PS424</td>
<td>1000</td>
<td>7-6</td>
<td>1.02</td>
<td>Peroxide or Plasms</td>
</tr>
<tr>
<td>PS426</td>
<td>1000</td>
<td>10</td>
<td>1.02</td>
<td>Peroxide or Plasms</td>
</tr>
<tr>
<td><strong>Vinylidimethyl, Dimethylsiloxane Copolymer, Vinyl Dimethyl Terminated</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS483</td>
<td>1000</td>
<td></td>
<td>1.02</td>
<td>Peroxide or Plasms</td>
</tr>
<tr>
<td><strong>Divinylmethyl Terminated, Polydimethyl Siloxanes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS483</td>
<td>1000</td>
<td></td>
<td>1.02</td>
<td>Peroxide or Plasms</td>
</tr>
<tr>
<td>PS488</td>
<td>100,000</td>
<td></td>
<td>1.02</td>
<td>Peroxide or Plasms</td>
</tr>
<tr>
<td><strong>Vinyl Q-resin Dispersions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS496</td>
<td>4000-6000</td>
<td></td>
<td>1.02</td>
<td>High strength RTV systems</td>
</tr>
<tr>
<td>PS498</td>
<td>100,000</td>
<td></td>
<td>1.02</td>
<td>High strength RTV systems</td>
</tr>
<tr>
<td><strong>Vinylphenylmethyl Terminated Dimethyl Siloxane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS463</td>
<td>1000</td>
<td></td>
<td>1.02</td>
<td>High strength RTV systems</td>
</tr>
<tr>
<td><strong>T-structure Polydimethylsiloxane with vinyl at branchpoint</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS408</td>
<td>50-75</td>
<td></td>
<td>0.99</td>
<td>High strength RTV systems</td>
</tr>
<tr>
<td><strong>T-structure Polydimethylsiloxane with vinyl at branch terminus</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS410</td>
<td>300-500</td>
<td></td>
<td>0.99</td>
<td>High strength RTV systems</td>
</tr>
<tr>
<td>PS925</td>
<td>3-7</td>
<td></td>
<td>0.99</td>
<td>High strength RTV systems</td>
</tr>
</tbody>
</table>
Table 23 UCT’s Hydrosilicones

<table>
<thead>
<tr>
<th>Description</th>
<th>Viscosity in centistokes</th>
<th>Mole % Methyl Hydro</th>
<th>Specific Gravity</th>
<th>Refractive Index</th>
<th>Flash Point</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylhydrolysiloxanes, Trimethylsilyl Terminated CAS No. [63148-57-2]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS118 2-5</td>
<td></td>
<td></td>
<td>1.382</td>
<td>80°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS119 20</td>
<td>0.99</td>
<td>1.395</td>
<td>100°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS120 30</td>
<td>0.99</td>
<td>1.396</td>
<td>121°</td>
<td>Blowing Agent Crosslinkers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS122 85</td>
<td>0.99</td>
<td>1.397</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Hydro, Dimethylsiloxane Copolymers, Trimethylsilyl Terminated CAS No. [68037-59-2]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS122.5 10-15</td>
<td>(50-55%)</td>
<td>0.99</td>
<td>1.394</td>
<td>70°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS123 25-30</td>
<td>(30-35%)</td>
<td>0.99</td>
<td>1.399</td>
<td>125°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS123.5 25-35</td>
<td>(15-18%)</td>
<td>0.99</td>
<td>1.400</td>
<td></td>
<td>Crosslinkers for addition cured Pt catalyzed systems</td>
<td></td>
</tr>
<tr>
<td>PS123.8 7500±2500</td>
<td>(0.5-1.0%)</td>
<td>0.97</td>
<td>1.404</td>
<td>300°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS124.5 250-275</td>
<td>(4-6%)</td>
<td>0.97</td>
<td>1.404</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# Table 23 UCT’s Hydrosilicones (continued)

<table>
<thead>
<tr>
<th>Description [CAS #]</th>
<th>Viscosity in centistokes</th>
<th>Mole % Methyl Hydro</th>
<th>Specific Gravity</th>
<th>Refractive Index</th>
<th>Flash Point</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Hydro, Cyanopropylmethyl Siloxane Copolymer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS124</td>
<td>1000-3000</td>
<td>(3-4%)</td>
<td>1.07</td>
<td>1.446</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Hydro, Methyloctyl Siloxane Copolymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS125</td>
<td>200-400</td>
<td>(40-60%)</td>
<td>0.93</td>
<td>1.435</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS125.5</td>
<td>300-600</td>
<td>(25-30%)</td>
<td>0.91</td>
<td>1.440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Hydro, Phenylmethyl Siloxane Copolymer, Dimethylsiloxyl Terminated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS129.5</td>
<td>75-100</td>
<td>(45-50%)</td>
<td></td>
<td>1.500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymethylsiloxanes, Hydride Terminated Cas # [70900-21-9]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS537</td>
<td>2-3</td>
<td></td>
<td>0.905</td>
<td>1.395</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS542</td>
<td>500</td>
<td></td>
<td>0.971</td>
<td>1.403</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS543</td>
<td>1000</td>
<td></td>
<td>0.971</td>
<td>1.403</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS545</td>
<td>10,000</td>
<td></td>
<td>0.974</td>
<td>1.403</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Other monomeric short chain silane end cappers, crosslinkers and chain extenders are employed where the formulator desires a more rigid structure or more tightly defined stoichiometry. Figure 5 lists the most commonly available commercial products and their United Chemical Technologies catalog numbers.
Figure 5 Typical Hydrosilane Chain Extenders, Crosslinkers and Endcappers

M8830 Crosslinker
T1915 Crosslinker
T2000 Crosslinker
T2030 Chain extender, Endcapper

H7010 Endcapper
H7322 Chain extender
O9814 Chain extender
P0100 Endcapper
Typical formulated silicone rubber systems require substantial molar excesses of hydrosilicone over vinyl fluid to achieve optimal physical properties. The desired mix ratio depends on the chain length of the vinyl terminated silicone and percent hydride in the backbone of the crosslinker. Table 24 lists theoretical mix ratios for three commercial United Chemical Technologies vinyl fluids when compounded with three hydrosilicones of varying hydride content (refer to Tables 22 and 23). Ratios are computed at a 1.5/1.0 SiH/Vinyl molar ratio. Less potent crosslinkers, such as PS123.8, and higher viscosity vinyl fluids, such as PS445, give softer cures at equivalent molar ratios.
# Table 24 Starting Ratios

Starting Ratios of Hydrosilicones (parts) to 100 parts of Vinylsiloxanes

<table>
<thead>
<tr>
<th>Vinylsiloxane</th>
<th>Hydrosilicone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS123.8</td>
</tr>
<tr>
<td>PS443</td>
<td>80.8</td>
</tr>
<tr>
<td></td>
<td>PS123.5</td>
</tr>
<tr>
<td>PS445</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>PS123.0</td>
</tr>
<tr>
<td>PS735</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Formulation is based upon molar ratio of 1.5 Si-H to 1.0 vinyl.

Filled formulations may require up to 3x the amounts listed for optimal physical properties.
Simple formulating technique for small scale development work is illustrated in Figure 6. No expensive equipment is required and physical properties such as Shore A durometer hardness and elongation are easily measured. Other physical properties such as tear strength or modulus will require more sophisticated instrumentation.
1. **WEIGHING**: Weigh A and B in the recommended ratios.

2. **MIXING**: Use a spatula to make a homogenous mixture of A and B.

3. **DEAIRING**: Place the mixed silicone in a vacuum chamber (desiccator) and apply vacuum until foam collapses.

4. **POURING**: Pour mix into mold or form avoiding entrapment of air.
5. CURING: Follow the recommended cure schedule

6. DEMOLDING THE FINISHED PART
In contrast, scale up to commercial bulk silicone resin manufacturing will require specialized blending equipment to achieve uniform mixing. High viscosities and filler levels necessitate such an investment. Alternatively, formulations may be sub contracted to experienced adhesives manufacturers. Figure 7 shows typical large scale equipment and Figure 8 illustrates intermediate scale equipment for scale up to kilogram level.
Figure 7 Typical Large Scale Industrial Mixing Equipment

“50 gallon high speed disperser – produced by Applied Silicone Corp, Ventura, California”
Figure 8  Intermediate Scale Industrial Mixing Equipment

“Hauschild Speed Mix from FlackTek Inc., Landrum South Carolina”

“One gallon Double Planetary Mixer” produced by Charles Ross & Son Company, Hauppauge, New York”
In summary, zero valent homogeneous Karstedt type catalysts have been shown to have substantial advantages and benefits over older tin or peroxide based curing technologies. United Chemical Technologies (UCT) manufactures a high quality version of these materials. Table 25 summarizes the benefits of the UCT product line.
Table 25 Features and Benefits

**Features**

- Consistent reactivity profile.
- High Clarity, Low Color.
- Customized platinum levels available.
- Specialized packaging available.
- Wide variety of catalyst activities for room temperature and high temperature cure profiles.
- Complete catalyst product line to serve Platinum-based, Peroxide-based, and Condensation-based Silicone cures.

**Benefits**

- Just in time delivery, very competitive pricing.
- Less customer problems with final cured product.
- Our Pt catalysts are more reactive and selective than chloroplatinic acid.
- Our Pt catalysts require lower formulated platinum concentrations (2-20ppm).
- Platinum catalyzed cures evolve no volatile byproducts.
- Our homogenous platinum catalysts have more consistent reactivity than heterogeneous catalysts due to irregular surface effects in the latter.
References


5) “A convenient and novel route to Bis-Alkyne platinum (0) and other platinum (0) complexes from Speiers hydrosilylation catalyst, X-Ray Structures”, Grish Chandra, Peter Y. Lo, Peter B. Hitchcock, Michael F. Lappert, Organometallics, (1987), 6, 191-192.