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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

15 April 2002

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Rusty Blanski et al. (PRSM), "Hybrid Inorganic-Organic Performance Fluids Based on Polyhedral  
Oligomeric Silsesquioxanes (POSS)"

**SAMPE Industry Conference**  
**(Long Beach, CA, 12-15 May 2002) (Deadline: 12 May 2002)**

**(Statement A)**

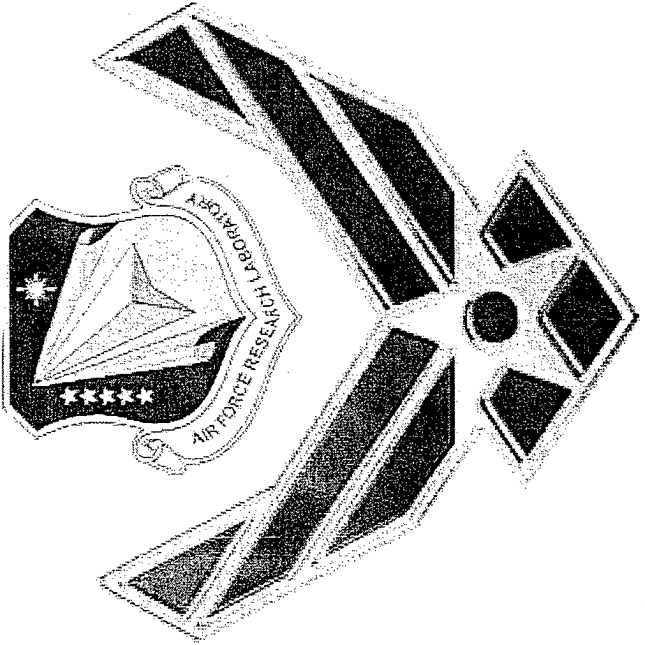
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# HYBRID INORGANIC PERFORMANCE FLUIDS BASED ON POLYHEDRAL OLIGOMERIC

*CC rec'd from*  
*B. Viers 4/24/02*  
**UIOXANES (POSS)**

*za*



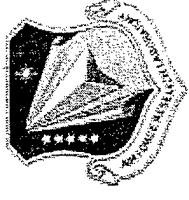
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**Rusty Blanski, Justin Leland,  
Brent Viers and Shawn H. Phillips**  
**PRSM**

**Air Force Research Laboratory**



# Hybrid Fluids Introduction

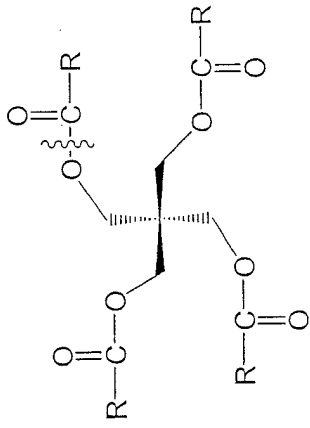
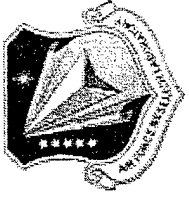


Hybrid Performance Fluids are fluids that can operate at elevated temperatures under extreme conditions for a variety of applications such as hydraulic and transmission fluids as well as lubricants. One area the AF is interested in is high temperature lubricants.

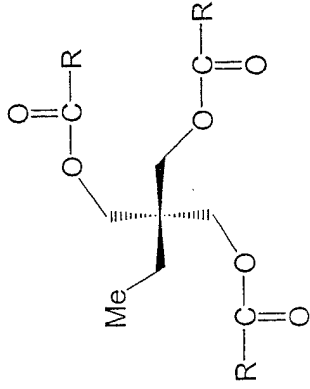
- Goals - Develop a lubricant that can withstand high temperatures ( $\gg 200\text{ }^{\circ}\text{C}$ ) and flows at  $-40\text{ }^{\circ}\text{C}$  (20K centistoke) (High temp gas turbine engines: jets)
- Higher temperature lubes means higher operating temperature  $\gg$  more power: increase in thrust:weight ratio
- Objective - Synthesize an oil with an operating range of  $-40\text{ }^{\circ}\text{C}$  to  $\gg 200\text{ }^{\circ}\text{C}$



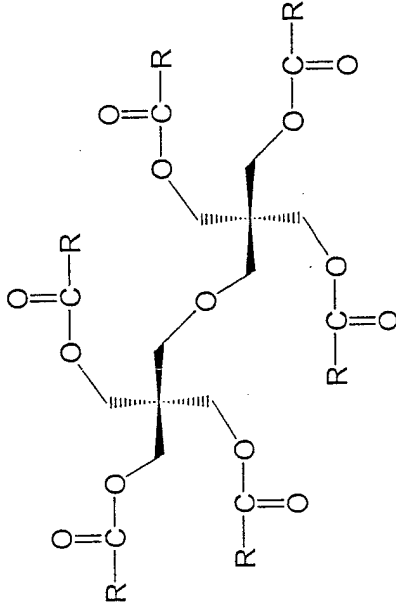
# Present AF Lubricants Technology



Pentaerithritol Ester



Trimethylpropane Ester

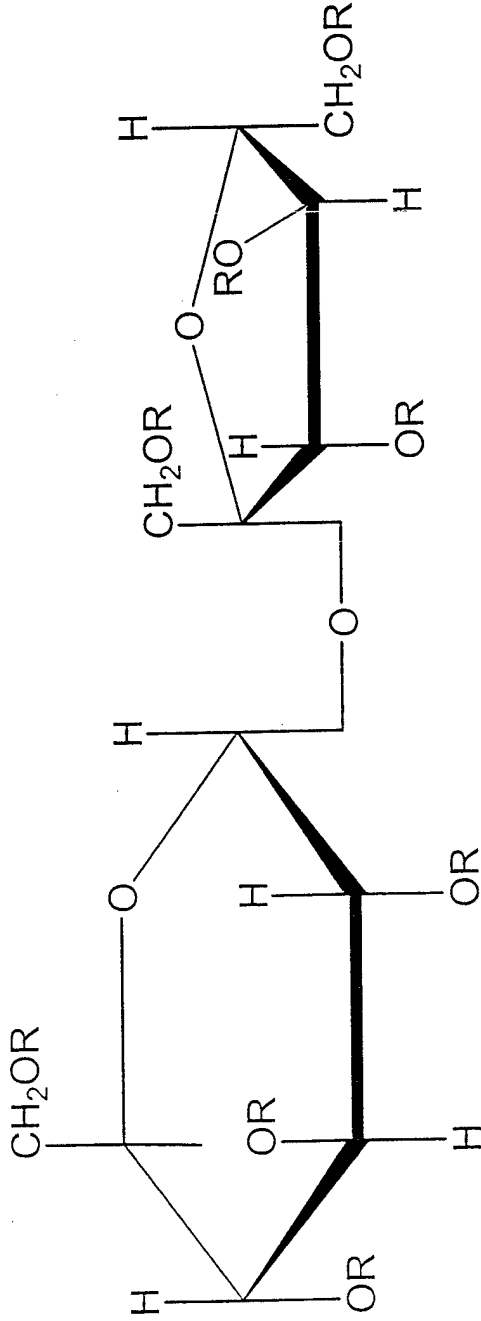
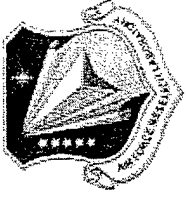


Pentaerithritol Dimer Ester

- The above polyol ester compounds are the main components of some AF turbine lubricants
- Operating range of  $-40^{\circ}\text{C}$  to  $200^{\circ}\text{C}$
- In house calculations show that ester C-O linkage breaks at  $200^{\circ}\text{C}$



# Olestra as a Lubricant?



Olestra  $R = C_5H_{13}C=O, C_6H_{15}C=O, C_7H_{13}C=O$  (Merck Index)

Our Sample: sludge w/unsaturated fatty esters present (NMR)

Average chain length: 15.7

**Isolated from a Bag of Lays WOW® Brand Potatoe Chips by ether extraction and hydrogenation**

**Solid at room temp at 200 °C (only 26% over 9 hours)**

**Good Mass loss at 200 °C (only 26% over 9 hours)**

**Remainder a caramelized sludge**



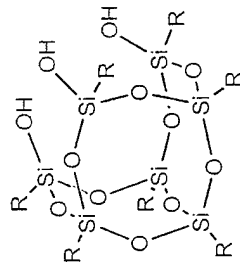
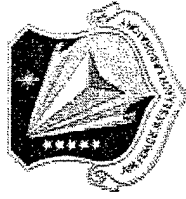
## What About a Hybrid Fluid?



- Hybrid organic/inorganic materials have in the past shown superior temperature stability
- One such material that has potential is POSS

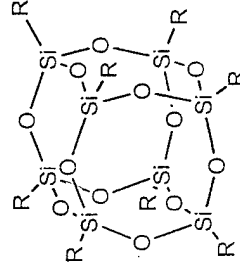


# POSS = Polyhedral Oligomeric Silsesquioxane: General Synthesis

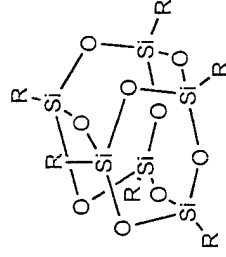


R = Cyclohexyl  
Cyclopentyl  
Cycloheptyl  
Vinyl  
Methyl

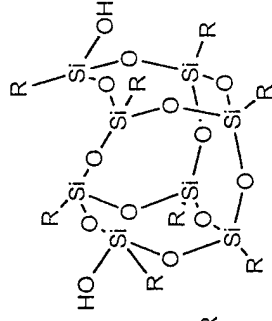
R = Cyclohexyl  
Cyclopentyl  
Cycloheptyl



R = Cyclohexyl  
Cyclopentyl  
Vinyl  
Methyl



R = Cyclohexyl



R = Cyclohexyl

R=Cyclohexyl: Brown and Vogt 1965

Fehér, Newman, Walzer 1989

Lichtenhan (AFRL, mid '90's) Optimized Purification

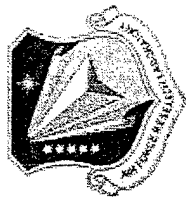
Cyclopentyl: Fehér, Budzichowski, Weller, Blanski, Ziller 1990

Lichtenhan (AFRL, 1993) Optimization

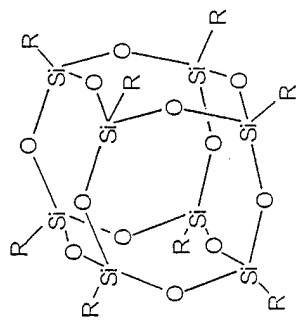
All of these materials are colorless solids at ambient temp



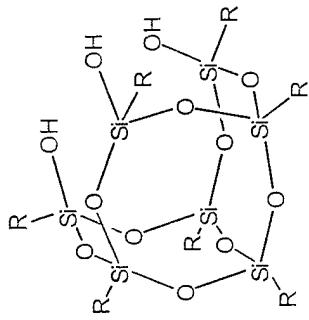
# New POSS Synthesis increases Diversity



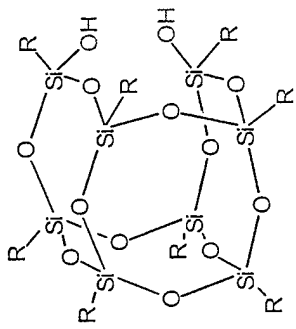
**Hybrid  
Plastics**



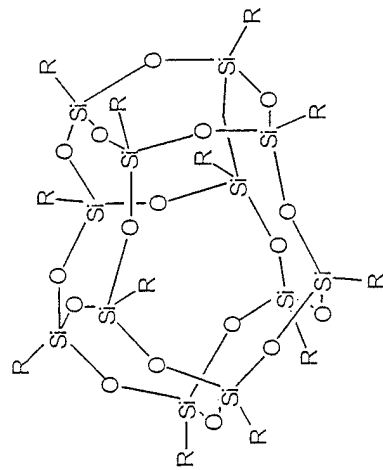
R = Methyl    Isooctyl  
Isobutyl    Phenyl  
Cyclopentyl    Phenethyl  
Cyclohexyl    Octadecene



R = Isobutyl  
Cyclopentyl  
Cyclohexyl  
Isooctyl  
Ethyl  
Phenyl

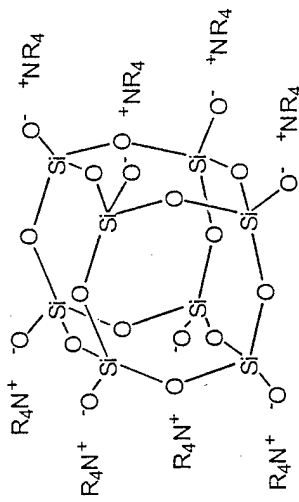


R = Isobutyl  
Cyclopentyl  
Cyclohexyl  
Isooctyl



R = Phenyl  
Trifluoromethylpropyl

## Polydisperse Cages (T<sub>8</sub>, T<sub>10</sub>, T<sub>12</sub>)

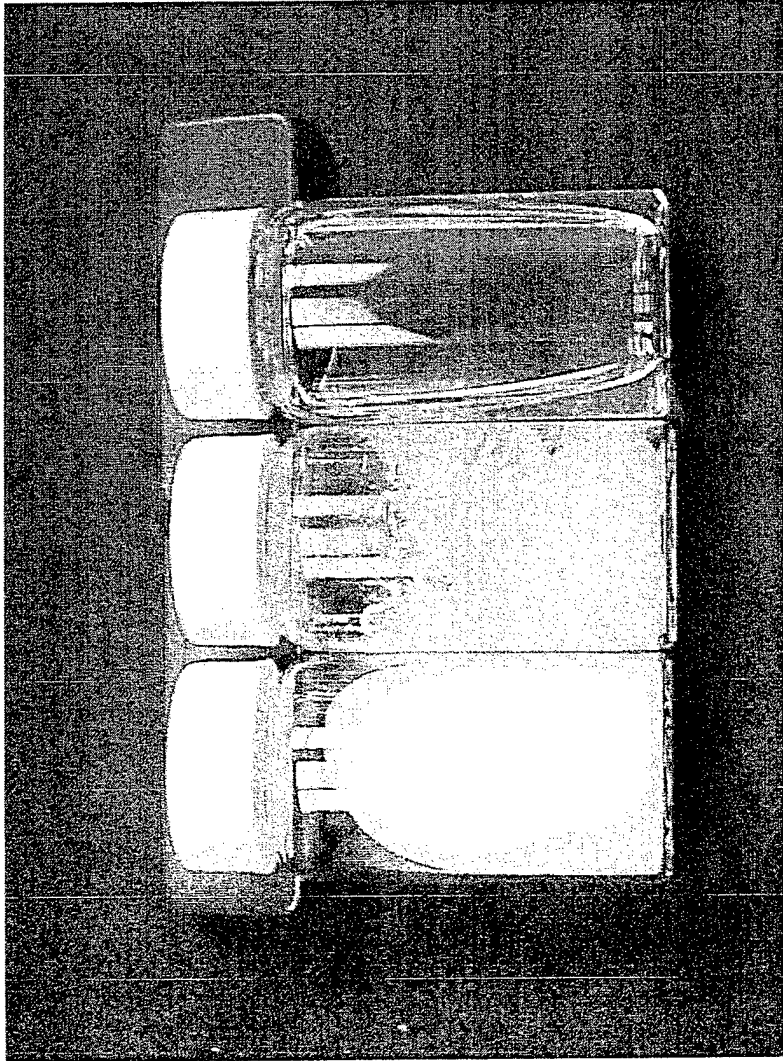
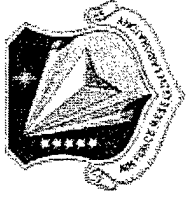


R = Vinyl  
Methacrylpropyl  
Phenethyl

R = Methyl



# Tech Challenges for Hybrid Oils



**Solids**

melts 24°C to 400°C+

**Waxes**

viscosity 40cSt. to 400cSt

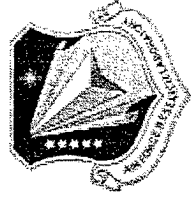
**Oils**

Known POSS molecules decompose to sand

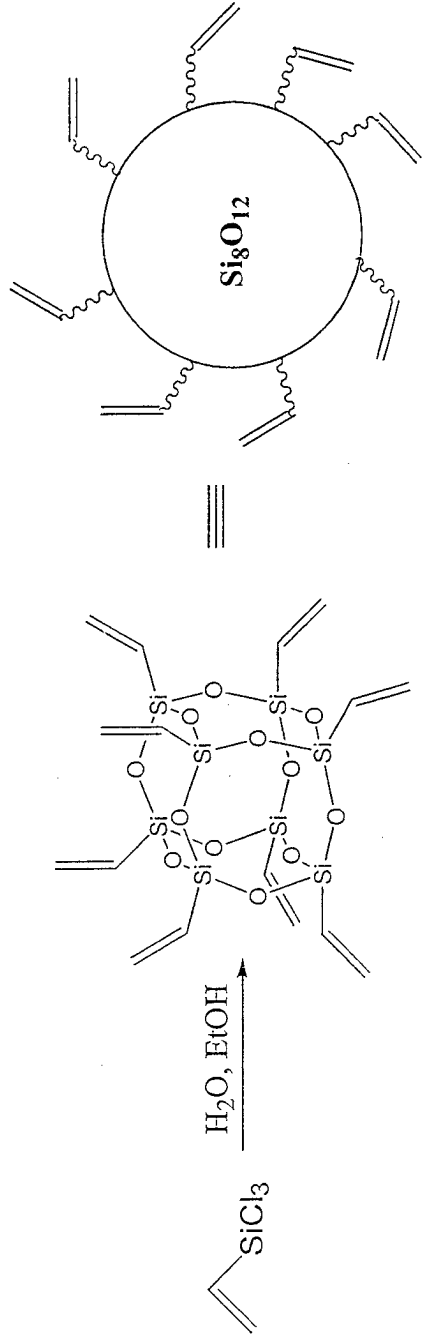
Most POSS molecules are solids at room temperature with only one exception (which does not meet the low temperature pumpability requirements)



# POSS Lubricants Project



## Synthesis of Vinyl<sub>8</sub>T<sub>8</sub> POSS Base Stock



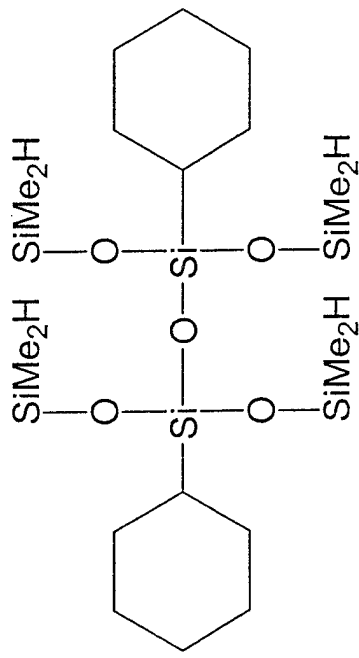
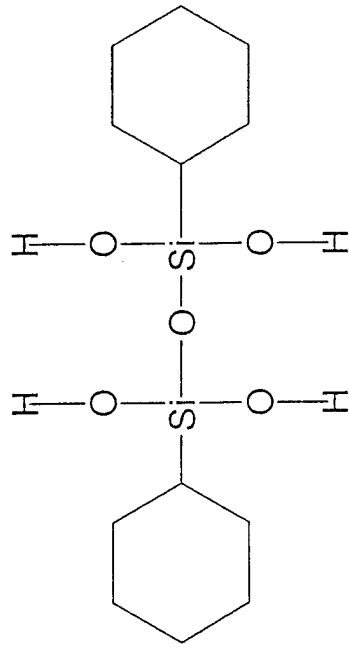
before: 20% yield (AFRL)

now: 40% yield (Hybrid Plastics)

- Least expensive octafunctionalized POSS to date
- Common starting point for octafunctional materials
- CRADA with Hybrid Plastics further reduces cost



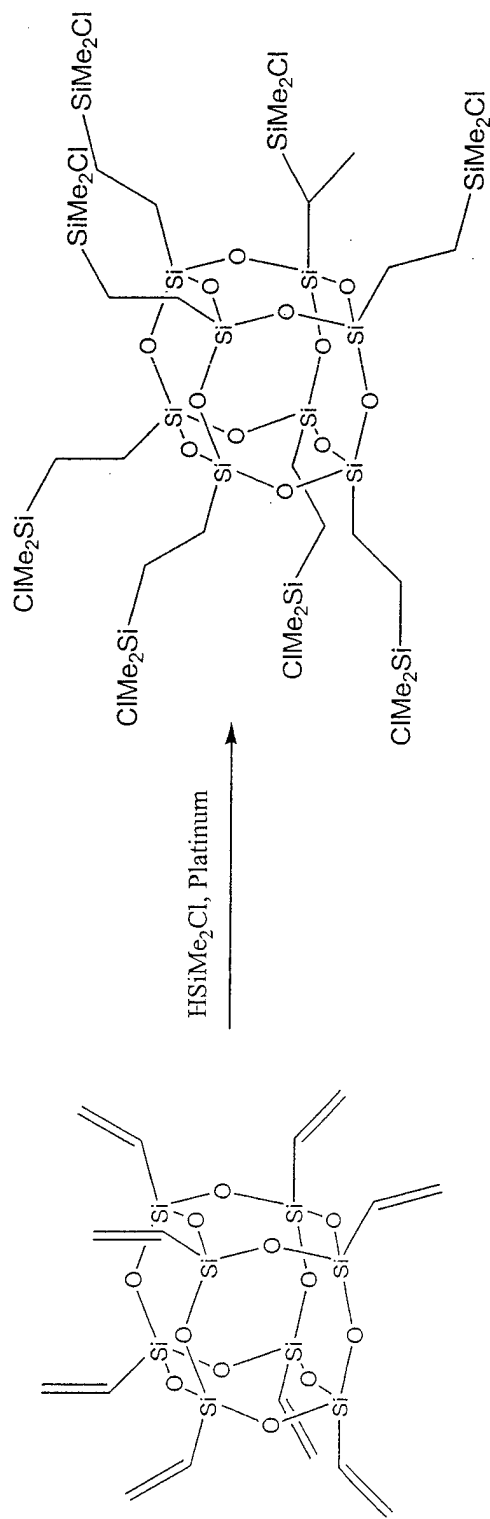
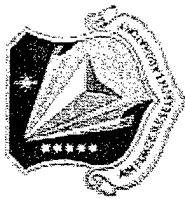
# POSS $\text{Cy}_2\text{T}_2$ Tetrahydride Synthesis



Clear Liquid



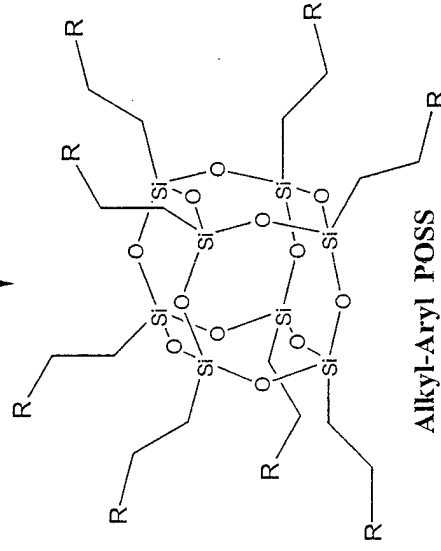
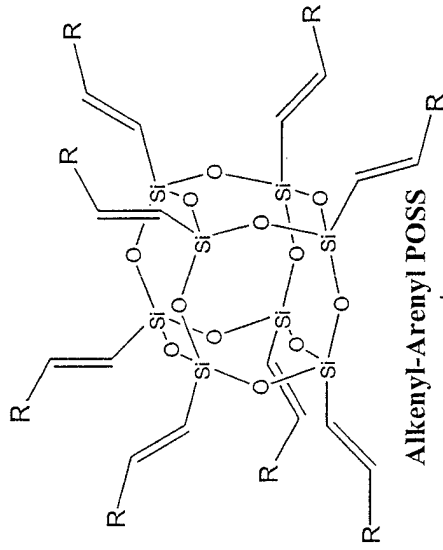
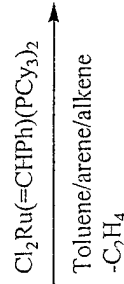
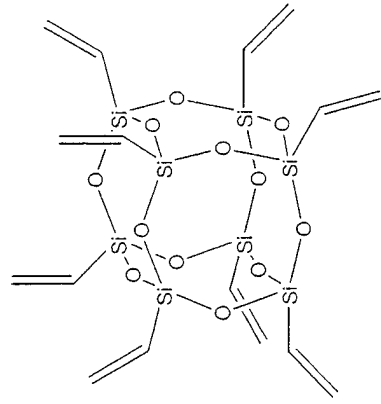
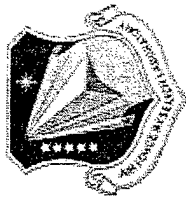
# POSS Synthesis Hydrosilylation





# POSS Synthesis

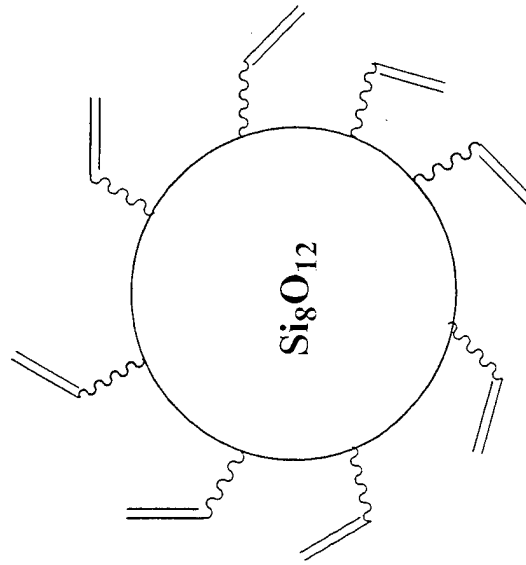
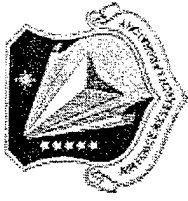
## Cross Metathesis/Hydrogenation



**Very useful reaction:  
Can potentially have  
8 different R groups  
on the Cage!**



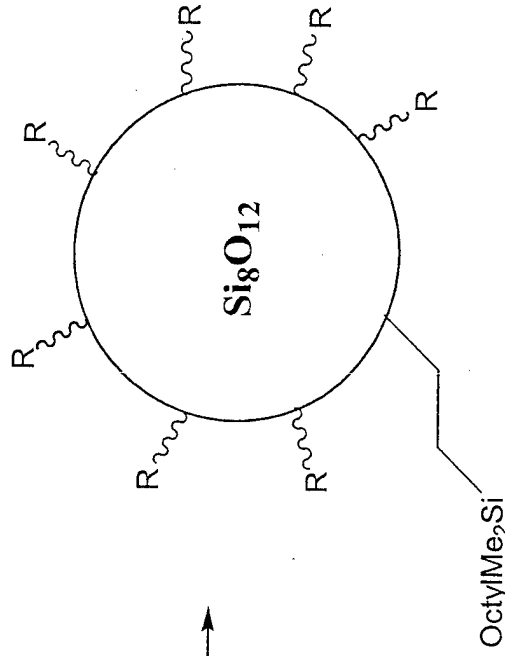
# POSS Lubricants/Blends Initial Studies



1.  $\text{HSiMe}_2\text{Cl}$ , Pt

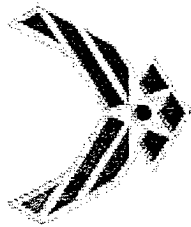
2.  $\text{OctylMgCl}$

or  
 $\text{HSiMe}_2\text{Octyl}$ , Pt



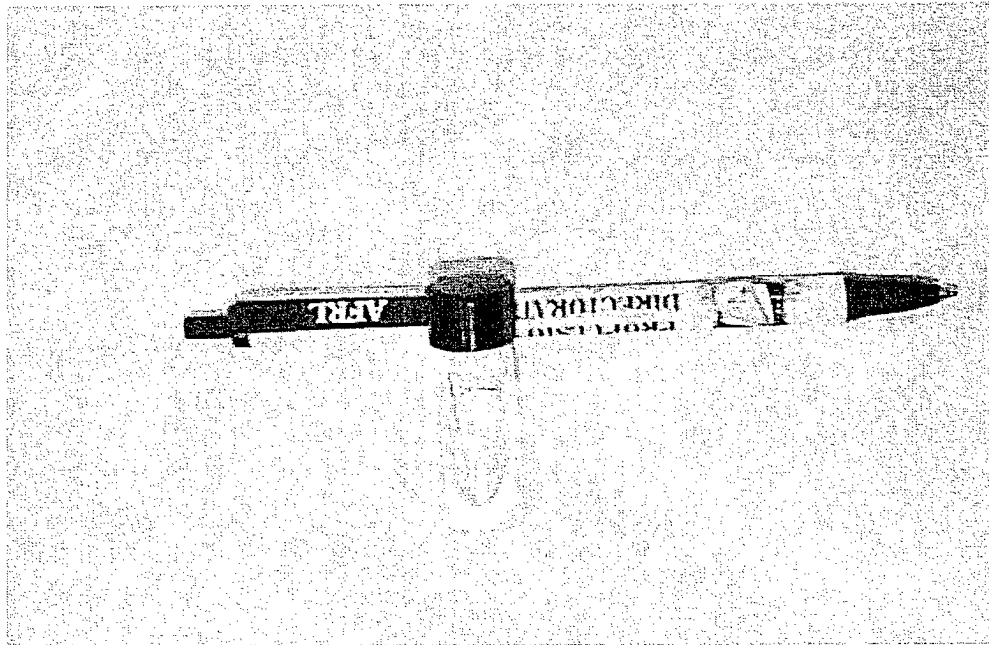
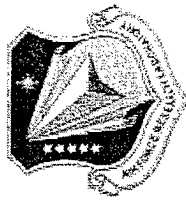
$\text{R} = \text{CH}_2\text{CH}_2\text{SiMe}_2\text{Octyl}$

OIL AT RT



# POSS Lubricants

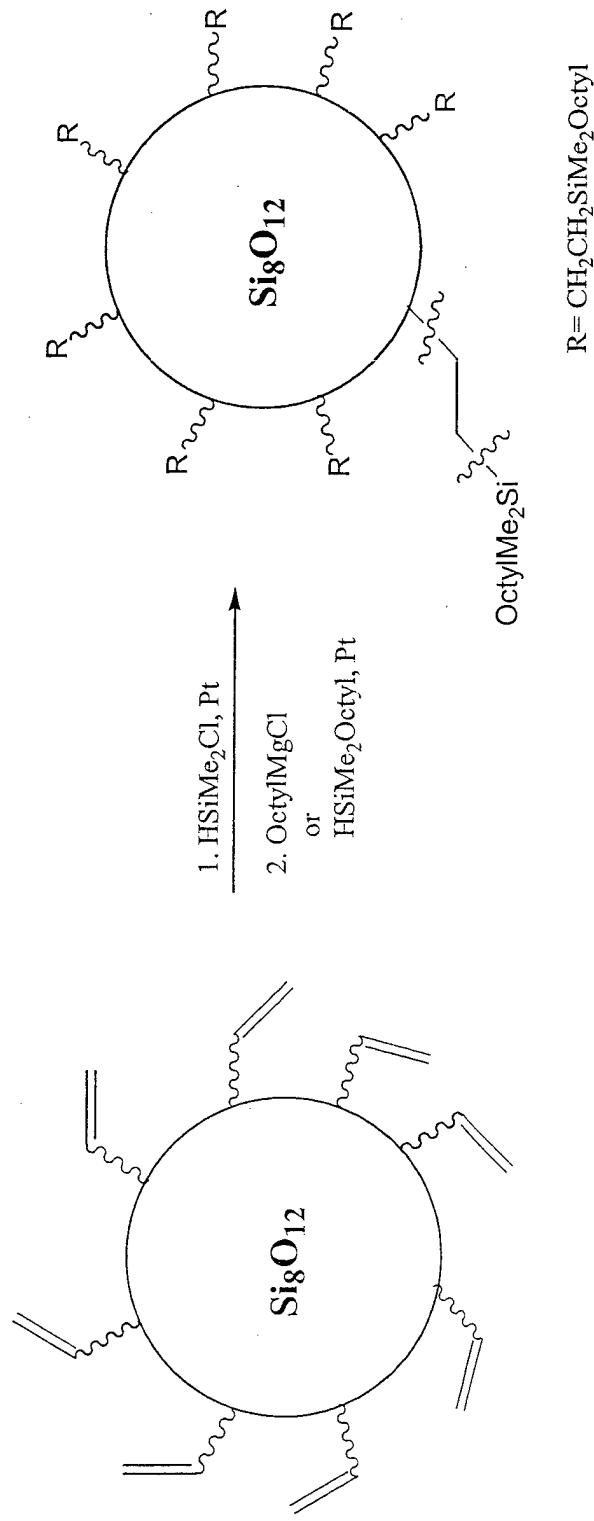
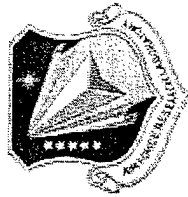
## $T_8[(CH_2CH_2)SiMe_2O]_8$





# POSS Lubricants/Blends

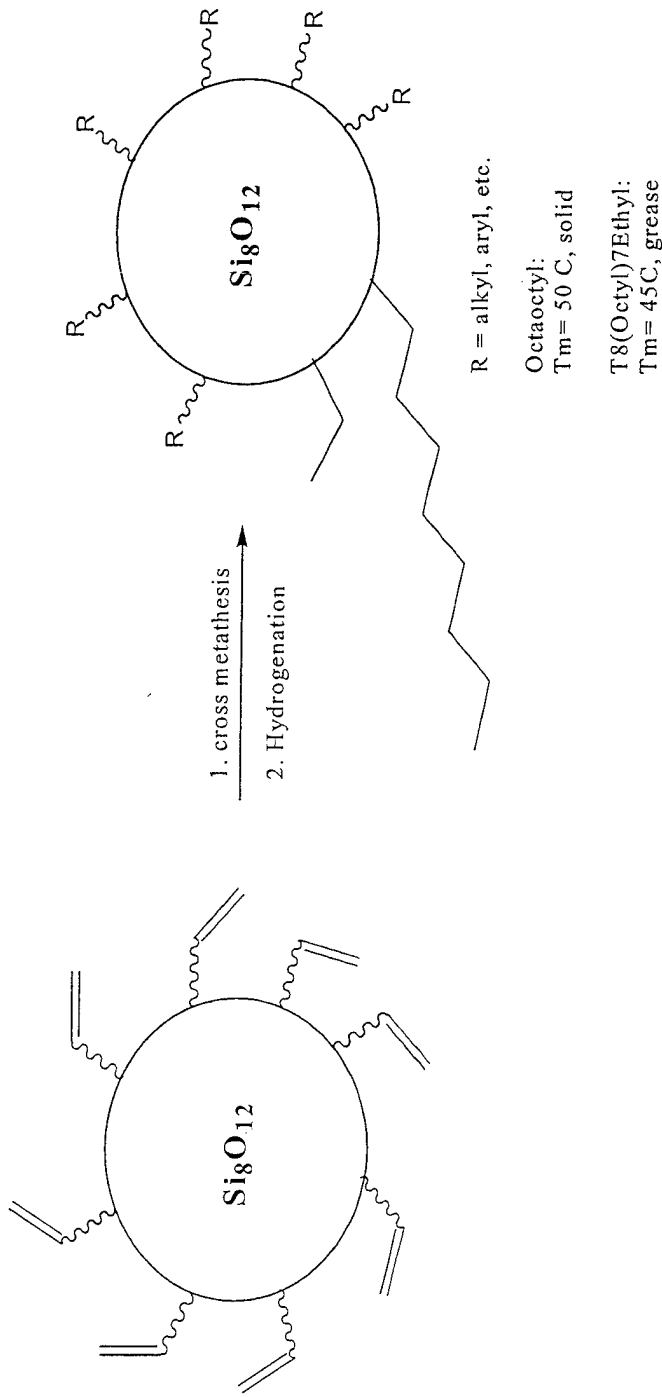
## Early work



**This class is NOT suitable for High Temp Lubes  
(Tdec < 200 °C) and decomposes to sand**



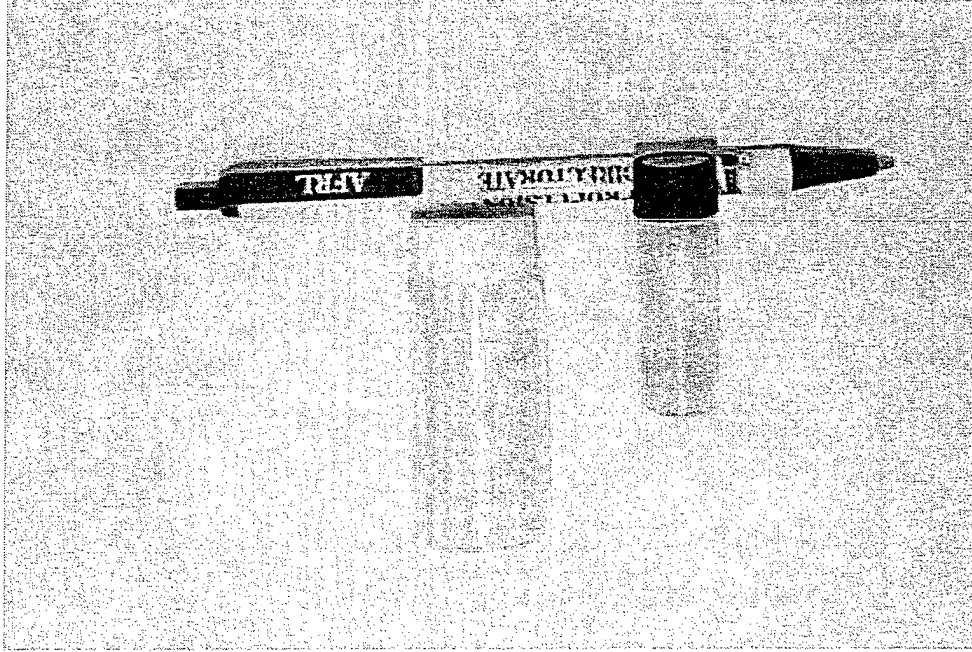
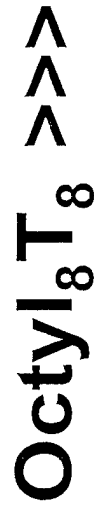
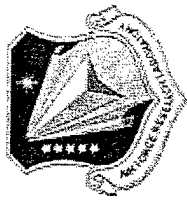
# POSS Lubricants: T8 Class



**Stable at 200 °C (TGA)**  
**Not an oil, but a possible pathway to oil is shown:**  
**Adjust the organic side groups to disturb any possible order and give a flowable compound**

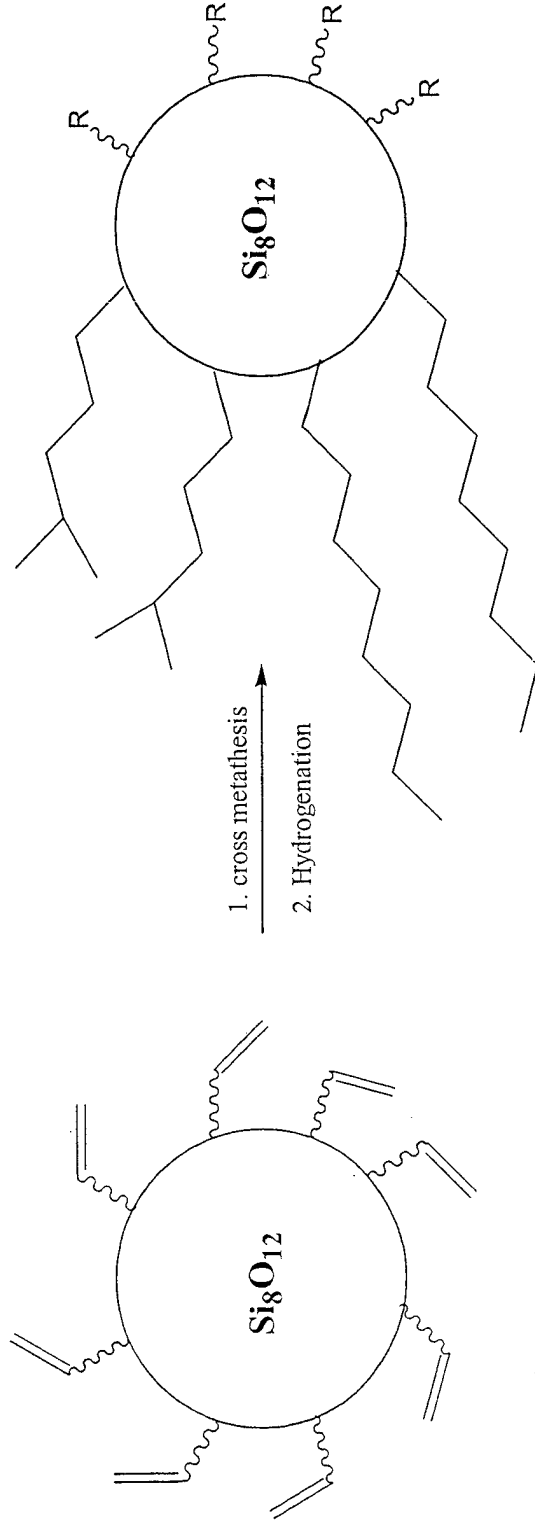


# POSS Lubricants: T8 Class





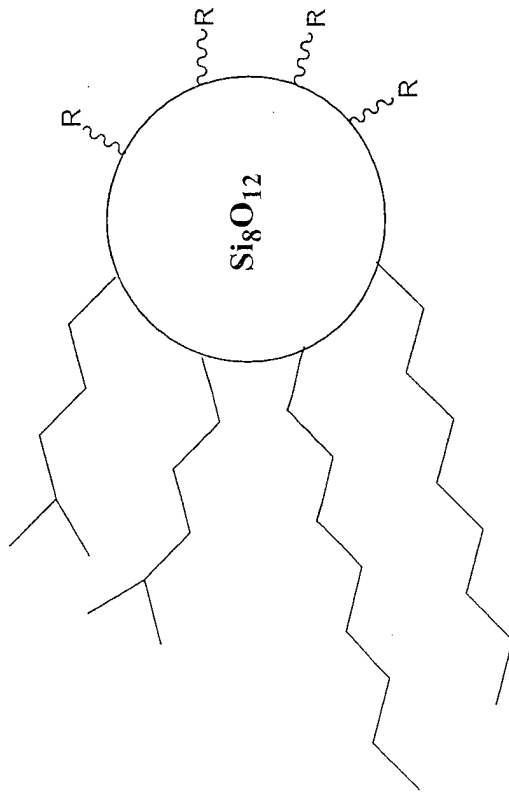
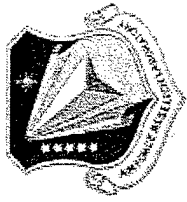
# POSS Lubricants Chain Adjustment Lowers Viscosity



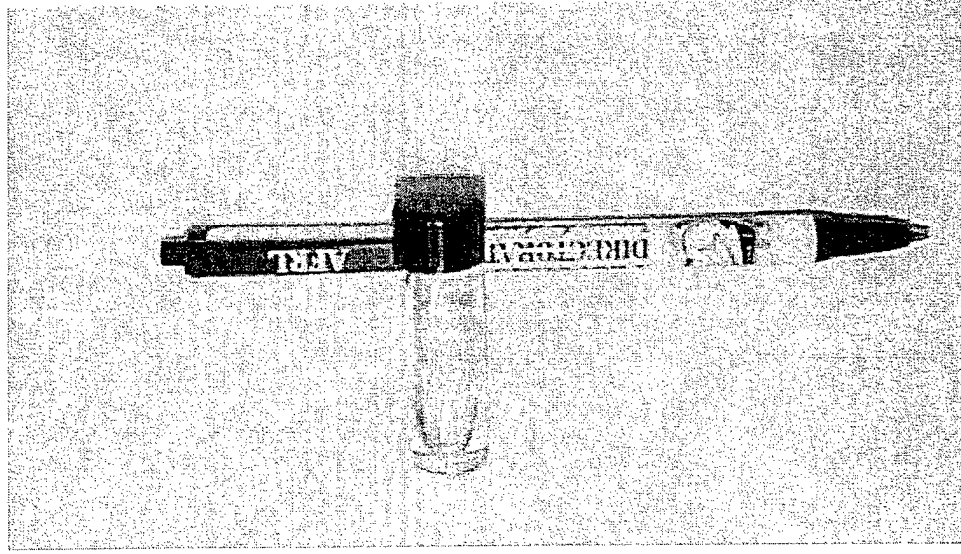
**Free flowing oil at room temperature**  
**Viscosity of 1650 centipoise at 0 °C**  
**Freezes at -12 °C**  
**Low volatility**



# POSS Lubricants Chain Adjustment Lowers Viscosity

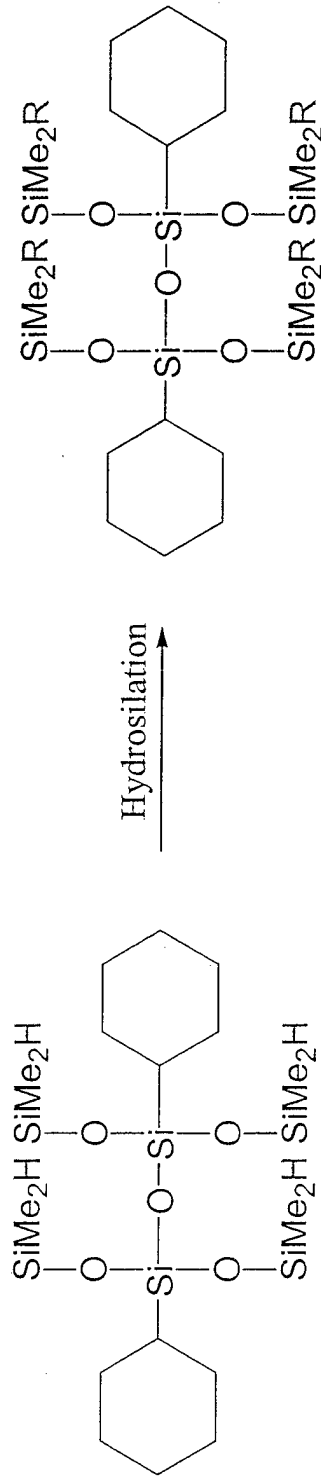
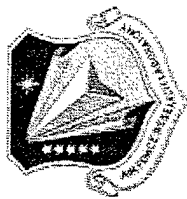


**Octyl<sub>4.6</sub>T<sub>8</sub>**  
**4-Methylpenyl<sub>3.4</sub>**





# POSS Lubricants Cyt<sub>2</sub> Class

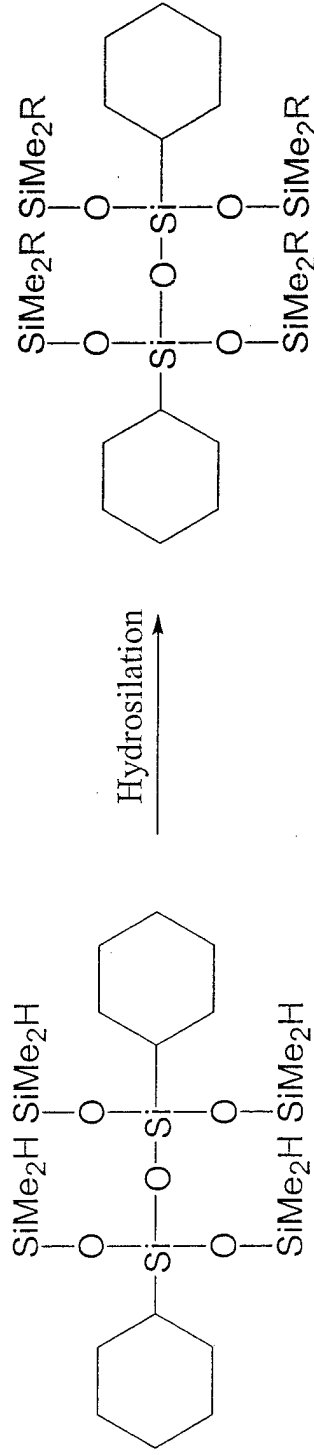


**Flows even at VERY low temperatures (-60 °C)**

**Volatility problem at 200 °C > Extend chain length**



# POSS Lubricants Cyt<sub>2</sub> Class



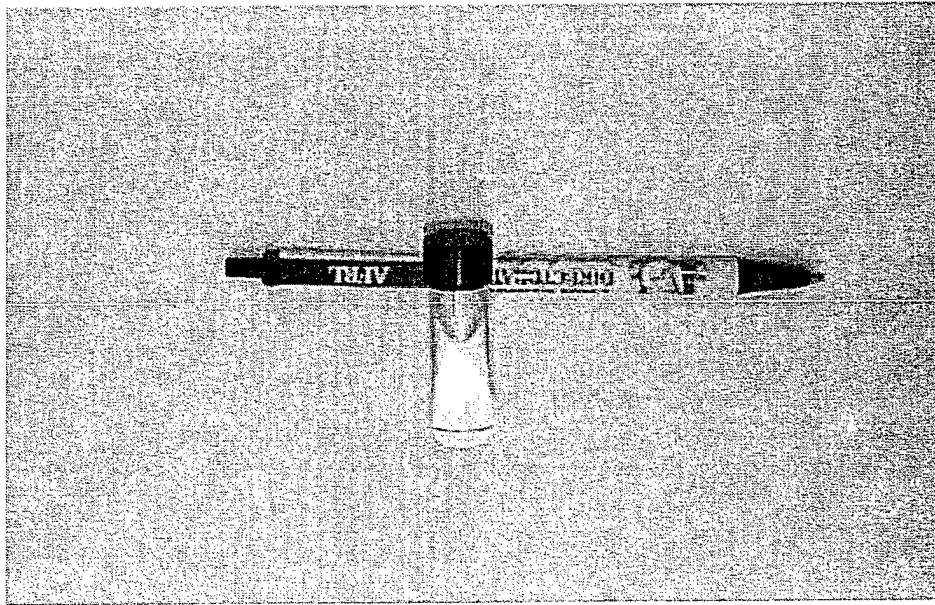
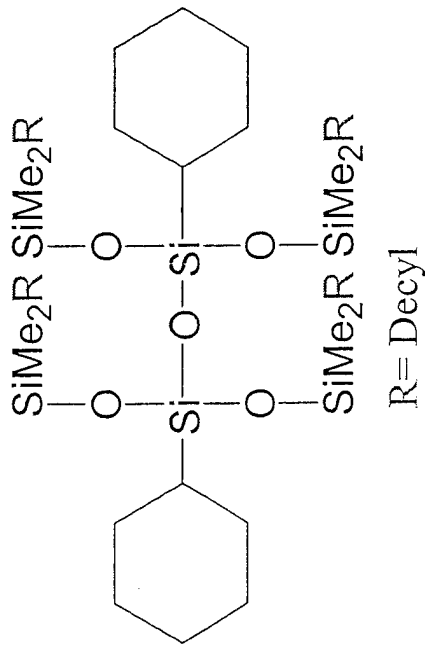
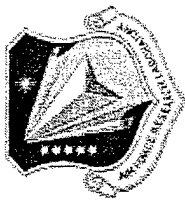
R= Decyl, Dodecyl,  
Tetradecyl, all liquids at RT

**When R=Decyl the viscosity at -40 °C is 4000 cP !!**  
**Stable at 200 °C with A/O present (TGA)**

**When R=Dodecyl, the freezing point is -12 °C**

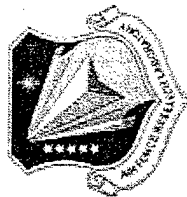


# POSS Lubricants Cyt<sub>2</sub> Class





# Viscosity of Lubricants

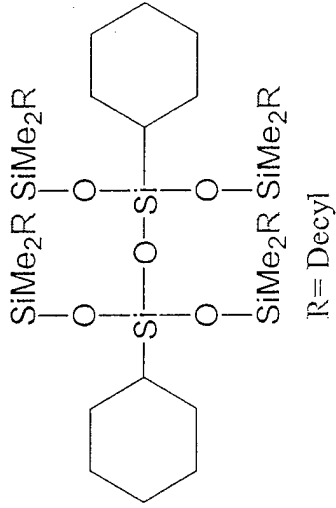


## Selected Data for POSS Lubes

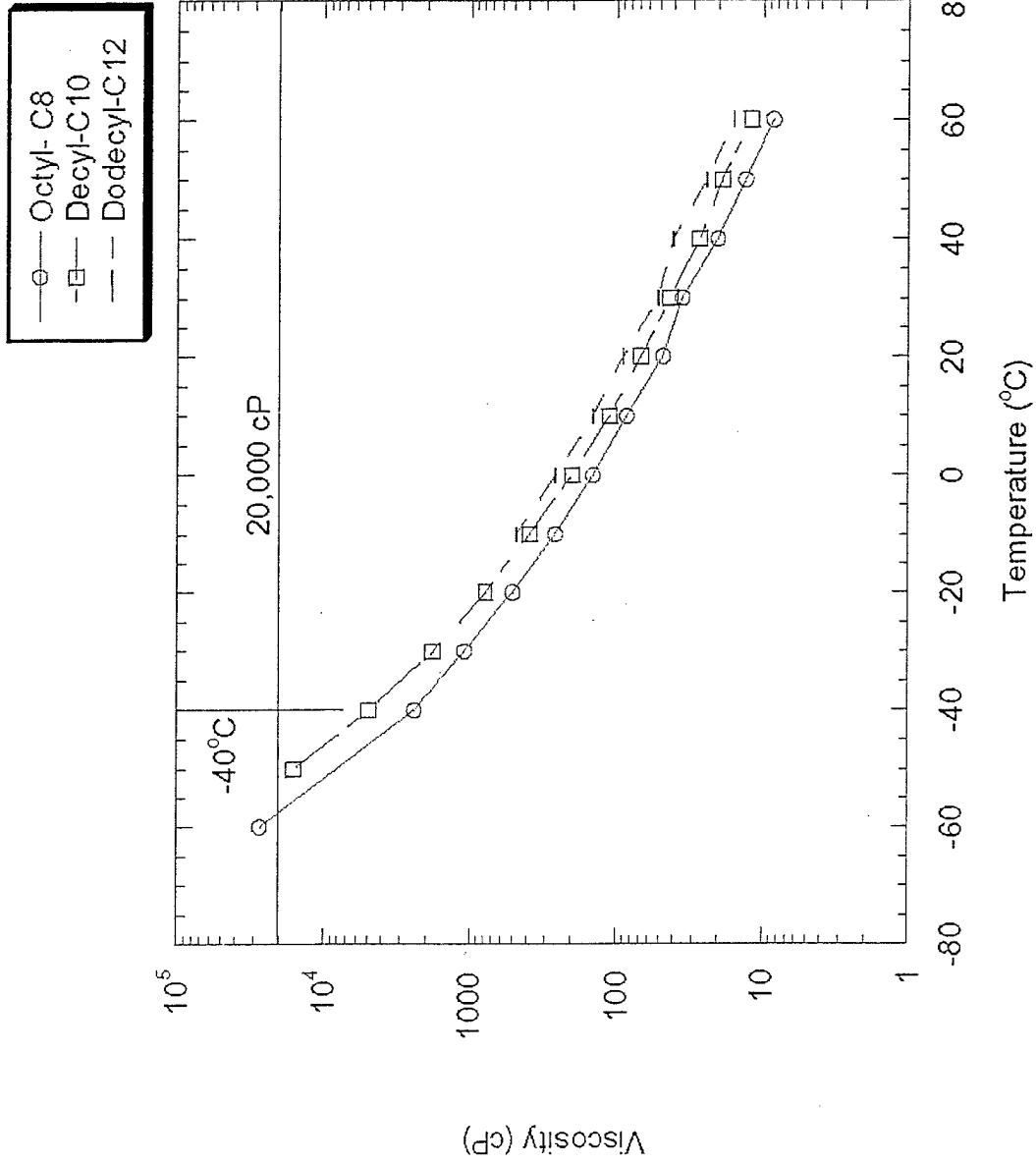
Reagent	mp °F	Viscosity cp (T <sub>1</sub> °F)	Viscosity cp (T <sub>2</sub> °F)	Viscosity cp (T <sub>3</sub> °F)
T <sub>8</sub> (octyl) <sub>4.5</sub> (4-methylpentyl) <sub>3.5</sub>	14	1650 (32)	11 (230)	1 (410)
Cy <sub>2</sub> T <sub>2</sub> (OSiMe <sub>2</sub> Octyl) <sub>4</sub>	< -76	28000(-76)	2600 (-40)	



# Viscosity of Lubricants

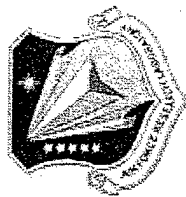


When R= octyl and decyl, the low temperature pumpable spec (20K cP@ -40 °C) is met!





# Decomposition of Lubricants



## Selected TGA Data for POSS Lubricants

Reagent	mp °C	iso temp °C	10% wt loss	% lost 9 hrs
Grade 4 Base stock	Liq rt	219.5	30 min	90
T <sub>8</sub> (octyl) <sub>8</sub>	50	218	60 min	27
T <sub>8</sub> (octyl) <sub>7</sub> (ethyl) <sub>1</sub>	45	216	225	11
T <sub>8</sub> (octyl) <sub>4.5</sub> (4-methylpentyl) <sub>3.5</sub>	-10	215	391 min	11.6
Cy <sub>2</sub> T <sub>2</sub> (OSiMe <sub>2</sub> Octyl) <sub>4</sub>	< -40	219	evaporated	100 (evap)
Cy <sub>2</sub> T <sub>2</sub> (OSiMe <sub>2</sub> Decyl) <sub>4</sub> w/AO	< -40	205	N/A	1 (4 hours)



## Conclusions: POSS Lubricants



- By adjusting organic side groups, POSS oils can be made to flow at low temperature and are stable at higher temperature (Both the  $T_{2s}$  and the larger  $T_{8s}$ )
- Addition of Antioxidant to T2 tetraalkyl derivatives slows down decomposition at 200 °C



# Acknowledgments



- Prof. Andre Lee (MSU) for viscosity measurements
- Lubrications Branch (AFRL/PRTM) for helpful discussions and advice
- Hybrid Plastics for materials