

REPORT DOCUMENTATION PAGE

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2 items enclosed = 210 + 213

⊗ Paper rec'd After 30-day Deadline = (22 days until Deadline)

FILE

MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

03 Sept 2002

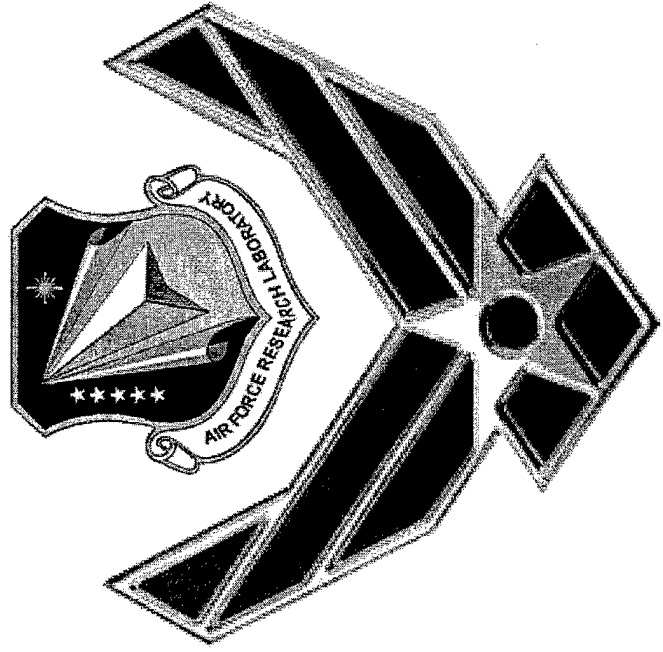
SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-210**
Rusty Blanski; Brent Viers; Rene Gonzalez; Andre Lee; Shawn Phillips (PRSM), "The Synthesis and
Characterization of Lubricants Based on POSS Technology" (viewgraphs)

POSS Nanotechnology Conference
(Huntington Beach, CA, 25-27 September 2002) (Deadline: 25 Sept 02)

(Statement A)

The Synthesis and Characterization of Lubricants Based on POSS Technology

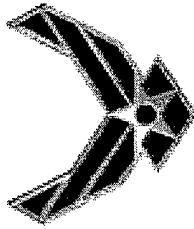
27 September 2002



Rusty Blanski, Brent Viers, Rene Gonzalez,
Andre Lee, and Shawn H. Phillips

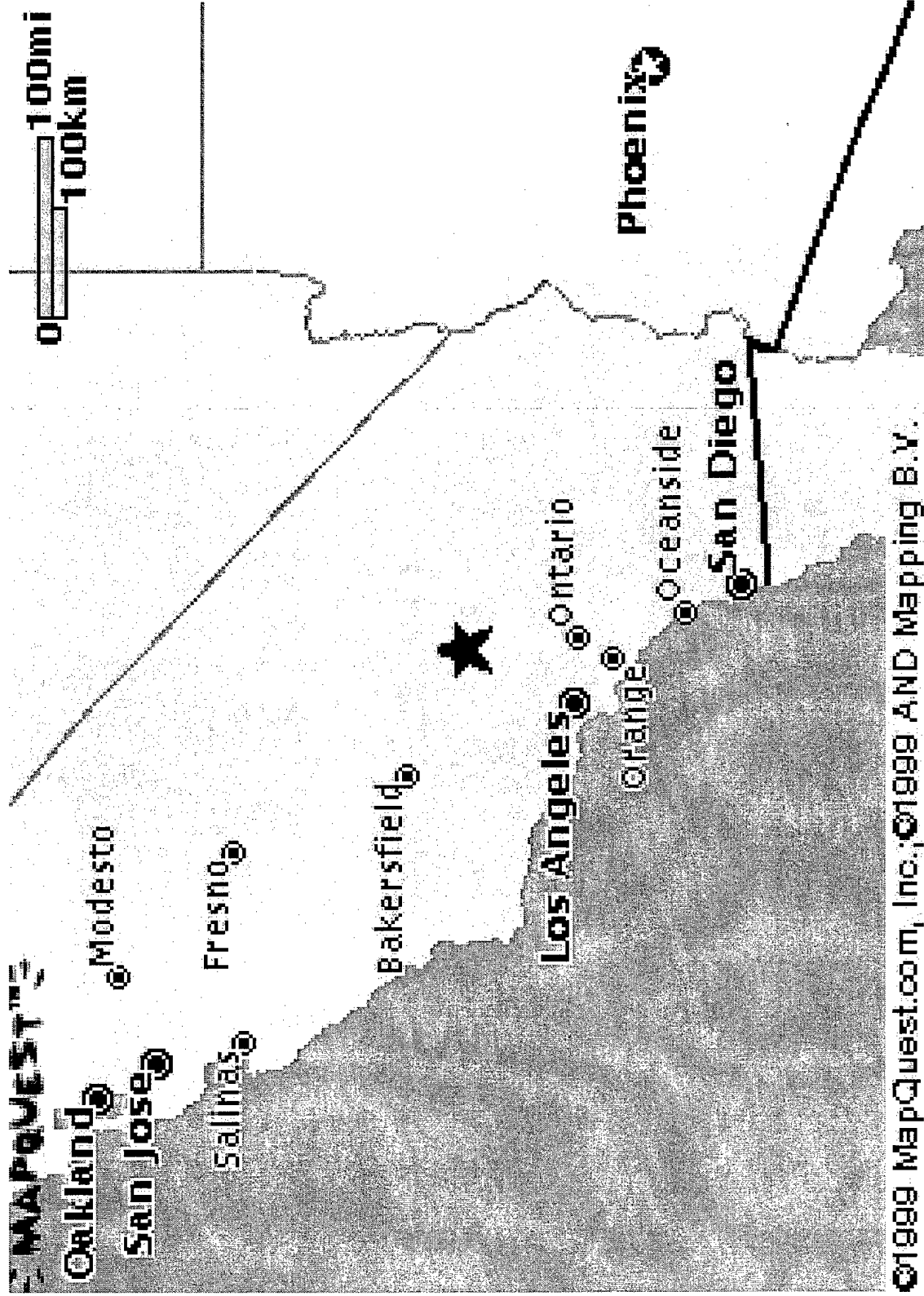
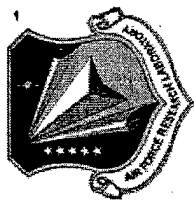
PRSM

Air Force Research Laboratory

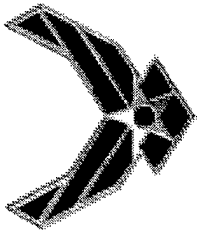


Air Force Research Laboratory

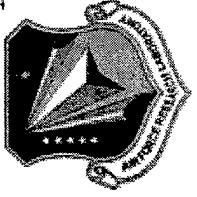
Located ~ 100 miles from LA



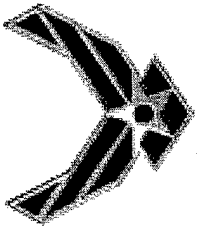
©1999 MapQuest.com, Inc.; ©1999 AND Mapping B.V.



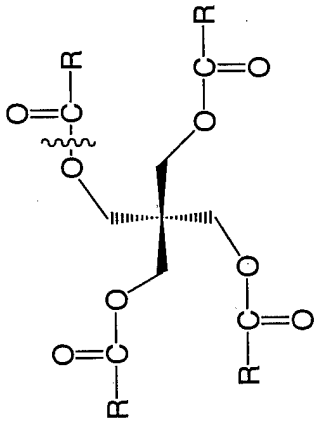
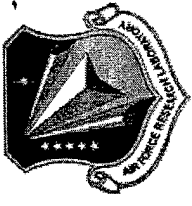
POSS Lubricants Project



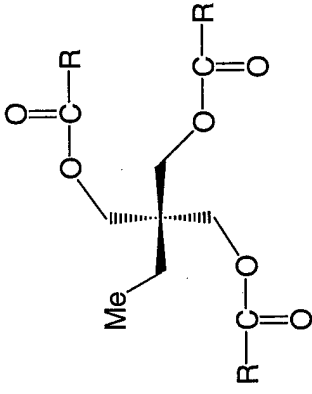
- Goal
 - Develop a lubricant that can withstand high temperatures (600 °F goal in IHPTET Phase III) and flows at -40 °C (20K centistoke) (High temp gas turbine engines: jets)
 - Higher temperature lubes means higher operating temperature which can lead to more power: increase in thrust:weight ratio
- Objective
 - Synthesize a POSS oil with an operating range of -40 °C to >> 400 °F (450 °F minimum)
 - Technical Hurdles:
 - Reaching High temperature operating minimum (450 °F)
 - Current Antioxidants in AF inventory decompose POSS



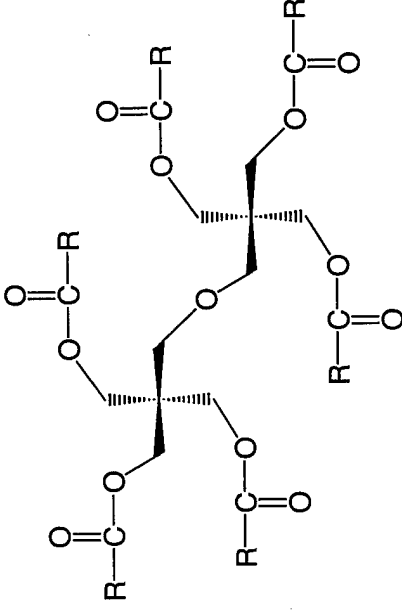
Present AF Lubricants Technology



Pentaerythritol Ester

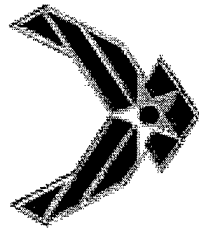


Trimethylolpropane Ester

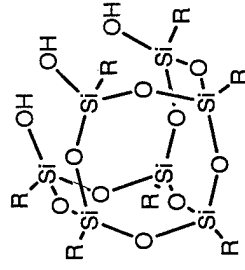
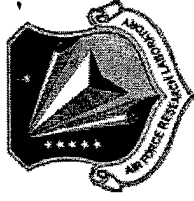


Pentaerythritol Dimer Ester

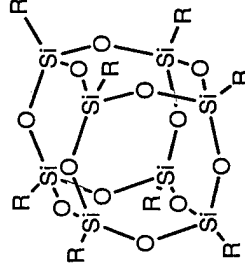
- The above polyol ester compounds are the main components of some AF turbine lubricants
- Operating range of -40°C to 200°C
- In house calculations show that ester C-O linkage breaks at 200°C
- Aminic antioxidants used



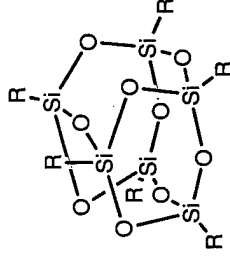
POSS = Polyhedral Oligomeric Silsesquioxane: Pre Hybrid Synthesis



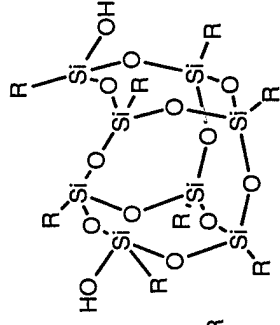
R = Cyclohexyl
Cyclopentyl
Cycloheptyl
Vinyl
Methyl



R = Cyclohexyl
Cyclopentyl
Cycloheptyl



R = Cyclohexyl



R = Cyclohexyl

R=Cyclohexyl: Brown and Vogt 1965

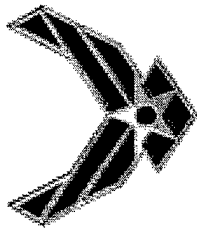
Fehér, Newman, Walzer 1989

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

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

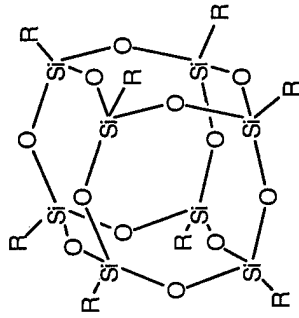
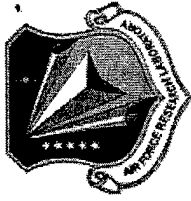
Lichtenhan (AFRL, 1993) Optimization

All of these materials are colorless solids at ambient temp

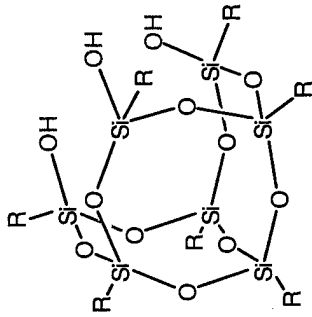


POSS Diversity

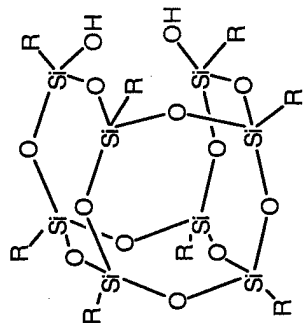
Hybrid Plastics



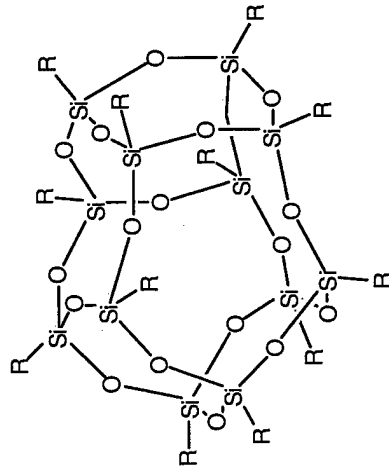
R = Methyl **Phenyl**
Isobutyl **Phenethyl**
Cyclopentyl **Octadecene**
Cyclohexyl



R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl
Ethyl



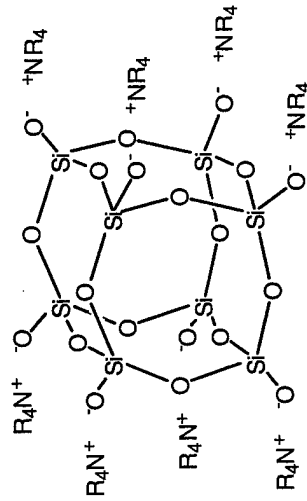
R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl



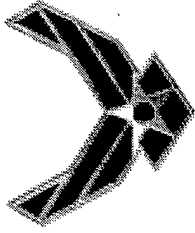
R = Phenyl
Trifluoromethylpropyl

Cage Mixtures
(T₈, T₁₀, T₁₂)

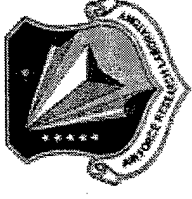
R = Vinyl
Phenethyl
Isooctyl



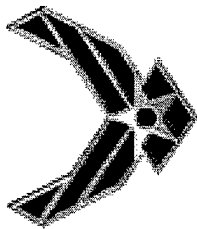
R = Methyl



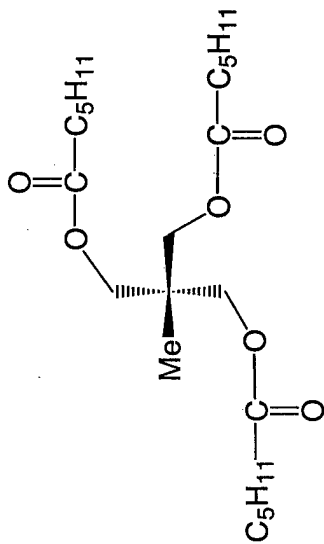
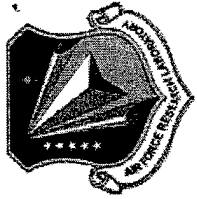
POSS Esters



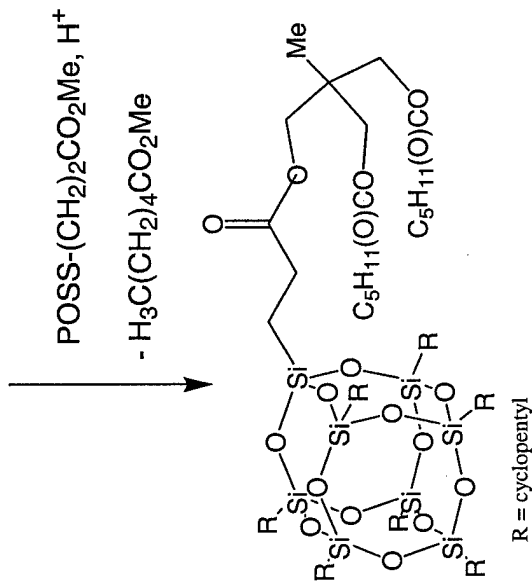
- **Goal: to synthesize a POSS Ester either as a lubricant additive or as a drop-in replacement**
- **It is believed that the POSS can act as a heat sink that will slow the ester decomposition so that higher temperatures can be reached (> 400 °F)**
- **Technical Issues:**
 - **- Lubricant Additives can be a solid (what all POSS esters are now) where an oil would be preferred**
 - **- Drop-in replacements need to follow the standard parameters (flows at – 40 °F)**



POSS Esters by Transesterification



Triethylpropane Ester

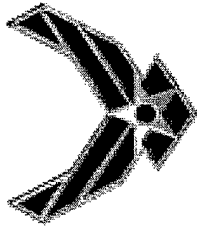


•The Transesterification of POSS into the triester would result in a “larger” lubricant

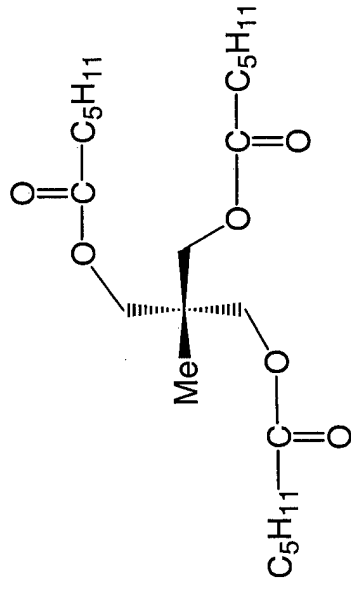
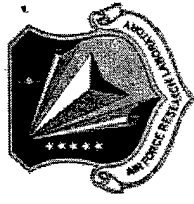
•A transesterification was done with the cyclopentyl POSS derivative, but there was a very low conversion and the product could not be separated from the POSS starting material

•Is there another POSS we can try?

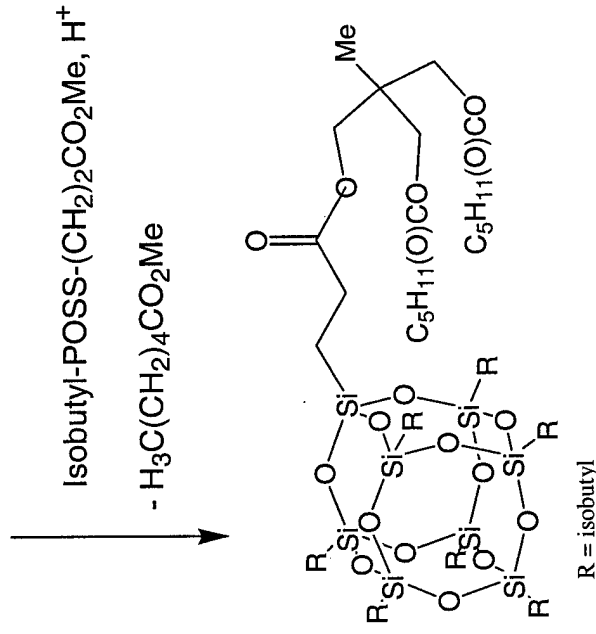
YES!



POSS Esters by Transesterification



Triethylpropane Ester

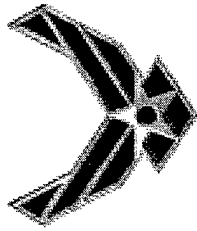


- The Transesterification of the new very soluble and lower melting isobutyl POSS was attempted with our model base stock

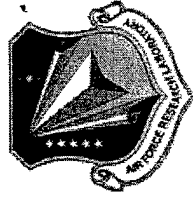
- The conversion for this reaction was much higher than the previous reaction

- Attempts at isolating the product from the starting material proved to be unsuccessful

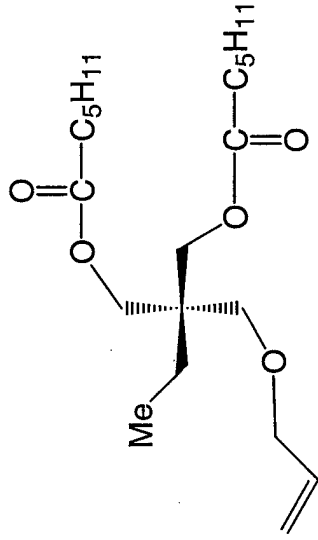
- Is there another pathway?



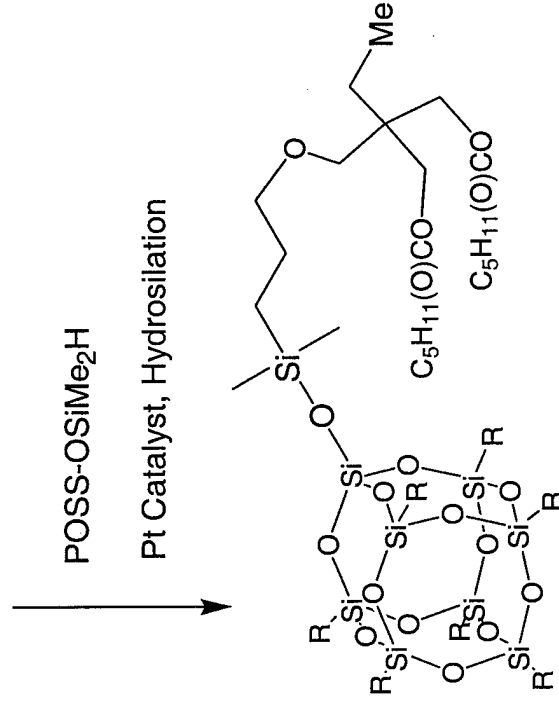
POSS Esters by Hydrosilation

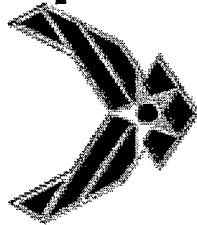


- After several attempts to make a POSS ester (discussed previously), the hydrosilation of a POSS hydride with TMP allyl ether dihexanoate does give a POSS diester
- 3 grams made
- Solid (as expected)
- Solubility in ester base stock: low (< 2%)
- Thermal stability can still be tested

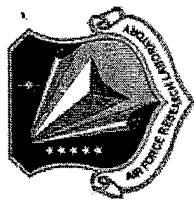


Triethylpropane Ester





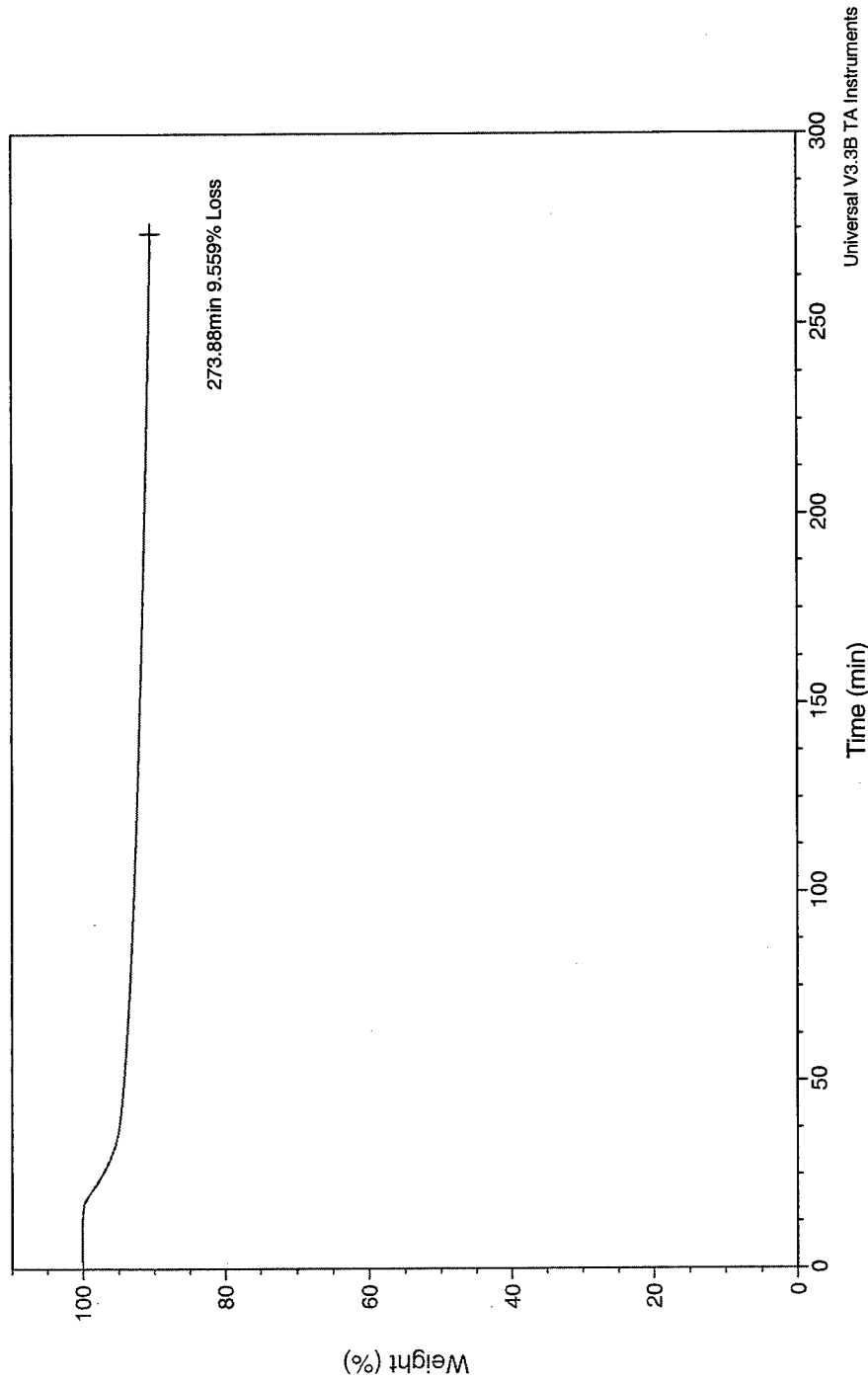
TGA Data For POSS Diester w/o AO

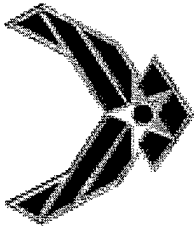


Sample: RLB-IV-5
Size: 30.9490 mg
Method: Isothermal Method
Comment: Air purge

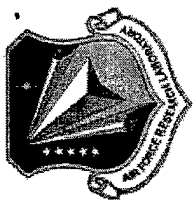
TGA

File: C:\...projects\Lubes\Lubes data\rb iv 5
Operator: Justin Leland
Run Date: 11-Jun-01 06:41
Instrument: 2050 TGA V5.4A





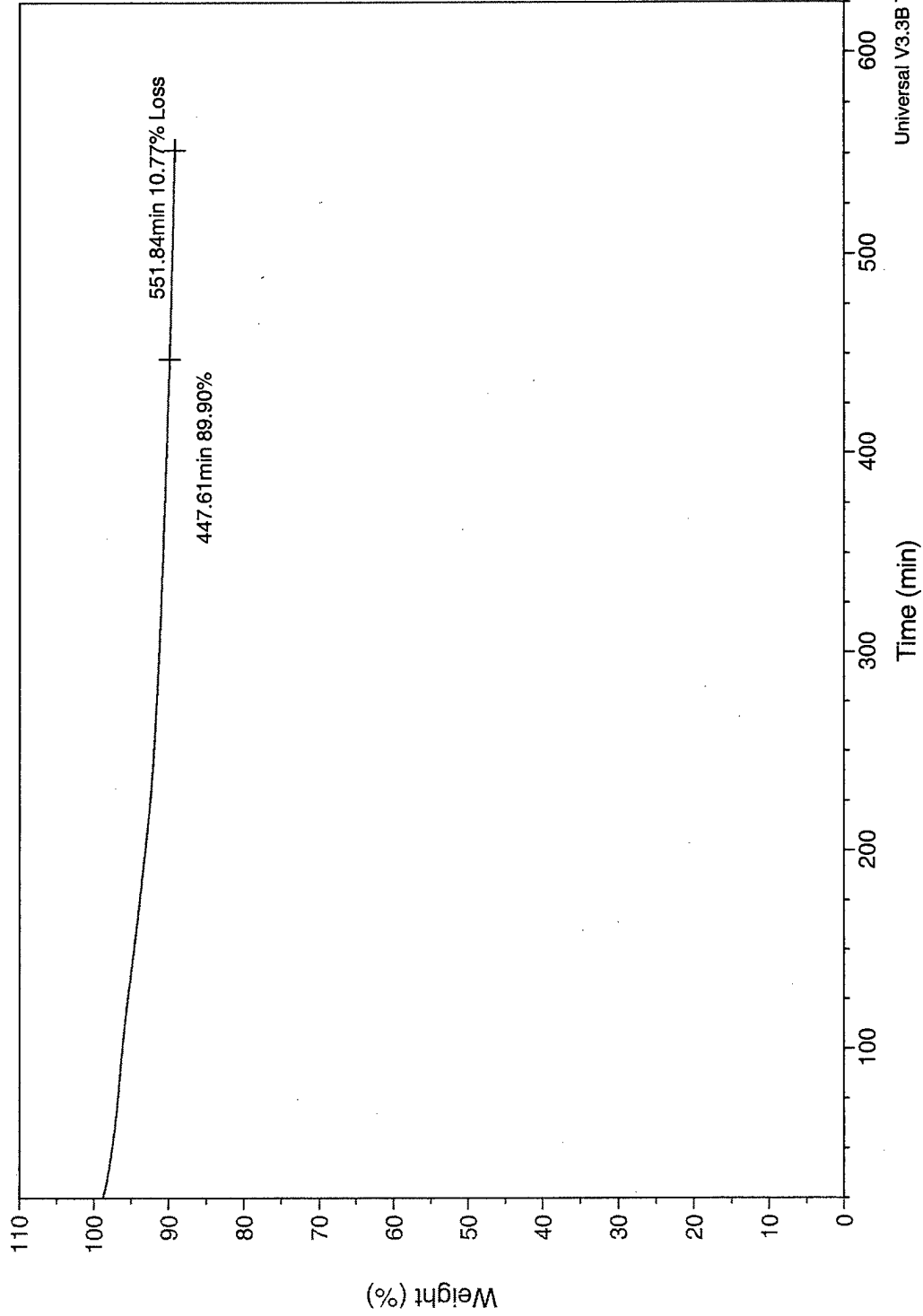
TGA Data For POSS Diester W/AO

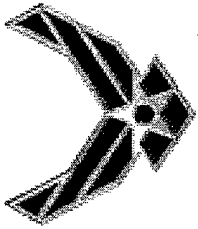


Sample: RLB-IV-5 w/AO
Size: 34.2630 mg
Method: Isothermal Method
Comment: Air purge

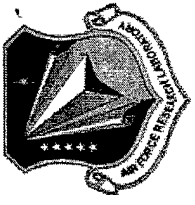
TGA

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Instrument: 2050 TGA V5.4A

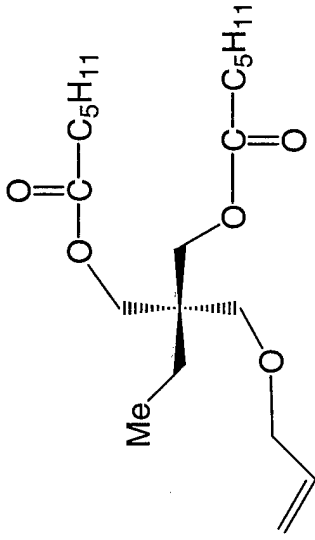




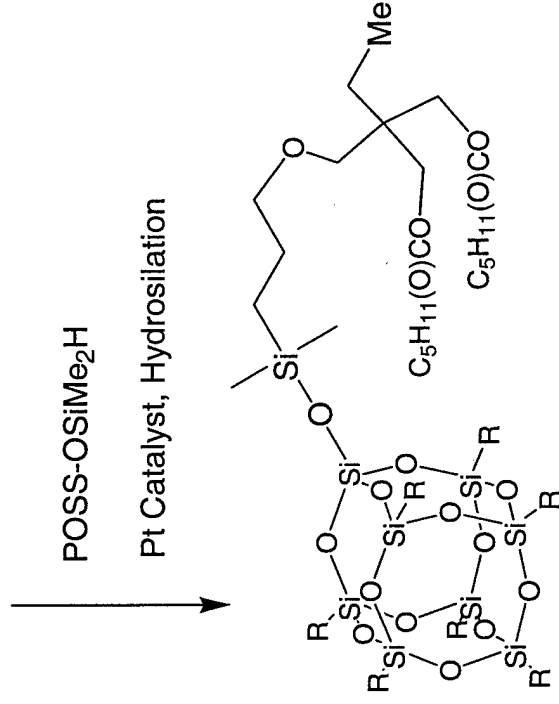
More Soluble POSS Diester



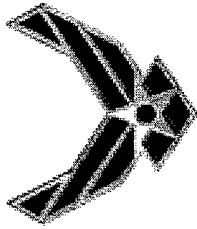
- A new POSS feedstock has come online with Hybrid Plastics: a POSS cage with isobutyl groups
- 3 grams made to prove concept
- Research problems (separation of unreacted TMP diester from POSS diester was not trivial due to similar solubilities) were overcome: vacuum distillation!
- Waxy Solid at room temperature
- Solubility in Grade 4 ester base stock: High, can be used in additive testing
- Further Physical testing will be done shortly



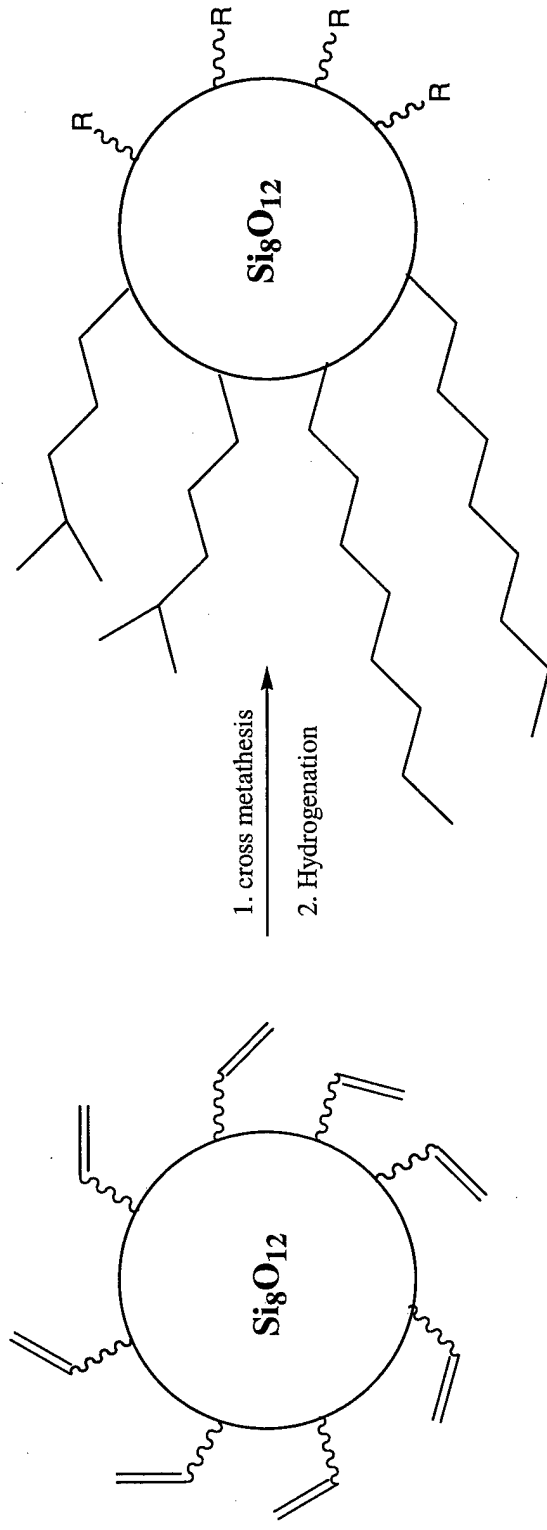
Triethylpropane Ester



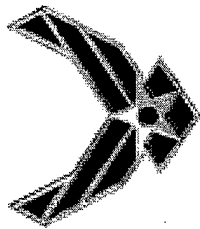
R = isobutyl



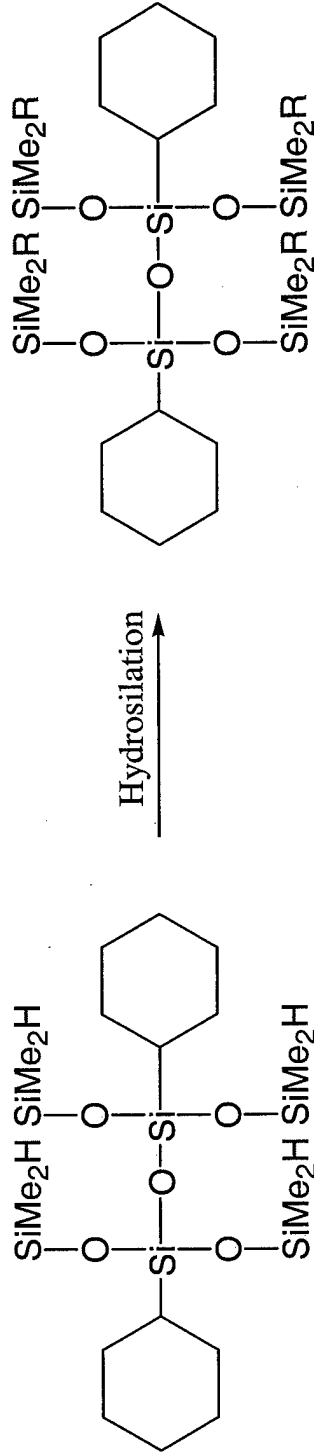
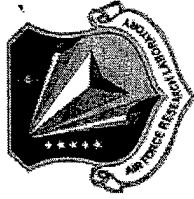
POSS Lubricants: T8 Class



- Stable above 200 °C (TGA)
- Oil at Room Temperature
- Through Cross Metathesis, Vinyl Groups allow adjustability of side groups

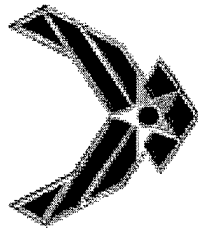


POSS Lubricants: Cyt_2 Class

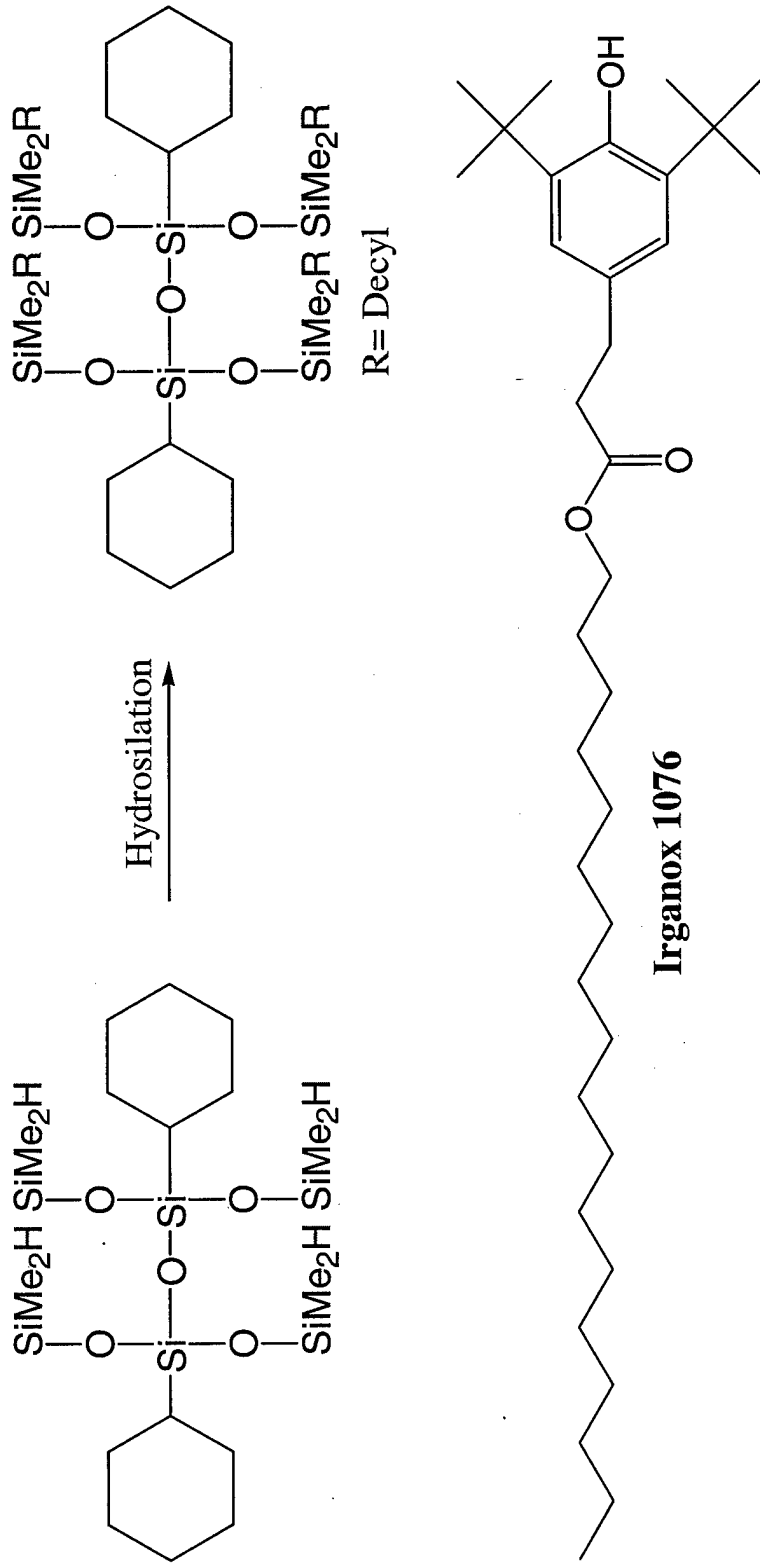
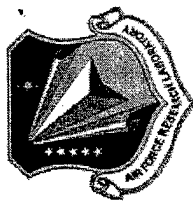


R= Decyl, Dodecyl,
Tetradecyl , all liquids at RT

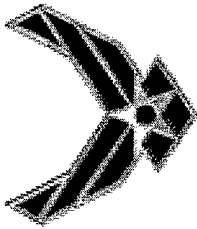
R=Octyl , flows at low Temp (-60 °C), evaporates at 200 °C
R=Decyl the viscosity at -40 °C is 4000 cP !!
R=Dodecyl, the freezing point is -12 °C
Stable at 200 °C with A/O present (TGA)



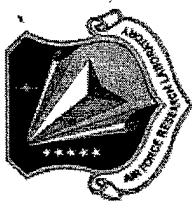
T₂ Tetradecyl System



- Aminic antioxidants reduce performance
- Irganox 1076 soluble to 4% level
- Higher temperature study performed:



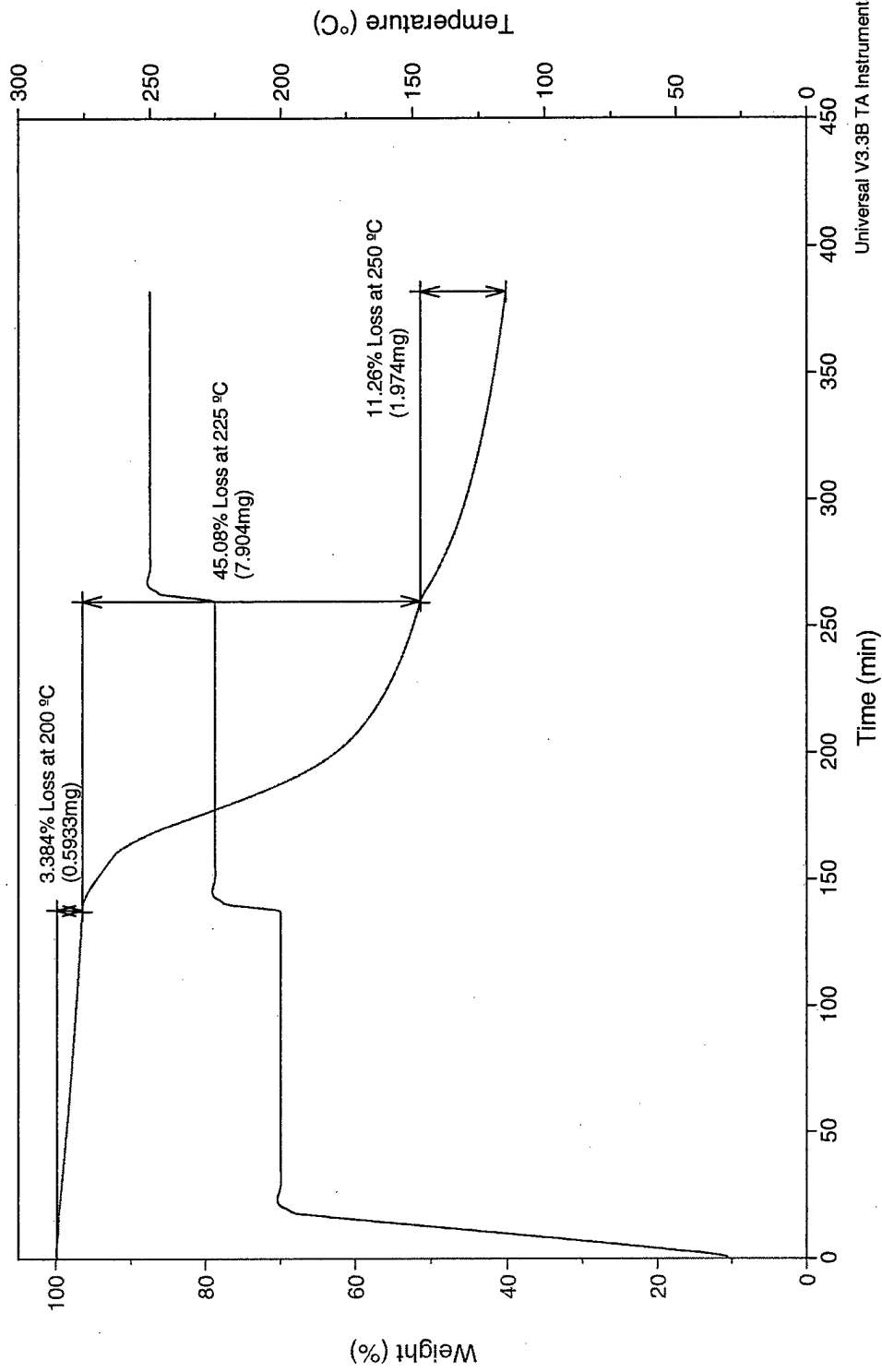
T₂ Tetradecyl System TGA

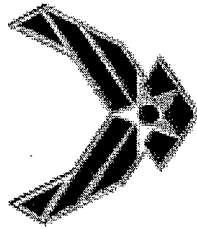


Sample: JTL1126 with 5% I-1076
Size: 17.5340 mg
Method: ramped isothermal
Comment: Air purge

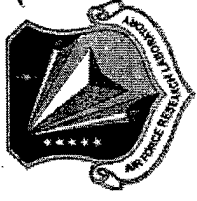
File: C:\TA\Data\Justin\TGA\5WT250
Operator: Justin Leland
Run Date: 7-May-01 07:05
Instrument: 2050 TGA V5.4A

TGA

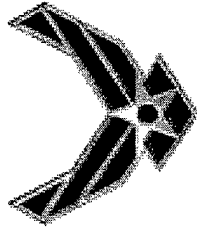




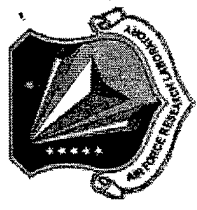
T₂Tetradecyl System



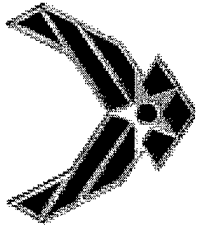
- While the T₂Tetradecyl system met the specifications for the state of the art (pourable at -40 °F and stable at 400 °F, the TGA data show that there are problems at higher temperatures: not an encouraging result
- To improve these results, a more efficient and compatible antioxidant may work → Further study
- While we do these studies, let's look into other systems.



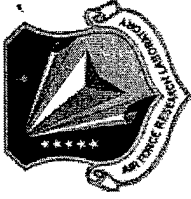
New POSS Compounds



- In conjunction with Hybrid Plastics a series of compounds was analyzed by several methods. One of these compounds was Isooctyl_nT_n, a commercially available product which is an oil at room temperature (13100 cP at 20 °C)
- One of these methods was Thermogravimetric analysis with an FTIR analysis of the effluent (TGA-FTIR)
- The POSS monomers usually did one of two things in the TGA-FTIR experiment: decomposed above 300 °C or volatilized around 250 °C. One sample however didn't volatilize until over 300 °C (570 °F): Isooctyl_nT_n
- What about using Isooctyl_nT_n as a lubricant?



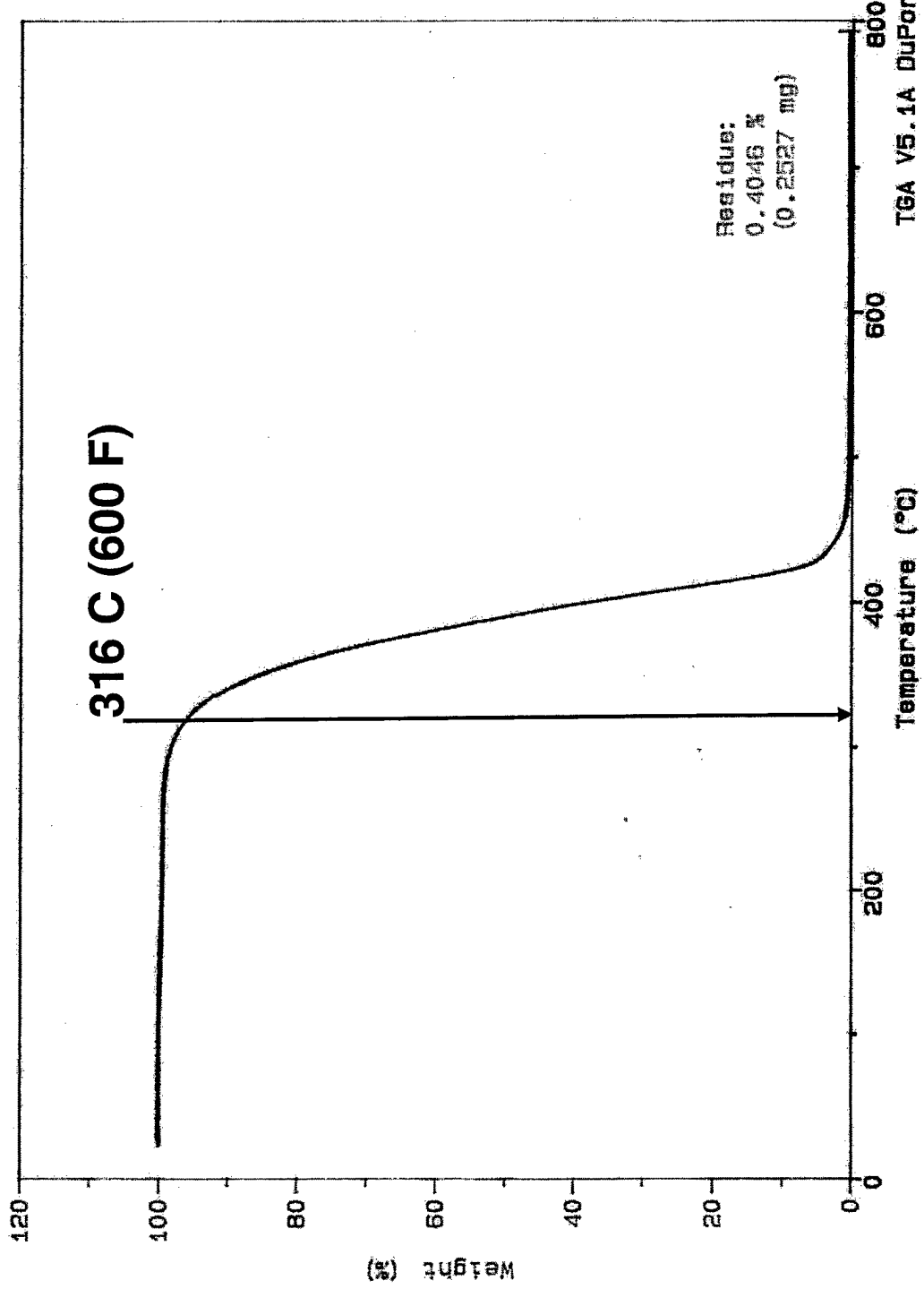
Isooctyl_nT_n as a Lubricant

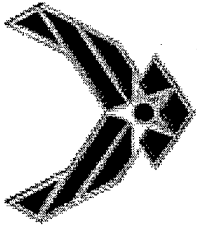


Sample: Isooctyl18T8 rerun
Size: 62.4530 mg
Method: POSS
Comment: GN2 100 mL/min, rate 10C/min to 800C

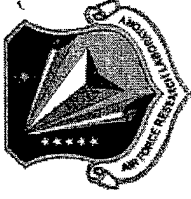
TGA

File: C: PBOYATP.28
Operator: Bianski
Run Date: 14-May-01 04:52

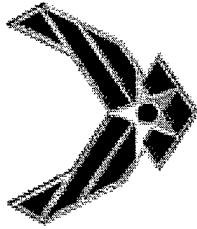




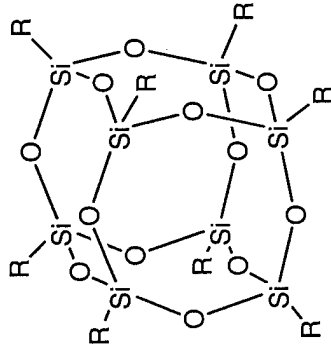
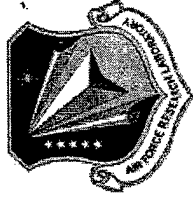
Isooctyl_nT_n as a Lubricant



- **Advantages of Isooctyl_nT_n as a lubricant: potential high temperature stability and relatively low cost.**
- **Technical Challenges for using Isooctyl_nT_n as a lubricant:**
- **Current supply of Isooctyl_nT_n contains a small amount of resin which should be removed because of reactivity and viscosity concerns**
- **No known method available separate a POSS oil monomer from oily resin: the usual method of selective crystallization is impossible**
- **Low Temperature pourability issues**
- **Goals:**
- **Develop method to separate POSS oil monomer from resin**
- **Characterize pure oil and test decomposition temperature**

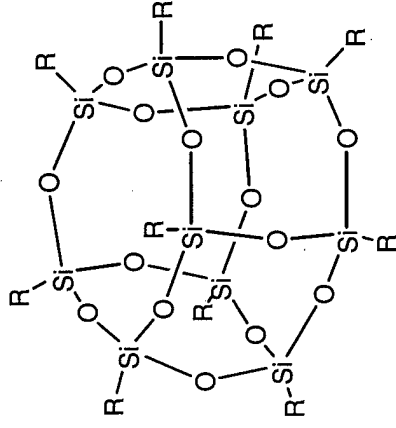


Isooctyl_nT_n as a Lubricant



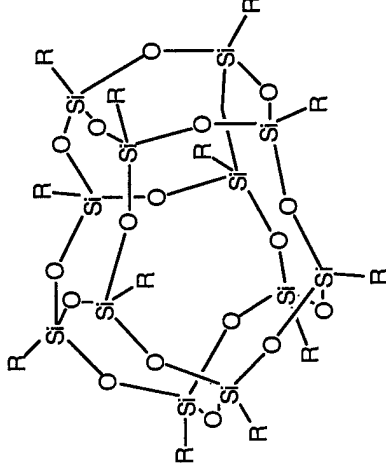
R = Isooctyl

minor component



R = Isooctyl

major component

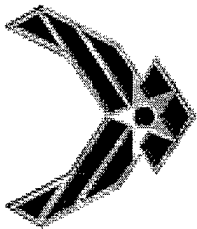


R = Isooctyl

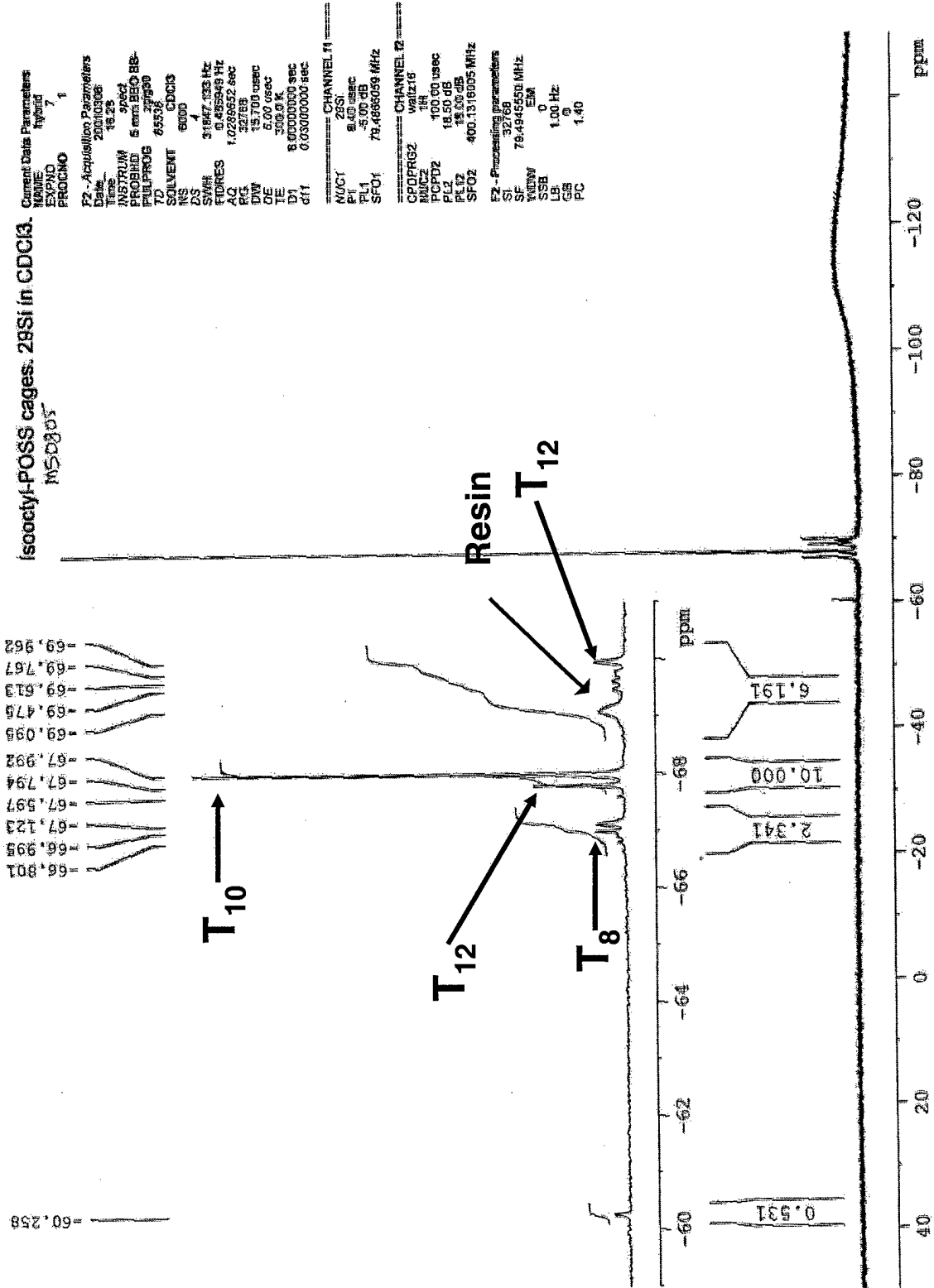
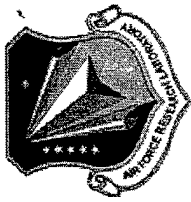
minor component

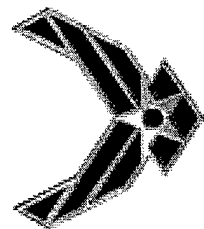
Since Isooctyl_nT_n volatilizes without decomposing (TGA-FTIR confirms this) what about distillation?

Since distillation at 300 °C is difficult, a vacuum distillation with a Kugelrohr (short path distillation under High Vacuum) was attempted

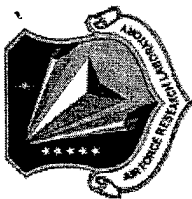


Isocetyl_nT_n Before Distillation

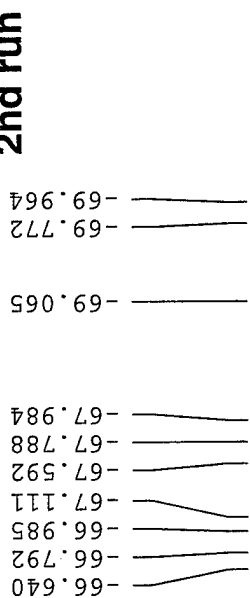




Isooctyl_nT_n After Distillation



Isooctyl8T8 distilled 250C 5 microns 29Si CDC13 Blanski
2nd run



```

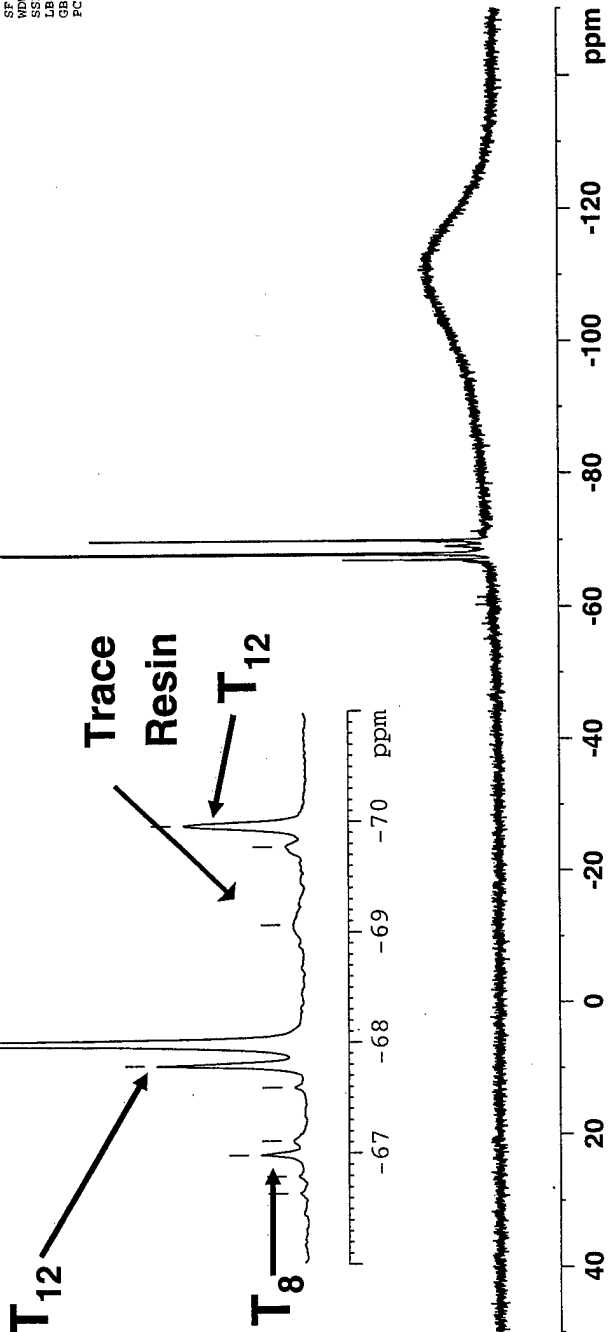
Current Data Parameters
NAME      isooctyl8T8
EXPNO     2
PROCNO    1

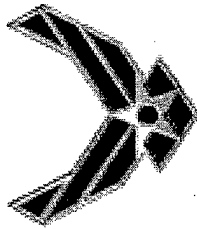
F2 - Acquisition Parameters
Time      24031100
Date_     16-09
INSTRUM   spect
PROBHD    5 mm QNP 1H
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         5124
DS         4
SWH        23809.523 Hz
FIDRES     0.363304 Hz
AQ         1.3763061 sec
RG         32768
DM         21.000 usec
DE         30.00 usec
DI         10.00000000 sec
d11        0.03000000 sec

===== CHANNEL f1 =====
NUC1       29Si
P1         10.00 usec
PL1        0.00 dB
SFO1       59.6214106 MHz

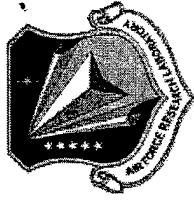
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        19.00 dB
PL12       20.00 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI         32768
SF         59.6273730 MHz
GB         0
LB         1.00 Hz
GB         0
PC         1.40
  
```

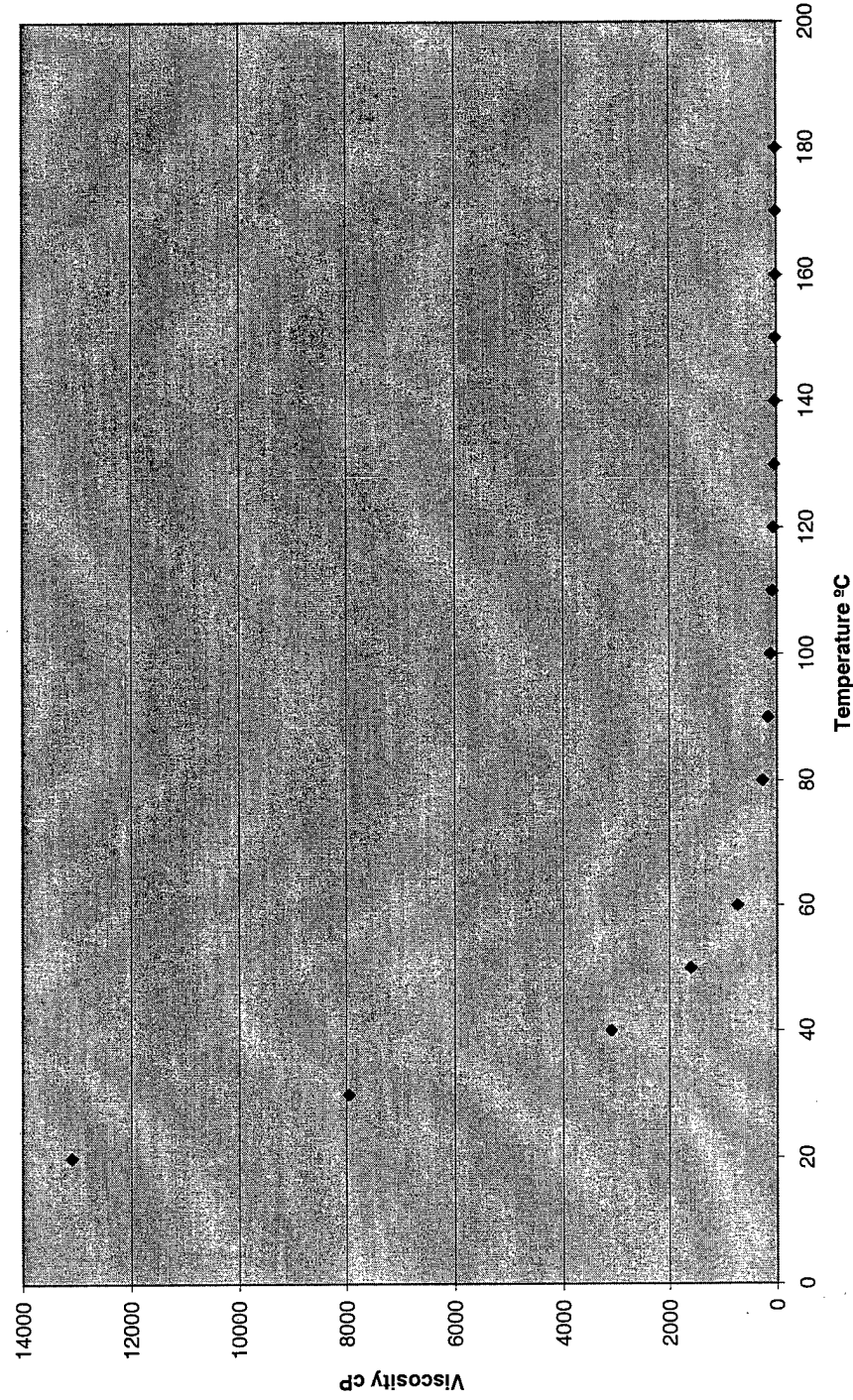




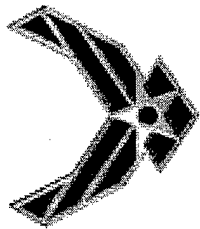
Viscosity of Distilled Isooctyl_nT_n



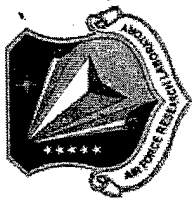
Viscosity of Isooctyl₈T₈



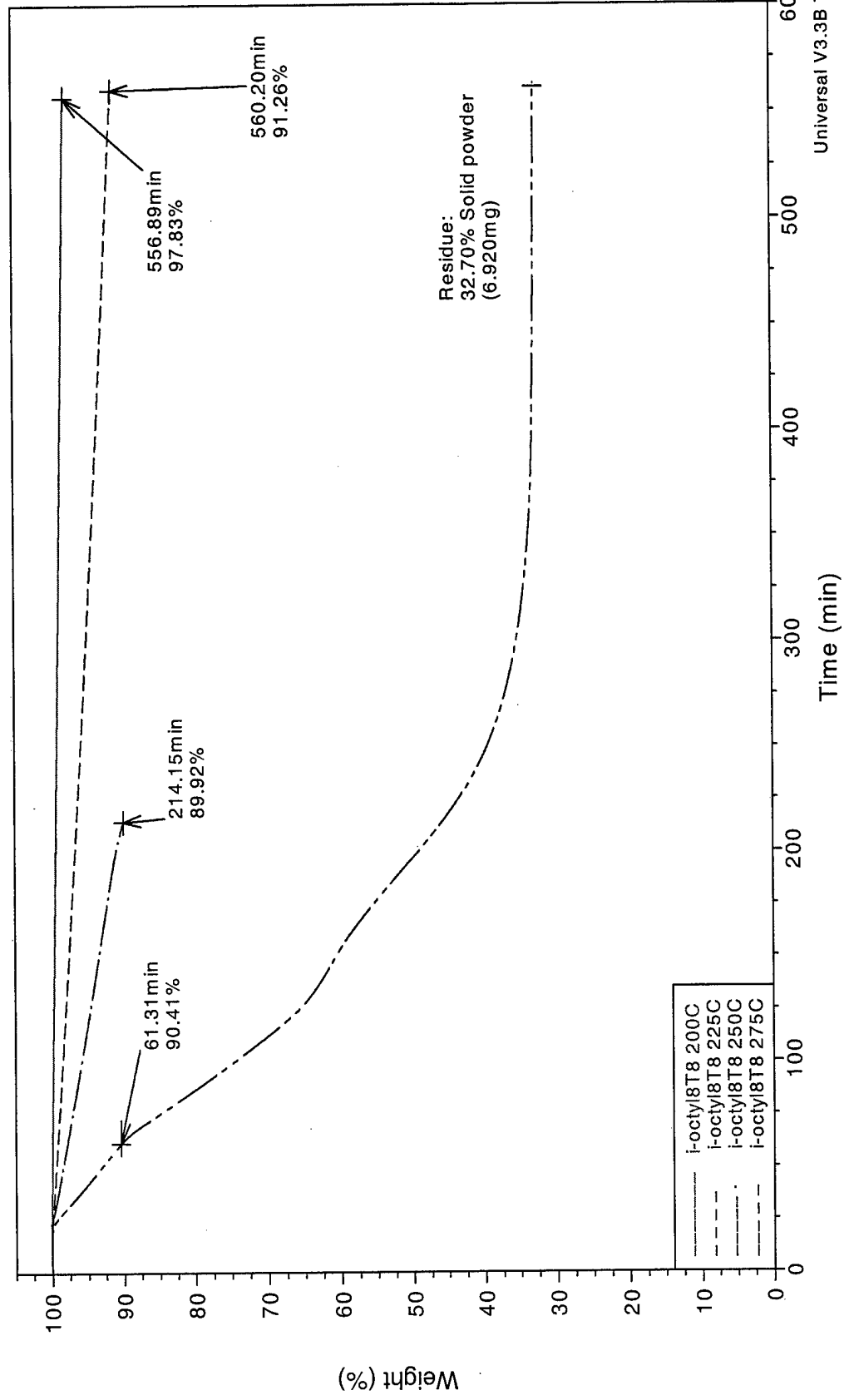
Temp °C	Vis cP
20	13100
30	7950
40	3100
50	1600
60	725
80	260
90	166
100	112.6
110	79
120	57
130	44
140	32
150	25
160	20.4
170	16.3
180	13.86

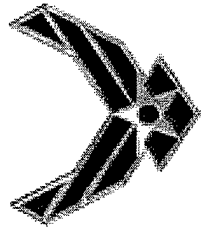


TGA of Isooctyl_nT_n w/AO

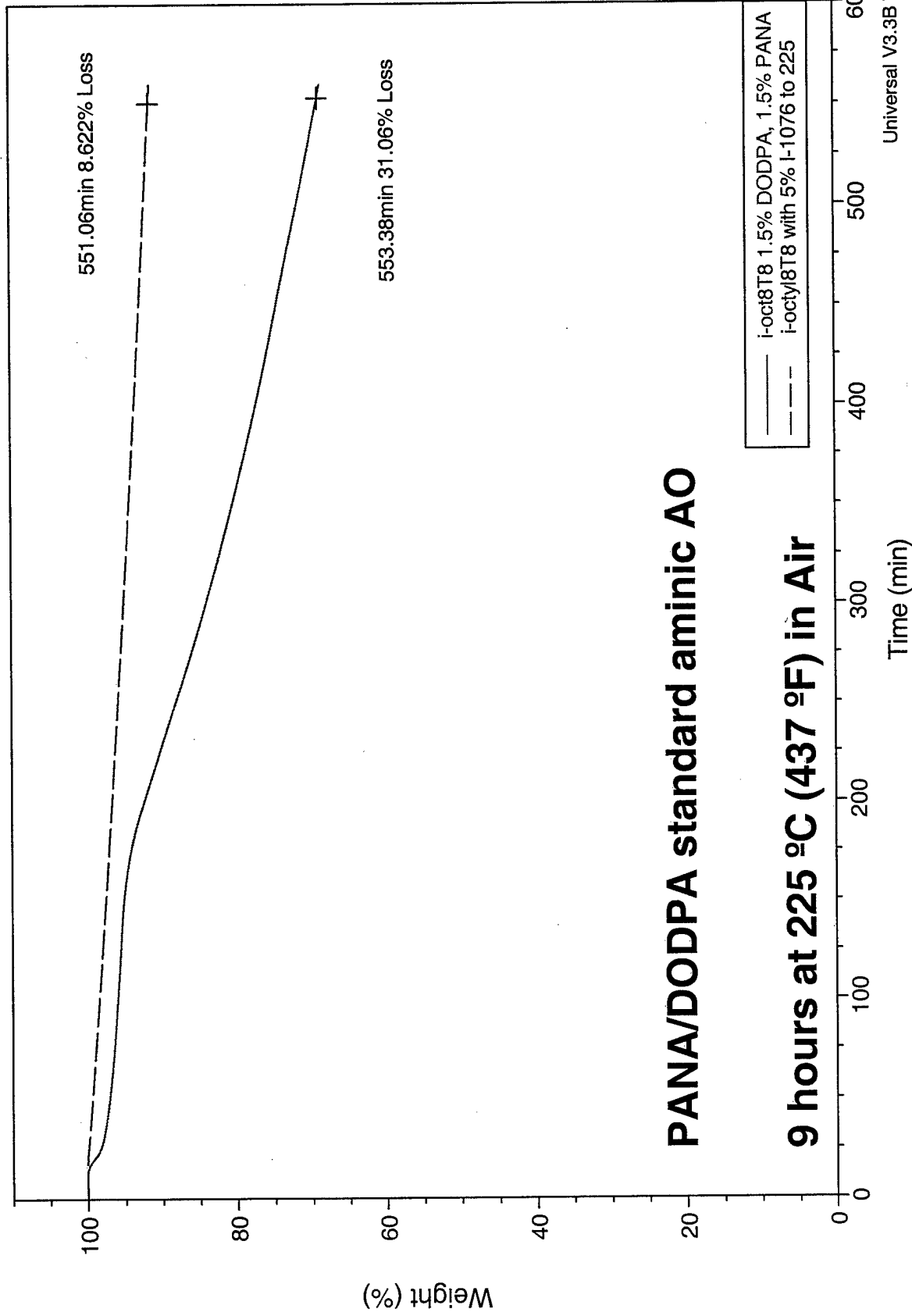
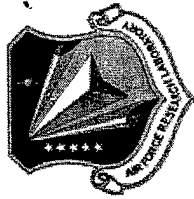


i-octyl 8T8. All samples contain 5 wt% I-1076.





TGA of Isooctyl_nT_n w/different AOs



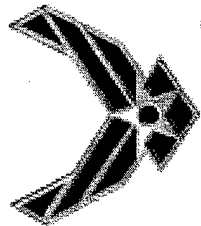
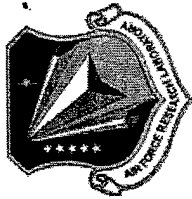
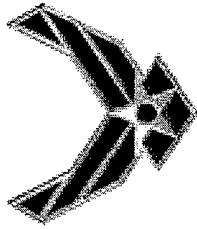


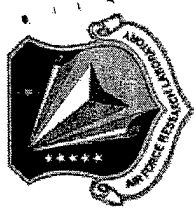
Table of TGA Data For POSS Samples



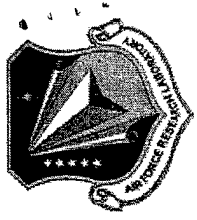
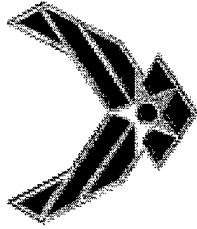
Material	TGA temp	TGA temp	Time to 10% mass loss	% lost after 9 hrs	residue
POSS Diester	200 °C	392 °F	4.6 hr	Stopped @ 4.6hrs	Solid
POSS Diester w/ AO	200 °C	392°F	7.5 hr	11	Solid
Isooctyl ₈ T ₈ with 5% I-1076	200 °C	392 °F	--	2.2	Oil
Isooctyl ₈ T ₈ with 5% I-1076	225 °C	437 °F	--	9.0	Oil
Isooctyl ₈ T ₈ with 5% I-1076	250 °C	482 °F	3.5 hrs	Stopped @ 3.5hrs	Oil
Isooctyl ₈ T ₈ with 5% I-1076	275 °C	527 °F	1hr	70	Grit



Future Work



- **Perform Testing on POSS diester and make a POSS diester which is an oil at room temperature**
- **Finish testing for T2 work to determine high temperature stability of this system**
- **Perform further testing on Isooctyl_nT_n (both purified and unpurified)**



Conclusions: POSS Lubes

- POSS Esters can be made by the Hydrosilation of POSS hydride and an allyl ether TMP diester
- 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})
- The discovery of IsooctylInTn and its high temperature stability (> 225 C) opens the door to high temperature applications