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Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

18 separate items enclosed

NOTIFIE[redacted]

12/1 CA9F

MEMORANDUM FOR PR (In-House Publication)

FROM: PROI (TI) (STINFO)

30 November 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-1999-0229**
Phillips, S., et al., "Hybrid POSS Polymer Technology for Rocket & Space Applications" (BFI)

49th JANNAF Propulsion Meeting (Tucson, AZ, 14-16 Dec 1999) **(Statement A)**

"Hybrid POSS Polymer Technology for Rocket & Space Applications"

JANNAF December 1999

Dr. Shawn H. Phillips
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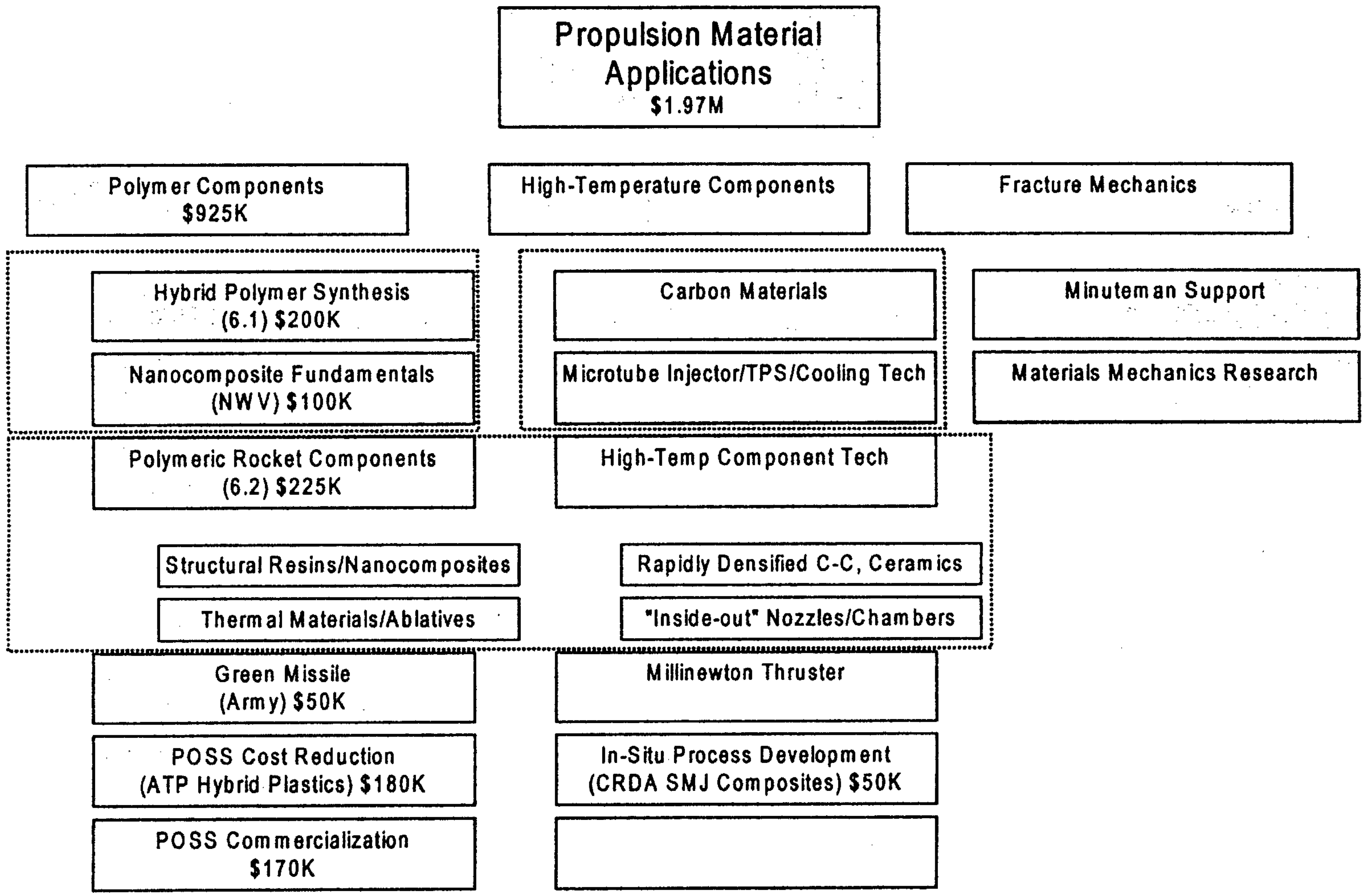
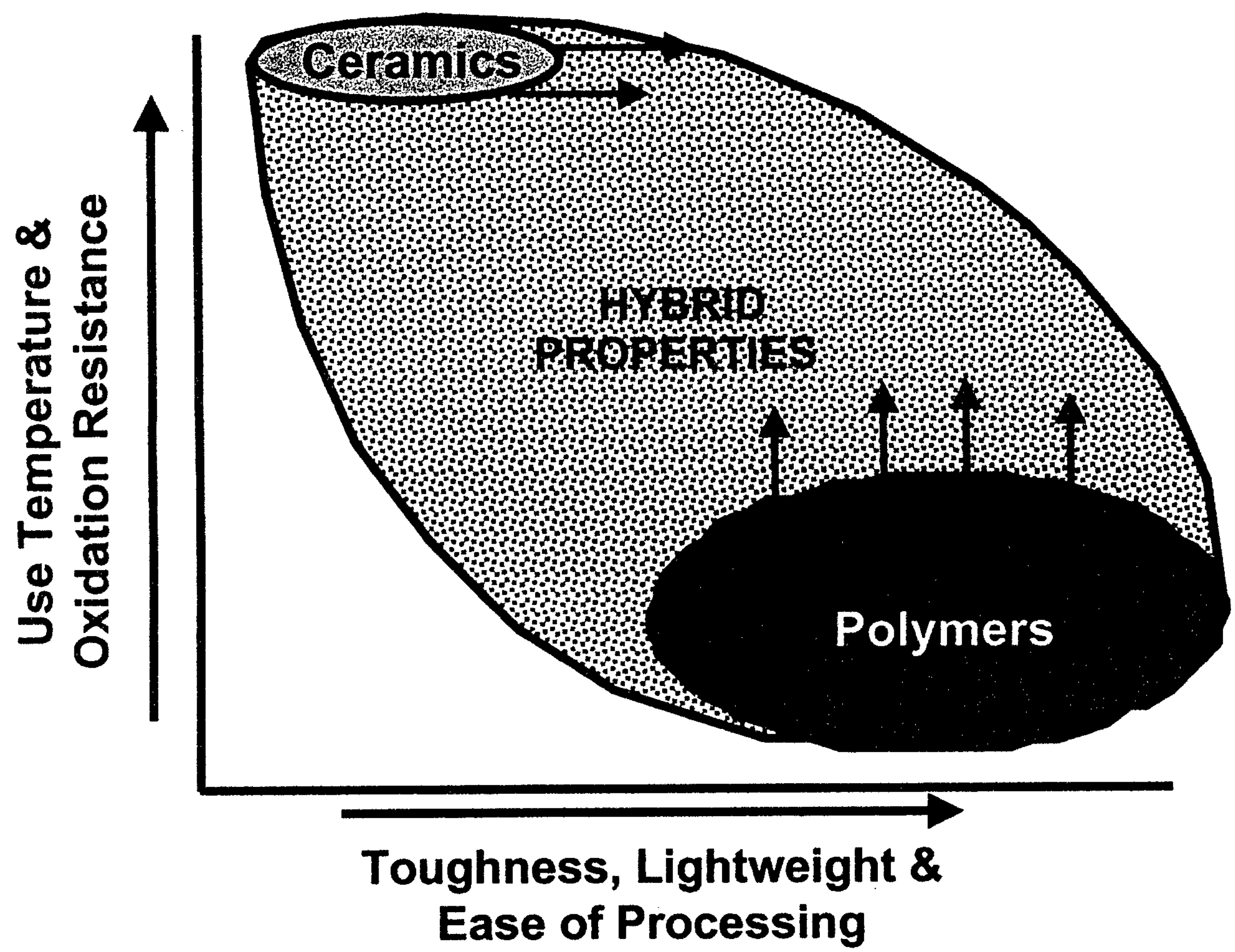
Propulsion Sciences Division
Edwards Air Force Research Lab

PRSM Work Breakdown Structure



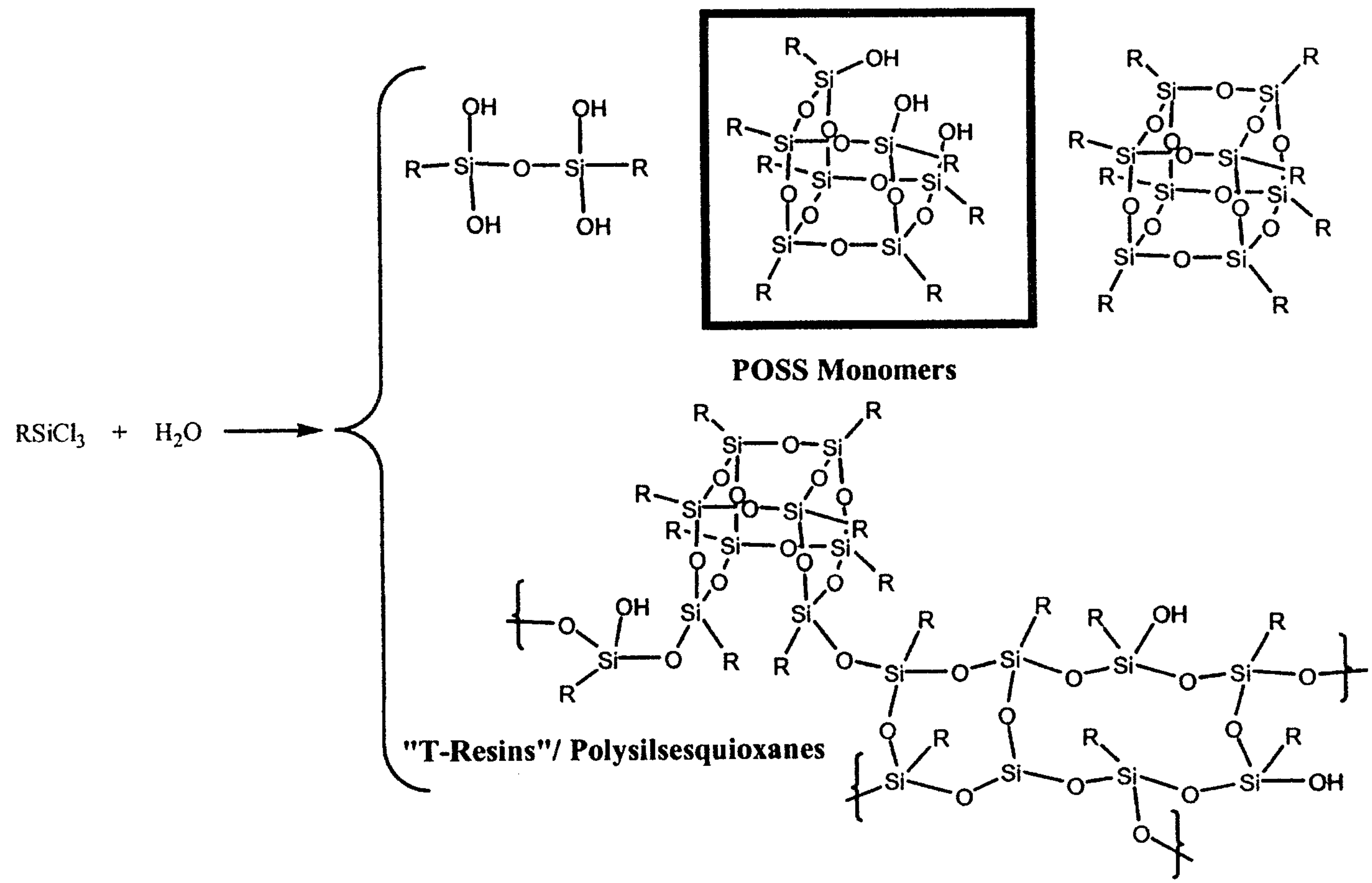
Propulsion (Air Force) Technology is Limited by Material Properties

Goal: Develop High Performance Polymers that REDEFINE material properties



- Hybrid plastics can bridge the barrier between ceramics and polymers

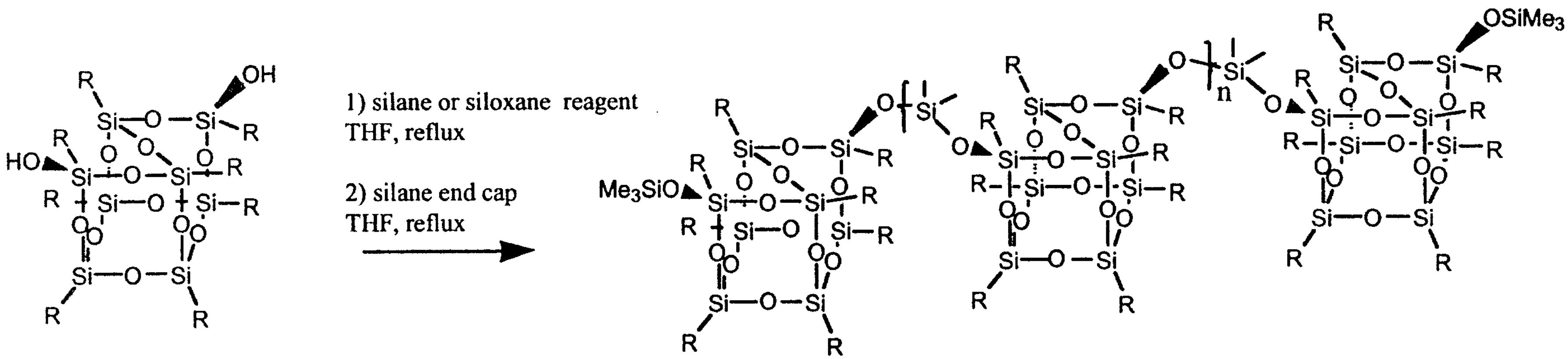
POSS = Polyhedral Oligomeric Silsesquioxane

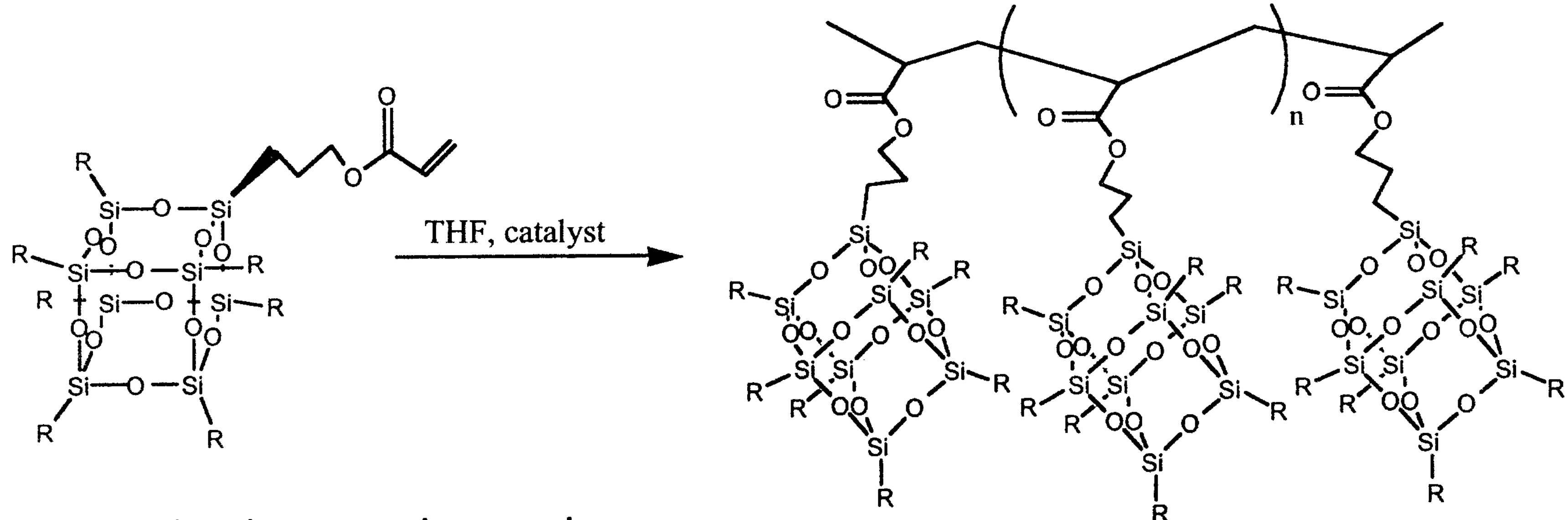


- **Traditional silsesquioxane chemistry focused on "T-Resins"**
- **The maximization of property enhancements in polymers results from interaction at the nano-level (Edwards AFRL/PRSM ---> POSS monomers)**

POSS-Based Hybrid Polymers

POSS-macromers can be employed in the same manner as "common" organics





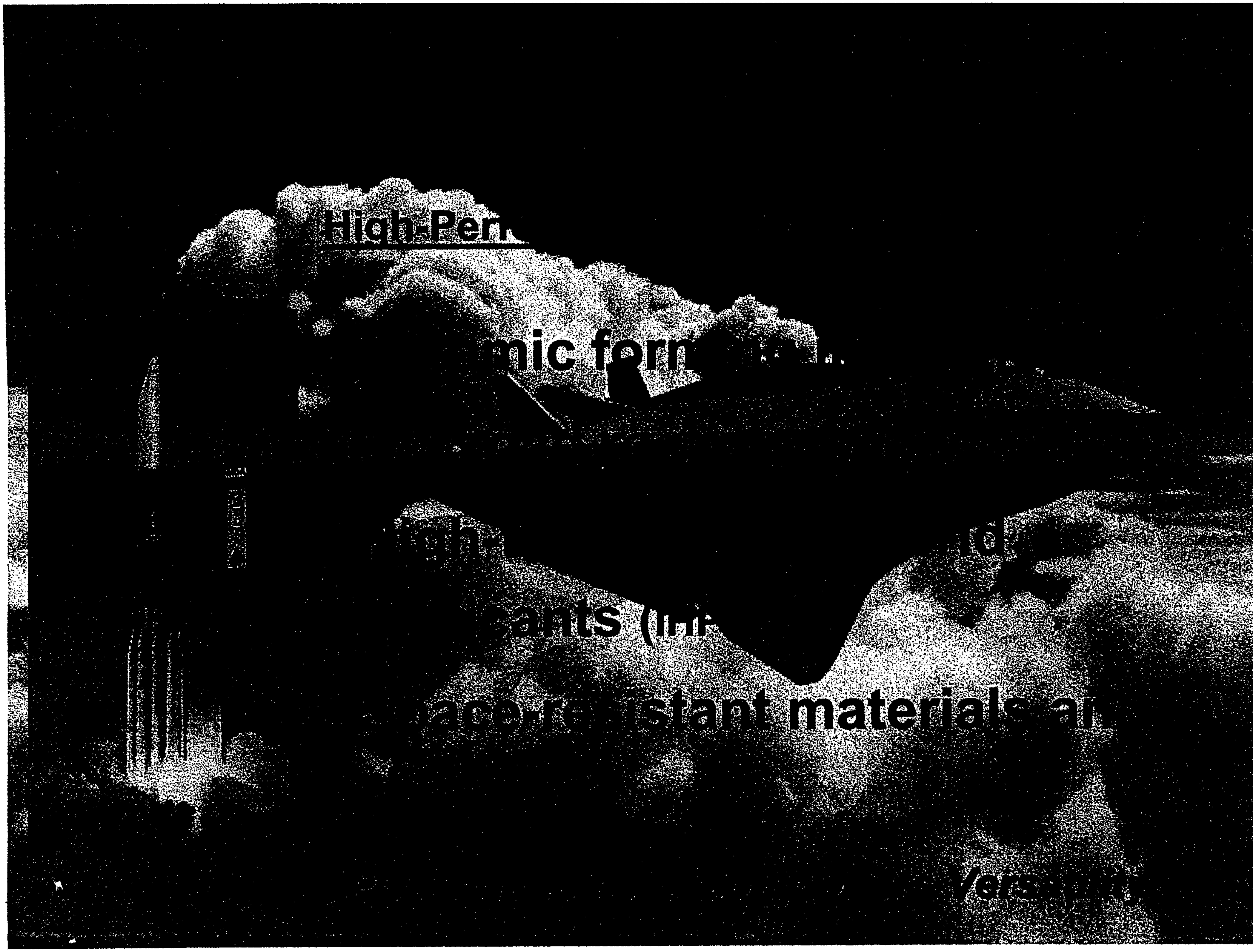
POSS-technology can be used in either monomer or polymer form.

Lichtenhan et. al. *Macromolecules* **1993**, *26*, 2141
Lichtenhan et. al. *Macromolecules* **1995**, *28*, 8435
Lichtenhan. *Comments on Inorganic Chemistry*, **1995**, *17*, 115

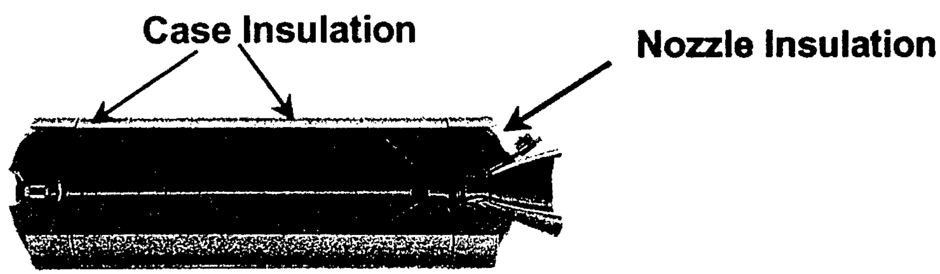
Property Enhancements via POSS

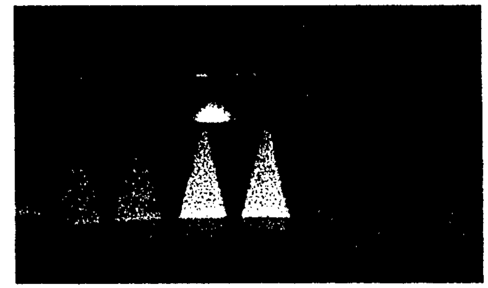
Observed in POSS-Copolymers and Blends

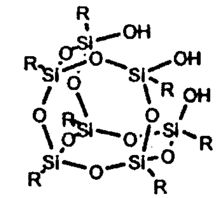
- increased T_g
- increased T_{dec}
- enhanced blend miscibility
- reduced flammability
- extended temperature range
- oxidation resistance
- reduced heat evolution
- increased oxygen permeability
- altered mechanicals
- lower density
- lower thermal conductivity
- reduced viscosity
- disposal as silica
- thermoplastic or curable


materials

Solid Rocket Motor Nozzle Insulation







Char Motor Polymer Insulation Samples

Goal: 50% Lower Erosion of Insulation (44 % weight reduction, 7.4% booster payload increase) – Phase III IHPRPT

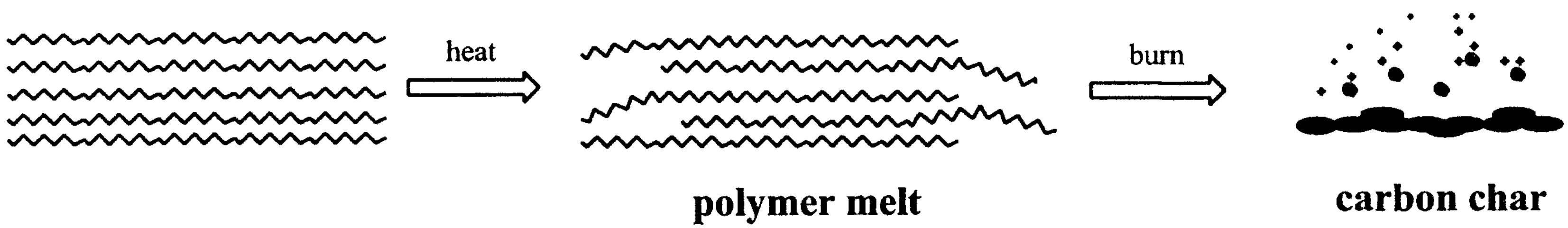
Objective: Development of Ceramic Forming Polymer

Technical Challenges:

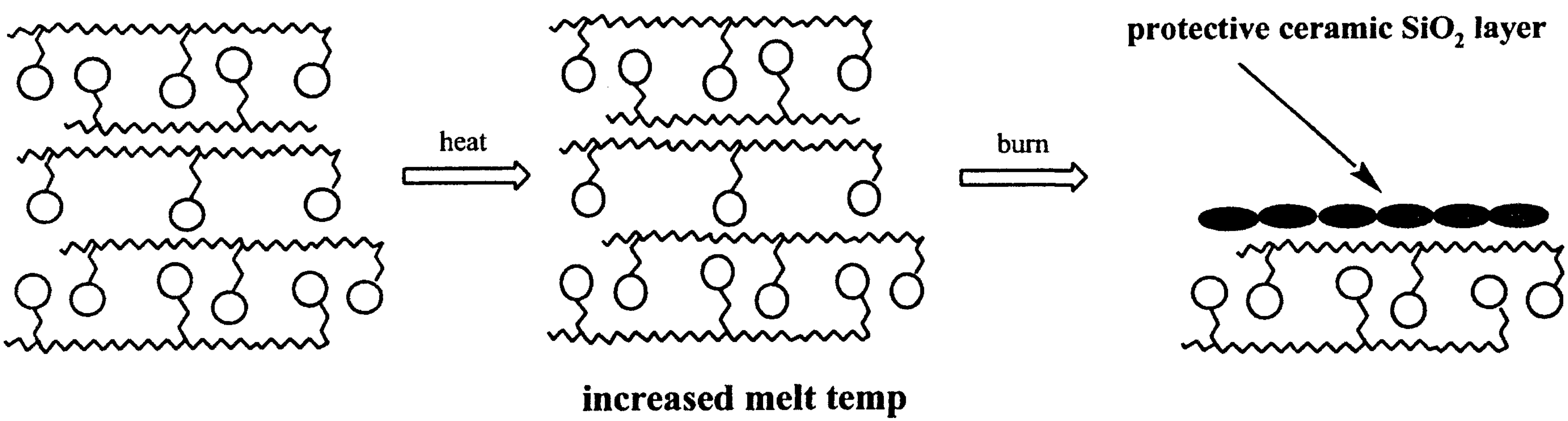
- Development/modification of insulation chemistry to incorporate pre-ceramic polymers
- Char formation/erosion under different operational conditions/prediction capabilities
- Achieving good adhesion and physical properties at the insulation/case interface

POSS for Flame Retardant Materials

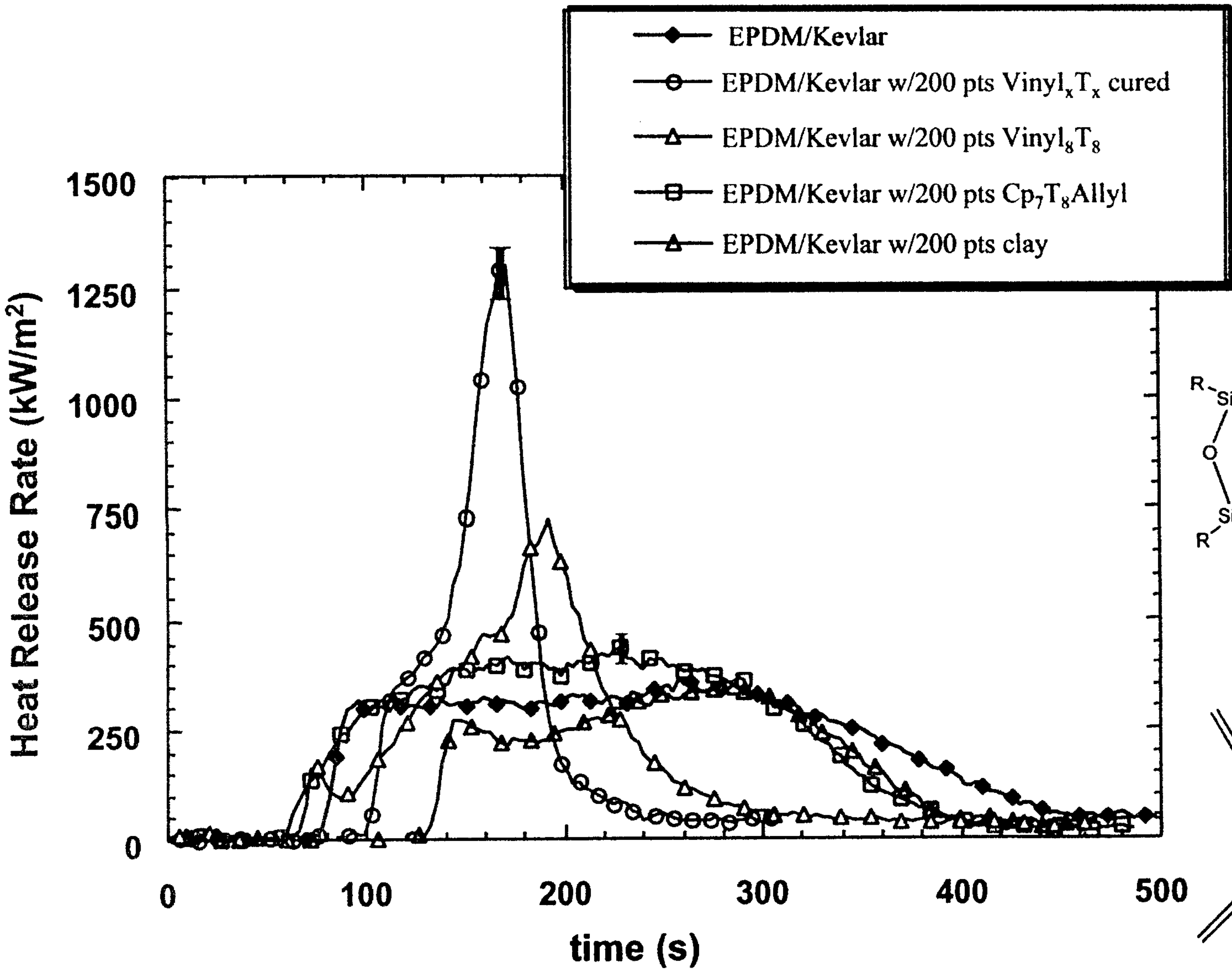
Traditional Polymer

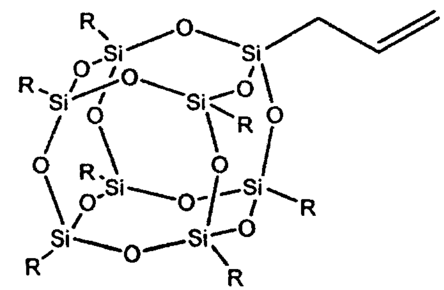


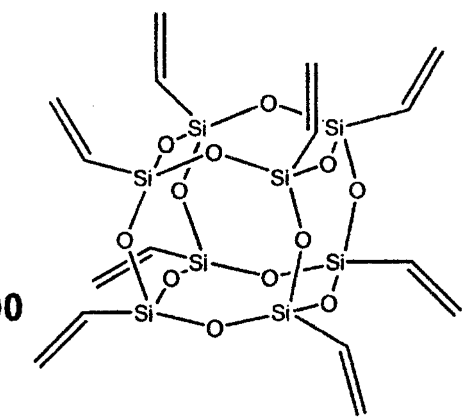
POSS Polymer



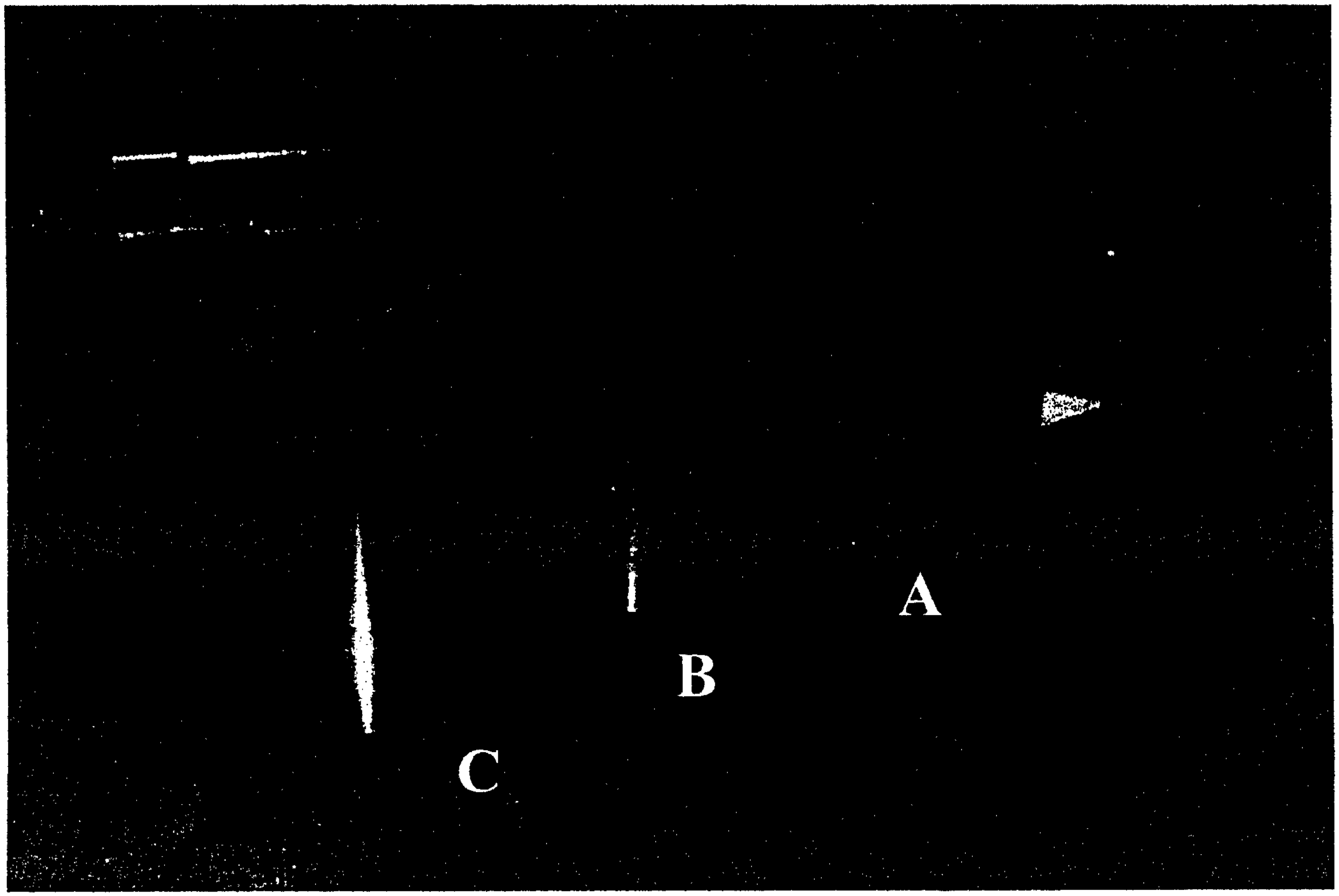
Cone Calorimeter Data







Solid Rocket Motors Insulation



A) Insulation containing POSS monomers
B) Convergent Cone
C) Convergent Cone + Insulation

Convergent Cone SRM Insulation Tests

Propellant			XXXX			XXXXX		
Ave Pressure			1340 psi			1310 psi		
Duration			6.5 sec			6.3 sec		
Insulation /Filler			[redacted]	POSS-Allyl (25%)	POSS-Octavinyl (25%)	[redacted]	Poss-Allyl (50%)	Poss-Octavinyl (50%)
Stn No.	e	Ma No.	[redacted]	%Ablated Depth	%Ablated Depth	[redacted]	%Ablated Depth	%Ablated Depth
0	3.5	.17	[redacted]	200	154	[redacted]	350	100
1	4.0	.15	[redacted]	115	121	[redacted]	200	111
2	6.6	.09	[redacted]	100	123	[redacted]	100	85
3	9.8	.06	[redacted]	100	100	[redacted]	200	137
4	13	.05	[redacted]	100	100	[redacted]	200	60
5	21	.03	[redacted]	100	100	[redacted]	100	-300
6	33	.02	[redacted]	100	100	[redacted]	-200	-500
7	47	.01	[redacted]	100	100	[redacted]	-500	-750

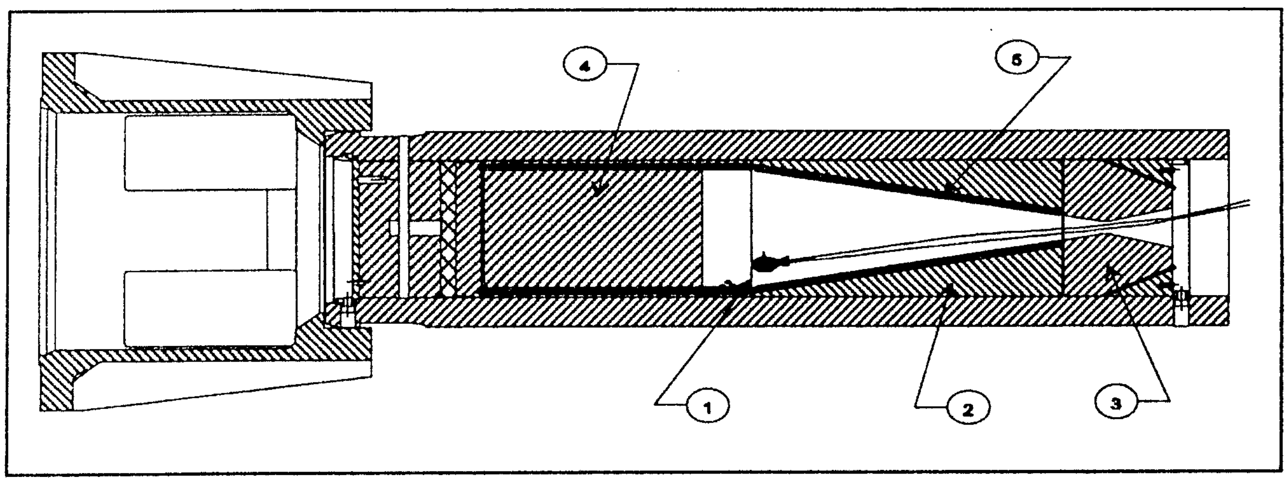
Negative numbers represent the formation of a structural char

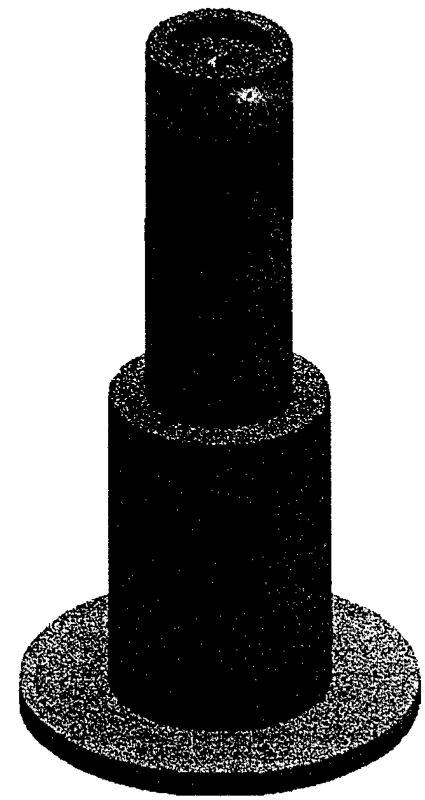
In-House SRM Insulation Testing

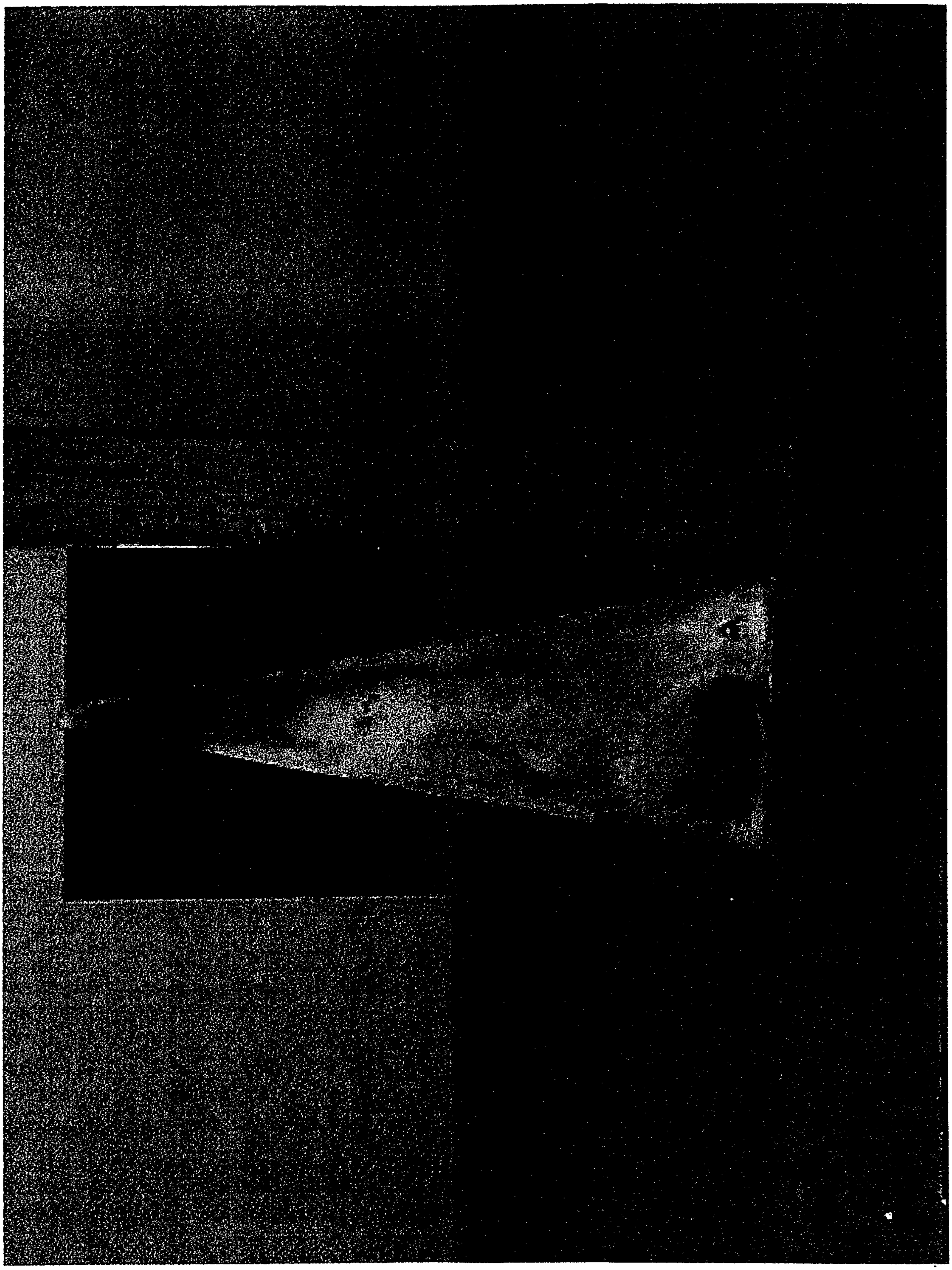
Objective: Los Cost/Low Volume Screening of New Materials for Rocket Motor Insulation

Capabilities:

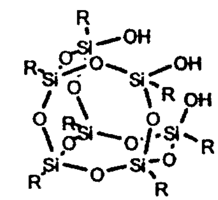
- Test facilities developed at Edwards AFRL (2 ¾" Pi-K Motor)
- Volume of material reduced from 5 Kg to 75 g
- Cost (synthesis, part fabrication, ablation test, analysis) reduced to 1K!!
- Rapid testing of 5-6 samples per day.







Solid Rocket Motors Insulation



FY99 Accomplishments:

- 25% weight reduction & ceramic layer formed (industrial testing)
- Restart of small rocket motor testing, Area 1-30
- Organization of 30 lb. synthesis of POSS monomers from HP

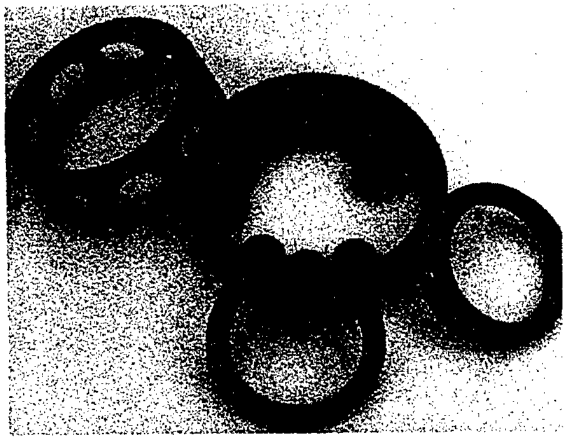
FY00 Objectives:

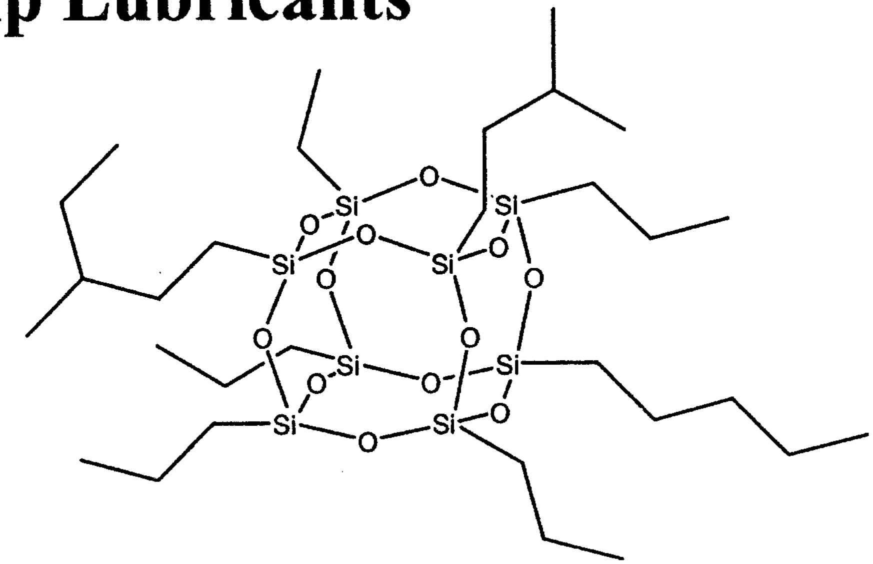
- Incorporation of POSS monomers into insulation
- 8 large-scale rocket motor firings with industrial partner (binding mode, monomer type, ablation & loading maximum)
- 30 small SRM tests utilizing metal oxides nanopowders & POSS
- modeling simulation of nanoparticle aggregation (NIST)

Tasks/Schedules:

TASK	FY98 (30K)	FY99 (80K)	FY00 (100K)	FY01 (120K)
Nozzle Insulation (XX)	◆ Insulation	◆ SRM test; ◆ Insulation	◇ SRM test	◇ Insul.; ◇ SRM test
Nozzle Insulation (PR)	◆ Demo tests complete	◆ Re-set	◆ POSS testing	◇ Nano-testing; ◇ Report

High Temp Lubricants



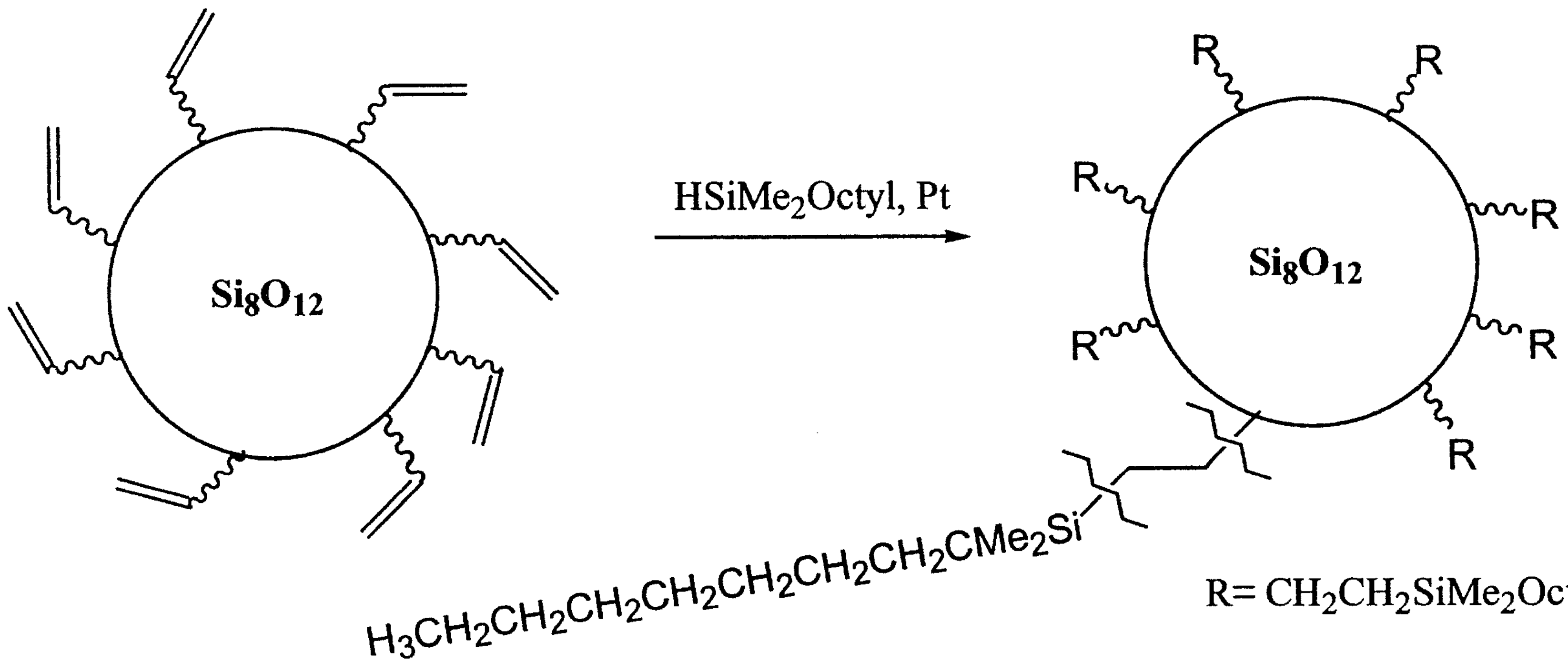


Goal: Replace ester-based lubricant with modified POSS lubricant.

Objectives:

- Fluid with working temperature range of -40° to 600° F (IHPTET)
- Ester lubricants limited to 400 °F: POSS monomer T_{dec} = 590 °F
- 600 °F lube = 1.5-1.6 T/W improvement

Generation I POSS Lubes

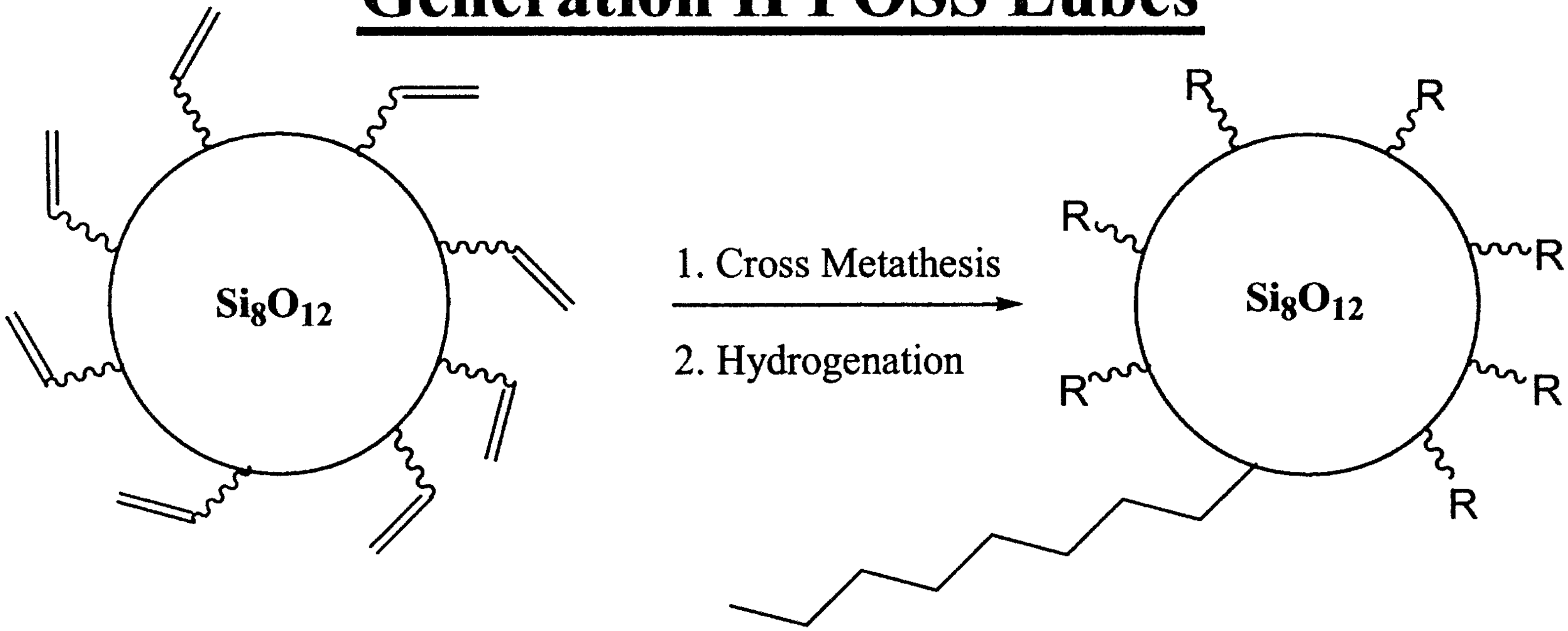


R= $CH_2CH_2SiMe_2Octyl$

OIL AT Room Temp.
T_{dec} low (< 200 °C)

This class is NOT suitable for High Temp Lubes, but may be suitable for blendables

Generation II POSS Lubes



Decomposition of POSS Lubes – TGA Data

Reagent	mp °C	iso temp °C	time for 10% loss (min)	% lost over 9 hours
Grade 4 Base stock	liq	219	30	90
$T_8(CH_2CH_2SiMe_2Octyl)_8$	liq	218	41	39
$T_8(octyl)_7(ethyl)_1$-grease	45	216	225	11
$T_8(octyl)_8$-solid	50	218	60	27
Cy_2T_2 $(OSiMe_2Octyl)_4$	liq	219	evaporated	100 (evap)

Decomposition of Lubricants

Three Ball and Disk Test for Selected Lubes

Table 4. 75°C TBOD wear test results
(0.5-mL sample, 246 rpm, 20-kg load, M50 balls and disk, 3-hour tests)

Test Fluid	Additive (concentration)	Average COF	Wear Scar Length (mm)
Gen I POSS*	TCP (2%)	0.205 ± 0.022	4.132
O-86-2 basestock	-	0.100 ± 0.007	0.868
O-86-2 basestock	$T_8Octyl_7Et_1$ (5%)	0.138 ± 0.010	0.701
O-86-2 basestock	T_8Octyl_8 (5%)	0.118 ± 0.011	0.645
O-86-2 basestock	$CyT_2(octyl)_4$(5%)	0.109 ± 0.006	0.581

*Test was suspended after 1 hour

Merging Technical Issues:

- Control viscosity of POSS lubes (-40° to 600° F)

- Decomposition of POSS lubes to silicate core (sand)

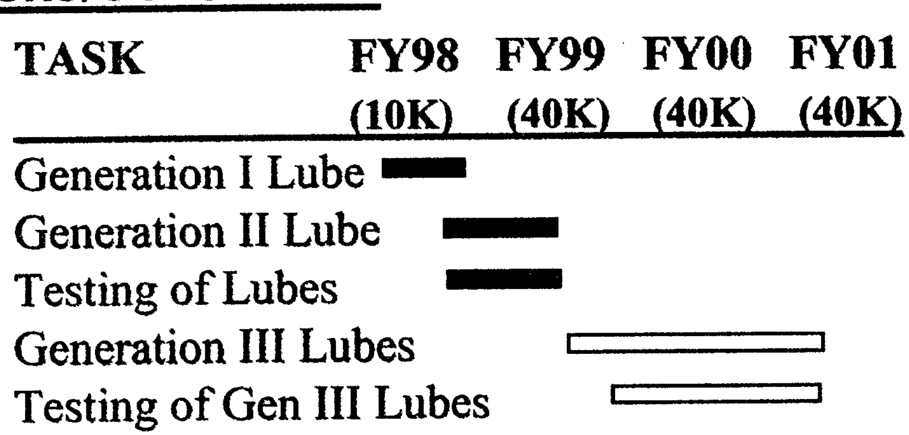
FY99 Accomplishments:

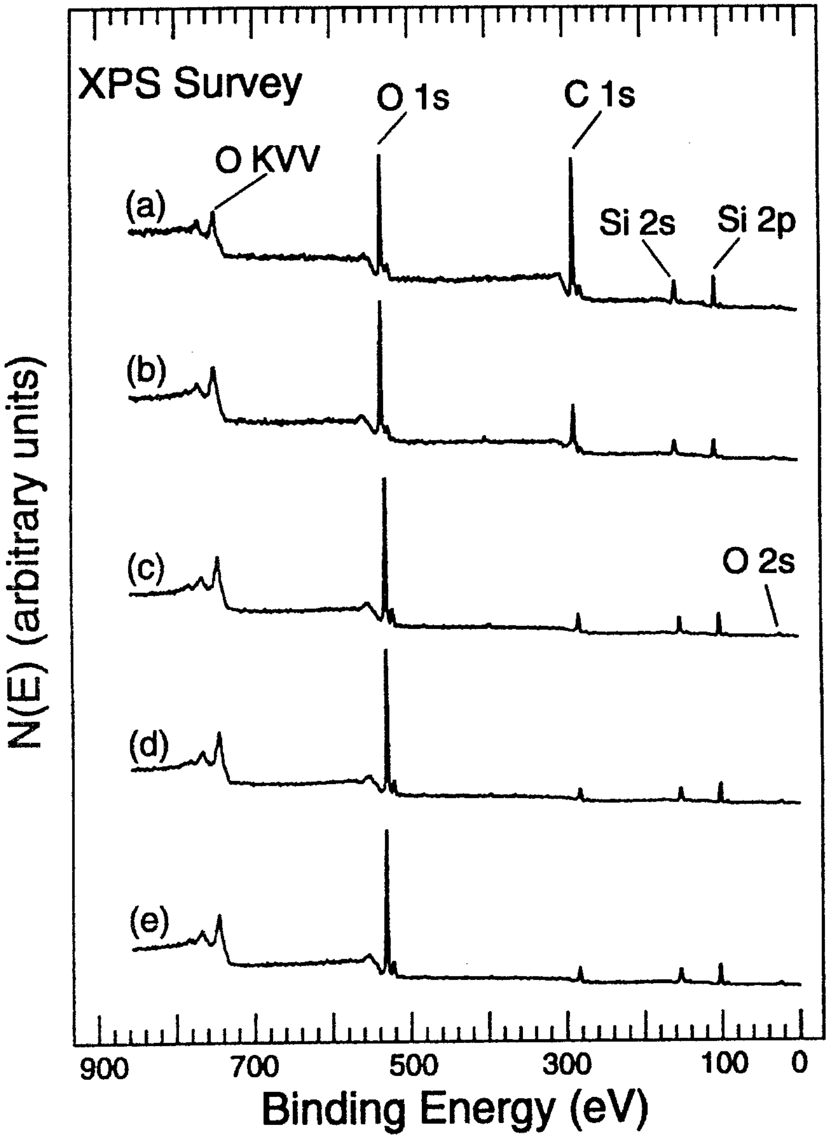
- Generation I POSS lube Delivered –> poor thermal stability
- Generation II POSS lube –> exceeded temperature stability of Ester base stock, and met or exceeded first round of wear tests (static coking tests, three ball and disc)

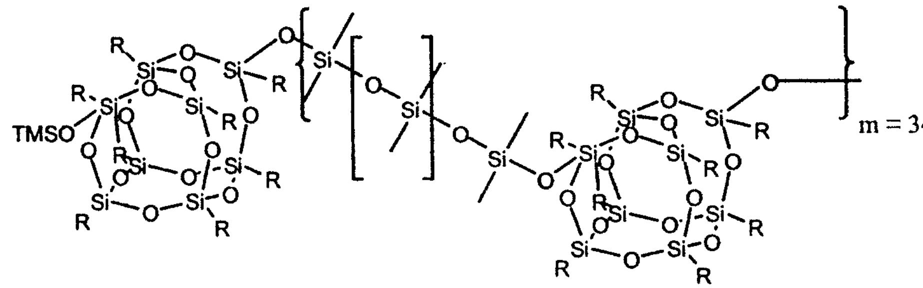
FY00 Objectives:

- Develop methodology for controlling viscosity (altering R groups)
- Determine additives needed to prevent decomposition to grit
- Perform rheological studies (viscosity, shear, stress-strain)
- Send limited samples to PRSL for further testing (static coking, 3-ball/disk)
- Select three best candidates for scale-up

Tasks/Schedules:





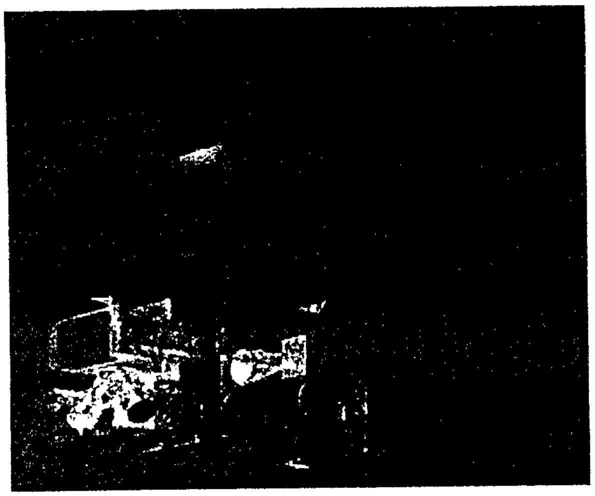


POSS-PDMS copolymers

Wt. % of Element

Exposure	O	C	Si
As entered	18.1	64.1	17.8
2-h	38.0	41.3	20.7
24-h	47.6	23.7	28.6
63-h	54.0	13.5	32.5
4.75-h air	54.6	18.1	27.3

Goal: Develop Multi-Functional, Space-Resistant Materials



Satellites & Space Systems

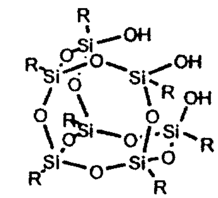
Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials by 10x

- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

POSS R&D Summary



Monomers & Polymers Research

- Fundamental studies ---> polymer property understanding (cage size, POSS miscibility, polymer type).
- Polymer Processing ---> reactive processing, polymer blends, composites
- Center of Excellence on POSS polymer research

Applications Research

- Lightweight, low-cost, high-temperature, high-strength
- Utilize economical small-scale SRM insulation screening for large scale testing
- Apply basic R&D work on POSS blends to POSS lubes to meet Phase III IHPTET Goals
- Initial work on space-resistant polymers is remarkable

Multi-Functional, Space-Resistant Materials

FY99 Accomplishments:

- **Collaboration with Prof. Gar Hoflund (U of Florida) for AO testing**
- **Synthesis of POSS-PDMS copolymer and thin-film casting**
- **AO testing of POSS-PDMS polymer →** Formation of protective layer, VUV resistance, Self-annealing!!
- **Synthesis of POSS-polyurethane of 20 and 60 wt. %**
- **Collaboration with JPL on POSS-epoxies**

FY00 Goals:

- **Synthesis & testing of nanocomposites (POSS-polyurethanes, POSS-polyimides, POSS-epoxies, Clay-Nylons)**
- **Incorporation of POSS into JPL space-epoxies**
- **Publications & Presentations!!**
- **Modeling of multiple source space damage**
- **Develop collaboration with VS**