BACKGROUND MATERIAL PROPERTIES OF SELECTED SILICONE POTTING COMPOUNDS AND RAW MATERIALS FOR THEIR SUBSTITUTES

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ABSTRACT

Since Dow Corning discontinued production of 93-119, 93-120, 93-122, Pantex joined with the Lawrence Livermore Laboratory to develop substitutes for these materials. Raw materials chosen for this project include Sylgard 184, Sylgard 186, Q3-6527 Dielectric Gel, Q3-6559 Accelerator, DC 1107 and Cab-o-Sil MS-75. This report deals with physical and chemical properties of these materials. Subsequent reports will be written to detail the work for specific substitutes.

INTRODUCTION

With the discontinuation of production of several Dow Corning addition cured potting compounds used by the DoE Weapons Complex, it became necessary to develop substitutes or alternate materials. This task was undertaken jointly by Pantex and the Lawrence Livermore Laboratory (LLL). This report gives the materials' properties, both chemical and physical, of the discontinued materials (93-119, 93-120, and 93-122) and the substitutes starting raw materials (Sylgard 184, 186, Q3-6559 Accelerator, Q3-6527 Dielectric Gel, DC 1107 and Cab-o-Sil* MS-75), as determined by Pantex.

Product of Cabot Corp.

DISCUSSION

One of the starting raw materials to be used in substitute formulations is Sylgard 184. It is a two-component silicone elastomer of medium viscosity (~ 3 - 4 Pa·S) and moderate pot life (time to double viscosity approximately 2 hrs at 25 C). It will cure to a clear material with a Shore A of about 35 and a tensile strength of about 6.2 MPa. Lot 31, representing the higher end of available viscosity material, and Lot 36, representing the lower end, were used in the study.

Another material is Sylgard 186 which is a two-component silicone elastomer of high viscosity (~ 50 Pa·S) and moderate pot life (time to double

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viscosity approximately 2-1/2 hours at 25 C). It will cure to a translucent material with a Shore A of about 30 and a tensile strength of about 4.8 MPa. Lot 47, representing the higher end of available viscosity material, and Lot 64, representing the lower end, were used in the study.

Dielectric Gel Q3-6527 is a low viscosity ($\sim$ 0.4 Pa•S) two-component silicone potting compound. It has a very long pot life (time to double viscosity approximately 6 to 10 hours at 25 C) and eventually cures to a clear elastomer with a Shore A of about 10 and a tensile strength of about 0.3 MPa. In the substitution work this material is used either as a viscosity modifying diluent or as a strength reducer.

Accelerator Q3-6559 is a Dow Corning one-component liquid of restricted availability. It can be added to the resin (A component) of the above materials to increase the cure rate by about a factor of 10.

Dow Corning DC 1107 is a one-component liquid generally used as a surface treatment for free flowing powders. When used in small quantities with the curing agent (B component) of the above materials, it accelerates the cure rate of the system up to several orders of magnitude.

Cab-o-Sil MS-75 is a fumed silicone dioxide. This material is used as an inert filler for increasing viscosities.

Viscosity

Viscosities of all of the materials (A, B and curing system) were determined at 25 C. In addition, the curing system viscosities for some materials were also determined at 20 and 30 C. The thinner materials were measured on Brookfield rotating spindle viscometers. The thicker, highly filled systems such as 93-122 were measured on a Rheometrics Mechanical Spectrometer between two oscillating parallel plates (Table I).

Typical viscosity time curves at different temperatures for several of the materials are shown in Figs. 1 through 7.

Specific Gravity (at 25 C)

The specific gravity of the A and B components as well as cured samples were determined for all of the raw materials. The thinner liquids were measured using a standard pycnometer technique and the cured samples were measured using the principle of Archimedes, i.e. weighing the sample suspended by a wire in air, then in water and calculating the specific gravity.

Determining the specific gravity of Sylgard 186A presented a problem due to the high viscosity of the A component. Entrapped air and incomplete filling of the pycnometer introduced large errors. A narrow, pre-weighed, open on both ends, glass tube was filled with water to an etched mark, re-weighed and its volume determined from the density of water at that temperature. Vacuum suction applied to the tube was then used to draw pre-deaerated Sylgard 186A material up to the mark. The filled tube was then re-weighed and specific gravity calculated (Table II).

Table I. Viscosity

Material	Condition*	Temperature (C)	10 Minute Viscosity (Pa·S)
93-119 (37) A&B	LVT - No. 3 @ 12	20	2.74
		25	2.65
		30	2.70
93-120 (34) A&B	LVT - No. 3 @ 3	20	9.32
		25	9.12
93-120 (29) A&B	LVT - No. 3 @ 3	30	9.84
93-122 (29) A	Mechanical Spect.	25	300.00
93-122 (30) B	LVT - No. 1 @ 30	25	0.16
93-122 (31) A&B	Mechanical Spect.	25	290.00
Sylgard 184 (31) A	LVF - No. 4 @ 60	25	6.4
(36) A		25	3.9
Sylgard 184 (31) B	LVT - No. 1 @ 30	25	0.069
(36) B		25	0.074
Sylgard 184 (31) A&B	LVT - No. 3 @ 6	20	4.0
		25	3.1
		30	3.2
Sylgard 184 (36) A&B	LVT - No. 3 @ 6	20	2.8
		25	2.6
		30	2.6
Sylgard 186 (47) A	HAF - No. 6 @ 5	25	149.0
(64) A		25	111.0
Sylgard 186 (47) B	LVT - No. 3 @ 12	25	1.08
(64) B		25	1.35
Sylgard 186 (47) A&B	HAF - No. 6 @ 10	20	50.0
		25	46.0
		30	62.0
Sylgard 186 (64) A&B	HAF - No. 6 @ 10	20	40.0
		25	41.0
		30	39.0
Dielectric Gel (31) A	LVT - No. 3 @ 60	25	0.25
(31) B	LVT - No. 3 @ 60	25	0.24
(31) A&B	LVT - No. 3 @ 60	20	0.29
		25	0.26
		30	0.25
Accelerator (56)	LVT - N0. 3 @ 60	25	0.36
DC 1107 (69)	LVT - No. 3 @ 60	25	0.03
(77)		25	0.03

**Model - Spindle No. at Speed (rpm).*

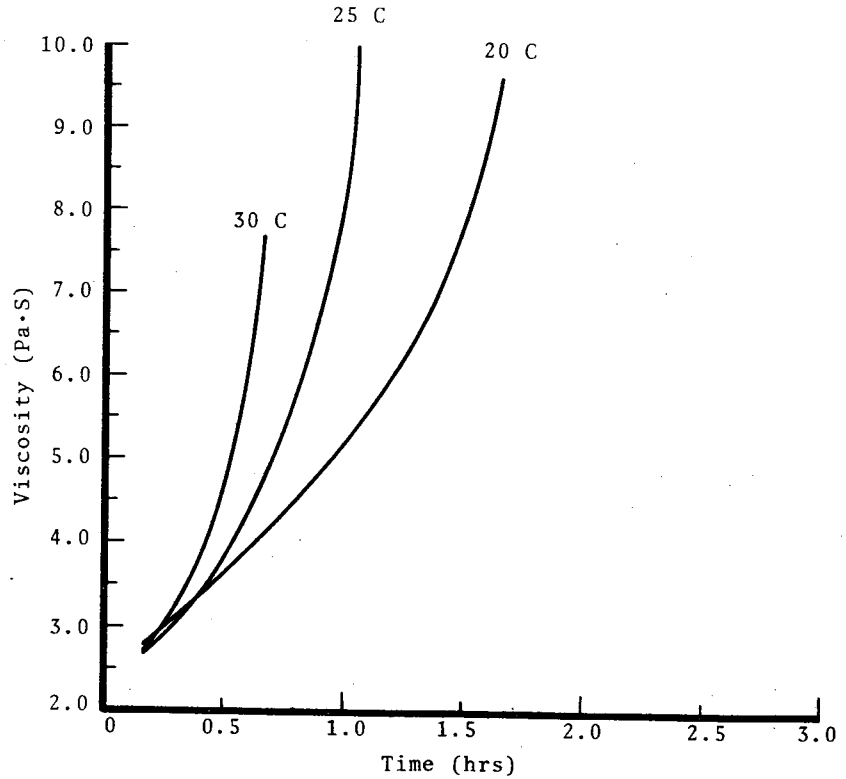


Fig. 1. 93-119 (Lot 37)

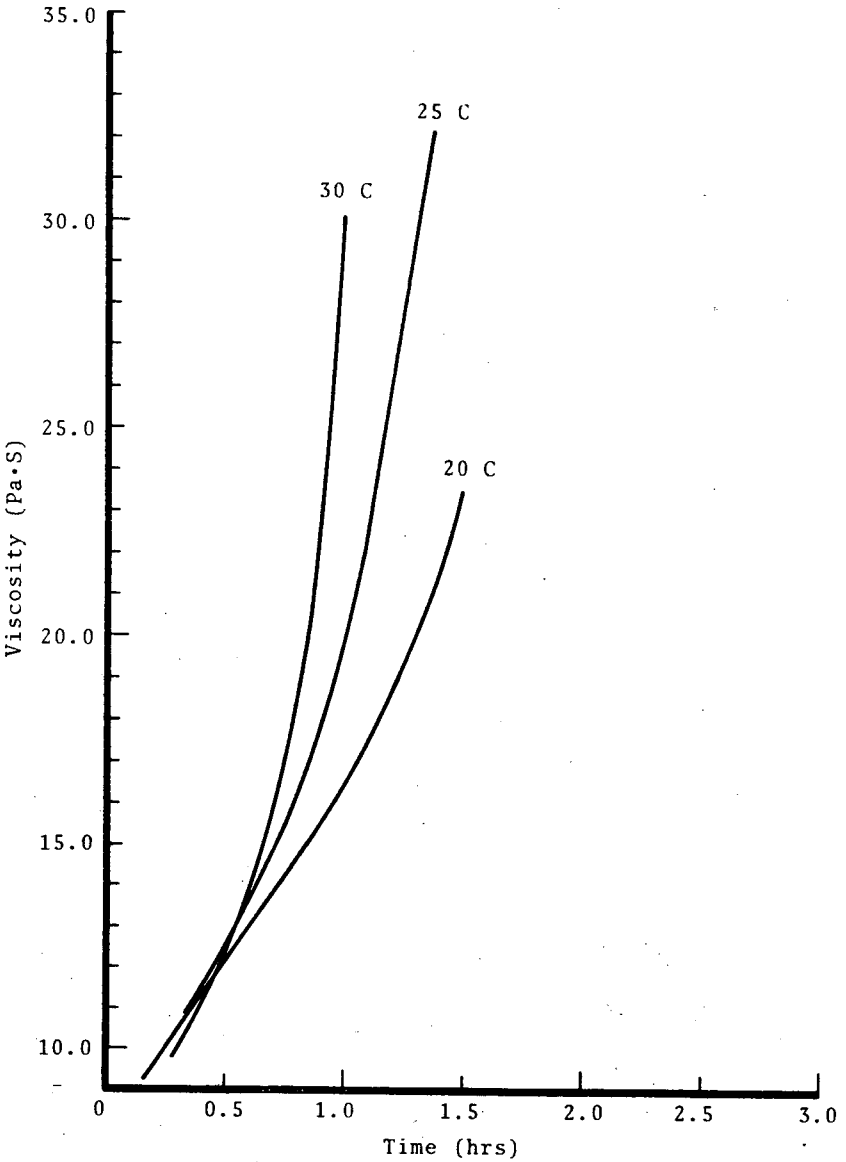


Fig. 2. 93-120 (Lot 34)

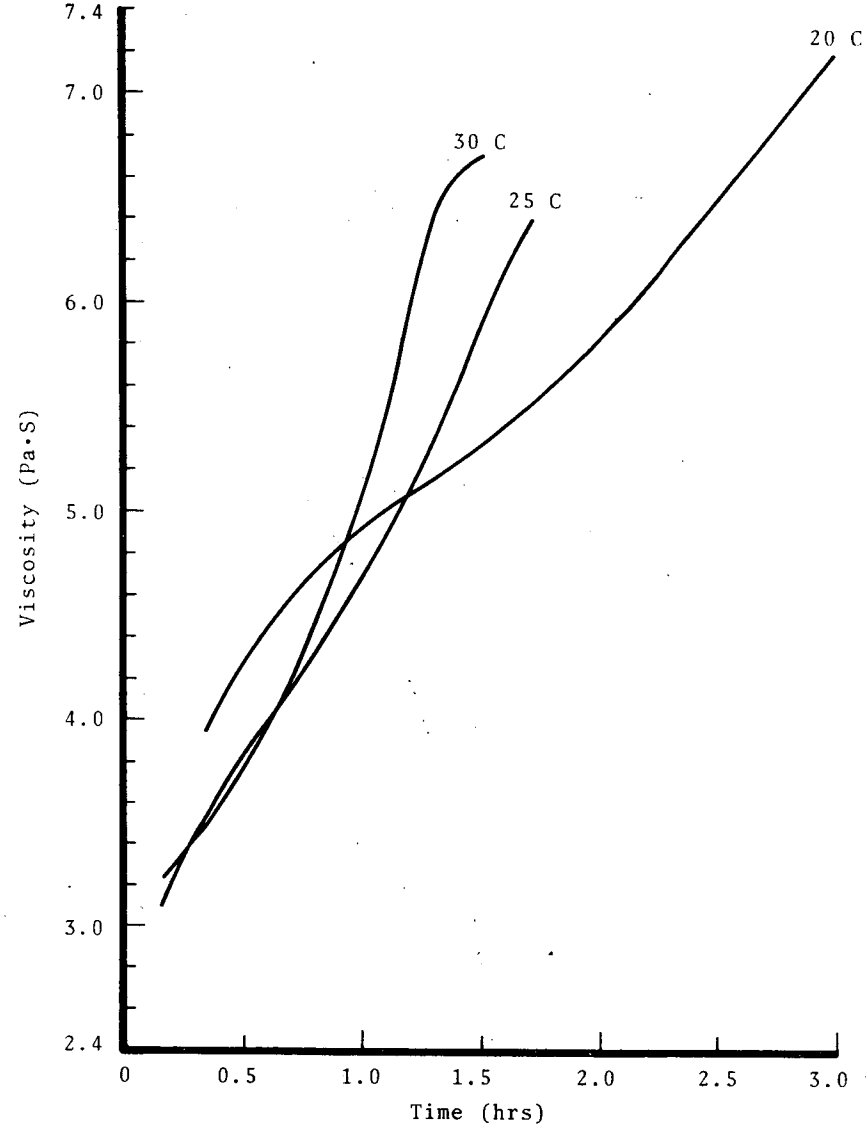


Fig. 3. Sylgard 184 (Lot 31)

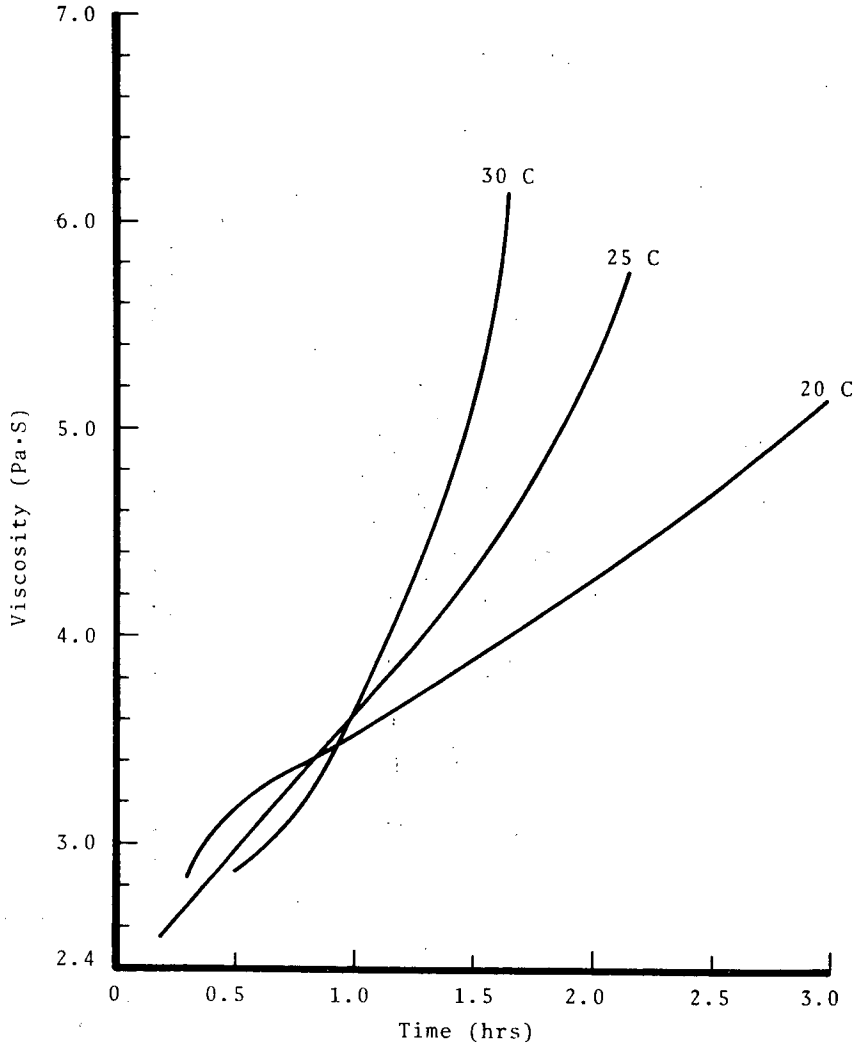


Fig. 4. Sylgard 184 (Lot 36)

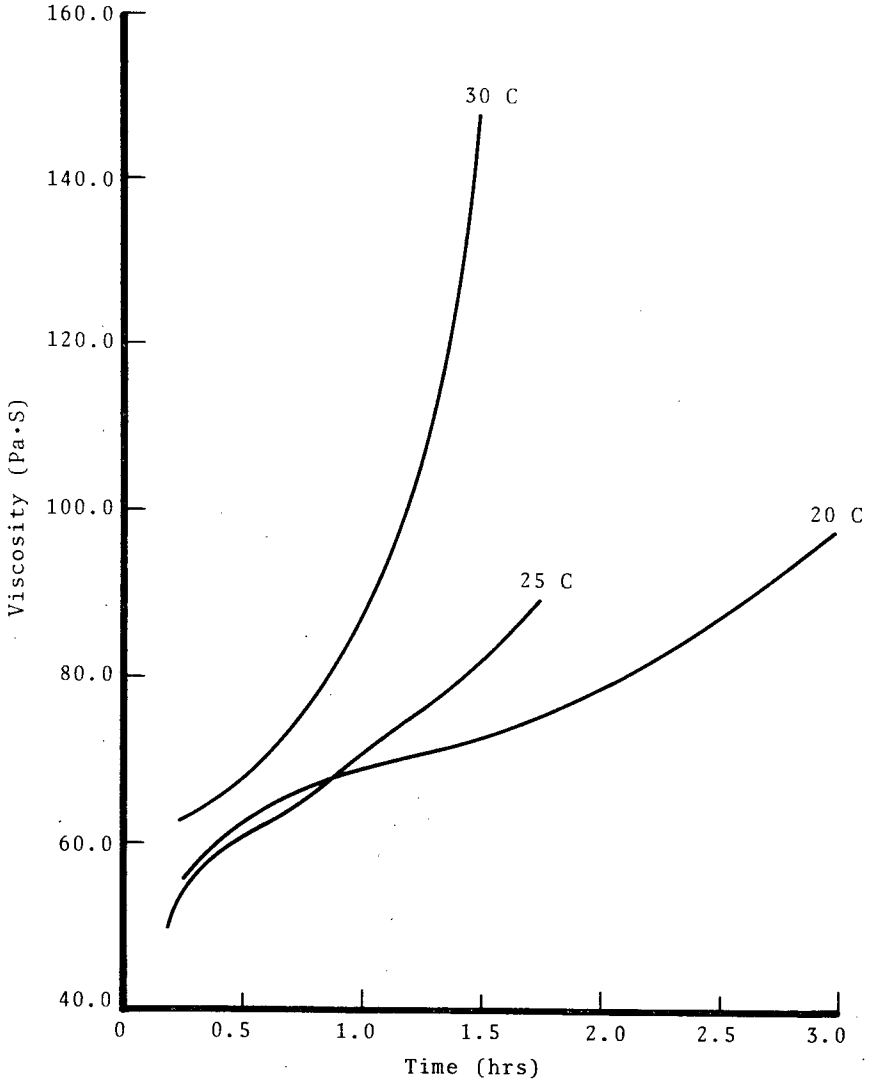


Fig. 5. Sylgard 186 (Lot 47)

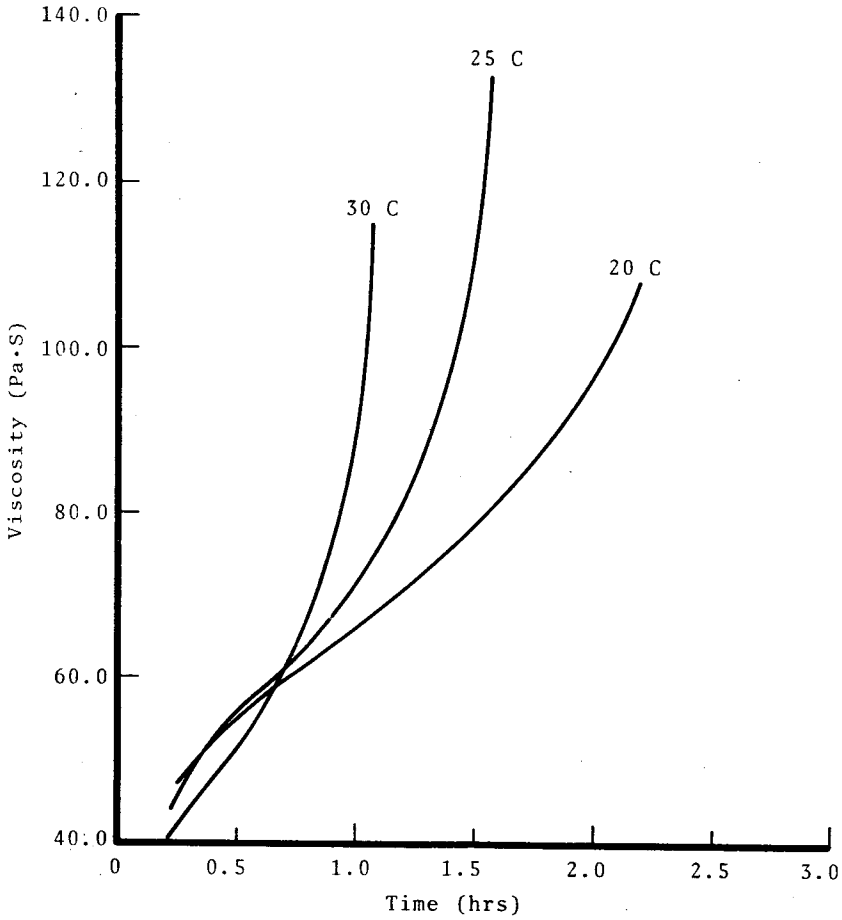


Fig. 6. Sylgard 186 (Lot 64)

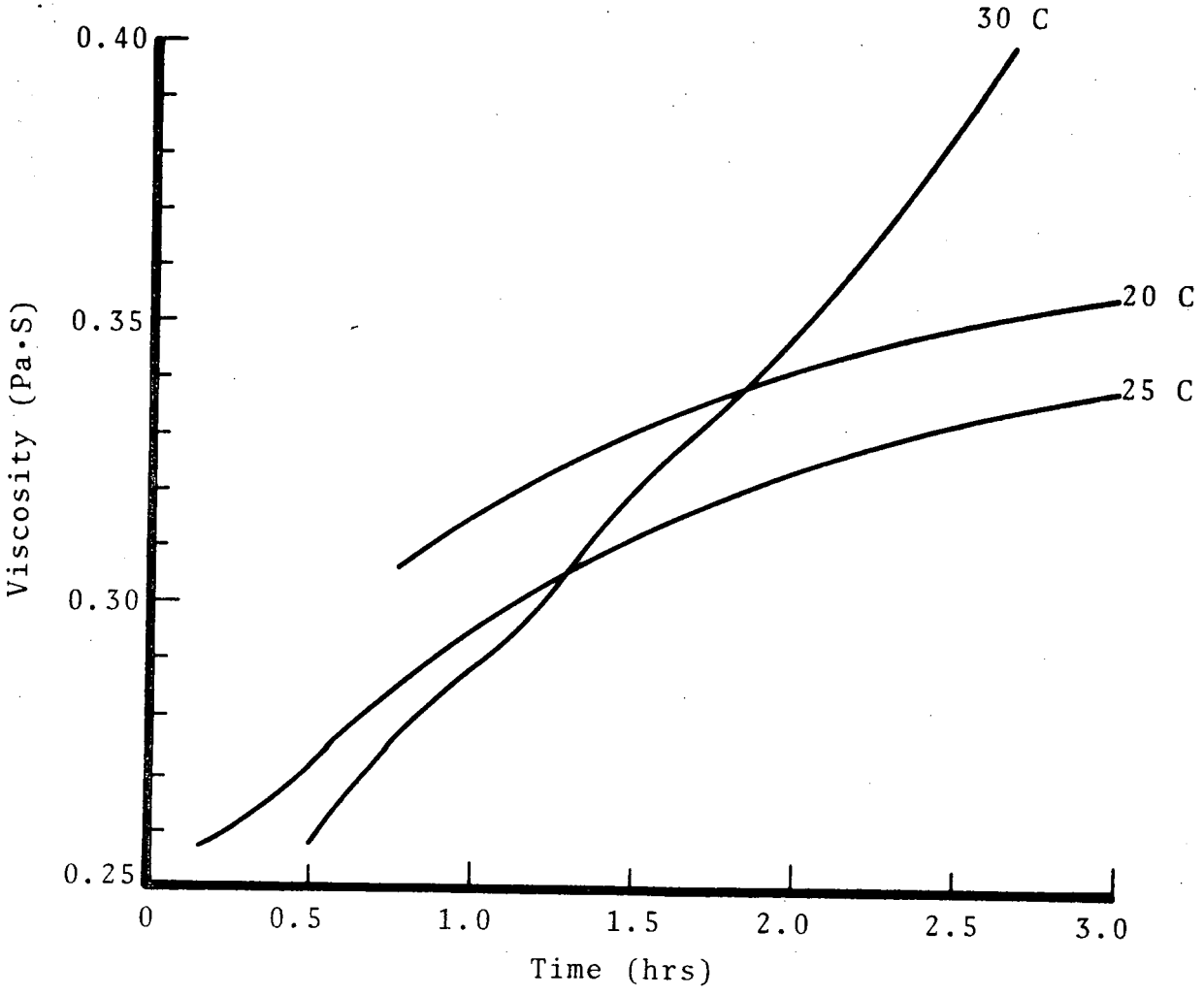


Fig. 7. Dielectric Gel

Table II. Specific Gravity

Material	Specific Gravity (A)	Specific Gravity (B)	Specific Gravity (Mix)
Sylgard 184 (31)	0.96	0.94	1.04
Sylgard 184 (36)	1.03	0.98	1.03
Sylgard 186 (47)	1.13	0.98	1.11
Sylgard 186 (64)	1.12	0.92	1.11
Dielectric Gel (31)	0.98	0.98	0.96
Accelerator (56)	0.98	-	-
DC 1107 (69)	-	1.00	-
DC 1107 (77)	-	1.01	-

Molecular Weight

Molecular weight was determined by using a Waters Associates gel permeation chromatograph. The carrier was tetrahydrofuran (THF) and the columns were 10^3, 10^4, 10^5 and 10^6 angstrom columns packed with corigel. All samples were filtered through a 1.0 μm filter and diluted 12.5:1 with the carrier prior to injection at a flow rate of 1 mℓ/min.

Molecular weight data (Table III) for all of the materials except 93-122A and Sylgard 186A are based on polystyrene equivalent molecular weights. A typical calibration curve of known polystyrene standard molecular weights versus column retention time is shown in Fig. 8. All of the materials except 93-122A and Sylgard 186A fell well within the linear portion of the curve. However, the 93-122A and Sylgard 186A materials exhibited bimodal peaks, one falling within the linear portion and the other higher molecular weight component falling in the undefined non-linear portion of the curve.

By making an extension of the linear portion of the curve, a "relative" molecular weight for the components could be established. This is quite satisfactory for this application since the main purpose for this test is to be able to compare lot-to-lot variations in the material. This extremely high molecular weight peak is probably related to the Cab-o-Sil filler even though every effort was made to remove it by filtration.

Table III. Molecular Weight Data

Material	Lot No.	Component A			Component B		
		M_n	M_w	MWD	M_n	M_w	MWD
93-119	30	12,300	42,500	3.46	12.200	44,300	3.63
93-119	32	15,800	40,300	3.18	15,300	45,200	2.95
93-120	35	11,700	62,400	5.33	4,220	14,000	3.32
93-120	36	13,700	80,000	5.84	4,700	14,600	3.05
93-122	30	3,900,000 7,350	6,380,000 43,300	1.64 5.89	6,730	24,500	3.64
93-122	31	3,850,000 6,770	6,630,000 43,500	1.72 6.43	6,580	23,600	3.59
Sylgard 184	31	5,800	24,100	4.16	7,472	28,000	3.75
Sylgard 184	36	6,190	27,700	4.47	6,770	26,000	3.84
Sylgard 186	47	4,780,000 8,460	8,480,000 44,300	1.77 5.24	15,500	43,200	2.79
Sylgard 186	64	3,060,000 7,160	6,500,000 45,600	2.12 6.37	15,100	44,300	2.93
Dielectric Gel	31	5,450	14,400	2.64	5,090	13,900	2.73
Accelerator	56	7,000	19,800	2.83	-	-	-

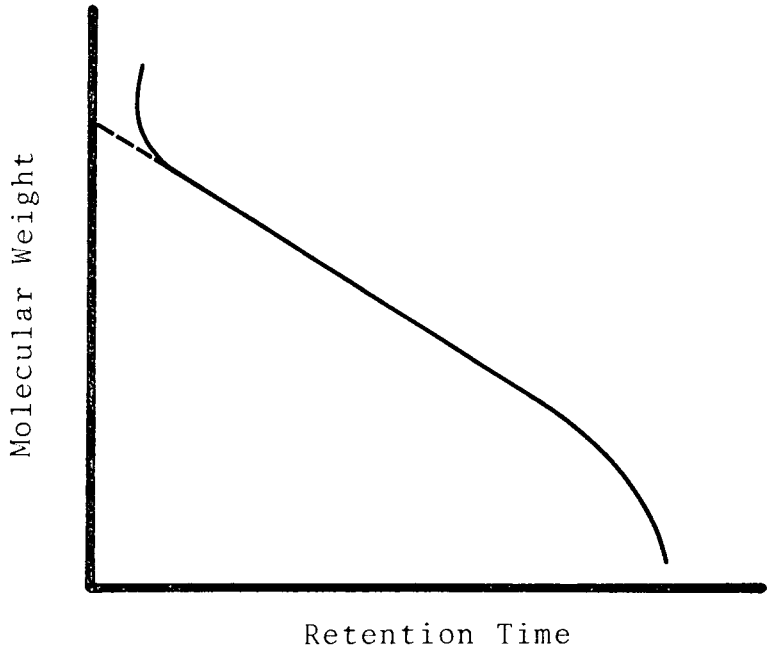


Fig. 8. Molecular Weight Versus Retention Time in GPC Analysis

Platinum

Trace analysis for total platinum in the resins was performed using atomic absorption spectroscopy. Samples were prepared by overnight decomposition with fuming nitric and concentrated hydrofluoric acids. Results were then calculated from a plot of absorbance versus concentration based on responses to standard solutions.

Material	Platinum (ppm)
93-119A*	8.9
93-120A*	8.7
93-122A (26)	10.0
Sylgard 184A (31)	8.5
Sylgard 184A (36)	6.5
Sylgard 186A (47)	6.8
Sylgard 186A (64)	5.0
Dielectric Gel (31)	15.5
Accelerator (56)	184.0

**Pantex historical data of many lots.*

Vinyl

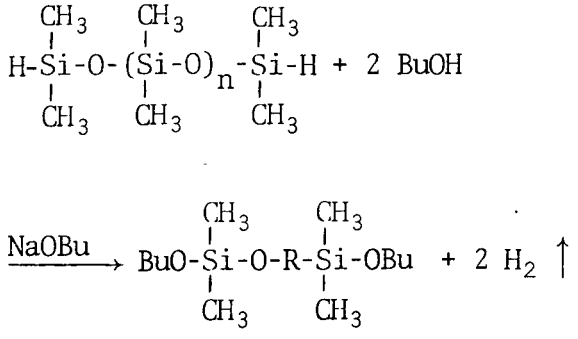
Vinyl content was determined for both A and B components by a 1 to 2 hour darkroom addition reaction of iodine monochloride (ICl) in glacial acetic acid. The solution was then titrated to determine the amount of ICl consumed in adding to the double bonds which gives the vinyl content (Table IV).

Table IV. Vinyl Content

Material	Vinyl in A (Wt. %)	Vinyl in B (Wt. %)
93-119 (030)	0.17	1.88
93-120 (036)	0.19	2.71
93-122 (26)	0.11	-
93-122 (30)	-	2.45
Sylgard 184 (31)	0.60	2.32
Sylgard 184 (36)	0.60	2.14
Sylgard 186 (47)	0.25	1.91
Sylgard 186 (64)	0.54	1.93
Dielectric Gel (31)	0.79	1.21
Accelerator (56)	0.77	-
DC 1107	-	3.87

Active Hydrogen

Active or silane hydrogen, was determined by reacting the material with sodium butoxide and manometrically determining the amount of evolved hydrogen. The more violent reaction and considerably larger quantities of evolved hydrogen from DC 1107 presents a difficult handling problem. The reaction equation for active hydrogen is



Material	Active Hydrogen (Wt. %)
93-119B*	0.152
93-120B*	0.151
93-122B (26)	0.308
Sylgard 184B (31)	0.456
Sylgard 184B (36)	0.442
Sylgard 186B (47)	0.088
Sylgard 186B (64)	0.097
Dielectric Gel B (31)	0.180
DC 1107	1.575

**Pantex historical data of many lots.*

Hydroxyl Content

Standard procedures for hydroxyl determination such as ASTM 222 or 9981017 do not allow the determination of hydroxyl contents less than about 1%. Since the expected concentrations were approximately one-tenth of this, another method had to be found.

A new method was developed by Dow Corning and employs the reaction of lithium aluminum hydride ($LiAlH_4$) with the silicones hydroxyl groups (HOH, COH, SiOH, or COOH) to liberate hydrogen. The evolved gas, equivalent to the hydroxyl reacted, is measured in a manometric apparatus. The reaction equation is

$$4\ ROH + LiAlH_4 \rightarrow 4\ H_2 \uparrow + LiAl(OR)_4$$

Material	A Hydroxyl (Wt. %)	B Hydroxyl (Wt. %)
93-119 (39)	0.04	0.48
93-120 (36)	0.03	0.38
93-122 (40)	0.39	0.93
Sylgard 184 (31)	0.15	0.11
Sylgard 184 (36)	0.13	0.10
Sylgard 186 (47)	0.36	0.05
Sylgard 186 (64)	0.29	0.04
Dielectric Gel (31)	0.06	0.52

Toluene Extractables

Toluene extractables are determined by placing a 2.5 g sample of the cured material in a Soxhlet extractor containing toluene. As the sample is repeatedly washed with hot toluene, material which is soluble in toluene is extracted, this being primarily unpolymerized material. After a period of time, the sample is dried in a vacuum oven and reweighed. This test may be repeated on the same sample until the weight loss approaches a limiting value, or the test may be done one time over some specified long time period.

Tests for samples which were 3 days old and 1 month old were done in a Soxhlet extractor for 24 to 36 hours of continuous extraction. Results are given in Table V.

Table V

Material	Precent Toluene Extractables 3 Day (Wt %)	1 Month (Wt %)
Sylgard 184 (31)	5.4	3.3
Sylgard 184 (36)	5.6	5.2
Sylgard 186 (47)	5.2	5.2
Sylgard 186 (64)	5.8	4.1
Dielectric Gel (31)	>20.0	>20.0
93-119*	4.03	-
93-120*	4.6	-
93-122 (30)	6.4	6.2

**Pantex historical data from many lots.*

Percent toluene extractables are then calculated as,

$$\frac{OSW - FSW}{OSW} \times 100$$

OSW = Original Sample Weight
FSW = Final Sample Weight

Since the percent toluene extractables is a measure of unpolymerized material left in the cured sample, the value might be expected to change with the age of the cured sample if further polymerization is taking place. Samples of 93-119 (31) A and B, 93-120 (35) A and B, and 93-120 (35) A/93-122 (29) B were prepared and tested at different ages ranging from 3 days to 12 weeks (see Fig. 9 and Table VI).

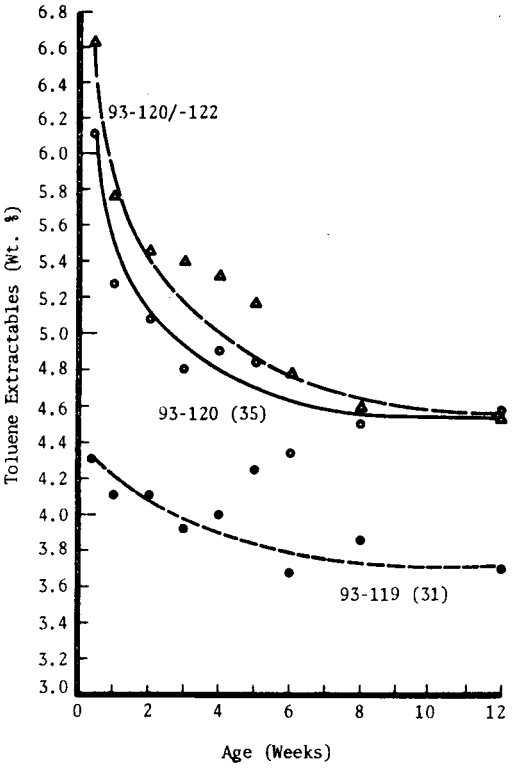


Fig. 9. Toluene Extractables Versus Sample Age

Table VI. Average Toluene Extractables (Wt. %) as a Function of Sample Age

Age	93-119 (31) $\bar{X}$	93-119 (31) σ	93-120 (35) $\bar{X}$	93-120 (35) σ	93-120 (35)/ 93-122 (29) $\bar{X}$	93-120 (35)/ 93-122 (29) σ
Days						
3	4.50	0.44	6.51	0.04	7.33	0.15
Weeks						
1	4.28	0.15	5.57	0.25	6.10	0.20
2	4.28	0.05	5.36	0.05	5.98	0.26
4	4.19	0.02	5.63	0.04	5.14	0.11
6	3.83	0.07	4.55	0.09	5.03	0.08
8	3.90	0.07	4.73	0.15	4.81	0.06
12	3.83	0.01	4.77	0.10	4.60	0.08

Chemical Reactivity Test (CRT)

The CRT is a standard test in the DoE complex. It was designed to provide an early indication of compatibility between a material sample and a high explosive (HE). The test involves placing a sample in a container, evacuating the container and backfilling with helium. The container is then subjected to 120 C for 22 hours and the evolved gases measured. A 0.250 g sample of the material of interest is processed, followed by a 0.250 g sample of the HE of interest and then a mixture of 0.250 g of the test material and 0.250 g of the HE. The evolved gases (decomposition products such as N_2, CO, NO, CO_2, N_2O, etc) are determined on a gas chromatograph. Should the amount of gases evolved from the mix be significantly greater than the algebraic sum of the gases from the two individual components, the material is said to be incompatible with the HE.

The starting raw materials as well as the materials to be replaced were tested against PBX 9404, PBX 9501, HMX, RDX, and PETN. No problems were encountered with any of the materials (Table VII).

Table VII. CRT Data

Material	Lot No.	Run No.	Elastomeric Material (Only)	PBX 9404	PBX 9501	HMX	RDX	PETN
HE		1		0.412	0.021	0.020	0.015	0.089
		2		0.399	0.016	0.005	0.018	0.100
		3		0.401	0.039	0.016	0.021	0.069
		4		0.405	0.038	0.017	0.027	0.561
		5				0.027		0.287
93-119	38	1	0.009	0.376	0.021	0.018	0.013	0.158
		2	0.009	0.384	0.025	0.029	0.012	0.176
		3	0.011					
		4	0.004					
		5	0.014					
93-120	30	1	0.012	0.355	0.025	0.041	0.016	0.207
		2	0.018	0.378	0.028	0.025	0.017	0.208
		3	0.015					
		4	0.014					
		5	0.010					
93-122	28	1	0.011	0.341	0.045	0.025	0.039	0.165
		2	0.011	0.353	0.039	0.024	0.045	0.184
		3	0.002					
93-120/-122	30/28	1	0.006	0.352	0.042	0.019	0.017	0.268
		2	0.007	0.360	0.041	0.024	0.013	0.264
		3	0.012					
		4	0.013					
Sylgard 184	31	1	0.005	0.354	0.035	0.016	0.025	0.221
		2	0.008	0.362	0.030	0.016	0.017	0.198
		3	0.006					
Sylgard 184	36	1	0.019	0.362	0.019	0.017	0.034	0.229
		2	0.011	0.367	0.028	0.016	0.018	0.209
		3	0.008					
		4	0.010					
Sylgard 186	47	1	0.018	0.358	0.019	0.013	0.030	0.191
		2	0.020	0.361	0.029	0.013		0.180
		3	0.005					
		4	0.007					
Sylgard 186	64	1	0.011	0.351	0.022	0.018	0.020	0.159
		2	0.014	0.352	0.028	0.020	0.015	0.152
		3	0.012					
		4	0.011					
Dielectric Gel	31	1	0.013	0.375	0.020	0.012	0.012	0.155
		2	0.007	0.344	0.012	0.017	0.013	0.161
		3	0.008					
		4	0.011					

Thermal Mechanical Analysis (TMA)

The TMA test performed at Pantex employs a DuPont instrument. Essentially the test involves a small sample placed in an environmentally controlled quartz chamber. A special probe (the tip shape depending on the test) is placed in contact with the sample and the displacement of the probe measured as the temperature is varied. Using this test, the coefficient of thermal expansion (CTE), elastic modulus and primary and secondary transitions can be determined.

A TMA analysis was done on cured samples of 93-119, 93-120, 93-122, Sylgard 184, Sylgard 186, and a mixture of accelerated 184 and 186. The only observable difference in any of the materials was the glass transition temperature. The amplitude of the peak is more pronounced for 93-119, 93-120 and 93-122 than the other materials. In addition, Sylgard 184 as well as mixtures containing Sylgard 184 exhibit a glass transition temperature between -40 and -50 C whereas all other materials exhibit a glass transition between -30 and -40 C.

Cab-o-Sil Particle Characterization

Cab-o-Sil is a fumed silicone dioxide of very small particle size. Its unique properties enable it to hydrogen bond to its own surface hydroxyl groups in non-polar solutions forming a three dimensional chain network. Small quantities of water or other polar materials can hydrogen bond to the surface hydroxyls of the Cab-o-Sil preventing or reducing the chain formation and hence the "thickness" of the subsequent material. Excellent literature is available from Cabot Corporation on Cab-o-Sil.

Cab-o-Sil MS-75 was characterized by Zeiss Particle Analysis. This technique actually measures a large quantity of individual particles which have been magnified many times. Results of this analysis are given in Table VIII.

Table VIII. Zeiss Particle Analysis for Cab-o-Sil MS-75

Measurement	Arithmetic Mean, Based On Frequency	Arithmetic Mean, Based On Weight	Lowest Weight	Highest Weight
Length (μ)	9.64	23.52	5.34	61.18
Width (μ)	7.10	15.06	5.32	37.41
Length/Width	1.36	1.58	1.00	3.64
Cross Sectional Area (μ^2)	73.81	483.44	22.26	2288.84
Surface Area (μ^2)	325.95	2236.88	89.04	10847.52
Volume (μ^3)	629.79	11200.95	79.00	72778.63
Equivalent Circular Dia. (μ)	8.65	20.51	5.32	53.98
Equivalent Spherical Dia. (μ)	8.39	19.66	5.32	51.80
Degree of Sphericity	0.90	0.84	0.68	1.00

Density = 2.300 g/cm^3

Shape = Based on Frequency - 41.0% rectangular, 59.0% spherical
= Based on Weight - 70.2% rectangular, 29.8% spherical

Surface Area = 2250.01 cm^2/g

Dynamic Viscosity (η), Loss (G'') and Storage (G') Moduli

In order to measure the dynamic viscosity (η), the dynamic loss modulus (G'') and the dynamic storage modulus (G') of the material as it cures, a mechanical spectrometer manufactured by Rheometrics, Inc., was used. The test method for this material employed two parallel plates 25 mm in diameter separated by a gap of 1.4 mm. The bottom plate was attached to a torque measuring transducer and was stationary. The top plate was oscillated at a frequency of 1 hz at a maximum strain rate of 630%. After the sample was catalyzed it was placed between these two plates and monitored as it cured. A graph for 93-119 (38) is presented in Fig. 10, for 93-120 (30) in Fig. 11, and for 93-122 (28) in Fig. 12. Shore A durometer readings are shown in the same figure.

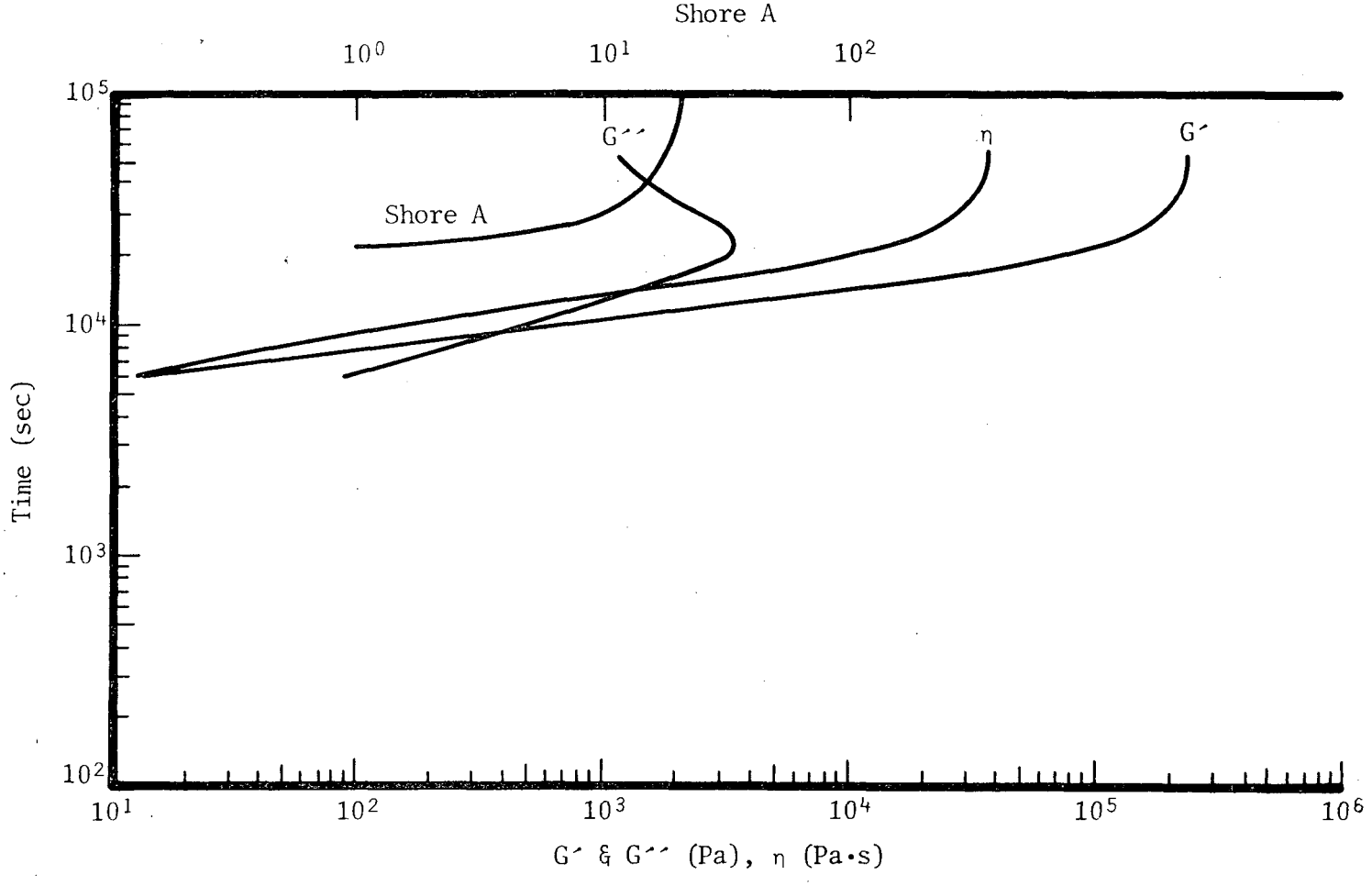


Fig. 10. Dynamic Properties and Hardness of 93-119 (38)

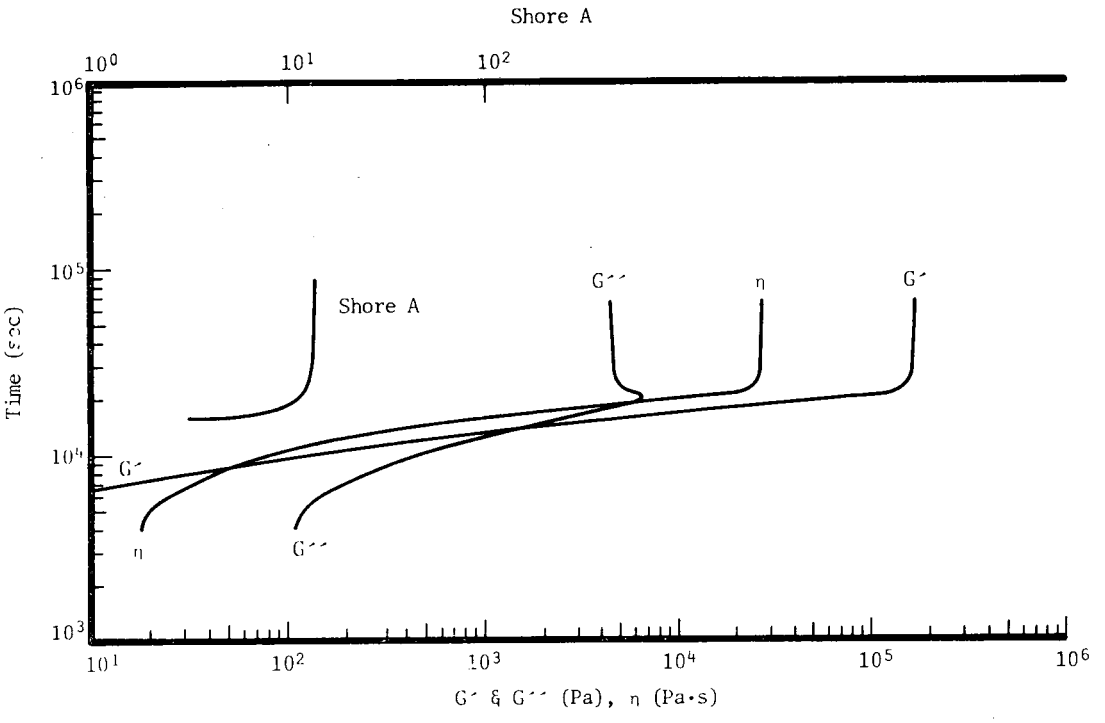


Fig. 11. Dynamic Properties and Hardness of 93-120 (30)

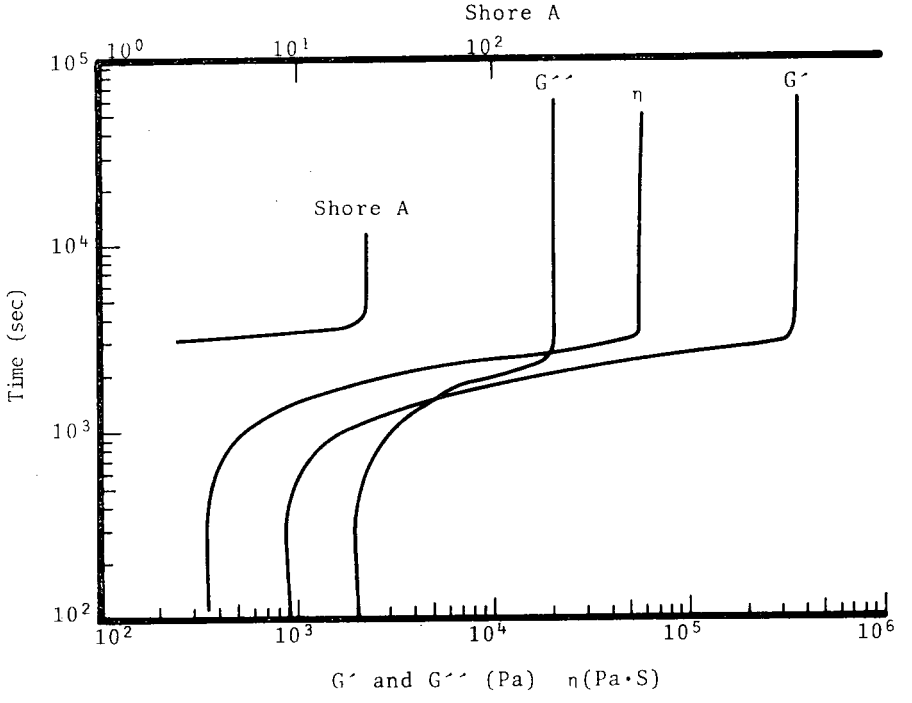


Fig. 12. Dynamic Properties and Hardness of 93-122 (Lot 28)

CONCLUSIONS & FUTURE WORK

This report is a background summary of both chemical and physical properties of addition cured silicone potting compounds no longer available from Dow Corning, and the raw materials to be used in the production of substitute materials. Other reports will be forthcoming that will detail the work on specific substitutes.

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