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INVESTIGATION AND DEVELOPMENT OF HIGH-TEMPERATURE STRUCTURAL ADHESIVES

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AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
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FOREWORD

This report was prepared by Mr. Alfred S. Kidwell and Mr. Kenneth L. McHugh of The Connecticut Hard Rubber Company, New Haven, Connecticut, under Air Force Contract No. AF 33(616)-2448. This contract was initiated under Project No. 3343, "Jet Rotors", Task No. 73496, "Heat Resistant Adhesives", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. F. W. Kuhn acting as project engineer.

This report covers work performed during the period 1 May 1955 to 1 November 1955 and is the third report on the subject by the same contractor.

ABSTRACT

Wide variations in the composition of the CHR-M-60 epoxy-modified DC-2103 silicone resin with Asbestine X filler, which has shown shear strength values as a metal-to-metal adhesive in excess of 1000 psi at 500°F, have been made and the results plotted to indicate composition areas yielding maximum shear strength values. Extended high-temperature aging tests have shown DC-803 silicone resin and epoxy-modified DC-803 to have better aging resistance than DC-2103 and epoxy-modified DC-2103, respectively. The DC-803 showed little loss in shear strength at 500°F after aging 1200 hours at 500°F on both aluminum panels and stainless steel panels (residual shear strength about 300 psi at 500°F). This resin also withstood 300 hours at 600°F on stainless steel and 200 hours on aluminum. The 20 percent epoxy-modified DC-803 lasted 800 hours at 500°F and 100 hours at 600°F (residual strength in each case about 350 psi at room temperature and 150 psi at 500°F).

A number of silicone-epoxy-phenolic resin blends were prepared, which showed shear strength values and high-temperature aging resistance slightly better than those for the epoxy-modified silicone resins.

Up to 20 percent of epoxy resin in epoxy-modified DC-2103 silicone resin was found to have relatively little effect on the change in shear strength values when tested over a temperature range from -70°F to +900°F; the epoxy resin mainly improved the strength over the lower half of the temperature range. Shear strength at 900°F was about 100 psi.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

Recent progress in the development of jet and rocket engines, promising to propel aircraft at speeds far beyond that of sound, has brought forth new requirements for metal-to-metal structural adhesives capable of maintaining strength at temperatures of 500°F and even 700°F. The silicone resins and elastomers are the outstanding synthetic polymers for high-temperature service, but until recently little work had been directed toward the application of these materials as structural adhesives. The present contract was created with the thought that a commercially-available silicone resin might be found which would provide the required strength at a temperature of 500°F to bond aluminum and stainless steel parts to each other. It was hoped that such an adhesive would withstand aging for several hundred hours at 500°F, and withstand brief exposure to a temperature of 700°F.

A thorough survey of existing commercial silicone resins and elastomers was made and reported in WADC Technical Report 54-98. Shear strengths of more than 400 psi at 500°F were found to be available. During the second phase of this research (WADC TR 54-98 Part 2) commercially available silicone resins were modified by reaction with epoxy and other organic resins, resulting in a raising of the shear strength at 500°F to 1000 psi. Relationships were also determined between chemical composition and adhesive strength with silicone resins synthesized in the laboratory. In the current phase of this research, covered in this report, a study was made of variations in the composition of the best epoxy-modified silicone resin adhesive selected from previous work, and of the preparation and evaluation of similar epoxy-modified and epoxy-phenolic-modified commercial and experimental silicone resins.

I. EXPERIMENTAL

A. EPOXY-MODIFIED COMMERCIAL SILICONE RESINS

Object: To prepare epoxy-modified silicone resins from commercial silicone and epoxy resins, and to evaluate these resins as metal-to-metal adhesives.

Results: A series of thirty epoxy-modified silicone resins have been prepared which cover a composition range of 5 - 40 percent epoxy with a series of epoxy resins. These resins have all been tested as adhesives on aluminum panels and selected resins have been tested on stainless steel.

The combination of high room-temperature shear strength with high shear strength at 500°F was found generally in a composition range of 10 to 30 percent epoxy resin in the modified silicone resins (see Section E on Fillers).

In general, Epon 834, and Araldite 6020 have consistently resulted in better modifications with silicone resins than other resins of the series. These epoxy resins, which are almost identical in composition, have an average molecular weight of 650 and an epoxide equivalent of 3.1 to 3.5 epoxy-groups per kilogram of resin. They also contain at least one hydroxyl group per molecule. These resins show good compatibility with the silicone resins and presented no difficulties during modification.

The stainless steel bonds showed about the same shear strength values at room temperature as the aluminum bonds, but at 500°F the values for the stainless steel panels were considerably lower.

Materials:	DC-2103	(silicone)	Araldite	6010	(epoxy)
	DC-2103HV	"	"	6020	"
	DC-2103LV	"	"	6030	"
	DC-803	"	"	6040	"
	DC-840	"	"	6060	"
	Epon 834	(epoxy)			
	" 864	"			
	" 1001	"			

Procedure: The resin-modifications were prepared in a 500 cc-capacity resin reaction flask fitted with a paddle-type stirrer, a thermometer and a Barrett tube-condenser assembly (Figure 1). One hundred and twenty grams (solids) of the silicone resin (50 percent solution in xylene) were placed in a beaker, and the required weight of epoxy resin was added. The mixture was heated on a steam bath to melt the organic resin, and was blended by stirring. The resin mix was then poured into the reaction flask. The stirrer and the heat were then turned on, and the reaction mixture was allowed to come to a gentle reflux (pot temperature, 120°-140°C). The water formed in the reaction was collected and withdrawn by means of the Barrett tube. When the formation of water, as observed in the Barrett tube, was no longer significant, the reaction was cooled and the resin was poured out. The heating period was generally about two hours.

One specific epoxy and silicone resin combination (80 parts DC-803 and 20 parts Epon 834) was selected for a brief study of controlled variations in the modification procedure. Modification M-187 was prepared in the standard manner described above, the temperature of the reaction mixture averaging 140°C. M-188 was prepared in the same manner except that a stream of nitrogen was passed through the mixture during the entire reaction period, resulting in a reaction mixture temperature of 130°C. Diethyl carbitol was used as the reaction solvent in M-189, and the reaction mixture was refluxed at 195°C under a nitrogen atmosphere. M-190 was prepared in the standard manner except that "Mini-lab" equipment (see Procedure under Section B) was used instead of the larger reaction equipment used for M-187.

Lap joints were prepared and tested as described in the Appendix to this report.

Data: The results of the shear strength tests on the epoxy-modified commercial silicone resins appear in Table I.

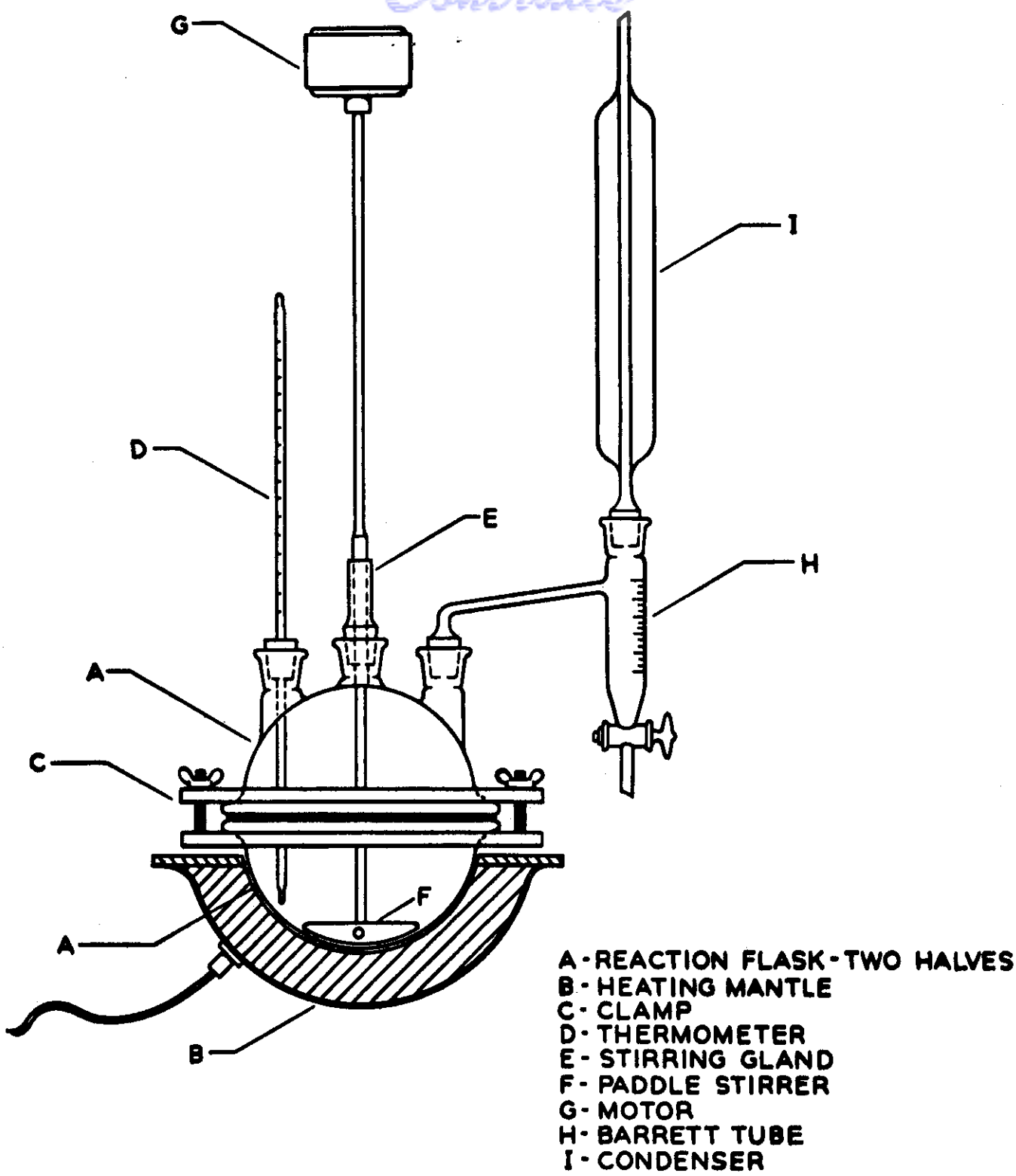

FIGURE 1 - APPARATUS FOR ORGANO-MODIFIED SILICONE RESINS.

TABLE I

EPOXY-MODIFIED COMMERCIAL SILICONE RESINS

Resin No.	Composition: Silicone	Composition: Organic	Composition: %	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
ALUMINUM													
M-187[a]	DC-803	Epon 834	20	2-2	1485	1500	1470	2	350	390	310	2	100
M-188	"	"	20	2-2	1250	1300	1200	2	240	260	220	2	"
M-189	"	"	20	2-2	1800	2000	1600	2	395	410	380	2	"
M-190	"	"	20	2-2	1685	1710	1660	2	485	500	470	2	"
M-236	"	Araldite 6020	20	2-2	945	960	930	2	395	410	380	2	"
M-127	DC-840	Epon 834	20	1-1	1485	1510	1460	2	345	380	310	2	"
M-108	DC-2103	"	5	1-1	1060	1150	950	4	335	340	320	4	"
M-109	"	"	10	1-1	960	1030	845	4	340	380	300	4	"
M-110	"	"	15	1-1	995	1150	840	4	325	440	200	4	"
M-154	"	"	20	1-1	1040	1100	940	6	400	470	280	6	"
M-111	"	"	25	1-1	900	930	890	4	265	280	250	4	"
M-112	"	"	30	1-1	1050	1300	900	4	245	300	210	4	"
M-153	"	"	40	2-2	1380	1510	1180	6	260	340	200	6	"
M-150	"	Epon 864	10	2-2	1270	1340	960	6	470	640	370	6	"
M-151	"	"	20	2-1	1100	1120	1080	4	295	350	240	4	"
M-152	"	"	30	2-2	960	1000	900	6	310	340	290	6	"
M-195	"	Epon 1001	10	2-2	1775	1930	1620	2	405	400	410	2	"
M-196	"	"	20	2-2	930	1000	860	2	260	290	230	2	"
M-104	"	Araldite 6010	20	1-1	1150	1250	930	4	300	310	270	4	"
M-128	"	Araldite 6020	10	1-1	1010	1010	1010	2	525	540	510	2	"

TABLE I (Cont'd.)

EPOXY-MODIFIED COMMERCIAL SILICONE RESINS

Resin No.	Composition: Silicone	Composition: Organic	Composition: %	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
M-105	DC-2103	Araldite 6020	20	1-1	1030	1100	950	4	450	510	380	4	100
M-106	"	Araldite 6030	20	1-1	1075	1180	975	4	320	360	220	4	"
M-193	"	Araldite 6040	10	2-2	1415	1470	1360	2	335	370	300	2	"
M-123	"	"	20	1-1	800	960	640	4	375	390	360	4	"
M-194	"	"	30	2-2	1605	1620	1590	2	660	670	650	2	"
M-101	DC-2103HV	Epon 834	10	2-2	490	600	400	4	190	230	180	4	90
M-191	DC-2103LV	"	10	2-2	1155	1200	1110	2	525	540	510	2	100
M-192	"	"	20	2-2	1135	1170	1100	2	455	480	430	2	"
STAINLESS STEEL													
M-187[a]	DC-803	"	20	2-2	1600	1670	1530	2	145	170	120	2	"
M-188	"	"	20	2-2	1660	1720	1600	2	115	140	90	2	"
M-189	"	"	20	2-2	1415	1440	1390	2	35	70	0	2	"
M-190	"	"	20	2-2	1775	1890	1660	2	130	150	110	2	"
M-191	DC-2103LV	"	10	2-2	1635	1720	1550	2	185	200	170	2	"
M-192	"	"	20	2-2	1550	1620	1480	2	230	270	190	2	"

a. Resins M-187, M-188, M-189 and M-190 were prepared with variations in the modification procedure. (See Procedure under Section A)

B. EPOXY-MODIFIED CHR SILICONE RESINS

Object: To prepare epoxy-modified silicone resins from commercial epoxy resins and silicone resins of known composition prepared in this laboratory, under different controlled conditions, and to evaluate these resins as metal-to-metal adhesives.

Results: Epoxy-modifications of CHR-122, the hardest of the three silicone resins compared in this group, displayed shear strength values at 500°F (400 to 700 psi) which were somewhat better than those of the other epoxy-modified silicone resins. Neutralizing the hydrolysis medium during preparation of CHR-122 resin produced, in general, lower shear strength values; and maintaining the hydrolysis medium at a constant temperature of 18°C had little effect on the shear strength values.

Variations in the method of preparing CHR-141 resin produced, in each case, shear strength values somewhat lower than those obtained by the standard method. Variations in the preparation of CHR-183 resin produced shear strength values slightly higher than those normally obtained. Adding the silane monomers separately to the hydrolysis medium produced poor results with each of the resins.

A resin (CHR-203) somewhat harder than CHR-122 (lower R/Si ratio and higher methyl content) was prepared and epoxy-modifications made and tested. Shear strength values, while nearly equivalent, were no better than those for CHR-122.

Materials:

Epon 834
Monomers for:
CHR-122 Resin (R/Si = 1.20; 50% methyl, 50% phenyl)
CHR-141 Resin (R/Si = 1.40; 57% methyl, 43% phenyl)
CHR-183 Resin (R/Si = 1.30; 46% methyl, 54% phenyl)
CHR-203 Resin (R/Si = 1.10; 54% methyl, 46% phenyl)

Procedure: The following procedures were used to prepare the silicone resins. The code letters added to the resin numbers in Table II correspond to the four different procedures outlined below.

Standard Method: Approximately one-half pound of each of the CHR silicone resins listed above was prepared in the following manner. The monomeric organochlorosilanes were weighed into a glass-stoppered Erlenmeyer flask, and 250 cc of distilled, dried, trichloroethylene was added. This

solution was added dropwise into the bottom (solvent) layer of a two-phase system of 250 cc of trichloroethylene and three liters of water. The mixture was well stirred during the addition, no attempt being made to cool the solution. The hydrolysis mixture was stirred for one-half hour after complete addition of the monomers (approximately forty-five minutes). The two layers were separated, and the trichloroethylene-silicone resin layer was washed in a separatory funnel as follows: 3 washings of 2 liters each of water, 1 washing with 2 liters of 5 percent sodium bicarbonate solution, 3 washings of 2 liters each of water. The trichloroethylene was distilled off until the resin solution became rather viscous. Two hundred and fifty cc of xylene was then added, and the resin was refluxed for 30 minutes to insure complete solution. The resin was then poured into a storage bottle, and a small sample was removed for a solids determination and a Karl Fischer silanol end-group titration.

T-(Isothermal Hydrolysis): The procedure and quantities of materials were identical to those used in the standard method except that the entire flask was immersed in an ice bath and the internal temperature of the hydrolysis mixture was maintained at 18° ± 1°C.

N-(Neutralized Hydrolysis): The procedure was identical to the standard method except that a quantity of sodium bicarbonate, sufficient to neutralize all of the hydrochloric acid formed in the hydrolysis or the organochlorosilanes, was added. Also, in earlier runs, the frothing accompanying the neutralization was quite troublesome, and it was found necessary to use half the quantity of monomeric organochlorosilanes, diluted with 250 cc of trichloroethylene, in order to reduce the frothing to a point at which it could be controlled. The trichloroethylene-silicone resin mixture was washed 3 times with 2 liters of water. No attempt was made to cool the reaction mixture.

NT-(Isothermal and Neutralized Hydrolysis): This procedure was identical to that of "N" with the exception that the temperature of the reaction mixture was maintained at 18° ± 1°C throughout the hydrolysis.

I-(Incremental Addition of the Monomers): The procedure was identical to the standard method except in the manner in which the monomeric organochlorosilanes were added. Only two monomers were required in the preparation of CHR-141 and CHR-183 resins. The monomers for these resins were weighed, diluted with trichloroethylene, and added to the hydrolysis

medium individually. The least reactive monomer, dimethylchlorosilane, was added first, over a period of 15 minutes, and then the more reactive monomer, phenyltrichlorosilane, over a period of 30 minutes. Since three monomers were required in the preparation of CHR-122 resin, at least two combinations of staggered addition were possible, i.e., adding the three monomers consecutively, or adding the two least reactive monomers first, and then the most reactive. Both procedures were used. The temperature was not controlled during the hydrolysis.

Each of the silicone resins was then modified with Epon 834 in the proportions indicated in Table II. In order to utilize best the quantity of silicone resin produced above, these modifications were prepared in "Mini-lab" 1/ equipment. This equipment is similar in design but considerably smaller than the apparatus used in Section I - A. The minimum capacity resin-reaction flask for the larger apparatus is 500 cc while the maximum capacity flask for the "Mini-lab" equipment is 100 cc, thus permitting preparation of more modifications from one lot of silicone resin. Actual testing requires only a small amount of resin.

The silicone and organic resins were weighed into a tared beaker and warmed on a steam bath. The mixture was blended with a stirring rod and transferred to the "Mini-lab" reaction flask. The stirrer and the heat were turned on, and the mixture was brought to and maintained at a gentle reflux until the distillate no longer contained a significant amount of water (usually 1½ to 2 hours). The reaction mixture was cooled and poured into a storage bottle.

The CHR-203 resin was prepared and modified by the standard methods described above.

Lap joints were prepared and tested as described in the Appendix to this report.

Data: The results of the shear strength tests on the epoxy-modified CHR silicone resins appear in Table II.

Remarks: The preparation of the resins proceeded with no difficulty except for the "I" series. In several attempts to prepare CHR 122I and CHR 183I, the resins gelled either during the hydrolysis or washing steps.

1/ Ace Glass Co., Vineland, N.J.

TABLE II

EPOXY-MODIFIED CHR SILICONE RESINS

Resin No.	Composition: Silicone	Composition: Organic	Composition: %	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
ALUMINUM													
CHR-122	--	--	--	1-1	755	980	630	2	495	510	480	2	100
M-117	CHR-122	Epon 834	10	2-2	845	860	830	2	680	710	650	2	"
M-118	"	"	20	2-2	955	990	920	2	395	420	370	2	"
M-119	"	"	30	2-2	1220	1240	1200	2	405	410	400	2	"
CHR-122N[a]	--	--	--	2-2	655	670	640	2	350	390	310	2	"
M-132	CHR-122N	Epon 834	10	2-2	1055	1060	1050	2	380	440	320	2	"
M-133	"	"	20	2-2	910	920	900	2	380	400	360	2	"
M-134	"	"	30	2-2	900	910	890	2	455	520	390	2	"
CHR-122T	--	--	--	1-1	770	800	740	2	390	400	380	2	"
M-135	CHR-122T	Epon 834	10	2-2	1175	1190	1160	2	420	430	410	2	"
M-136	"	"	20	2-2	975	980	970	2	535	600	470	2	"
CHR-122NT	--	--	--	2-2	665	710	620	2	360	380	340	2	"
M-138	CHR-122NT	Epon 834	10	2-2	1180	1250	1110	2	545	590	500	2	"
M-139	"	"	20	2-2	1255	190	1220	2	495	520	470	2	"
CHR-183	--	--	--	2-2	615	640	590	2	355	380	330	2	"
M-114	CHR-183	Epon 834	10	2-2	880	1040	720	4	410	500	320	4	"
M-115	"	"	20	2-2	1160	1280	1040	4	180	220	160	4	"
M-116	"	"	30	2-2	1225	1270	1180	4	205	230	180	4	"
CHR-183N	--	--	--	2-2	790	820	760	2	370	380	360	2	"
M-141	CHR-183N	Epon 834	10	2-2	1075	1210	1040	2	410	430	390	2	"
M-142	"	"	20	2-2	1120	1260	780	6	280	340	115	6	"

TABLE II (Cont'd.)

EPOXY-MODIFIED CHR SILICONE RESINS

Resin No.	Composition: Silicone	Composition: Organic	Composition: %	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
CHR-183T	--	--	--	2-2	720	740	700	2	400	410	390	2	100
M-144	CHR-183T	Epon 834	10	2-2	1350	1380	1320	2	470	490	450	2	"
M-145	"	"	20	2-2	960	1120	800	2	205	220	190	2	"
M-146	"	"	30	2-2	1170	1360	980	2	285	290	280	2	"
CHR-183NT	--	--	--	2-2	800	810	790	2	315	390	240	2	"
M-147	CHR-183NT	Epon 834	10	2-2	1125	1160	1090	2	320	360	280	2	"
M-148	"	"	20	2-2	1240	1280	1200	2	305	310	300	2	"
CHR-141	--	--	--	2-2	990	1000	980	2	385	390	380	2	"
M-120	CHR-141	Epon 834	10	1-1	1130	1240	1020	4	205	210	200	4	"
M-121	"	"	20	1-1	1300	1420	1240	4	340	430	290	4	"
M-122	"	"	30	1-1	1360	1400	1320	4	490	540	380	4	"
CHR-141N	--	--	--	2-2	650	900	400	2	165	180	150	2	"
M-180	CHR-141N	Epon 834	10	2-2	1375	1380	1370	2	255	270	240	2	"
M-181	"	"	20	2-2	1300	1380	1220	2	395	420	370	2	"
CHR-141T	--	--	--	2-2	870	880	860	2	215	230	200	2	"
M-183	CHR-141T	Epon 834	10	2-2	1315	1390	1240	2	310	330	290	2	"
M-184	"	"	20	2-2	1220	1260	1180	2	325	420	230	2	"
M-185	"	"	30	2-2	1490	1500	1480	2	340	340	340	2	"
CHR-141I	--	--	--	1-1	0	0	0	2	0	0	0	2	"
M-124	CHR-141I	Epon 834	10	1-1	400	400	0	2	140	170	110	2	"
M-125	"	"	20	1-1	675	710	640	2	200	200	200	2	"
M-126	"	"	30	1-1	380	380	0	2	0	0	0	2	"
CHR-203	--	--	--	2-2	705	780	640	4	420	430	400	4	"
M-235	CHR-203	Epon 834	10	2-2	1010	1020	1000	2	590	610	570	2	"
M-234	"	"	20	2-2	835	860	810	2	320	340	300	2	"

TABLE II (Cont'd.)

EPOXY-MODIFIED CHR SILICONE RESINS

Resin No.	Composition: Silicone	Composition: Organic	Composition: %	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
STAINLESS STEEL													
M-132	CHR-122N	Epon 834	10	2-2	1570	1590	1550	2	350	360	340	2	100
M-133	"	"	20	2-2	1680	1760	1600	2	190	200	180	2	"
M-134	"	"	30	2-2	1720	1760	1680	2	210	260	160	2	"
M-135	CHR-122T	"	10	2-2	685	770	600	2	155	180	130	2	"
M-136	"	"	20	2-2	2000+	2000+	2000	2	185	200	170	2	"
M-138	CHR-122NT	"	10	2-2	1565	1590	1540	2	190	200	180	2	"
M-139	"	"	20	2-2	1685	1730	1640	2	210	250	170	2	"
M-141	CHR-183N	"	10	2-2	1415	1420	1410	2	115	140	90	2	"
M-142	"	"	20	2-2	1540	1580	1500	2	195	200	190	2	"
M-144	CHR-183T	"	10	2-2	1690	1710	1670	2	90	100	80	2	"
M-145	"	"	20	2-2	1410	1520	1300	2	45	50	40	2	"
M-146	"	"	30	2-2	1175	1210	1140	2	0	0	0	2	"
M-147	CHR-183NT	"	10	2-2	1625	1630	1620	2	25	50	0	2	"
M-148	"	"	20	2-2	1550	1590	1510	2	130	140	120	2	"
M-180	CHR-141N	"	10	2-2	1430	1460	1400	2	60	70	50	2	"
M-181	"	"	20	2-2	1665	1840	1490	2	150	190	110	2	"
M-183	CHR-141T	"	10	2-2	1565	1620	1510	2	110	130	90	2	"
M-184	"	"	20	2-2	1570	1570	1570	2	105	110	100	2	"
M-185	"	"	30	2-2	1910	1970	1850	2	110	140	80	2	"

a. See Procedure under Section B for explanation of the suffix letters.

C. PHENOLIC-MODIFIED SILICONE RESINS

Object: The preparation of a phenolic-modified silicone resin.

Results: No satisfactory phenolic-modified silicone resin was prepared. In every case the two materials separated after a brief period of time and were not considered worth testing.

Materials: Phenolic Resins: Plyophen 5015, 5023, 5516
Silicone Resins: CHR-183 (R/Si = 1.30, 46% Methyl)
DC-803

Procedure and Observations:

1. 240 grams of DC-803 solution (50 percent solids) was poured into a resin reaction flask fitted with a paddle-type stirrer, a thermometer, and a Barrett tube-condenser assembly (Figure 1). While being stirred, the resin solution was heated to reflux temperature (125-130°C). 40 grams of Plyophen 5023 solution (80 percent solids in methanol) was diluted to 100 grams with methanol and added dropwise to the silicone resin solution over a period of 45 minutes. After approximately 15 minutes of this addition, the phenolic resin was observed to be solidifying into small bead-like particles. After complete addition, the resin mixture was cooled and filtered. The solid material was washed, dried, and weighed, and was found to correspond closely to the weight of phenolic resin added. The material was discarded.

2. The above procedure was repeated using the same quantities of materials, with the phenolic resin neutralized and made just acid by means of 5 percent aqueous hydrochloric acid. The same effect as above was noted with the exception that the hard bead-like particles of procedure (1) were, in this case, soft and gummy but were easily filtered out of the mixture.

3. 240 grams of DC-803 solution was weighed into a tared beaker and 40 grams of Plyophen 5023 was neutralized, made just acid (pH5), and added to the silicone with stirring. The mixture was heated on a steam bath with intermittent stirring for four hours. At the end of this time, the mixture was stirred vigorously and then allowed to stand overnight. The phenolic resin again separated and formed a skin over the liquid similar to that found on paint which has been allowed to stand in air.

4. A 240 gram sample of DC-803 was placed in a vacuum oven and heated under reduced pressure (40°C and approximately 25 millimeters of mercury) until a constant weight was obtained (corresponding to 90 percent removal of solvent). The resin was then divided into three equal portions of 44 grams each. Each of the three portions was dissolved in a different solvent, viz. methanol, ethanol, and acetone. 14 grams of Plyophen 5023 (pH5) was added to each of the three portions, mixed with a stirring rod and then mixed for 5 minutes in a Waring Blendor. The resin mixtures in the alcohols separated within one hour after removal from the Waring Blendor. The resin-mixture in acetone required almost 24 hours to separate. When the latter mixture was heated on a steam bath, however, separation occurred within three hours.

5. CHR-183 resin (R/Si 1.3, Methyl 46%) was dissolved in acetone, and three equal portions of 40 grams (solids) each were weighed into individual beakers. To each of these three portions was added 14 grams (solids) of each of the following phenolic resins diluted to 40 grams with acetone and neutralized with 5 percent hydrochloric acid: Plyophen 5015, 5023, 5516. The resin mixtures were blended with a stirring rod and poured into a Waring Blendor, mixed for ten minutes, then poured into beakers. As before, all of the phenolic resins settled slowly, but after standing one day they were found separated into two distinct layers. Each mixture was again blended in the Waring Blendor and heated for two hours on a steam bath. The mixtures were allowed to stand in bottles and were remixed daily by shaking. Over a period of two weeks, all of the phenolic resins gelled.

The combination of CHR-183 and Plyophen 5015 appeared to be the most compatible mixture tested, although all were considered poor.

D. SILICONE-EPOXY-PHENOLIC RESIN SOLUTION BLENDS

Object: To prepare solution blends of a ternary mixture of a silicone resin, an epoxy resin and a phenolic resin.

Results: Certain phenolic and epoxy resins were found to be readily miscible, and the mixtures did not separate easily on standing. Upon the addition of silicone resins, however, these mixtures showed a definite tendency to separate, the phenolic dropping out of solution and the epoxy remaining in solution. This separation was found to take place anywhere from one hour to approximately four days after mixture, depending on the resins involved. Refrigeration greatly extended the shelf life of these mixtures. Lap joints prepared from the freshly mixed blends yielded good shear strength values at 500°F. Of the twenty blends tested in the initial series, eight showed high-temperature shear strength values in excess of 600 psi, while more than half of the values were over 500 psi. A blend of six parts of DC-803, one part of Epon 1001 and one part of Plyophen 5010 displayed average shear strength values of 1380 at 70°F and 920 psi at 500°F.

A second series of ternary blends based on DC-803 and Epon 834 showed good, although somewhat lower, adhesion values. The use of fresh lots of phenolic resins showed a small overall improvement. (The results of adding fillers and oven aging are described in later sections.)

Materials:

DC-803 (50% in xylene)	Plyophen 5010 (60% in alcohol)
DC-2103 (60% in toluene)	" 5012 (60% in alcohol)
	" 5015 (65% in water)
Epon 828	" 5023 (80% in alcohol)
" 834	" 5027 (70% in water)
" 1001	" 5516 (60% in water)

(As received, percent solids and solvent in parentheses)

Procedure: A series of epoxy-phenolic mixtures (1:1) were prepared from the three epoxy resins and the six phenolic resins listed above (all resins or solutions were used as received, except Epon 1001, a solid, which was used as a 50 percent solution in acetone). All of the mixtures appeared compatible even after prolonged standing. Portions of these mixtures were then added to each of the two silicone resin solutions, DC-803 and DC-2103, to produce final resin mixtures of 6 parts silicone resin, 1 part epoxy resin, and 1 part phenolic

resin (by weight of resin solids). After the blends had been thoroughly mixed, lap joints were prepared and tested, as described in the Appendix to this report.

Portions of the blends were then allowed to stand undisturbed, at room temperature, and the time of separation was noted. Separate portions of the blends (M-200 to M-205) (Table III) were placed under refrigeration (40°F) and the time and extent of separation was noted. Of this particular series, the blends containing Plyophen 5015 and 5516 separated first, and incidentally gave the poorest high-temperature shear strength values.

The second series of blends shown in Table III were prepared by blending the organic resins and adding to the silicone resin solutions, as above.

Data: The results of the shear strength tests on the silicone-epoxy-phenolic resin solution blends appear in Table III.

Remarks: The blends which separated immediately were considered incompatible. A serious problem of shelf storage exists, however, on those considered compatible, in that the phenolic resins polymerize slowly at room temperature and eventually separate from solution. It should be noted here that three of the blends which separated in four days at room temperature still remained homogeneous after fifteen days at 40°F.

TABLE III

SILICONE-EPOXY-PHENOLIC RESIN SOLUTION BLENDS

Resin No.	Composition						Glue Line, Mils	Shear Strength, psi								Failure, % Adhesive
								Room Temperature				500°F				
	Silicone	%	Epoxy	%	Phenolic	%		Aver.	High	Low	No. Tests	Aver.	High	Low	No. Tests	
M-204	DC-803	75	Ep-828	12.5	Pl-5010	12.5	2-2	1050	1070	1030	2	375	380	370	2	100
M-205	"	"	"	"	Pl-5012	"	2-2	1115	1140	1090	2	350	370	330	2	"
M-201	"	"	"	"	Pl-5015	"	2-2	1020	1040	1000	2	315	380	250	2	"
M-200	"	"	"	"	Pl-5023	"	2-2	1140	1160	1120	2	650	800	490	2	"
M-203	"	"	"	"	Pl-5027	"	2-2	1100	1160	1040	2	435	470	400	2	"
M-202	"	"	"	"	Pl-5516	"	2-2	1275	1350	1200	2	255	300	210	2	"
M-207	"	"	Ep-1001	"	Pl-5010	"	2-2	1380	1380	1380	2	920	1000	840	2	50
M-208	"	"	"	"	Pl-5012	"	2-2	1260	1500	1020	2	635	690	580	2	"
M-210	"	"	"	"	Pl-5015	"	2-2	1110	1140	1080	2	640	680	600	2	"
M-209	"	"	"	"	Pl-5023	"	2-2	1320	1320	1320	2	645	700	590	2	"
M-206	"	"	"	"	Pl-5027	"	2-2	1375	1400	1350	2	590	610	570	2	"
M-211	"	"	"	"	Pl-5516	"	2-2	1285	1320	1250	2	455	470	440	2	"
M-213	DC-2103	"	"	"	Pl-5010	"	2-2	1250	1400	1100	2	470	480	460	2	75
M-214	"	"	"	"	Pl-5012	"	2-2	1215	1220	1210	2	510	510	510	2	"
M-216	"	"	"	"	Pl-5015	"	2-2	990	1020	960	2	495	520	470	2	"
M-215	"	"	"	"	Pl-5023	"	2-2	875	890	860	2	455	460	450	2	"
M-212	"	"	"	"	Pl-5027	"	2-2	1125	1200	1050	2	505	520	490	2	"
M-217	"	"	"	"	Pl-5516	"	2-2	1115	1130	1100	2	645	680	610	2	"
M-198	"	40	Ep-834	30	Pl-5023	30	2-2	1265	1290	1240	2	605	610	600	2	50
M-199	"	60	"	20	Pl-5023	20	2-2	1255	1310	1190	2	765	800	730	2	"

TABLE III (Cont'd.)

SILICONE-EPOXY-PHENOLIC RESIN SOLUTION BLENDS

Resin No.	Composition: Silicone	%	Epoxy	%	Phenolic	%	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	High	Low	No. Tests	500°F: Aver.	High	Low	No. Tests	Failure, % Adhesive
M-218	DC-803	80	Ep-834	10	Pl-5010	10	2-2	1250	1410	1100	4	400	610	300	4	100
M-219	"	60	"	20	"	20	2-2	1190	1290	1100	4	400	430	390	4	"
M-220	"	80	"	5	"	15	2-2	1110	1200	1010	4	205	270	180	4	"
M-221	"	80	"	15	"	5	2-2	1440	1560	1340	4	325	390	240	4	"
M-222	"	80	"	10	Pl-5023	10	2-2	1235	1440	1030	4	535	590	400	4	"
M-223	"	60	"	20	"	20	2-2	1085	1160	980	4	430	510	360	4	"
M-224	"	80	"	5	"	15	2-2	1170	1280	1020	4	580	650	520	4	"
M-225	"	80	"	15	"	5	2-2	1135	1370	1020	4	435	530	360	4	"
M-218A[a]	"	80	"	10	Pl-5010	10	2-2	1140	1100	1180	2	555	560	550	2	"
M-220A	"	80	"	5	"	15	2-2	1290	1300	1280	2	450	480	420	2	"
M-222A	"	80	"	10	Pl-5023	10	2-2	1820	1880	1760	2	205	230	180	2	"
M-224A	"	80	"	5	"	15	2-2	1350	1390	1310	2	355	360	350	2	"

a. The modified resins labeled "A" were prepared using fresh lots of the phenolic resins.

E. EVALUATION OF FILLERS

Object: To determine the effect of a group of selected inorganic fillers on a pure silicone resin and on epoxy and epoxy-phenolic modifications of that silicone resin, and to select the optimum filler loading in several selected modified silicone resins.

Results: As in previous work, the use of fillers in conjunction with pure silicone resins was found to offer little significant improvement in the shear strength values. In the case of only one filler, ferric oxide, was there a small general improvement in both room-temperature and high-temperature shear strengths. Asbestine X and Titanium dioxide offered some improvement in the shear strength values of the epoxy-modified silicone resin. It will be noted in Table VI that the Asbestine 5X produced shear strength values at 500°F somewhat superior to those of the other Asbestine types. In later data, the 5X appeared equivalent or slightly better than the X.

Earlier data on the three-component system, DC-2103, Epon 834 and Asbestine X, were plotted on triangular graphs (Figures 2A and 2B), and new data were produced to fill in promising areas. A similar series of samples was prepared for the systems DC-803, Epon 834, and Asbestine X, and CHR-122, Epon 834, and Asbestine X (Figures 3 and 4). The effect of filler loading varies somewhat in the three systems, but, in general, 50 to 100 parts is about the optimum loading in the epoxy-modified silicone resins.

Two hours of ball-mill grinding appeared to be sufficient to blend a 50 part loading of Asbestine X with epoxy-modified DC-2103 silicone resin. Further milling showed no significant improvement in the shear strength values (Table IV).

Procedure: The resin solutions were adjusted to 50 percent solids (by addition of xylene). The resin solution was weighed directly in the ball-mill jar, and the quantity of filler indicated in Tables IV to XI was added. The same number of one-half inch porcelain balls was used in each test. The jars were rolled for sixteen hours (except as indicated in Table IV), and the resin-filler mixtures were separated from the balls by filtration. Lap joints were prepared immediately and tested as described in the Appendix to this report.

Data: The results of the shear strength tests appear in Tables IV through XI.

Remarks: Although the data in Table IV showed that two hours of grinding on the ball mill was sufficient, sixteen hours was selected as a convenient period which would insure wetting of the different types of filler materials at the various loadings.

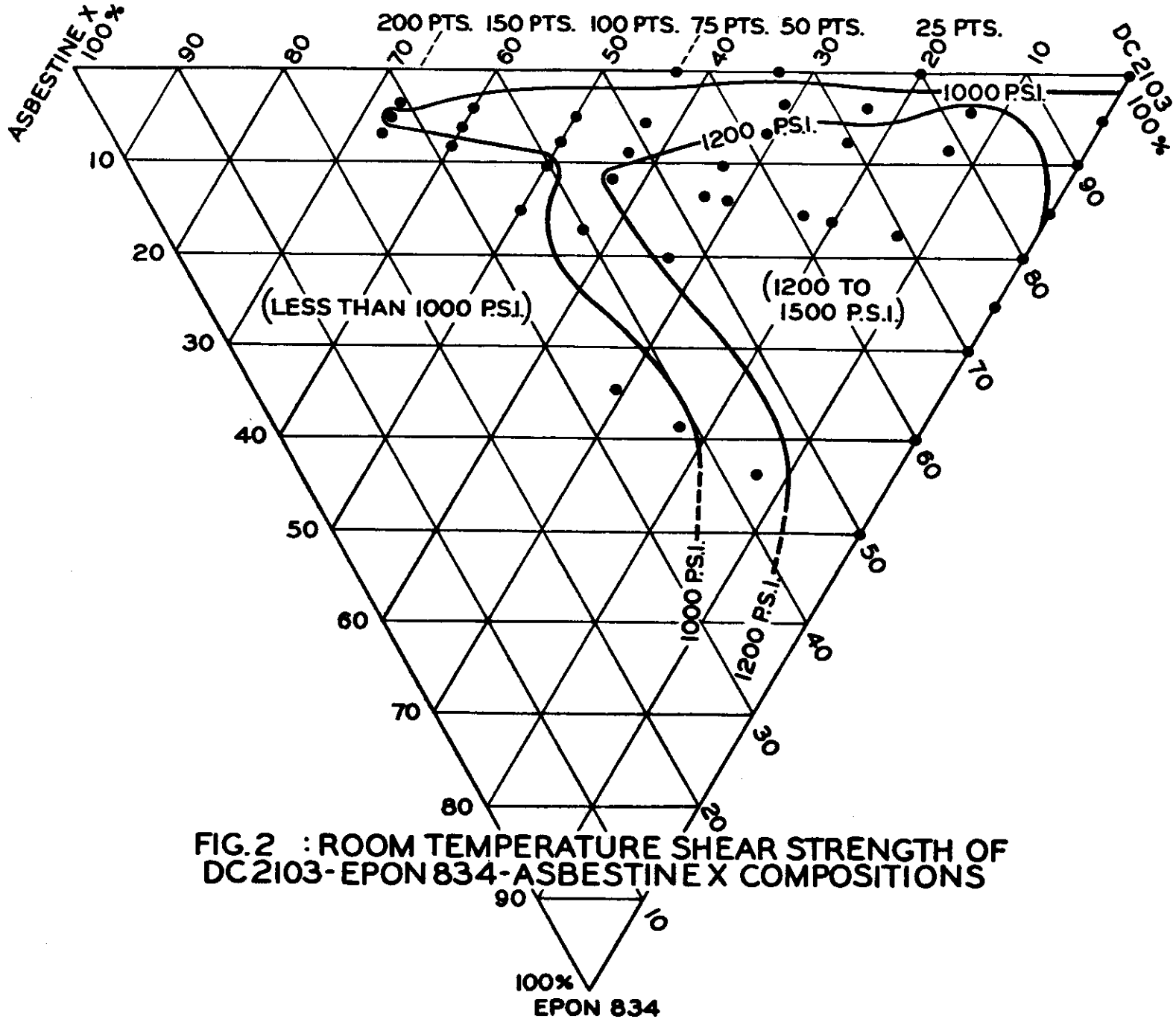

FIG. 2 : ROOM TEMPERATURE SHEAR STRENGTH OF DC2103-EPON 834-ASBESTINE X COMPOSITIONS

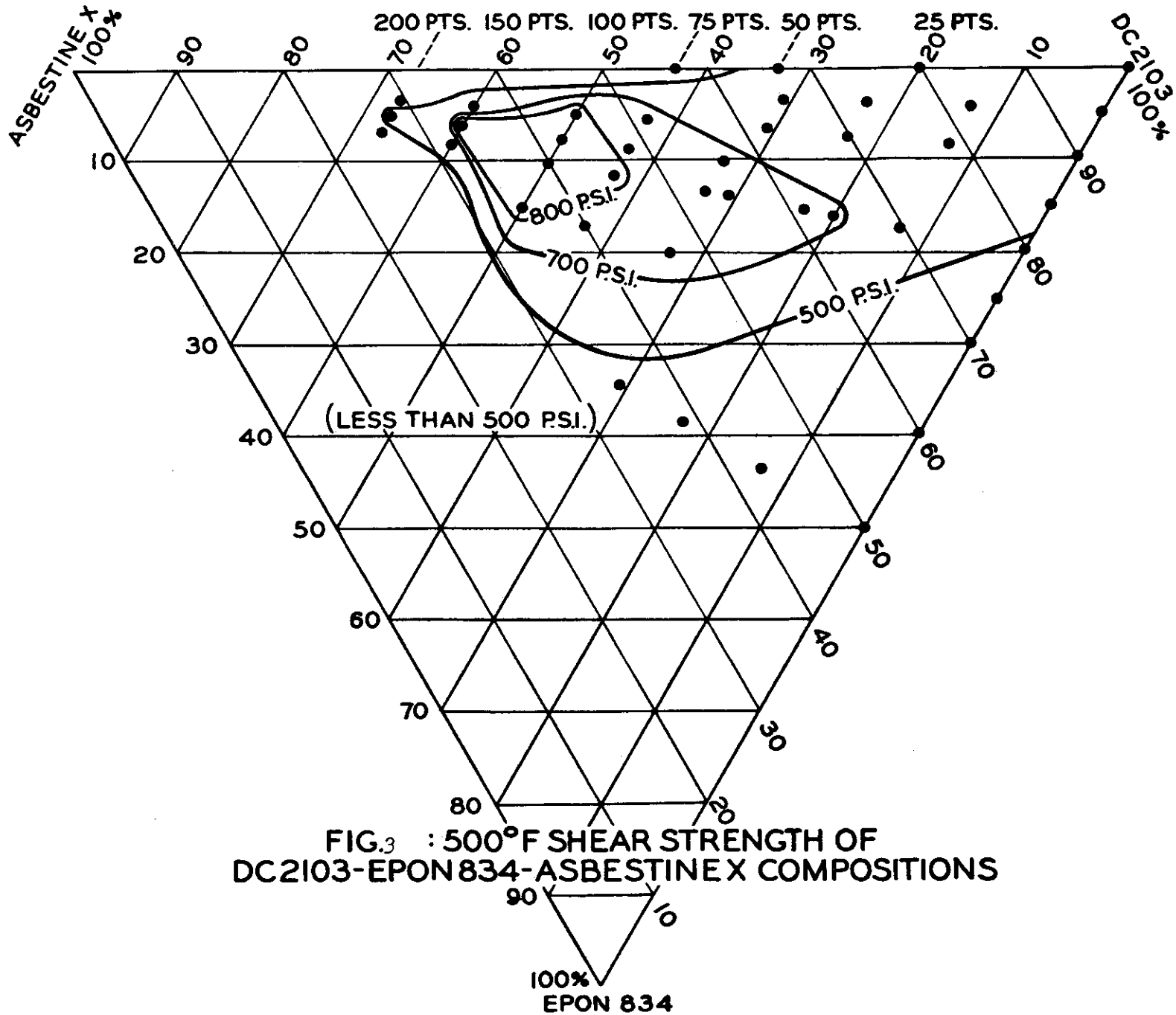

FIG. 3 : 500°F SHEAR STRENGTH OF DC2103-EPON 834-ASBESTINE X COMPOSITIONS

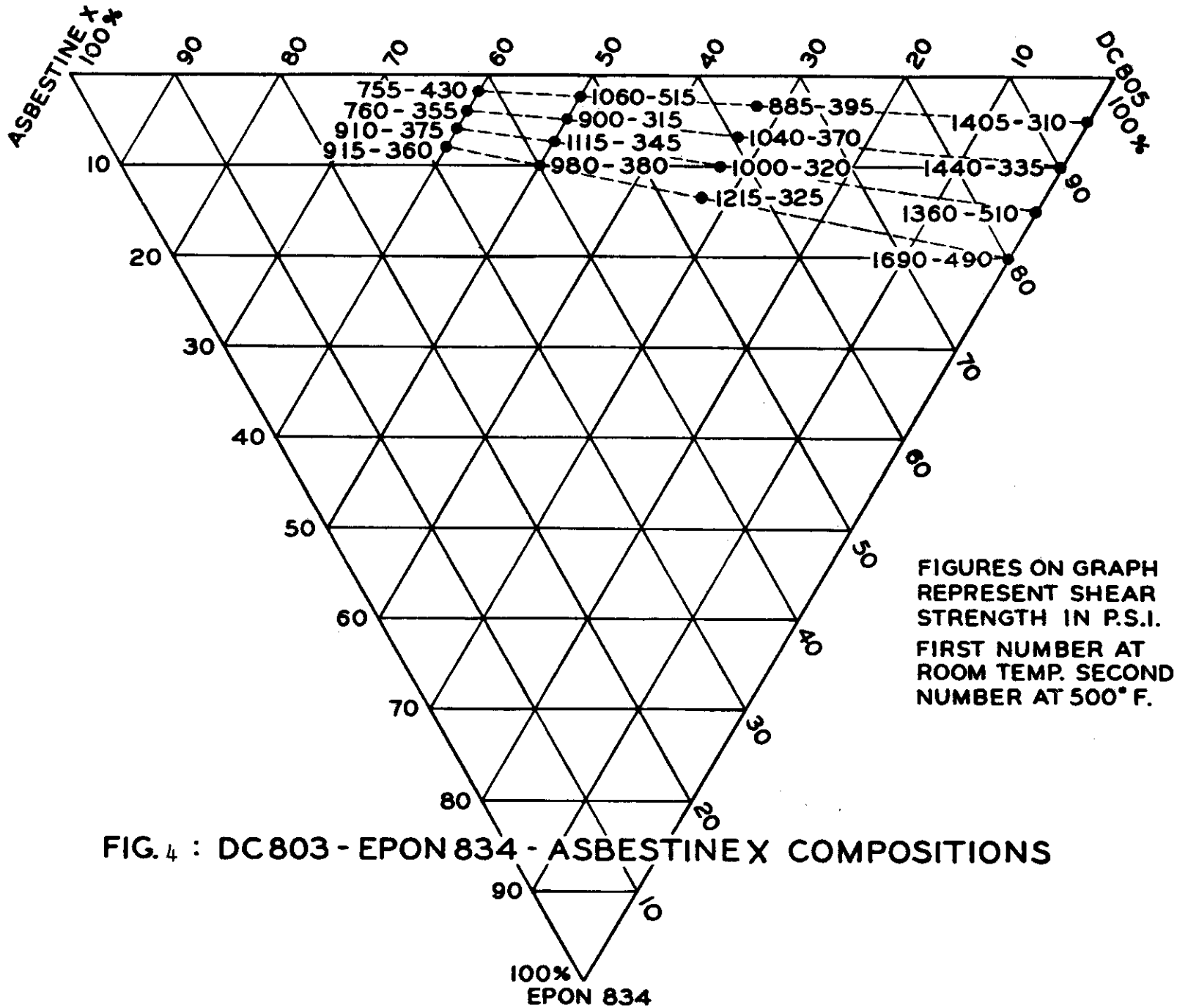

FIG. 4 : DC 803 - EPON 834 - ASBESTINE X COMPOSITIONS

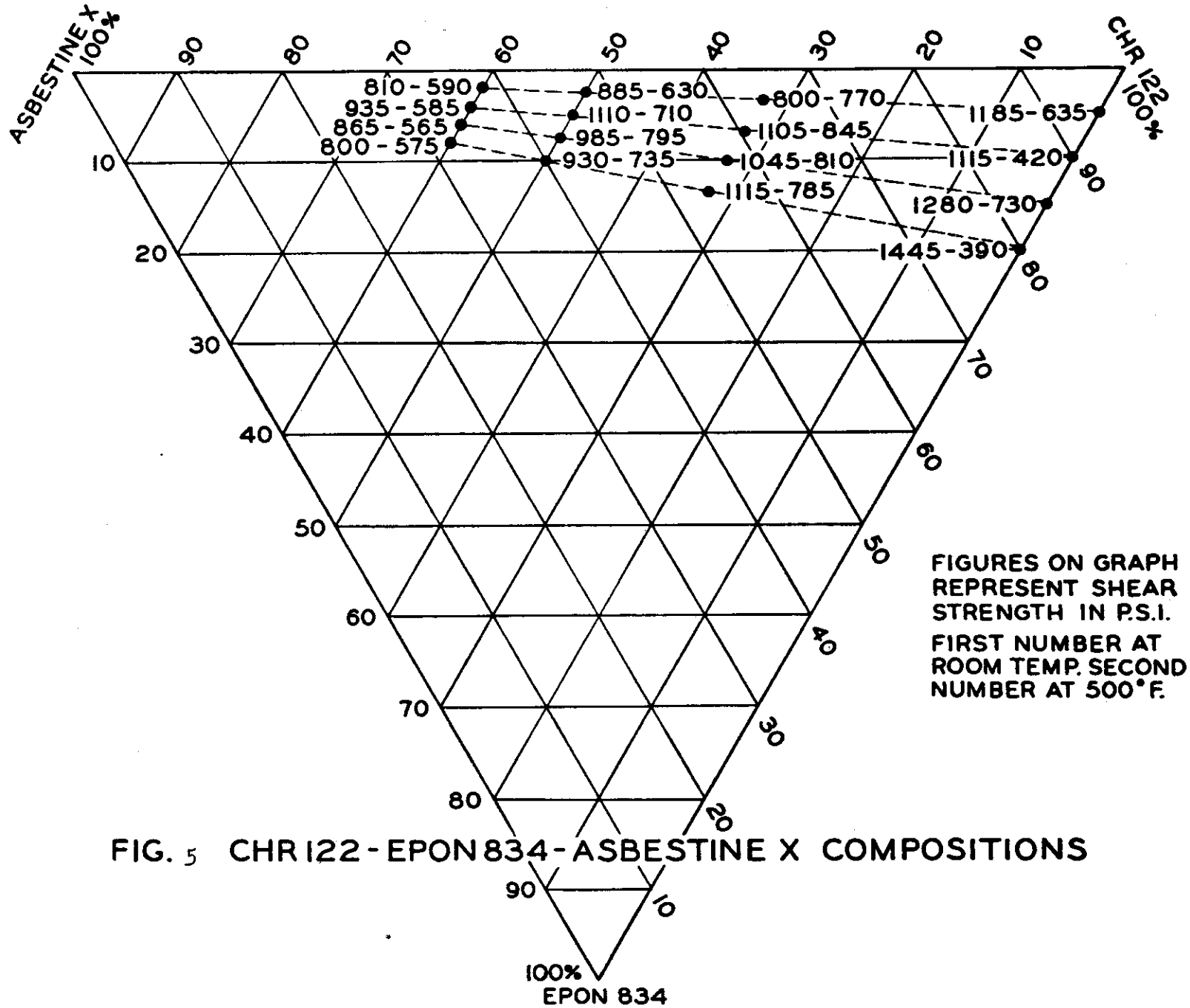

FIG. 5 CHR 122 - EPON 834 - ASBESTINE X COMPOSITIONS

TABLE IV

BALL-MILL BLENDING OF ASBESTINE X AND CHR-M-60 RESIN

Resin No.	Filler	phr[a]	Blending Method	Hrs.	Glue Line, Mils	Shear Strength, psi[c] Room Temperature Aver.	Room Temperature High	Room Temperature Low	500°F Aver.	500°F High	500°F Low	Failure, % Adhesive
DC-2103	(none)				1-1	920	920	920	590	640	540	100
Epon 834	"				1-1	1750	1820	1680	180	200	160	50
M-60[b]	"				2-2	1040	1180	900	390	410	370	80
"	Asbestine X	50	Hand-ground	--	2-2	810	880	740	400	400	400	50
"	"	"	Ball-mill	1	2-2	1130	1220	1040	340	400	280	"
"	"	"	"	2	2-2	980	1020	940	450	520	380	"
"	"	"	"	4	2-2	[illegible]0	880	880	355	360	350	"
"	"	"	"	8	2-2	910	1020	800	420	440	400	"
"	"	"	"	16	2-2	1070	1140	1000	370	430	310	"
"	"	"	"	1	2-2	900	1060	740	350	400	320	"
"	"	"	"	2	2-2	875	950	800	420	530	300	"
"	"	"	"	4	2-2	1030	1060	1000	470	520	440	"
"	"	"	"	8	2-2	955	970	940	420	470	340	"

a. Parts per hundred of resin
b. Blend of 80 percent DC-2103, 20 percent Epon 834
c. All values average of two tests

TABLE V-

FILLERS IN DC-2103 RESIN

Filler	phr	Glue Line, Mils	Shear Strength, psi: Room Temperature Aver.	Room Temperature High	Room Temperature Low	Room Temperature No. Tests	500°F Aver.	500°F High	500°F Low	500°F No. Tests	Failure, % Adhesive
Control	--	2-2	910	930	860	4	630	670	580	4	100
Asbestine X	25	1-1	720	760	680	2	615	650	580	2	"
"	50	2-2	900	900	900	2	620	640	600	2	"
"	75	2-2	610	630	590	2	365	400	330	2	"
Alum. Dust	25	2-2	885	900	870	2	700	710	690	2	"
"	50	2-2	905	910	900	2	385	410	360	2	"
"	75	1-1	850	870	830	2	640	700	580	2	"
Titanox (RA-168-LO)	25	1-1	1000	1020	980	2	300	360	240	2	"
"	50	1-1	1040	1070	1010	2	355	400	310	2	"
"	75	1-1	975	990	960	2	290	330	250	2	"
Titanox (RA)	25	2-2	1030	1040	1020	2	300	310	290	2	"
"	50	3-3	695	700	690	2	225	270	180	2	"
"	75	2-2	565	570	560	2	245	300	190	2	"
Fe_2O_3	25	2-2	955	1020	890	2	685	690	680	2	"
"	50	2-2	985	1000	970	2	720	740	700	2	"
"	75	2-2	910	910	910	2	675	730	620	2	"

TABLE VI

FILLERS IN CHR-M-60 RESIN

Filler	phr	Glue Line, Mils	Shear Strength, psi: Room Temperature Aver.	Room Temperature High	Room Temperature Low	Room Temperature No. Tests	500°F Aver.	500°F High	500°F Low	500°F No. Tests	Failure, % Adhesive
Control	--	3-3	1475	1490	1460	2	735	760	710	2	100
Asbestine X	25	3-3	1475	1490	1460	2	735	760	710	2	"
"	50	3-3	1370	1390	1350	2	650	740	560	2	50
"	75	3-3	1270	1300	1240	2	955	990	920	2	"
Alum. Dust	25	3-3	1350	1390	1310	2	790	860	720	2	"
"	50	3-3	1390	1410	1370	2	585	650	520	2	"
"	75	3-3	925	940	910	2	655	670	640	2	"
Titanox (RA-168-LO)	25	3-3	1390	1400	1380	2	585	600	570	2	100
"	50	3-3	1410	1420	1400	2	665	690	640	2	"
"	75	3-3	1485	1510	1460	2	535	560	510	2	"
Titanox (RA)	25	3-3	1530	1620	1440	2	820	910	730	2	"
"	50	3-3	1170	1210	1130	2	890	900	880	2	"
"	75	3-3	1185	1200	1170	2	490	580	400	2	"
Fe_2O_3	25	2-2	1090	1100	1080	2	460	480	440	2	"
"	50	2-2	1180	1220	1140	2	485	510	460	2	"
"	75	3-3	1115	1180	1050	2	420	430	410	2	"

TABLE VII

ASBESTINE FILLERS IN CHR-M-60 EPOXY-MODIFIED SILICONE RESIN[a]

Resin No.	Filler[b]	Glue Line, Mils	Shear Strength, psi: Room Temperature Aver.	Room Temperature High	Room Temperature Low	Room Temperature No. Tests	500°F Aver.	500°F High	500°F Low	500°F No. Tests	Failure, % Adhesive
M-60[c]	None	2-2	1155	1180	1110	6	670	810	540	6	50
"	Asbestine X	3-3	1165	1220	1080	6	680	720	640	6	"
"	Asbestine 3X	2-2	960	1030	830	4	575	600	550	4	"
"	Asbestine 5X	2-2	995	1020	970	4	725	800	580	4	"
"	Asbestine FT	2-2	945	1040	920	4	585	600	560	4	"
"	None	4-4	1375	1450	1300	2	420	440	400	2	100
"	Asbestine X	4-4	1345	1390	1300	2	530	450	500	2	50
"	Asbestine 3X	3-3	1230	1270	1190	2	580	620	540	2	"
"	Asbestine 5X	5-5	1330	1340	1320	2	705	780	630	2	"
"	Asbestine FT	4-4	1220	1280	1160	2	595	600	590	2	"
M-60[d]	None	4-4	1405	1600	1210	2	330	360	300	2	"
"	Asbestine X	3-3	1170	1230	1110	2	605	630	580	2	"
"	Asbestine 3X	3-3	1120	1140	1100	2	610	790	430	2	"
"	Asbestine 5X	3-3	1220	1250	1190	2	635	650	620	2	"
"	Asbestine FT	3-3	1140	1160	1120	2	420	440	400	2	"

a. Blends of 80 percent DC-2103, 20 percent Epon 834
b. 30 parts filler per hundred parts resin
c. Batches prepared at different times by the standard method
d. Prepared by room-temperature solution blending at the same time as standard batch directly above.

TABLE VIII

DC-2103 - EPON 834 - ASBESTINE X COMPOSITIONS

Resin No.	Composition: DC-2103, %	Composition: Epon 834, %	Composition: Asbestine X, phr[a]	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
M-109	90	10	75	3-3	1165	1270	1060	2	760	790	730	2	75
"	"	"	100	3-3	1160	1190	1130	2	860	890	830	2	"
"	"	"	150	3-3	1115	1130	1100	2	525	540	510	2	"
"	"	"	200	3-3	665	670	660	2	400	410	390	2	"
M-110	85	15	50	3-3	840	1000	680	2	595	600	590	2	100
"	"	"	75	3-3	1000	1020	980	2	630	640	620	2	"
"	"	"	100	3-3	1000	1010	990	2	700	770	630	2	"
"	"	"	150	3-3	1205	1310	1100	2	760	780	740	2	"
"	"	"	200	3-3	1010	1140	980	2	570	600	540	2	"
M-60	80	20	50	3-3	1155	1210	1100	2	800	810	790	2	50
"	"	"	60	3-3	970	980	960	2	610	610	610	2	"
"	"	"	70	3-3	1005	1010	1000	2	685	700	670	2	"
"	"	"	80	3-3	975	980	970	2	600	630	570	2	"
"	"	"	90	3-3	860	900	920	2	550	560	540	2	"
"	"	"	100	3-3	800	860	740	2	650	650	650	2	"
"	"	"	150	3-3	645	690	600	2	590	600	580	2	75
"	"	"	200	3-3	255	270	240	2	195	200	190	2	100

a. Parts per hundred of resin

TABLE IX

DC-803 - EPON 834 - ASBESTINE X COMPOSITIONS

Resin No.	Composition: DC-803, %	Composition: Epon 834, %	Composition: Asbestine X, phr	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
M-230	95	5	None	1-1	1405	1420	1390	2	310	330	290	2	100
"	"	"	50	3-3	885	910	860	2	395	400	390	2	"
"	"	"	100	3-3	1060	1120	1000	2	515	530	500	2	"
"	"	"	150	3-3	755	820	710	2	430	440	420	2	"
M-231	90	10	None	1-1	1440	1470	1410	2	335	340	330	2	"
"	"	"	50	3-3	1040	1100	980	2	370	400	340	2	"
"	"	"	100	3-3	900	930	870	2	315	330	300	2	"
"	"	"	150	3-3	760	780	740	2	355	360	350	2	"
M-232	85	15	None	1-1	1300	1360	1240	2	510	530	490	2	"
"	"	"	50	3-3	1000	1000	1000	2	320	340	300	2	"
"	"	"	100	3-3	1115	1140	1090	2	345	360	310	2	"
"	"	"	150	3-3	910	920	900	2	375	380	370	2	"
M-233	80	20	None	1-1	1690	1720	1660	2	490	490	490	2	"
"	"	"	50	3-3	1215	1230	1200	2	325	340	310	2	"
"	"	"	100	3-3	980	1010	950	2	380	400	360	2	"
"	"	"	150	3-3	915	940	890	2	360	370	350	2	"

TABLE X

CHR-122 - EPON 834 - ASBESTINE X COMPOSITIONS

Resin No.	Composition: CHR-122, %	Composition: Epon 834, %	Composition: Asbestine X phr	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure % Adhesive
M-226	95	5	None	2-2	1185	1190	1180	2	635	640	610	2	100
"	"	"	50	3-3	800	800	800	2	770	800	640	2	"
"	"	"	100	3-3	885	980	790	2	630	650	610	2	"
"	"	"	150	3-3	810	890	730	2	590	600	580	2	"
M-227	90	10	None	2-2	1115	1270	960	2	420	440	400	2	"
"	"	"	50	3-3	1105	1120	1090	2	845	860	810	2	"
"	"	"	100	3-3	1110	1120	1100	2	710	730	690	2	"
"	"	"	150	3-3	935	980	890	2	585	600	570	2	"
M-228	85	15	None	2-2	1280	1420	1140	2	730	760	700	2	"
"	"	"	50	3-3	1045	1160	930	2	810	820	800	2	"
"	"	"	100	3-3	985	1010	960	2	795	820	770	2	"
"	"	"	150	3-3	865	890	840	2	565	590	540	2	"
M-229	80	20	None	2-2	1445	1570	1320	2	390	400	380	2	"
"	"	"	50	3-3	1115	1130	1100	2	785	820	750	2	"
"	"	"	100	3-3	930	940	920	2	735	780	690	2	"
"	"	"	150	3-3	800	860	740	2	575	610	540	2	"

TABLE XI

ASBESTINE 5X FILLER IN EPOXY-MODIFIED SILICONE RESINS

Resin No.	Composition: Silicone	Composition: Organic	Composition: %	Filler, phr	Glue Line, Mils	Shear Strength, psi: Room Temperature: Aver.	Room Temperature: High	Room Temperature: Low	Room Temperature: No. Tests	500°F: Aver.	500°F: High	500°F: Low	500°F: No. Tests	Failure, % Adhesive
M-189	DC-803	Epon 834	20	25	3-3	980	980	980	2	75	90	60	2	100
"	"	"	20	50	3-3	1070	1100	1040	2	300	310	290	2	"
"	"	"	20	75	3-3	1225	1260	1190	2	895	930	860	2	50
M-236	"	Araldite 6020	20	100	2-2	685	730	640	2	515	540	490	2	100
M-193	DC-2103	Araldite 6040	10	25	3-3	915	970	860	2	775	940	610	2	50
"	"	"	10	50	3-3	1180	1180	1180	2	580	590	570	2	75
"	"	"	10	75	3-3	1075	1080	1070	2	620	640	600	2	75
M-194	"	"	30	25	3-3	595	600	590	2	500	520	480	2	75
"	"	"	30	50	3-3	616	700	530	2	535	570	500	2	75
"	"	"	30	75	3-3	610	620	600	2	460	530	390	2	100
M-191	DC-2103LV	Epon 834	10	25	3-3	1280	1290	1270	2	675	690	660	2	"
"	"	"	10	50	3-3	1130	1140	1120	2	870	910	830	2	75
"	"	"	10	75	3-3	735	760	710	2	205	210	200	2	100
M-122	CHR-141	"	30	25	3-3	920	940	900	2	590	610	570	2	50
"	"	"	30	50	3-3	925	950	900	2	625	630	620	2	"
"	"	"	30	75	3-3	960	970	950	2	610	670	550	2	"
M-235	CHR-203	"	10	100	2-2	685	700	670	2	465	500	430	2	100
M-234	"	"	20	100	2-2	680	720	640	2	485	510	460	2	"

TABLE XII

FILLERS IN SILICONE-EPOXY-PHENOLIC RESIN BLENDS

Resin No.	Composition: Silicone	%	Epoxy	%	Phenolic	%	Filler	phr	Glue Line, Mils	Shear Strength, psi: Room Temperature Aver.	High	Low	No. Tests	500°F Aver.	High	Low	No. Tests	Failure, % Adhesive
M-207	DC-803	75	Ep-1001	12.5	Pl-5010	12.5	Alum. Dust	25	4-4	895	1110	680	2	665	700	630	2	100
"	"	75	"	12.5	"	12.5	"	50	4-4	695	700	690	2	495	510	480	2	"
"	"	75	"	12.5	"	12.5	"	100	4-4	940	980	900	2	470	480	460	2	"
M-209	"	75	"	12.5	Pl-5023	12.5	"	25	4-4	635	780	490	2	415	500	330	2	"
"	"	75	"	12.5	"	12.5	"	50	4-4	655	680	630	2	525	560	490	2	"
"	"	75	"	12.5	"	12.5	"	100	4-4	585	600	570	2	450	490	410	2	"
M-218A[a]	"	80	Ep-834	10	Pl-5010	10	Asb.5X	100	3-3	990	1010	980	2	575	590	560	2	"
M-220A	"	80	"	5	"	15	"	100	3-3	960	960	960	2	580	600	560	2	"
M-222A	"	80	"	10	Pl-5023	10	"	100	3-3	955	1000	910	2	435	480	390	2	"
M-224A	"	80	"	5	"	15	"	100	3-3	885	900	870	2	290	300	280	2	"

a. The modified resins marked "A" were prepared using fresh lots of phenolic resins (see Table III)

F. CURING CATALYSTS FOR EPOXY-MODIFIED SILICONE RESIN

Object: To develop a curing agent for epoxy-modified silicone resins which would substantially reduce both the time and temperature of the cure required to produce maximum adhesive strength.

Results: One formulation tested in this preliminary study offered definite promise as a curing agent for the epoxy-modified silicone resins. The addition to CHR-M-60 epoxy-modified silicone resin of a mixture of one part of dicyandiamide dissolved in two parts of dimethyl formamide produced in three hours at 320°F 80 percent of the average room-temperature shear strength developed after the long high-temperature cure, (16 hours at 480°F). The test results were, however, quite erratic.

Materials:

- DC-2103
- CHR-M-60 resin
- Phthalic anhydride
- Dicyandiamide
- Dimethyl formamide
- m-Phenylene diamine
- Triethanolamine

Procedure: Phthalic anhydride and dicyandiamide were thoroughly ground into separate samples of CHR-M-60 or DC-2103 resin solutions. The solution of dicyandiamide in dimethyl formamide and the amines were blended into the resin solution by stirring. The mixtures were applied to aluminum panels, and allowed to stand for one and one-half hours at room temperature to allow evaporation of solvent. The lap joints were then assembled in the jigs and oven-cured at 320°F under 25 psi for the period of time indicated in Table XII.

Data: The results of the shear strength tests appear in Table XII.

TABLE XIII

CURING CATALYSTS FOR EPOXY-MODIFIED SILICONE RESIN

Resin No.	Curing Catalyst	phr	Cure, Hours at 320°F	Glue Line, Mils	Shear Strength, psi: Room Temperature Aver.	Room Temperature High	Room Temperature Low	Room Temperature No. Tests	500°F Aver.	500°F High	500°F Low	500°F No. Tests	Failure, % Adhesive
M-60	None	--	--[a]	2-2	1155	1180	1110	6	670	810	540	6	50
"	"	--	3	1-1	80	160	0	2	0	0	0	2	100
"	Phthalic anhydride	4	4	1-1	130	260	0	2	45	90	0	2	"
"	Dicyandiamide	0.5	4	2-2	0	0	0	2	0	0	0	2	"
"	"	1	4	2-2	510	530	490	2	180	200	160	2	"
"	"	4	4	1-1	180	200	160	2	0	0	0	2	"
"	"	5	4	2-2	80	160	0	2	0	0	0	2	"
"	"	1	3	2-2	215	240	190	2	150	190	110	2	"
"	Dimethylformamide	2	3	2-2	440	470	410	2	210	240	180	2	"
"	1 Dicyandiamide:2 Dimethylformamide	3	3	2-2	835	860	820	2	350	390	310	2	"
"	" "	3	4	2-2	818	980	730	4	115	190	0	4	"
"	" "	3	6	2-2	730	970	560	4	225	370	140	4	"
"	" "	3	8	2-2	842	1030	400	4	0	0	0	4	"
"	" "	3	24	2-2	970	1010	940	4	400	520	190	4	"
"	" "	4	3	3-3	515	810	160	4	335	370	330	4	"
"	" "	5	3	3-3	795	920	660	4	125	190	80	4	"
"	" "	6	3	3-3	655	780	540	4	55	120	0	4	"
"	m-Phenylene diamine	1	3	2-2	40	80	0	2	0	0	0	2	"
"	Triethanolamine	1	3	2-2	165	210	120	2	60	120	0	2	"
DC-2103	None	--	--[a]	2-2	910	930	860	4	630	670	580	4	"
"	Dicyandiamide	0.5	4	2-2	185	200	170	2	205	220	190	2	"
"	"	1	4	2-2	520	520	520	2	185	200	170	2	"
"	"	5	4	2-2	775	940	610	2	440	560	320	2	"

a. Standard cure, 16 hours at 480°F

G. SHEAR STRENGTH OF RESINS AT TEMPERATURES FROM -70° to 900°F

Object: To determine the effect of increasing amounts of epoxy resin on the shear strength of a silicone resin at elevated temperatures.

Results: The silicone and epoxy-modified silicone resins exhibited a consistent decrease in shear strength as the temperature was raised from -70°F to +900°F (Figure 5). The epoxy resin (uncatalyzed) displayed an increase in shear strength between -70°F and +70°F, and then exhibited a steady and rather rapid decrease.

It is interesting to note in Figure 5 that the shear strength of the three silicone adhesives had a tendency to level off at 700°F to 900°F, and the adhesives showed at least a significant retention of strength at 900°F.

Materials: DC-2103
Epon 834
CHR-M-109 (90 percent DC-2103: 10 percent Epon 834)
CHR-M-60 (80 percent DC-2103: 20 percent Epon 834)

Procedure: The resins were applied to aluminum panels, and lap joints were prepared as described in the Appendix to this report (cured 16 hours at 480°F). Lap joints were pulled at each temperature after a ten-minute soak at that temperature, with the exception of the tests at 900°F.

In our normal testing procedure, the thermocouple is attached to the panels at the lap joint. The portable furnace is then placed around the lap joint which had previously been clamped in the jaws of the test machine. It was found that the wire clip used to attach the thermocouple wire began to fail after five minutes of heating at 900°F. In addition, the temperature did not show a continuous rise; instead, it climbed to approximately 820°F in 45 to 50 seconds, thereupon leveled off until the metal became a dull red color (approximately 2½ minutes), and then resumed its climb to 900°F (approximately 15 seconds). A one-minute soak at 900°F was allowed, and then the shear strength was determined.

Data: The results of the shear strength tests are listed in Table XIII and are shown graphically in Figure 5.

Remarks: It should be noted that no curing catalyst was added to the epoxy resin (or other resins). It is known that higher shear strength values would be shown by the epoxy resin if it contained a curing catalyst and if less rigorous curing conditions were used.

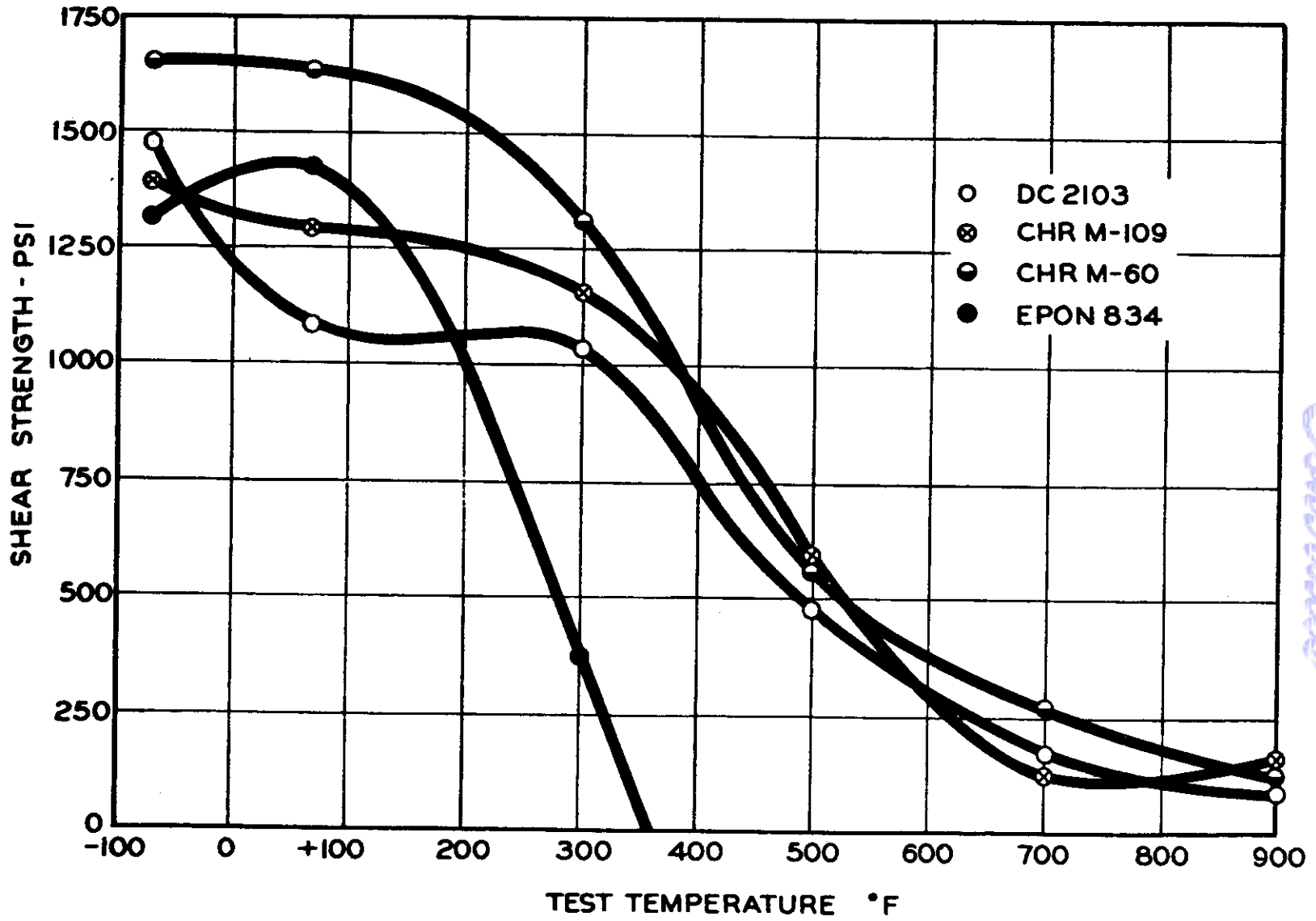

FIG. 6 SHEAR STRENGTH VS. TEMPERATURE

TABLE XIV

SHEAR STRENGTH OF RESINS AT TEMPERATURES FROM -70°F to 900°F

Resin No.	Test Temperature	Glue Line, Mils	Shear Strength, psi[a] Aver.	High	Low	No. Tests
DC-2103	-70°F	2-2	1480	1510	1450	2
"	70°F	2-2	1075	1140	1010	2
"	300°F	2-2	1020	1040	1000	2
"	500°F	2-2	480	500	460	2
"	700°F	2-2	190	200	180	2
"	900°F	2-2	100	110	90	2
Epon 834	-70°F	2-2	1330	1390	1270	2
"	70°F	2-2	1415	1430	1400	2
"	300°F	2-2	375	390	360	2
"	500°F	2-2	0	0	0	2
"	700°F	2-2	0	0	0	2
"	900°F	2-2	0	0	0	2
M-109[b]	-70°F	2-2	1385	1420	1350	2
"	70°F	2-2	1315	1340	1290	2
"	300°F	2-2	1155	1170	1140	2
"	500°F	2-2	590	670	510	2
"	700°F	2-2	120	130	110	2
"	900°F	2-2	115	130	105	2
M-60[c]	-70°F	2-2	1645	1670	1620	2
"	70°F	2-2	1630	1700	1560	2
"	300°F	2-2	1305	1390	1220	2
"	500°F	2-2	570	590	550	2
"	700°F	2-2	260	270	250	2
"	900°F	2-2	105	130	80	2

a. Failure, in every case, was 100 percent adhesive
b. 90 percent DC-2103, 10 percent Epon 834
c. 80 percent DC-2103, 20 percent Epon 834

H. HIGH-TEMPERATURE AGING STUDIES

Object: The object of these experiments was twofold: (1) to study the effect of high-temperature aging on silicone and epoxy-modified silicone structural adhesives, and (2) to to correlate the effect of aging at 600°F with the effect of aging at 500°F, to set up an accelerated aging test.

Results: The effect on the shear strength of the resins when aged at both 500°F and 600°F in the initial aging experiment is shown in Figures 6 to 13 and Tables XIV-A and XIV-B. DC-803 exhibited considerably better resistance to aging than DC-2103; and, similarly, the modification of DC-803 with Epon 834 showed better resistance to aging than did the modification of DC-2103 with Epon 834. The room-temperature shear strength values with the stainless steel panels were about 40 percent higher than those with aluminum panels, but no corresponding increase was found in the high-temperature shear strength values.

Selected modified silicone resins, filled with Asbestine X or aluminum powder, were aged for 24 hours and 72 hours at 600°F. All of the samples containing Asbestine X filler lasted through the 72-hour aging period, and showed shear strength values at 500°F ranging from 165 psi to 310 psi. Those containing aluminum powder showed considerably less resistance to aging.

Three resins, a pure silicone, an epoxy-modification of that silicone, and an epoxy-phenolic-silicone blend, were aged for 72, 100, and 200 hours at 600°F. All three of the resins showed fair room temperature strength after the 200-hour accelerated aging, but only the pure silicone resin was useful at 500°F after the 200-hour aging. The ternary blend showed good retention of strength at 500°F after 72 hours at 600°F, but failed on the high-temperature test after 100 hours. The epoxy-modified silicone resin showed considerable loss of high-temperature strength after 72 hours at 600°F.

Procedure: For the initial aging experiment (Tables XIV-A and XIV-B), a large number of lap joints, sufficient for the entire aging study, were prepared as described in the Appendix to this report. Lap joints for each resin were tested after the initial cure of 16 hours at 480°F, and thereafter four lap joints which had been aged for the period specified were tested (two at 70°F and two at 500°F).

Data: The results of the shear strength tests appear in Tables XIV-A and B, XV, and XVI, and in Figures 6 to 13.

Remarks: The scales of Figures 6 to 13 were adjusted so that the time of failure of the resins at 600°F could be compared with the time of failure at 500°F. Although the relation of aging at 600°F to that at 500°F appears to be different for each resin and metal, it is felt that a short accelerated aging test at 600°F (e.g., 72 or 120 hours) can be extremely helpful in screening various adhesives, instead of a prohibitively long (seven weeks) aging test at 500°F.

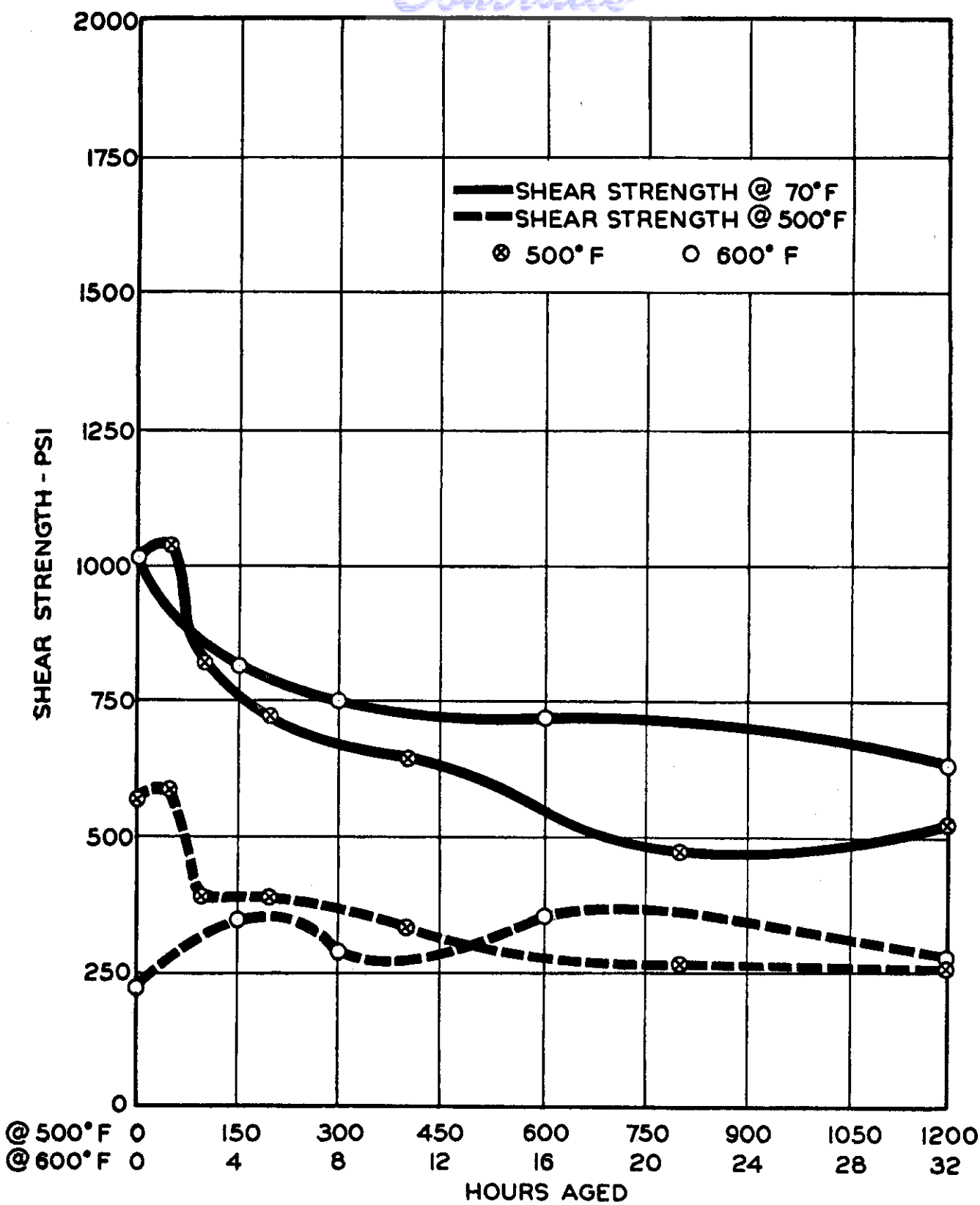

FIG. 7 500°F AND 600°F AGING OF DC 2103 ON ALUMINUM

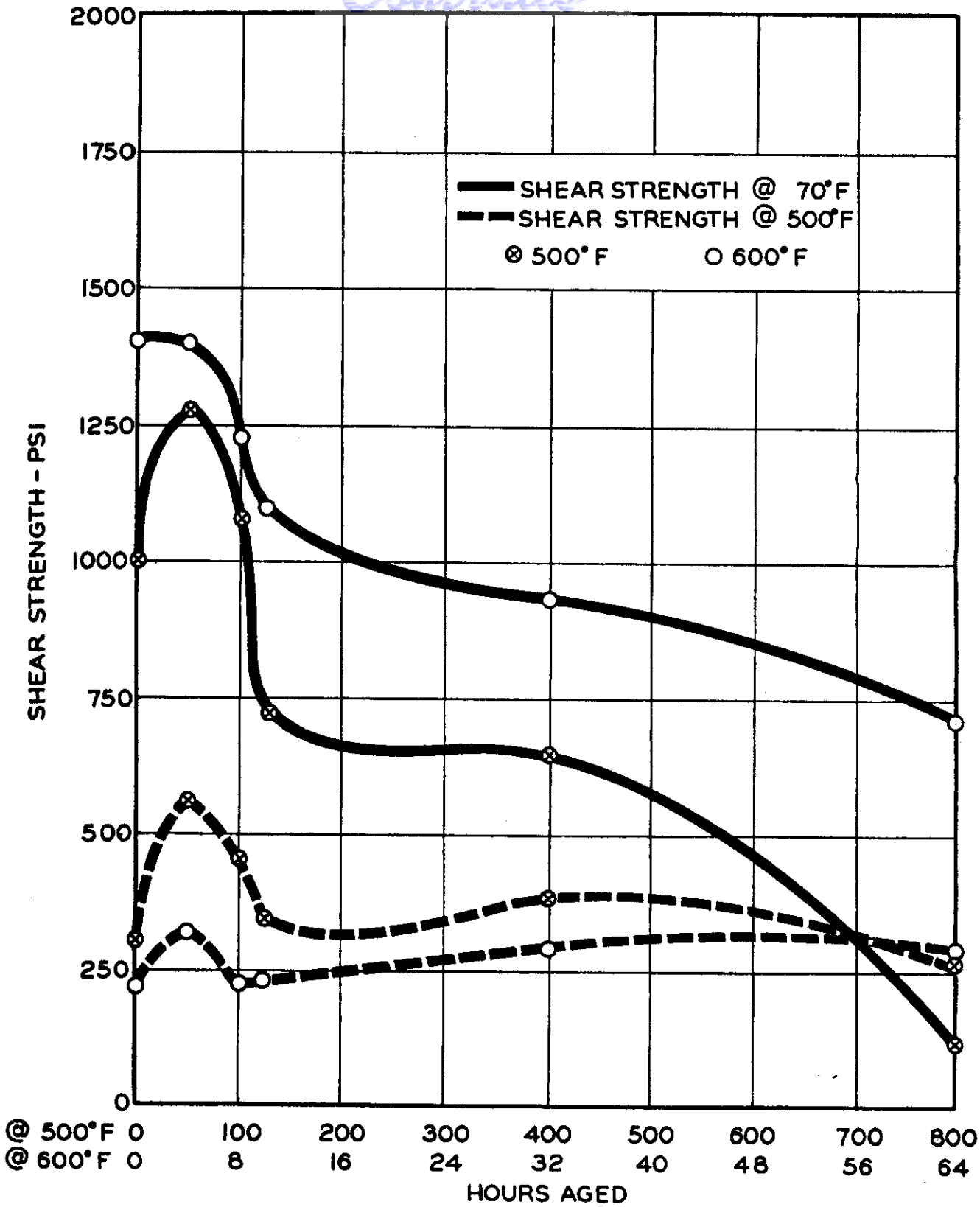

FIG. 8 500° F AND 600°F AGING OF DC 2103 ON STAINLESS STEEL

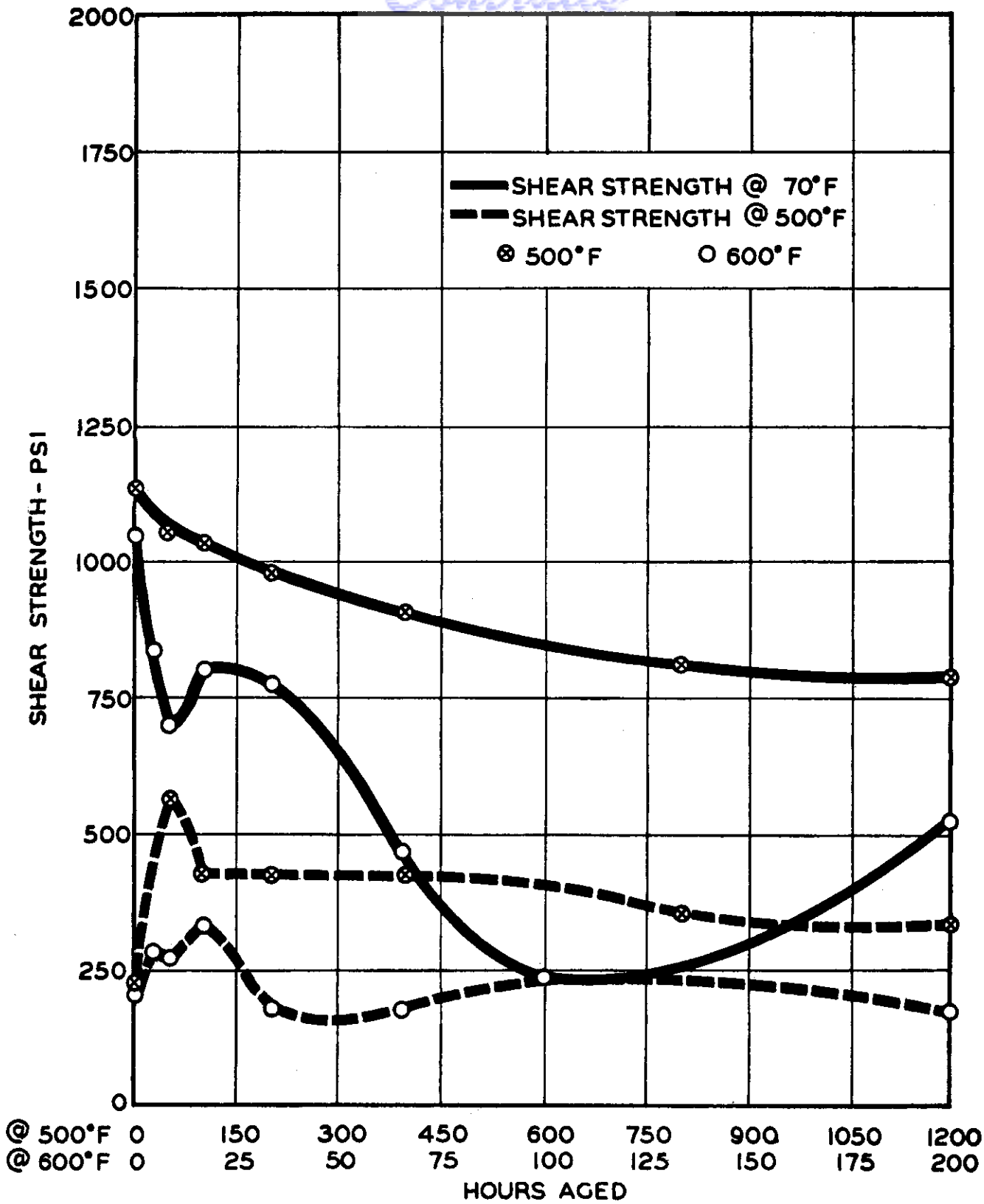

FIG. 9 500° F AND 600° F AGING OF DC 803 ON ALUMINUM

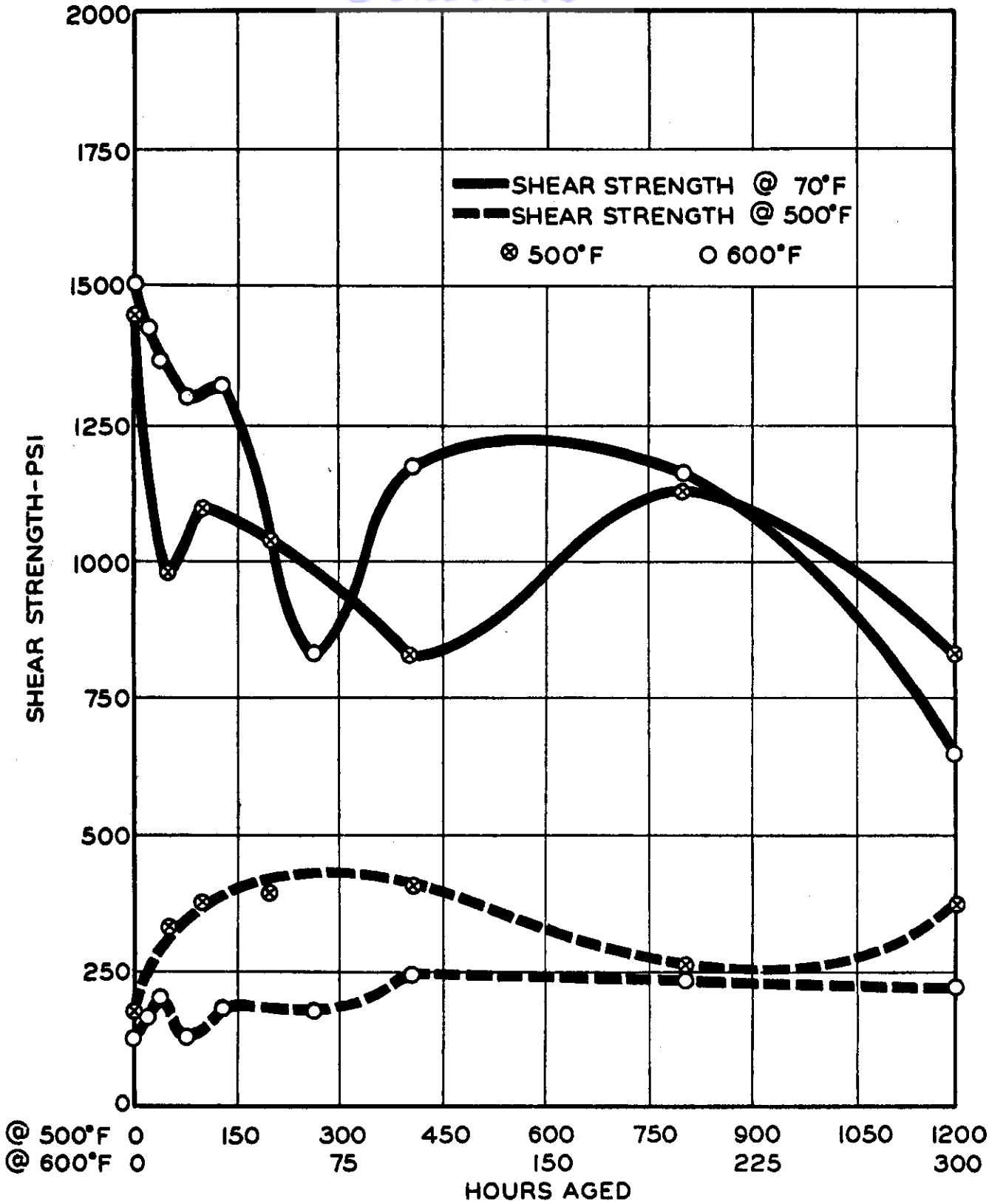

FIG. 10 500° F AND 600°F AGING OF DC 803 ON STAINLESS STEEL

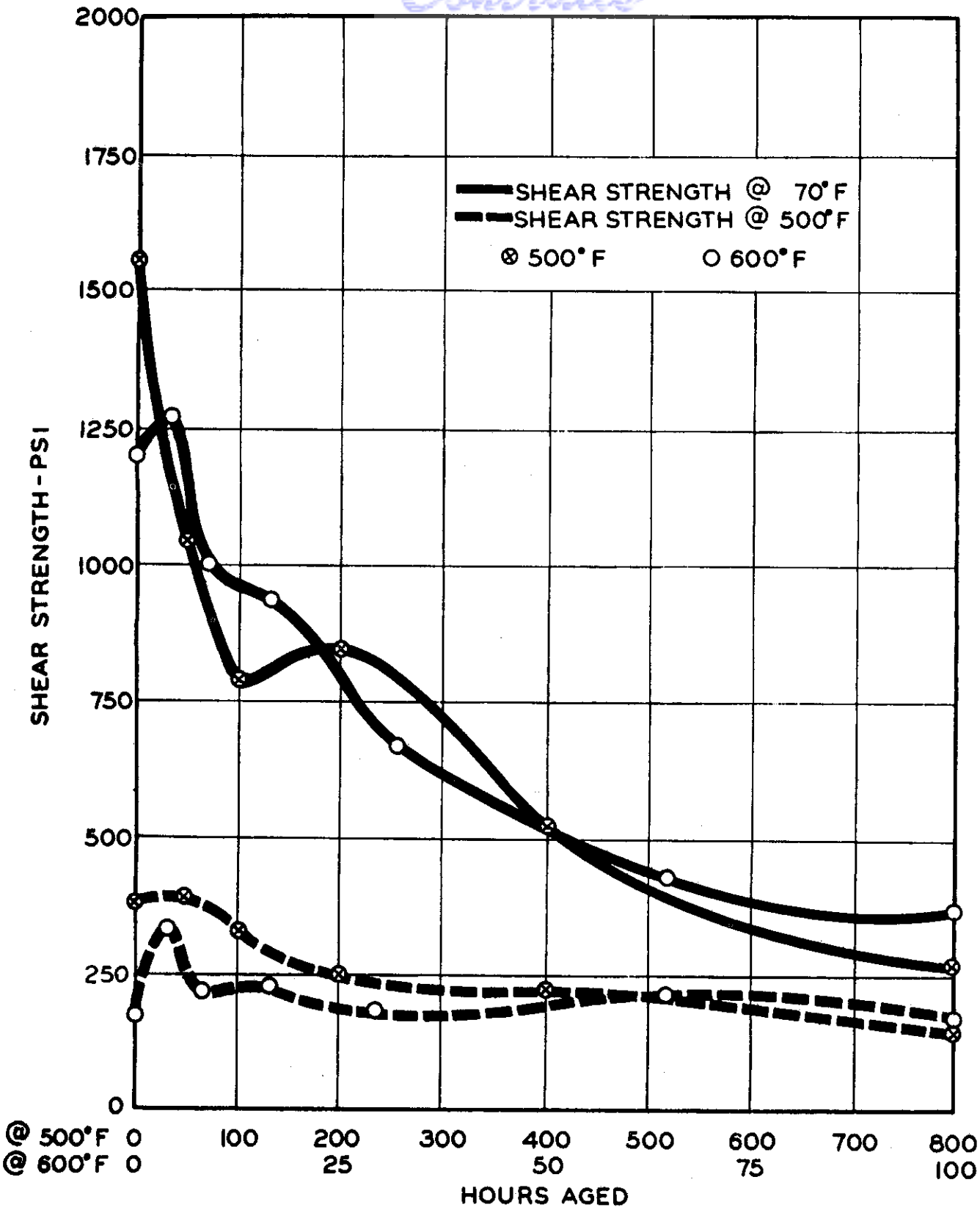

FIG. 11 500°F AND 600°F AGING OF CHR M-42 ON ALUMINUM

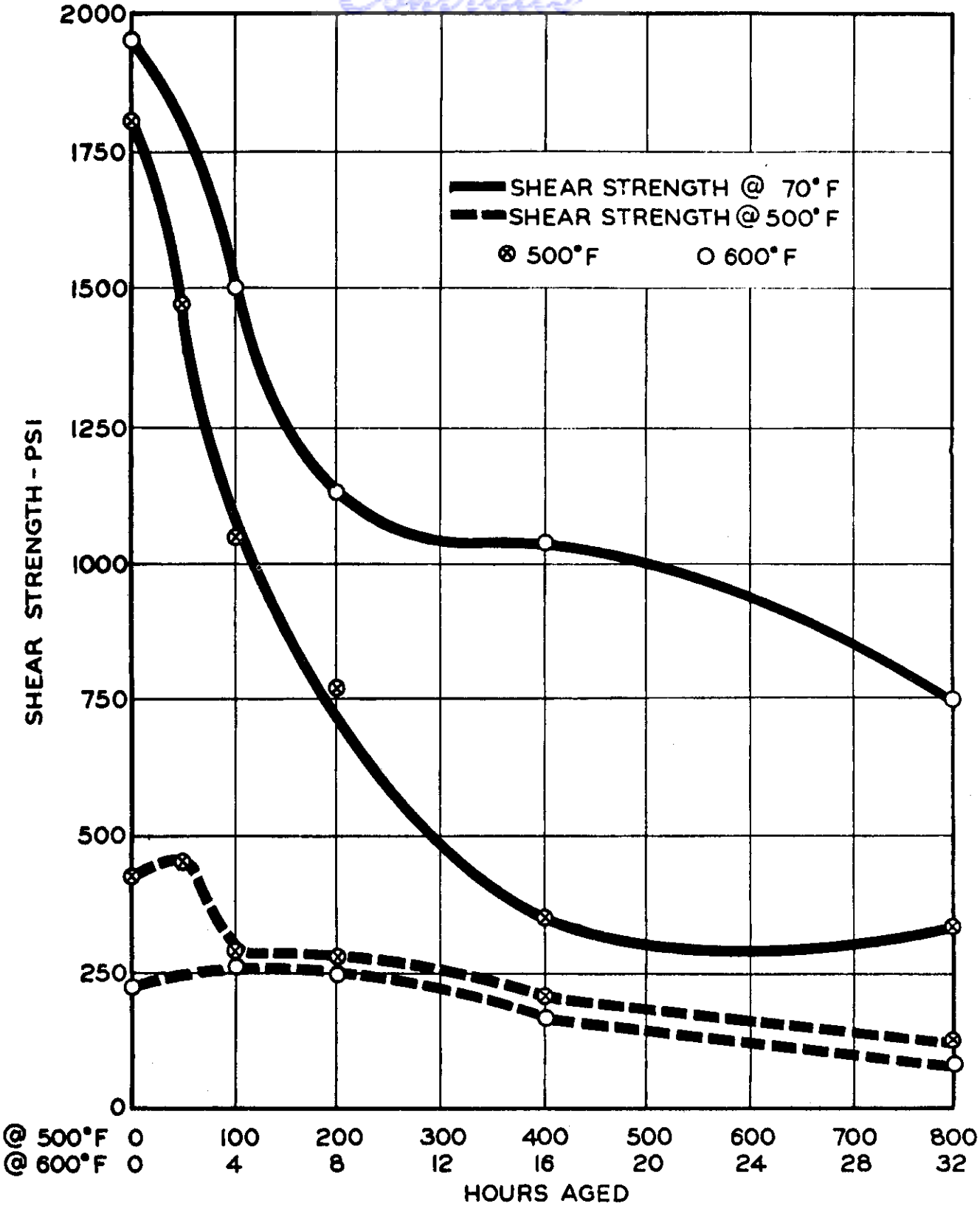

FIG. 12 500° F AND 600° F AGING OF CHR M-42 ON STAINLESS STEEL

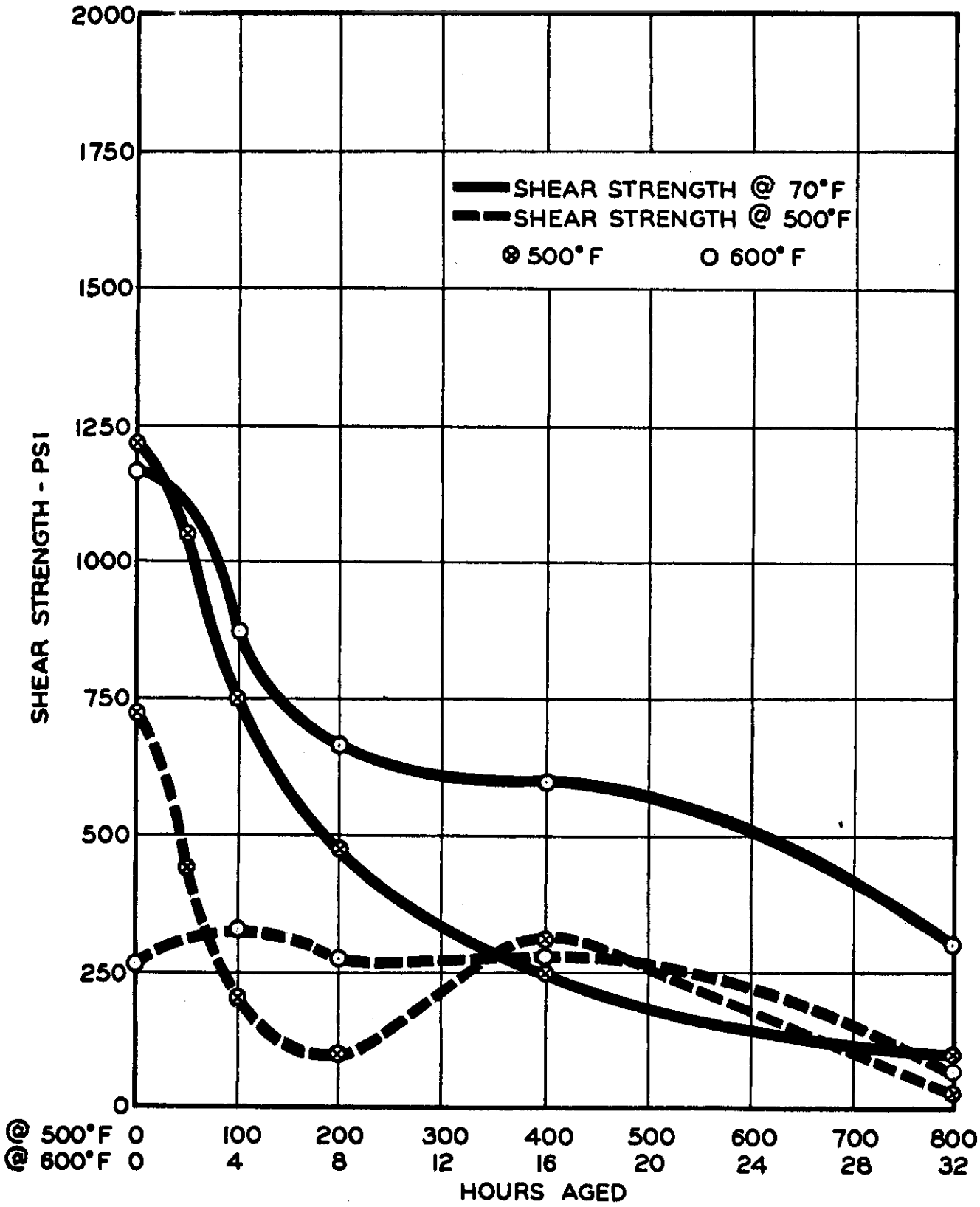

FIG. 13 500°F AND 600°F AGING OF CHR M-60 ON ALUMINUM

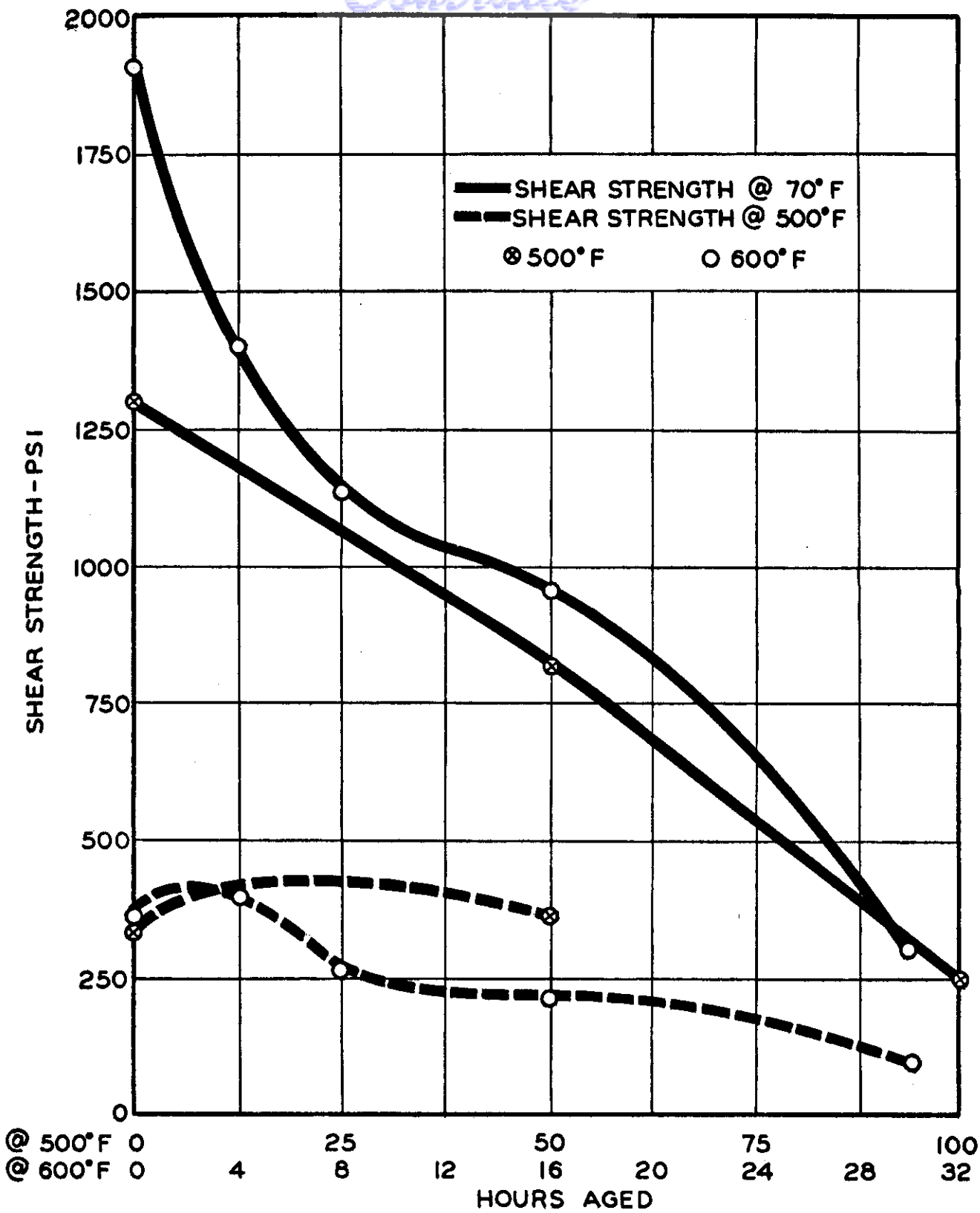

FIG. 14 500° F AND 600° F AGING OF CHR M-60 ON STAINLESS STEEL

TABLE XV

HIGH-TEMPERATURE AGING COMPARISON, 500°F AND 600°F (ALUMINUM PANELS)

Resin No.	Testing Temperature, °F	Initial Value	Shear Strength, psi, After Aging: Hours Aged at 500°F					
			50	100	200	400	800	1200
DC-2103	70	1025	1045	825	730	655	485	525
"	500	565	585	385	390	330	0	255
DC-803	70	1135	1065	1040	990	905	815	790
"	500	235	565	415	415	415	355	330
M-60[a]	70	1215	1030	755	485	250	100	0
"	500	725	435	205	100[c]	0	0	0
M-42[b]	70	1560	1055	790	850	525	270	0
"	500	385	395	325	250	225	150[c]	0
Epon 834	70	2000	0	800	0	0	0	0
"	500	260	0	155	0	0	0	0

Resin No.	Testing Temperature, °F	Initial Value	Hours Aged at 600°F							
			4	8	16	32	64	100	200	300
DC-2103	70	1020	820	750	720	640	0	0	0	0
"	500	235	350	285	355	260	0	0	0	0
DC-803	70	1050	840	700	800	780	450	0	520	0
"	500	245	285	270	340	190	190	240[c]	190	0
M-60[a]	70	1170	880	660	600	300	0	0	0	0
"	500	260	325	275	270	80	0	0	0	0
M-42[b]	70	1200	1270	100	940	670	440[c]	380[c]	0	0
"	500	180	320	215	230	190	210[c]	160[c]	0	0
Epon 834	70	1750	0	0	0	0	0	0	0	0
"	500	180	0	0	0	0	0	0	0	0

a. 80 percent DC-2103, 20 percent Epon 834
b. 80 percent DC-803, 20 percent Epon 834
c. One value only, all others average of two values

TABLE XVI

HIGH-TEMPERATURE AGING COMPARISON 500°F AND 600°F (STAINLESS STEEL PANELS)

Resin No.	Testing Temperature, °F	Initial Value	Shear Strength, psi, After Aging							
			Hours Aged at 500°F							
			50	100	200	400	800	1200		
DC-2103	70	1000	1290	1090	740[c]	645	110[c]	0		
"	500	310	560	460	345	390	260	0		
DC-803	70	1455	995	1100	1030	810	1130	820		
"	500	175	330	380	395	410	240	280		
M-60[a]	70	1305	815	250[c]	0	0	0	0		
"	500	340	370	0	0	0	0	0		
M-42[b]	70	1810	1475	1050	765	355	340[c]	0		
"	500	430	455	285	280	205	120[c]	0		
			Hours Aged at 600°F							
			4	8	16	32	64	100	200	300
DC-2103	70	1400	1400	1240	1100	940	740[c]	0	0	0
"	500	220	320	230	235	295	260[c]	0	0	0
DC-803	70	1500	1430	1380	1300	1320	830	1180	1150	640
"	500	130	170	200	130	190	180	255	240	220[c]
M-60[a]	70	1900	1400	1140	960	300	0	0	0	0
"	500	350	400	265	210	100[c]	0	0	0	0
M-42[b]	70	1950	1500	1130	1040	750	0	0	0	0
"	500	230	265	250	190	90	0	0	0	0

a. 80 percent DC-2103, 20 percent Epon 834
b. 80 percent DC-803, 20 percent Epon 834
c. One value only, all others average of two values

TABLE XVII

600°F AGING OF SILICONE-ORGANIC RESIN BLENDS

Resin No.	Composition: Silicone	%	Epoxy	%	Phenolic	%	Filler	phr	Glue Line, Mils	Shear Strength, psi[a]; Hours Aging at 600°F: Room Temperature: Initial	24 Hrs.	72 Hrs.	500°F: Initial	24 Hrs.	72 Hrs.
M-230	DC-803	95	Ep-834	5	None		Asbest.X	100	4	1075	780	615	445	425	220
M-232	"	85	"	15	"		"	100	4	1030	845	645	395	385	295
M-227	CHR-122	90	"	10	"		"	50	4	1000	695	605	780	460	205
M-228	"	85	"	15	"		"	50	4	890	860	450	545	295	165
M-207	DC-803	75	Ep-1001	12.5	Pl-5010	12.5	None		2	955	480	510	615	360	365
M-222	"	80	Ep-834	10	Pl-5023	10	Asbest.X	50	4	890	715	540	410	315	255
"	"	80	"	10	"	10	"	100	4	880	665	565	305	445	310
"	"	80	"	10	"	10	"	150	4	840	685	595	360	410	220
M-224	"	80	"	5	"	15	"	50	4	790	660	415	530	395	230
"	"	80	"	5	"	15	"	100	4	685	605	510	295	310	170
"	"	80	"	5	"	15	"	150	4	680	620	510	300	385	275
M-222	"	80	"	10	"	10	Alum.Dust	50	3	930	295	0	475	190	0
"	"	80	"	10	"	10	"	100	3	755	385	115	490	145	0
"	"	80	"	10	"	10	"	150	3	715	320	170	535	165	0
M-224	"	80	"	5	"	15	"	50	3	630	175	0	455	0	0
"	"	80	"	5	"	15	"	100	3	800	225	115	500	0	0
"	"	80	"	5	"	15	"	150	3	905	230	190	520	0	0

a. All values average of two tests

TABLE XVIII

600°F AGING OF SILICONE-ORGANIC RESIN BLENDS

Resin No.	Glue Line, Mils	Shear Strength, psi[a]; Hours Aging at 600°F							
		Room Temperature				500°F			
		Initial	72 Hrs.	100 Hrs.	200 Hrs.	Initial	72 Hrs.	100 Hrs.	200 Hrs.
DC-803	2	1400	720	675	655	300	260	245	210
M-231[b]	2	1440	495	390	290	335	95	0	0
M-218A[c]	2	1140	470	420	410	555	370	0	0

a. All values average of two tests
b. 90 parts DC-803, 10 parts Epon 834
c. 80 parts DC-803, 10 parts Epon 834, 10 parts Pliophen 5010

TABLE XIX

DESCRIPTION AND SOURCE OF COMMERCIAL MATERIALS

Aluminum Company of America	
Atomized Aluminum Dust 101	Aluminum dust
Ciba Company, Inc.	
Araldite 6010	Epoxy resin
" 6020	" "
" 6030	" "
" 6040	" "
" 6060	" "
Dow Corning Corporation	
DC-803	Silicone protective coating resin
DC-840	Silicone blending resin
DC-2103	Silicone bonding resin
International Talc Co., Inc.	
Asbestine X	Natural magnesium silicate, crystalline
" 3X	" " " small amount fiber
" 5X	" " " large amount fiber
" FT	" " " fibrous
Reichhold Chemicals, Inc.	
Plyophen 5010	Phenolic resin
" 5012	" "
" 5015	" "
" 5023	" "
" 5027	" "
" 5516	" "
Shell Chemical Corporation	
Epon 828	Epoxy resin
" 834	" "
" 864	" "
" 1001	" "
Titanium Pigment Corporation	
Titanox RA	TiO_2, rutile, 0.4 micron
Titanox RA-168-LO	TiO_2, anatase, 0.3 micron

II. DISCUSSION

EXPERIMENTAL PROGRAM

The program for the experimental work under this phase may be broken down into two broad classifications: (1) a study of means of improving the CHR-M-60 epoxy-modified silicone resin developed previously under this contract, and (2) extension of the basic method of modification to other combinations of silicone and organic resins, with particular emphasis on silicone resins of known composition prepared in this laboratory. The first part of the program consisted of a detailed examination of the copolymerization or modification method, and a study of the composition variables of the CHR-M-60 adhesive mixture, including fillers and solvents. A brief study was made on the effect of curing agents as a means of shortening both the curing time and the curing temperature required to develop optimum shear strength of the resins. An extended aging study was also run with the CHR-M-60 epoxy-modified silicone resin on stainless steel and aluminum test panels at 500°F and at 600°F. One object of this study was to set up a relationship so that 600°F aging could be used as an accelerated aging test in place of the extended aging (1200 hours) at 500°F. A determination of the shear strength at temperatures from -65°F to +900°F was also made on the CHR-M-60 epoxy-modified silicone resin and the component resins.

The second phase of the program centered on the preparation of silicone resins in this laboratory and the use of those resins of known composition to prepare modifications with the organic resins which proved most successful with the commercial silicone resins.

The effect of variations in the preparatory procedure of the silicone resins, known to affect the extent and to some degree the direction of the polymerization, was studied as a means of improving the adhesive strength of the organo-modified silicones. An extension of this work was the modification of silicone resins with phenolic resins, and the preparation of ternary blends of silicone-epoxy-phenolic resins.

EPOXY-MODIFIED COMMERCIAL SILICONE RESINS

As indicated in the section above, initial work was based on the CHR-M-60 epoxy-modified silicone resin, consisting of 20 parts of Epon 834 and 80 parts of DC-2103 resins. A number of variations were made around this composition, covering a

range of 5 to 40 percent of epoxy resin, and using a series of Epon and Araldite epoxy resins. Epon 834 and Araldite 6020, which are very similar in composition and molecular weight, have consistently shown the best results when used to modify DC-2103 and other silicone resins. These epoxy resins have a molecular weight ranging from about 600 to 800, and contain an average of two epoxy groups and one hydroxyl group per molecule.

Modifications of DC-2103 showed the highest shear strength values at 500°F, and good room-temperature shear strength. DC-2103 LV (low viscosity) displayed shear strengths considerably better than those obtained with DC-2103 HV (high viscosity). Modifications of DC-803, while showing lower initial shear strength values than modifications of DC-2103, were found to have outstanding resistance to aging at 500° and 600°F (see High Temperature Aging Study, Section H). An epoxy modification of DC-840 showed good room-temperature shear strength, but only fair high-temperature shear strength.

Four samples of epoxy-modified DC-803 resin were prepared for a study of the effect of several variations in the modification procedure. The sample prepared in "Mini-lab" equipment showed a somewhat higher shear strength value at 500°F than the other samples. In the larger reaction flask, reduction of the reaction mixture temperature caused by passing nitrogen gas continuously through the mixture apparently resulted in noticeably lower shear strength values. A considerably higher reaction mixture temperature resulting from the addition of Diethyl Carbitol led to significantly higher shear strength values. This improvement in the modification procedure was found near the end of the work under this contract, too late to be incorporated as a change in the standard procedure.

Several of the epoxy-modified silicone resins were tested on stainless steel panels instead of the standard aluminum panels. These bonds showed normal shear strength at room temperature, but considerably lower shear strength at 500°F.

EPOXY-MODIFIED CHR SILICONE RESINS

Three different CHR silicone resins were prepared under neutralized and isothermal conditions, and by incremental addition of the silane monomers, and epoxy-modifications of these resins were prepared and tested. Shear strength data obtained in tests on these resins varied so little that only in a few cases could specific conclusions be drawn concerning the effect

of variations in the method of preparing the silicone resins.

Epoxy modifications of CHR-122, a relatively hard silicone resin with an R/Si ratio of 1.20 and containing 50 percent phenyl groups attached to the silicon-oxygen structure, showed somewhat better shear strength values at 500°F than the other modified silicone resins. Neutralization of the hydrolysis medium during preparation of CHR-122 resin produced, in general, lower shear strength values. Maintaining the hydrolysis medium at a constant temperature of 18°C had little effect on the shear strength values. With CHR-141 resin (R/Si ratio 1.40 and 57 percent methyl), variations in the method of preparing the resin produced, in each case, shear strength values somewhat lower than those obtained by the standard method. Variations in the preparation of CHR-183 resin (R/Si ratio 1.30 and 46 percent methyl) produced shear strength values slightly higher than those normally obtained. Adding the silane monomers separately to the hydrolysis media produced poor results in each of the three cases.

CHR-203 (R/Si ratio of 1.10 and 54 percent methyl), a somewhat harder resin than CHR-122, showed shear strength values nearly equivalent to CHR-122, but no better.

The bonds on stainless steel panels showed considerably higher shear strength values at room temperature and lower values at 500°F.

PHENOLIC-MODIFIED SILICONE RESINS

Attempts to modify the silicone adhesive-type resins directly with commercial reactable phenolics were unsuccessful. The phenolic resins as received from the manufacturer were "A" stage resins and contained some material such as hexamethylene tetramine which acted as a basic catalyst and supplied the necessary methylene cross-linking groups. The use of basic catalysts with the phenolic resins promotes a rapid reaction to form a reticulated polymer. Acid catalysts tend to form a more linear polymer at a somewhat slower speed. The initial modification experiments with the phenolic resins in basic medium failed due to rapid gelling and separation of the phenolic resin. The silicone condensation is known to proceed much more rapidly in an acidic medium than in a basic medium, therefore it was felt that an acidic medium might be more advantageous for this modification reaction. Indeed, the modification experiments with neutralized and slightly acidic phenolic resins indicated at least borderline compatibility. Later work on ternary blends (phenolic, epoxy, silicone, Section D) showed much more promising results.

SILICONE-EPOXY-PHENOLIC RESIN SOLUTION BLENDS

Earlier attempts to prepare phenolic-modified silicone resins (Section C) were not successful because of the lack of compatibility between the phenolic and silicone resins and the relatively high speed of polymerization, or cure, of the phenolic resin. Certain phenolic and epoxy resins, however, have been found to be readily miscible. These mixtures were added to silicone resin solutions, and relatively stable solution blends were produced. Lap joints prepared from the freshly mixed blends yielded good shear strength values at 500°F, several of these being in the range of 800 to 900 psi.

The various ternary blends were found to separate after standing at room temperature for periods of from one hour to four days. These same blends, stored in a refrigerator at 40°F, remained homogenous for periods from two weeks to more than three months. Apparently the gradual polymerization of the phenolic resins, which can be almost eliminated by refrigeration, caused a separation of the phenolic portions of the mixtures.

The shear strength values of these ternary blends approached those of the best modified silicone resins prepared to date. The results of filler addition and oven aging were also promising (see later sections of this discussion section).

EVALUATION OF FILLERS

A group of selected inorganic fillers was tested over a range of concentrations in DC-2103 silicone resin and in the epoxy-modified DC-2103 resin. The fillers provided little or no improvement in the high-temperature shear strength of the straight silicone resin. Iron oxide showed a 10 percent improvement in high-temperature shear strength; aluminum dust showed a small improvement; and Asbestine X at 25 and 50 parts loading caused no change in the high-temperature shear strength, and the 75 part loading caused a noticeable reduction in both the room-temperature and high-temperature shear strength values. Both types of titanium dioxide resulted in lower shear strength values at 500°F.

In the CHR-M-60 epoxy-modified silicone resin (80 percent DC-2103, 20 percent Epon 834), both the Asbestine X and one of the titanium dioxides improved the shear strength at 500°F, giving values of nearly 1000 psi. The other fillers provided little or no improvement in the shear strength of this resin.

As indicated under Experimental Section E, earlier data obtained on the three-component system, DC-2103, Epon 834, and Asbestine X, were plotted on triangular graphs to show the areas of highest shear strength values (see Figures 2A and 2B), and new data were produced to fill in the promising areas in the graphs. With few exceptions, the values fell into relatively well-defined areas according to shear strength at room temperature and at 500°F. On Figure 2A, it can be seen that the highest room-temperature shear strength values (1200 psi to 1500 psi) were found for compositions ranging from about 15 percent to 50 percent Epon 834, and 85 to 50 percent DC-2103 with loadings up to 75 parts of Asbestine X. The areas of high shear strength values at 500°F are much more closely defined than the areas for the room-temperature values. The highest shear strength values at 500°F (800 psi and above) were found in an area representing 10 to 30 percent Epon 834, 90 to 70 percent DC-2103, and 75 to 150 parts loading of Asbestine X. The points shown in Figures 2A and 2B indicate a thorough coverage of this epoxy-modified silicone resin system, representing the variations in composition of the CHR-M-60 resin (80 DC-2103, 20 Epon 834) indicated in the discussion of the experimental program, and cover a wide range of loadings with the best inorganic filler (Asbestine X) found for the epoxy-modified silicone resins.

High-temperature aging studies on the epoxy-modified silicone resins indicated the resins based on DC-803 or CHR-122 silicone resins to be considerably better in high-temperature aging resistance than the modified resins based on DC-2103 silicone resin. For this reason, selected samples were prepared covering the three-component systems, DC-803, Epon 834 and Asbestine X, and CHR-122, Epon 834 and Asbestine X, and data from these samples were plotted on triangular graphs (Figures 3 and 4). The DC-803 system showed a general decrease in room-temperature shear strength values with increasing loading of Asbestine X; the shear strength values at 500°F, however, covered a comparatively small range, from 300 psi to 500 psi, and the variations did not appear to correlate with composition. The CHR-122 series again showed a gradual decrease in room-temperature shear strength values with increased loading of Asbestine X; the shear strength values at 500°F showed comparatively little variation with resin composition over the small range covered here (5 to 20 percent epoxy) but showed a definite variation with Asbestine X loading, maximum shear strength values occurring at about 50 parts loading of the filler.

Several grades of the Asbestine filler, ranging from crystalline to fibrous, were tested in three different samples

of the CHR-M-60 epoxy-modified silicone resin at a loading of thirty parts of filler per hundred parts of resin. Little difference was found in shear strength values produced by the different grades of Asbestine at this filler loading, although, in each case, the Asbestine 5X provided high-temperature shear strength values slightly greater than those produced by the other Asbestine samples. Later data (Tables X and XI) confirmed the slight superiority of Asbestine 5X over Asbestine X.

Asbestine 5X filler in the silicone-epoxy-phenolic ternary blends effected a small general increase in the shear strength values at 500°F, but caused a decrease in the room temperature shear strength values (Table XI).

Aluminum dust was tested in several loadings in both the epoxy-modified silicone resin and in the silicone-epoxy-phenolic resin blends and showed no consistent improvement in shear strength values. In the high-temperature aging studies, the addition of aluminum dust to the silicone-epoxy-phenolic resin blends was found to reduce the life of the bonds considerably.

CURING CATALYSTS FOR EPOXY-MODIFIED SILICONE RESIN

A relatively long high-temperature cure (16 hours at 480°F) has been used in the standard evaluation procedure. Curing agents have been tested from time to time as a means of substantially reducing both the time and the temperature of the resin cure required to obtain the desired high adhesive strength, and not affect retention of this strength during long high-temperature aging. Data in Table XII revealed that the addition to CHR-M-60 epoxy-modified silicone resin of a mixture of one part of dicyandiamide dissolved in two parts of dimethyl formamide showed considerable promise of reducing the time and temperature of the cure. The results of this preliminary study, however, were quite erratic. Further tests should be made on other modified silicone resins, and aging studies carried out. In any further work, a curing agent may be selected which will be consumed during the cure as a result of reaction with epoxide or hydroxyl groups, and will shorten the cure time without harmful effect on high-temperature aging of the resin.

SHEAR STRENGTH OF RESINS AT TEMPERATURES FROM -70°F to 900°F

The effect of increasing amounts of epoxy resins on the shear strength of a silicone resin at elevated temperatures was determined. It will be noted from the curves in Figure 5 that the modification of DC-2103 silicone resin with amounts up to

20 percent of Epon 834 epoxy resin had comparatively little effect on the change in shear strength at temperatures up to 900°F. The main effect noted from the addition of the epoxy resin was that of considerably improved shear strength at temperatures below 500°F. From 500°F to 900°F, the epoxy-modified silicone resins still showed generally higher shear strength values than those of the pure silicone resin, but the differences between the shear strengths were relatively small at the elevated temperatures.

The silicone and modified silicone resins displayed a considerable decrease in shear strength between 500° and 700°F, but it is interesting to note that each of the three silicone adhesives showed at least a significant retention of strength at 900°F. It will be observed that these values were obtained on the unfilled resins; considerably higher shear strength values and less loss in strength at the elevated temperatures should be expected with filled resin compositions.

As noted in the experimental section, the low shear strength values for the pure epoxy resin were undoubtedly due to the lack of curing agent and the rigorous curing conditions.

HIGH TEMPERATURE AGING STUDIES

Four silicone-based resins were aged for total periods of 1200 hours at 500°F and 300 hours at 600°F. The four resins selected were two silicone resins, DC-2103 and DC-803, and epoxy modifications of those two silicone resins, CHR-M-60 and CHR-M-42. DC-803 and epoxy-modified DC-803 were found to be considerably more resistant to high-temperature aging than DC-2103 and its epoxy modification. The epoxy-modified resins showed significantly higher initial shear strength values than the pure silicone resins, but they also showed a more rapid loss in shear strength with aging and failed after a shorter period of time.

The difference between the two silicone resins was more pronounced on stainless steel panels than it was on aluminum panels. It should also be noted from the figures (6 through 13) that the stainless steel lap joints exhibited about 40 percent higher initial shear strength values at room temperature than the aluminum lap joints. The high-temperature shear strength values on stainless steel and on aluminum were found to be very nearly the same. The difference in the resistance of the resins to high-temperature aging on the aluminum panels as compared with the stainless steel panels varied somewhat with the different resins and did not appear to be significant.

The scales of the graphs were adjusted so that the time of failure of the resins at 600°F could be compared with the time of failure at 500°F. The relation of the effect of aging at 600°F with that at 500°F appears to be different for each resin and each metal. In spite of these differences, however, it was felt that a short accelerated aging test at 600°F (e.g., 72 or 120 hours) would be extremely helpful in screening various adhesives, instead of a prohibitively long (seven weeks) aging test at 500°F.

Various loadings of Asbestine X filler in selected modified silicone resins caused little improvement and no apparent harm in the accelerated aging (600°F) of those resins. It was quite apparent, however, that aluminum dust filler in the ternary resin blends (silicone-epoxy-phenolic) caused a serious reduction in the resistance to aging at 600°F (Table XV).

Three resins, DC-803 silicone resin, epoxy-modified DC-803, and a ternary blend of 80 parts DC-803, 10 parts epoxy and 10 parts phenolic, were selected and aged for periods up to 200 hours at 600°F. These resins were 100 percent, 90 percent and 80 percent silicone, respectively, and all three of the resins showed fair room-temperature strength after the 200 hour aging. Confirming the earlier high-temperature aging results, however, only the pure silicone resin was useful at 500°F after the 200-hour accelerated aging, retaining 70 percent of its initial high-temperature shear strength.

As a result of the aging studies on the various silicone and modified silicone resins, it appears that the best silicone-based structural adhesive resin would be one based on DC-803 or on a similar slow-curing, high-temperature-resistant silicone resin containing a small amount of an epoxy-phenolic resin combination as a means of obtaining high initial shear strength values from a catalyzed low-temperature cure. The organic resins should be present in sufficiently small amount so that they will not affect the long-term-high-temperature-resistance of the silicone resin. It is apparent that more thorough studies of the basic silicone resin, of filler reinforcement, and of silicone metal surface wetting are needed to raise the entire shear strength level of the basic silicone resin composition. It is quite probable that introduction of thermally stable, highly polar side groups on the silicone chain, such as in the chloro-substituted phenyl silicones which have shown such a marked

improvement in the metal surface wetting properties of silicone lubricants 1/, may add the needed increase in shear strength to the inherently stable silicone structural adhesive.

1/ Elliott, J.R., Prober, M., and George, P.D. Carbon Functionals - The New Silicone Frontier. Chemical and Engineering News. Volume 33. 24 October 1955. pp 4513-14.

III. SUMMARY AND CONCLUSIONS

1. The three-component system of epoxy-modified DC-2103 silicone resin containing Asbestine X filler, which, when tested as a structural adhesive for aluminum, produced shear strength values at 500°F better than the target requirement of 1000 psi, has been investigated thoroughly, and triangular graphs prepared showing composition areas yielding maximum shear strength values. Maximum room temperature shear strength values (1200 to 1500 psi) were found in a composition area ranging from 15 to 50 percent Epon 834 and 85 to 50 percent DC-2103, with loadings up to 75 parts of Asbestine X; maximum shear strength values at 500°F (800 to 1000 psi) were more closely defined in an area representing 10 to 30 percent Epon 834, 90 to 70 percent DC-2103, and 75 to 150 parts loading of Asbestine X. Similar graphs have been prepared for the systems, DC-803 silicone resin, Epon 834, and Asbestine X, and CHR-122 silicone resin, Epon 834, and Asbestine X. These systems showed considerably less variation in shear strength with composition over the limited range covered.

2. High-temperature aging studies for periods of 1200 hours at 500°F and 300 hours at 600°F were carried out on a group of silicone and epoxy-modified silicone resins. DC-803 silicone resin showed considerably better resistance to high-temperature aging than the DC-2103 silicone resin, and also the epoxy-modified DC-803 resin showed better resistance to aging than epoxy-modified DC-2103 resin (CHR-M-60). The DC-803 lasted the full 1200 hours at 500°F on both aluminum panels and stainless steel panels, and withstood 300 hours at 600°F on stainless steel and 200 hours on aluminum. These agings resulted in little or no loss of shear strength at 500°F for the DC-803 (200 to 350 psi residual shear strength), but a 30 to 50 percent loss in shear strength at room temperature (600 to 800 psi residual). The 20 percent epoxy-modified DC-803 resin lasted 800 hours at 500°F (residual 300 psi at room temperature and 150 psi at 500°F) and 100 hours at 600°F (residual 380 psi at room temperature and 160 psi at 500°F).

3. An accelerated aging test for periods up to 200 hours at 600°F verified the above results with DC-803 silicone resin. A ternary blend of 80 percent DC-803, 10 percent epoxy, and 10 percent phenolic resins, while showing fair retention of room temperature strength after the 200-hour aging, and only 33 percent loss in shear strength at 500°F after 72 hours, failed in the 500°F shear strength test after 100 hours of aging at 600°F.

4. The shear strengths of DC-2103 silicone resin and of several epoxy-modified DC-2103 resins were determined at temperatures from -70°F to +900°F. Up to 20 percent of epoxy resin showed little effect on the change in shear strength with temperature up to 900°F. The main effect of the epoxy resin was to improve the shear strength over the lower half of the temperature range, causing a large improvement at temperatures up to 500°F and very little improvement from 500°F up to 900°F (residual shear strength at 900°F was about 100 psi).

5. Ternary solution blends of silicone, epoxy and phenolic resins were prepared which showed shear strength values as good as the best epoxy-modified silicone resins prepared to date. The addition of Asbestine X filler showed some improvement in shear strength values. The ternary blends were somewhat more resistant to high-temperature aging than the epoxy-modified silicone resins, but considerably less resistant than the straight silicone resins.

6. A number of commercial and laboratory synthesized silicone resins have been modified with epoxy resins. Epon 834 and Araldite 6020, similar in composition and molecular weight, have consistently shown the best results in these modifications.

7. A mixture of dicyandiamide and dimethylformamide was found to be quite effective as a curing catalyst for epoxy-modified silicone resin in a brief investigation of curing agents.

8. The best reinforcing fillers found thus far for the epoxy-modified silicone resins are Asbestine 5X and Asbestine X. Aluminum dust caused no consistent improvement in shear strength values, and was found to reduce the high-temperature aging resistance of silicone-epoxy-phenolic resin blends.

9. Samples of the different types of silicone-based adhesives developed under the contract work were prepared, tested, and forwarded to Wright Air Development Center. Four samples were selected and submitted. Two samples were of epoxy-modified commercial silicone resins, one (M-60) which showed consistently the highest shear strength values at 500°F, and the other (M-42) which showed outstanding retention of strength after aging at 500°F. The third sample was M-117, selected as the best epoxy-modified CHR silicone resin, and the fourth was M-207, the ternary resin blend (silicone-epoxy-phenolic) showing the highest shear strength values at 500°F. A sample of unmodified DC-803

silicone resin was also included for comparison testing. Resins M-60 and M-117 were prepared with 75 parts and 50 parts respectively, of Asbestine X per hundred parts of resin; the other samples were supplied unfilled. Instructions for use were supplied with the samples.

IV. APPENDIX

PREPARATION OF LAP JOINTS

The resin solution was painted on the lap area of 24S-T3 clad aluminum panels (4 x 1 x 0.064 inch) which were previously degreased and chromic acid-cleaned by Method C-1 or on stainless steel panels, 18-8 half hard (4 x 1 x 0.050 inch), degreased and cleaned by Method C-5, (cleaning method described below). On the separate panels, the solvent was evaporated by heating at 150°F for one and one-half hours, and the resin was partially cured for one hour at 300°F. The lap joints were then assembled on a thin Teflon film in the jig (shown in Figure 5 WADC Technical Report 54-98, Part 2) to give a one-half inch overlap. (The Teflon film facilitated the removal of the lap joints later.) Eight complete lap joints (16 panels) were assembled in the jig at one time, care being taken to make proper alignment. Shims were used at each side of the jig to hold the panels level and establish the desired glue line. A shim 0.003 inch in excess of the panel thickness was normally used, but this procedure was sometimes changed to allow for various glue lines, as indicated in some of the tables. A thin Teflon film and the jig cover were placed on top of the lap joints to complete the assembly. Four jigs were stacked in an oven, and two fifty-pound steel weights, shaped to fit the jig cover, were placed on top of the jigs. This applied a pressure of 25 psi to the lap joints in the top jig, and an additional 2 psi for each succeeding lower jig, a maximum of 31 psi being applied to the lap joints in the bottom jig. The jigs were placed initially in an oven at 300°F and after 30 minutes moved to an oven at 480°F for the 16-hour cure.

After cure, the lap joints were tested for shear strength at room temperature and at 500°F.

CLEANING METHOD C-1 (for clad aluminum)

The 24S-T3 clad aluminum panels were degreased by immersion for at least 16 hours at room temperature in trichloroethylene. The degreased panels were air-dried and then were placed in a rack so that approximately one inch of each panel was immersed for 10 minutes in a chromic acid solution of the following composition by weight: 30 parts water, 10 parts concentrated sulfuric acid and 1 part crystalline sodium dichromate. This solution was maintained, with agitation, at a temperature of 150 to 160°F. The panels were rinsed six times with cold water and were allowed to dry for at least 30 minutes at room

temperature, or for 10 minutes in a circulating-air oven at 150 to 200°F. The cleaned and dried panels were stored in a desiccator.

CLEANING METHOD C-5 (for stainless steel)

The stainless steel panels were degreased with trichloroethylene, air-dried, and placed in a rack as in Method C-1, above. They were immersed to one inch for 5 minutes in a hydrochloric acid solution, containing 15 percent hydrogen chloride by weight, maintained at 80°F, followed by a water rinse. They were then immersed to one inch for 30 minutes in a nitric acid solution, containing 30 percent nitric acid by weight, maintained at 80°F. The panels were rinsed thoroughly with cold water, dried, and stored as in Method C-1.

MEASUREMENT OF SHEAR STRENGTH

Shear strengths were measured in a Dillon Dynamometer, Model K, having a range of 0 to 5000 psi and modified to have a loading rate of 1200 to 1400 psi per minute. All shear strength tests were run in duplicate.

The procedure and equipment used for shear strength measurement at elevated temperatures were described in some detail in WADC Technical Report 54-98. Briefly, the lap joints were heated and maintained at the desired temperature by means of a small electric tube furnace affixed between the jaws of the Dillon Dynamometer. The temperature of the test panel was indicated by an iron-constantan thermocouple wrapped around the bonded area, connected to a Simplytrol (0 to 750°F) pyrometer. The lap joints were inserted in the preheated jaws of the tester, and the temperature of the lap joints was raised to 500°F and maintained at that temperature for five minutes before applying the load.