INVESTIGATION AND DEVELOPMENT OF HIGH-TEMPERATURE STRUCTURAL ADHESIVES

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JANUARY 1956

FOREWORD

This report was prepared by Mr. Kenneth L. McHugh and
Mr. Alfred S. Kidwell 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," form-
erly RDO No. 582-218, "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
June 1954 to 1 May 1955 and is the second report on the same
subject by the same contractor. The first report was published
in August 1954 as WADC Technical Report 54-98 and covered the
work performed during the period 15 January 1953 to 15 January
1954 under Air Force Contract No. AF 33(616)-427.

WADC TR 54-98 Pt 2

ABSTRACT

An epoxy-modified silicone resin composition for use as a metal-to-metal adhesive has been developed which displays shear strength values slightly in excess of the target requirement of 1000 psi at 500°F, and shear strength values at room temperature of about 1100 psi. The highest shear strength value obtained at 500°F in an evaluation of seventy-seven commercial silicone and organo-modified silicone resins was 560 psi. A commercial organo-modified silicone resin produced a much higher shear strength at room temperature (average, 2300 psi), but a low shear strength at 500°F (average, less than 100 psi).

Experimental silicone resins were prepared which displayed shear strength values appreciably higher than those of the best commercial silicone resins. The best high-temperature shear strength values were found in resins having an R/Si ratio from 1.10 to 1.30 and a methyl content from 30 to 60 percent.
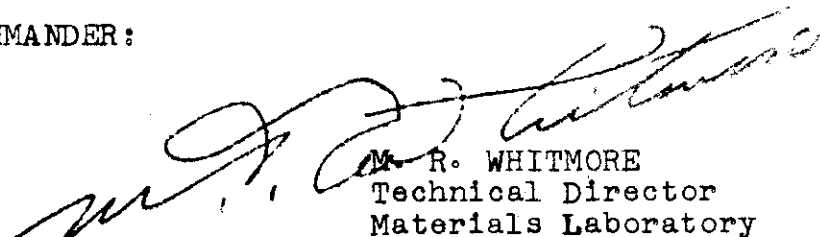
Epoxy-modified silicone resins were the most promising of almost one hundred modifications prepared with epoxy, alkyd, phenolic, and polyamine resins. Silicone-isocyanate copolymers, while not yet practical, showed interesting results. The Karl Fischer reagent was found useful for the determination of silanol groups in silicone resins.

Asbestine X and titanium dioxide fillers reinforced the silicone and organo-modified silicone resins to some extent. Glass fabric was of little or no value as a reinforcement.

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

Great progress was made during World War II in the development of adhesives of all types. This advance was to be expected as an indirect result of the tremendous development of synthetic resins and elastomers during and immediately preceding this period. Extension of the use of adhesives for the purpose of bonding metals began toward the end of World War II. Today, adhesives are available for bonding aluminum, stainless steel and other metals for service at temperatures as high as 300°F, as required for the manufacture of various types of sandwich construction, airframe wing sections, and helicopter rotor blades.

Another aspect of the remarkable progress in the aircraft industry is the development of the jet and rocket engines which promise to propel aircraft at speeds far beyond that of sound. Under these conditions, the entire aircraft is heated by the friction of air passing over its surface so that engineers must demand component parts having service temperatures as high as 500°F and even 700°F. An excellent review of the metal-to-metal adhesive problem in the aircraft industry today can be found in a recent book written by George Epstein (8).

The silicone resins and elastomers are the outstanding synthetics for high-temperature service, but 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, when used to bond aluminum and stainless steel. It was hoped that such an adhesive would withstand aging for several hundred hours at 500°F, and would stand 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 attainable. During the second phase of this research, covered in this report, commercially available silicone resins have been modified by reaction with epoxy and other organic resins for the purpose of raising the shear strength at 500°F to 1000psi. Based on this work, there is considerable basis for the hope that further research will make possible the development of a silicone-based structural adhesive for the bonding of modern high-speed aircraft.

I. EXPERIMENTAL

A. Synthesis of Resins and Resin Blends

Silicone Resins

The synthesis of silicone resins carried out in this work consisted in mixing the organohalosilane or organoethoxysilane monomers with water to hydrolyze them to the silanols, followed by polymerization, or condensation, of the silanols to highly cross-linked polymers.

The following general procedure, which was used in the preparation of most of the silicone resins listed in Table II, was developed gradually in the preparation of earlier resins. The apparatus is shown in Figure 1. Monomeric organosilanes were weighed accurately into a glass-stoppered Erlenmeyer flask containing approximately an equal weight of distilled and dried trichloroethylene (or other similar solvent such as perchloro-ethylene, carbon tetrachloride, etc.). Distilled water (600 cc) and trichloroethylene (100 cc) were placed in the three-neck reaction flask. The monomer-solvent mixture was placed in the dropping funnel, the stirrer was started, and the stopper was adjusted to allow slow, steady addition of the monomers over a period of 30 minutes. During this addition of monomers, the temperature of the reaction mixture increased gradually from room temperature to about 60° to 70°C.

The reaction mixture was stirred for an additional 15 minutes, and then the entire hydrolysis mixture was poured into a separatory funnel. The lower, trichloroethylene, layer was withdrawn, and the aqueous layer remaining was washed with a small quantity of trichloroethylene. The wash solvent was withdrawn and added to the original solution. The trichloro-ethylene-silicone polymer solution was then washed continuously with water until the wash water was neutral (to remove residual acid formed in the hydrolysis). The solution was again separated from the aqueous phase and distilled. Any water dissolved in the solution was removed by an azeotropic forerun. The distil-lation was continued until the solution in the flask became quite viscous. A quantity of the solvent desired as the vehicle for the final solution, generally toluene or xylene, was added, and the mixture was refluxed (usually 15 to 30 minutes) to effect complete solution. The resin solution was adjusted to the desired solids concentration (generally 50 percent) by addition of solvent, and then was filtered through glass wool into a storage bottle.

ENLARGED DETAIL
OF STIRRER
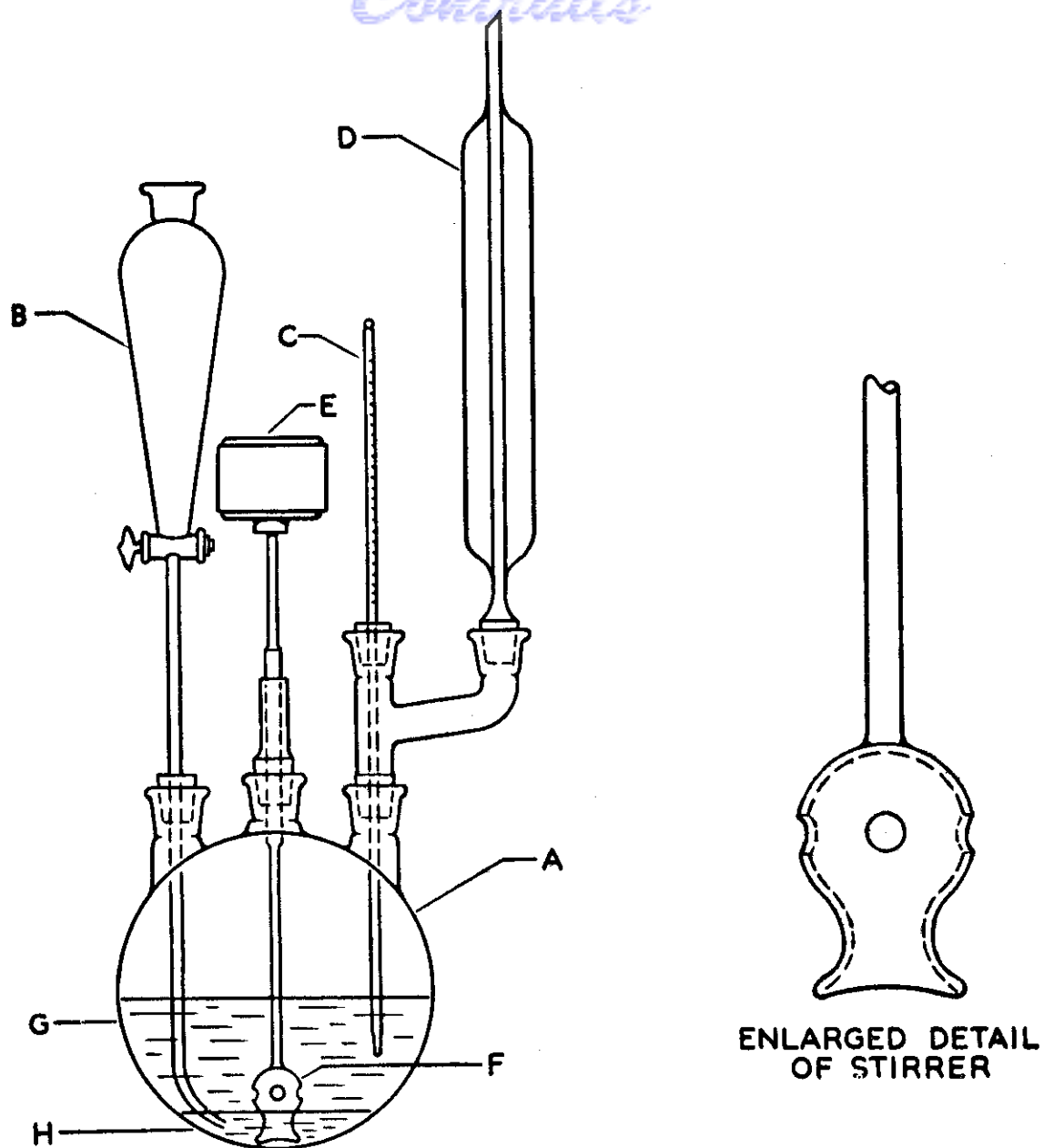
A - FLASK
B - DROPPING FUNNEL
C - THERMOMETER
D - CONDENSER
E - MOTOR
F - STIRRER
G - WATER PHASE
H - TRICHLOROETHYLENE PHASE

FIGURE I - APPARATUS FOR HYDROLYSIS
OF ORGANOHALOSILANES.

A number of variations of this general procedure were made for specific resins. These variations, where significant, are noted in footnotes to Table II, and are discussed in some detail in the Discussion Section of this report.

The types and proportions of the silicone monomers used in the preparation of the various silicone resins are indicated by the numbers in the first two columns in Table II. Except where noted by Footnote 3, the monomers were chlorosilanes ($RSiCl_3$, R_2SiCl_2 or $RR'SiCl_2$). Ethoxysilane ($RSi(OC_2H_5)_3$, $R_2Si(OC_2H_5)_2$ or $RR'Si(OC_2H_5)_2$) monomers were used with ten of the resins, (Footnote 3). The R group consisted of only methyl or phenyl, except in the case of two resins, CHR-132 and CHR-138, where vinyl ($CH_2{=}CH{-}$) silanes were used (Footnotes 1 and 2). The figures in the first two columns of Table II are based on mole percentages of the monomers used to prepare the resins. The weight of each monomer used was expressed in moles (the weight in grams of the monomer divided by the molecular weight of the monomer), and the mole percentage of each monomer in the mixture was determined. As an example, a monomer mixture of 30.0 grams of methyl trichlorosilane (CH_3SiCl_3), 25.9 grams of dimethyldichlorosilane ($(CH_3)_2SiCl_2$), and 126.6 grams of phenyltrichlorosilane ($C_6H_5SiCl_3$) would be indicated as follows in Table II:

	Wt., Grams	M.W.	Moles	Mole %	Mole % XnR*	Methyl	Phenyl
CH_3SiCl_3	30.0	150	0.20	20	20	20	
$(CH_3)_2SiCl_2$	25.9	129	0.20	20	40	40	
$C_6H_5SiCl_3$	126.6	211	0.60	60	60	—	60
Total			1.00	100	120	60	60

$$\text{R/Si ratio} = \frac{120}{100} = 1.20$$

$$\% \text{ Methyl} = \frac{60}{120} = 50\%$$

* Mole Percent times number of R groups

Organo-Modified Silicone Resins

Almost all of the modified resins listed in Table III were prepared with the use of the same general procedure. The apparatus shown in Figure 2 is extremely versatile for the laboratory synthesis of resinous materials. The flask (A) is composed of two sections joined by matched ground-glass flanges. A lower section having a 500 cc capacity was used in this work. The flask was fitted with a stirrer, a long-stem thermometer, a Barrett tube, and a condenser. The Barrett tube serves to isolate water formed and distilled from the reaction mixture. The amount of water indicates the progress and extent of the condensation reaction.

The desired proportions of silicone resin solution and organic resin were weighed and blended to yield a total weight (solids) of about 200 grams, and the resin mixture was poured into the reaction flask. The mixture was stirred and the temperature was raised sufficiently to reflux the solvent present as the silicone resin carrier. This solvent was generally toluene (B.P. 110°C) or xylene (B.P. 131°C), and the resin mixture temperature at reflux was about ten degrees above the boiling point of the solvent. As noted in Table II, most of the modification reactions did not proceed satisfactorily at that temperature. Therefore, to most of the resin-solvent mixtures, a higher boiling solvent such as diethyl carbitol (B.P. 188°C) or dibutyl carbitol (B.P. 256°C) was added. The resin-solvent mixture was heated, and the lower boiling solvent was allowed to collect in the Barrett tube where it was drawn off. The reaction temperature was thus raised to 200° or 270°C.

As indicated above, a simple means of following the progress and extent of the modification reaction was available. Water split off in the condensation reaction was immiscible in the solvent and was measured directly as it collected in the Barrett tube during the refluxing. The theoretical amount of water, based on the amount of organic resin, was calculated, and as the reaction approached completion the resin mixture was diluted with solvent and was allowed to cool. In instances of highly cross-linked silicone and organic resins, the resin mixtures gelled prior to complete reaction and the amount of water could not be used as a guide. In those cases, heating was stopped just as the resin mixture reached its gelation point, a small quantity of solvent was added and the solution was cooled.

A number of the early modified silicone resins (M-1, M-2, and M-13 through M-37) were made with the use of the Linde X-14

A · REACTION FLASK · TWO HALVES
B · HEATING MANTLE
C · CLAMP
D · THERMOMETER
E · STIRRING GLAND
F · PADDLE STIRRER
G · MOTOR
H · BARRETT TUBE
I · CONDENSER
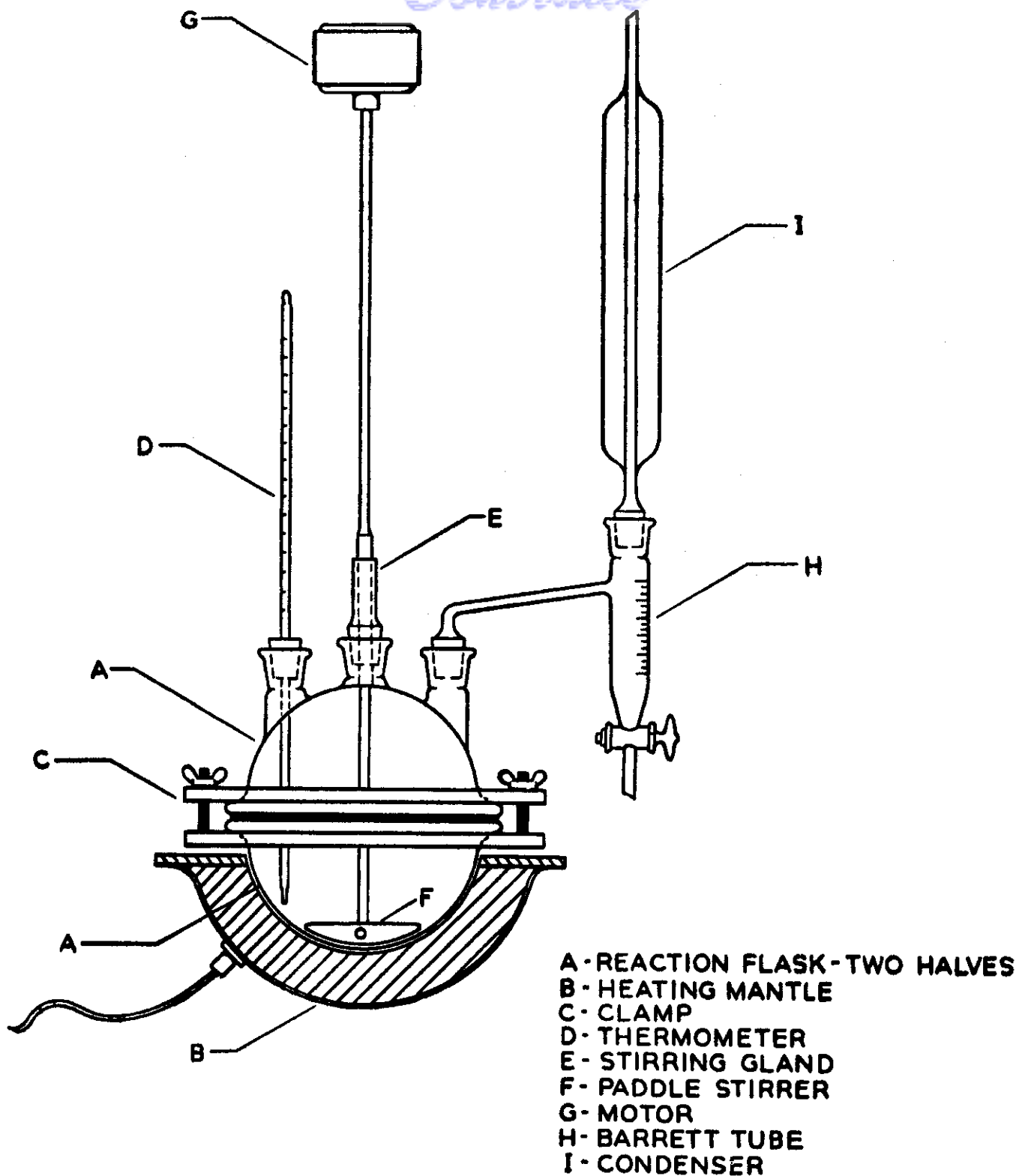
FIGURE 2 – APPARATUS FOR ORGANO-MODIFIED SILICONE RESINS.

(later designated as X-821) reactable silicone polymer. These condensations proceeded through the elimination of ethanol, which was soluble in the solvent, instead of water (see the Discussion Section). Here the ethanol-solvent distillate was withdrawn periodically from the Barrett tube and was titrated with water until a separate phase appeared. By means of phase diagrams, the amount of ethanol was quickly approximated.

Further modifications of this general procedure are brought out in the Discussion Section of this report.

The Karl Fischer reagent was used for titration of silanol end-groups in eight Dow-Corning resins (Table IV). A standard procedure and apparatus were used with minor variations as required by the polymeric nature of the samples (see the Discussion Section of this report). The apparatus shown in Figure 3 was designed to exclude moisture as much as possible. The extra hole in the stopper, normally fitted with a drying tube, permitted the addition of material. Before use, the beaker was thoroughly flushed with dry nitrogen gas to eliminate the possibility of moist air remaining in the beaker. The Karl Fischer reagent was standardized before use against a standard solution of methanol containing 1.04 milligrams of water per milliliter. Commercial anhydrous methanol, titrated to determine the water content, was used as a solvent for the resin. The resin sample to be titrated was dried in a vacuum oven overnight to remove the residual water and solvent. A resin sample was carefully weighed into a small stoppered flask, and, at the same time, a second sample was taken for a careful determination of the percent solids. Ordinarily, the sample would be added directly to the titration beaker containing a known volume of anhydrous methanol. In the case of the resins, however, 0.5 milliliters of Karl Fischer reagent was added to each flask and the samples were allowed to stand for 3 hours with intermittent shaking. The sample was then transferred into the titration beaker, a total of 50 cc of anhydrous methanol being used for rinsing and dilution. The beaker was flushed with dry nitrogen gas and was closed. The stirrer was started, the electrode circuit switch was closed, and the further addition of Karl Fischer reagent was initiated. As the titration neared the end point, the needle of the microammeter began to rise, attaining a maximum near the end point and remaining at that maximum. An excess of Karl Fischer reagent was added, and the meter was adjusted to read 20 microamperes. Then the reaction mixture was back-titrated with methanol, containing a known amount of water, until the needle suddenly dropped to zero. This method, known as the "dead stop" method, is favored in titrations of

A - SELF FILLING BURETTES.
B - RESERVOIR BOTTLES.
C - DRYING TUBES.
D - BEAKER, 250 ML. CAP. BELOW STOPPER.
E - ELECTRODES (PLATINUM WIRE SEALED
    IN GLASS - MERCURY CONTACT.)
F - MAGNETIC STIRRER.
G - MAGNET
H - ELECTRIC CIRCUIT AND METER.

SCHEMATIC OF CIRCUIT
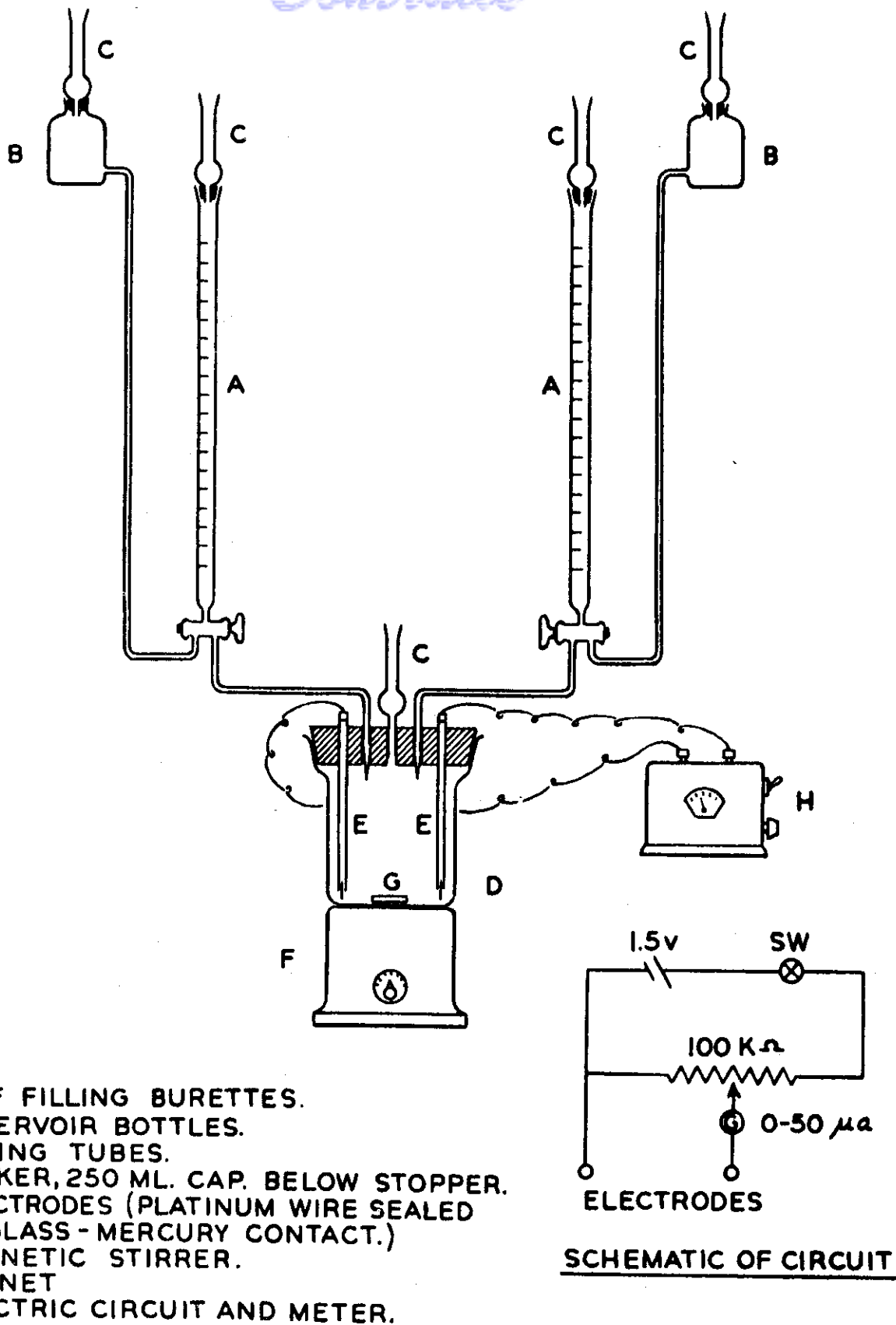
FIGURE 3 - APPARATUS FOR KARL FISCHER TITRATION

this general type (1). The amounts of water in the methanol
used as solvent and in the back-titration were deducted from
the water equivalent of the total Karl Fischer reagent used.
The figure remaining represented water formed through reaction
of the Karl Fischer reagent with the silanol end-groups. This
reaction appears below:

1. $CH_3OH + SO_3 \longrightarrow CH_3OSO_3H$ Solution No. 1 K.F. Reagent

2. $2C_5H_5N + I_2 \longrightarrow 2C_5H_5NI$ Solution No. 2 K.F. Reagent

3. $\equiv Si-OH + CH_3OH \quad \xrightarrow{CH_3OSO_3H} \quad \equiv Si-O-CH_3 + H_2O$
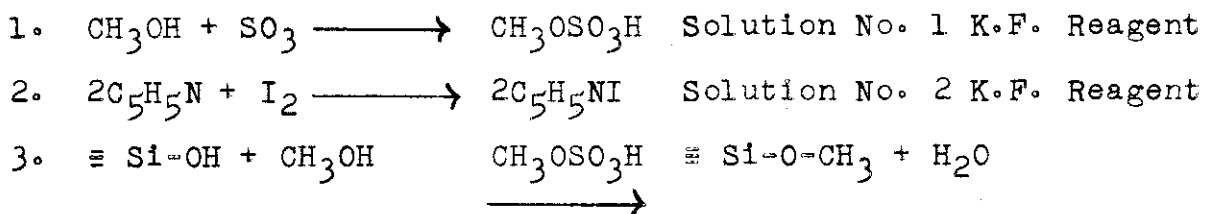
The water formed then reacts with the iodine-pyridine complex
to give a potentiometric end point.

Total K.F. reagent = cc originally added + cc used in titration

Total blank for methanol = cc of methanol solvent x equivalence
of solvent + cc used in back-titration x equivalence.

Total K.F. - blank = cc of K.F. required to neutralize water formed

$$\frac{cc \text{ of K.F. x K.F. water equivalent}}{\text{weight of sample}} = \text{mgs of water per gm of sample.}$$

Data obtained in the calibration of the Karl Fischer deter-
mination using recrystallized diphenylsilanediol are shown below:

Titration of Diphenylsilanediol with Karl Fischer Reagent

Grams $(C_6H_5)_2Si(OH)_2$	K.F. Reagent cc	mgH_2O	Theoretical
0.200	7.20	33.4	31.2
0.200	6.81	31.6	31.2
0.200	6.90	32.0	31.2

Standardization: 1 cc of K.F. reagent equivalent to 4.64 mg H_2O

An experiment set up to determine the required time for
reaction of a polymeric material with the Karl Fischer reagent
produced the following results:

Experiment with DC-804

Time after Addition of 0.5 cc K.F. Reagent, min	Wt. of DC-804 (solids) gms	K.F. Reagent cc	mg H$_2$O	mg H$_2$O/ gm Resin
0	2.831	3.65	15.1	5.33
20	3.316	6.10	25.2	7.69
30	3.846	8.55	35.3	9.18
60	3.467	8.15	33.6	9.70

Standardization: 1 cc of K.F. reagent equivalent to 4.12 mg H$_2$O

A discussion of the application and accuracy of this method is included in the Discussion Section of this report.

Silicone-Isocyanate Copolymers

A series of reactions were carried out using diphenyl-silanediol and 2,4-tolylene diisocyanate (TDI). To prepare silicone-isocyanate copolymers, 100 cc of dioxane (or toluene) were placed in a 250 cc flask fitted with a stirrer and a thermometer. Dried diphenylsilanediol (0.05 mole, 10.4 gms) was added and dissolved with stirring. The redistilled 2,4-tolylene diisocyanate (0.10 mole, 17.4 gms) was added dropwise, with stirring. Upon complete addition of the TDI, two drops of the triethylamine catalyst were added. After an induction period of one to two minutes, the color of the solution began to change from yellow to red-brown, accompanied by a rise in temperature. The reaction mixture temperature increased gradually to approximately 45° to 50°C and remained at that level. After 15 to 20 minutes, a solid began to form, as evidenced by increasing cloudiness of the solution. The solution was cooled to 20°C and was stirred for an additional 20 minutes. The solution was then filtered, and the solid precipitate was dried. The product was a tan, powdery solid which decomposed gradually at temperatures in excess of 325°C, and was insoluble in common organic solvents. With the use of toluene as a solvent in the above procedure and no catalyst (triethylamine), the product was found to show partial solubility in ethanol, acetone and benzene. Benzene was used to separate the product into two fractions, the benzene-soluble fraction being a white, flaky substance, and the benzene-insoluble material being a powdery, tan substance. The white flakes softened over a temperature range from 180° to 230°C, thereafter becoming discolored, and were found to contain approximately one iso-cyanate group for every 1.25 silicon atoms. The tan product decomposed above 200°C, and was found to contain about one

silicon atom for every 28 isocyanate groups.

The above general procedure was repeated, several variations of solvents and catalysts being used in an attempt to produce a soluble low-molecular-weight polymer. In none of these cases was a significant amount of soluble material produced.

Because of the insoluble and infusible nature of the above products, an attempt was made to form an adhesive bond in situ from the silanediol and the TDI. When dissolved in pyridine, tolylene diisocyanate forms a dimeric compound which can be isolated as a solid. The solid dimer undergoes cleavage when heated to 302°F and regenerates the monomer. The solid diphenylsilanediol melts at 300-310°F. Taking advantage of these close temperatures, an equimolar dry mixture of TDI dimer and diphenylsilanediol was dusted on aluminum panels, and lap joints were prepared in the standard bonding jigs. The lap joints were heated for 2 hours at 350°F and thereafter for 16 hours at 480°F (see standard evaluation procedure). These lap joints showed shear strengths of 820 and 420 psi at 70°F and 500°F respectively.

A brief study was made of the kinetics of the reaction of diphenylsilanediol and tolylene diisocyanate. The reaction was run in a flask fitted with a stirrer and suspended in a thermostatically controlled bath. At predetermined periods, a 10 cc aliquot was withdrawn and weighed in a stoppered flask, and the isocyanate content was determined by a method involving the addition of excess standard amine solution, and back-titrating the excess amine with standard hydrochloric acid (2). Two runs were made by this method, the first without catalyst; two drops of N-methyl morpholine were added as catalyst in the second run.

The reaction was found to be of second order. The second order kinetic equation is expressed as follows:

$$\frac{dx}{dt} = k\,(a-x)\,(b-x)$$

or, in its integrated form,

$$\frac{1}{a-b}\ \log\ \frac{a(b-x)}{b(a-x)}\ = k\,t$$

where:

a = the original number of millimoles of diphenylsilanediol
b = the original number of millimoles of TDI
x = the number of millimoles of TDI reacted
t = time
k = reaction constant (slope of the graph)

In the tables below, the number of cc of hydrochloric acid used to titrate the sample is subtracted from the blank determination and this result is multiplied by the normality of the hydrochloric acid to determine the amount of unreacted isocyanate.

First Run

Diphenylsilanediol 5.00 gms -Tolylene Diisocyanate 6.42 gms

Toluene 200 cc - Dioxane 10 cc

Blank 9.68 cc

Reaction temperature 75°C

Time, Min	HCl, cc Requd.	Unreacted Isocyanate, Millimoles (b-x)	Unreacted Silanediol, Millimoles (a-x)	Log (b-x)/ (a-x)
15	1.4	8.4	4.0	0.322
30	0.9	9.0	4.6	0.292
60	1.2	8.7	4.3	0.305
90	2.1	7.7	3.3	0.367
120	1.0	8.8	4.4	0.301
180	1.7	8.1	3.7	0.340
240	1.8	8.0	3.6	0.346

Second Run

Diphenylsilanediol 8.00 gms - Tolylene Diisocyanate 12.82 gms

Toluene 100cc - Dioxane 5 cc

N-methyl morpholine (catalyst) 2 drops

Blank 9.47 cc

Reaction temperature 75°C

Time, Min	HCl, cc Requd.	Unreacted Isocyanate Millimoles (b-x)	Unreacted Silanediol, Millimoles (a-x)	Log (b-x)/ (a-x)
30	0.05	9.59	2.62	0.564
60	0.38	9.25	2.28	0.609
120	1.98	7.62	0.65	1.069
180	1.84	7.77	0.80	0.970

These data are plotted in Figure 4.
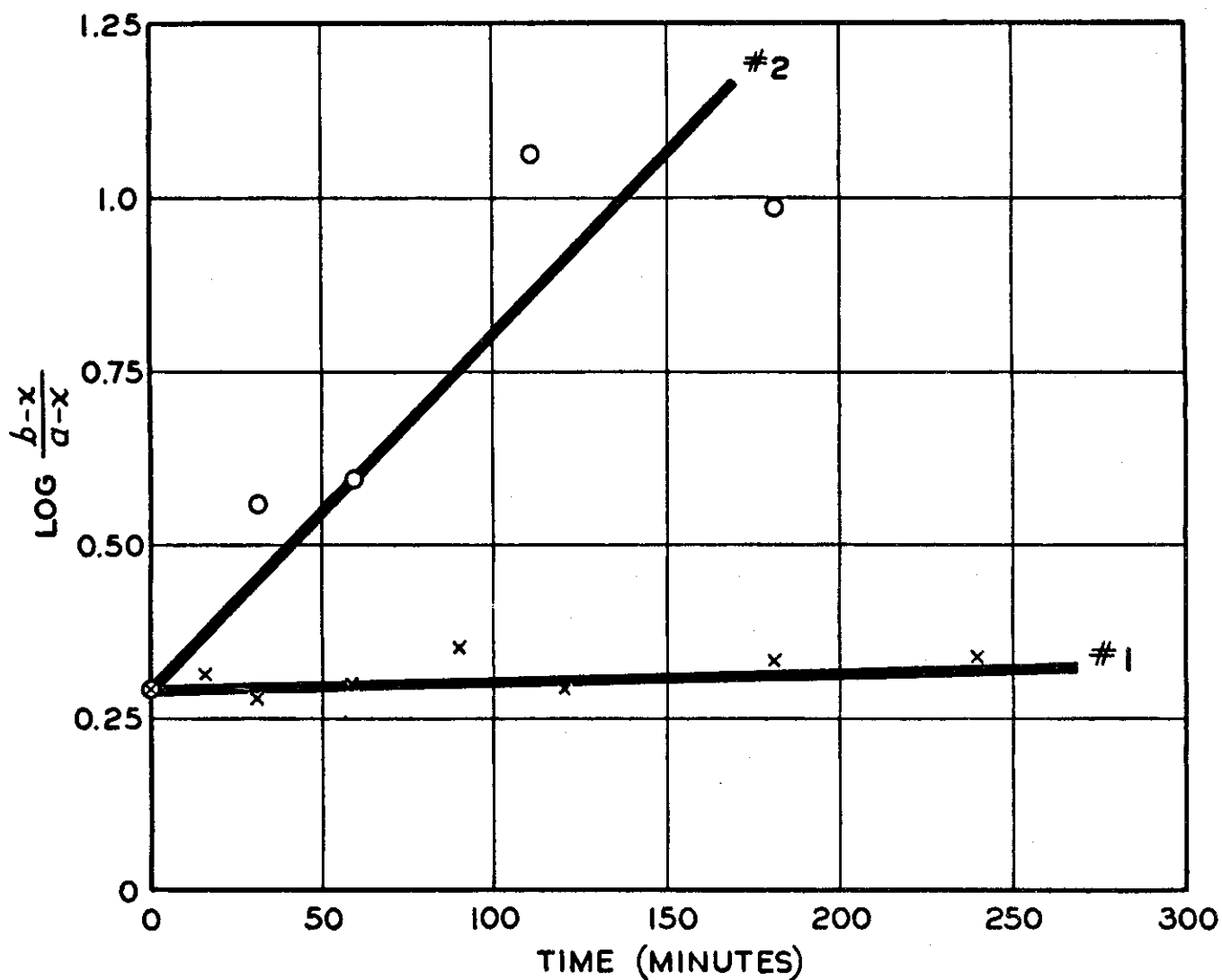
FIGURE 4 – PLOT OF EXPERIMENT DATA FOR
DETERMINATION OF RATE OF REACTION OF
DIPHENYLSILANEDIOL AND TOLYLENE DIISOCYANATE

B. Evaluation of Adhesives

Standard Procedure

For the purpose of screening and for direct comparison, all commercial silicone and modified silicone resins, as well as the silicone and modified silicone resins prepared in this laboratory, were evaluated as adhesives by a standard procedure. The results of the standard evaluation of commercial resins are listed in Table I; the data on the Connecticut Hard Rubber resins may be found in Tables II and III.

In the standard procedure, 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, described below under Primers and Surface Treatments. 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 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. Low pressure was applied to the jig by means of either Method B-1 or Method B-2, described below, and the lap joints were oven-cured for 16 hours at 480°F, unless otherwise specified in the tables.

In Method B-1, standard heavy-duty cast C-clamps with a four-inch span between the anvil and the foot were used to maintain contact pressure on the bonded panels during the oven cure. After assembly of the jig, it was placed in an hydraulic press under contact pressure for twenty minutes at 300°F. After removal from the press, two C-clamps were applied, at opposite ends of the jig, and were positioned to use the full two-inch depth of the clamps, and to distribute the pressure as evenly as possible across the jig. The clamps were tightened evenly, with finger pressure only, and the jigs were placed in an oven at 480°F for the 16-hour cure.

COVER

SHIM

8 TEST PANELS
CLAD AL 24S-T3
1" x 4" x .064"

½" OVERLAP

SHIM

9"

7 ½"
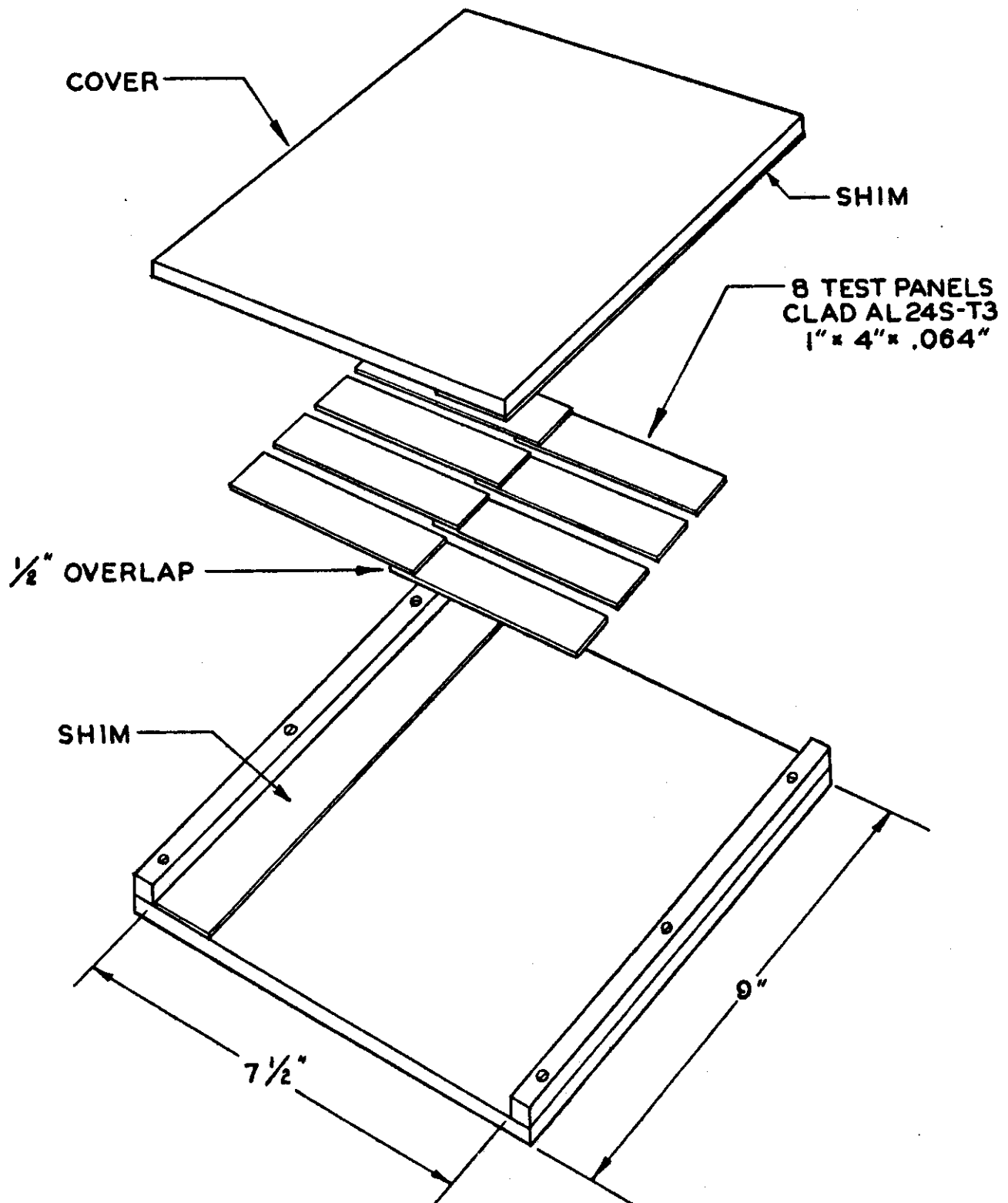
FIGURE 5-JIG FOR ASSEMBLING SHEAR PANELS

Method B-2 was a simplification and an improvement of Method B-1 in that neither press-cure nor C-clamps were required. The lap joints were assembled in the jig, as before. 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. Shear strengths were measured on 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 quadruplicate.

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. It should be noted that the pyrometer replaced a Leeds and Northrup potentiometer used in earlier work. The pyrometer could be read far easier and faster, and allowed a significant increase in the rate of testing samples. The pyrometer was calibrated against the potentiometer and was found to be quite sensitive and accurate, consistently indicating changes of less than 5°F at 500°F.

Except as otherwise noted on the tables, all bond failures were 100 percent adhesive.

Variations from the Standard Procedure

1. Special Curing and Catalyst Requirements

The cure times noted in Table V (Method B-1, above) ranged from 2 hours to 16 hours, instead of the standard 16-hour cure described above.

The curing catalysts indicated in Tables VI, VII and VIII were thoroughly blended into the resin solutions immediately prior to preparation of the lap joints. The catalyst concentrations were, in all cases, weight percentages based on resin solids.

2. Primers and Surface Treatments

The standard procedure for cleaning the aluminum test panels, Method C-1 mentioned above in the Standard Procedure, and in Table IX, was described in some detail in WADC TR 54-98. 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.

The other aluminum surface treatment specified in Table IX was that of electrical anodizing. In this table, half of the aluminum test panels are designated as "E-1a anodized", which has reference to Method E-1a described in the above-mentioned WADC Technical Report 54-98. Here, the aluminum panels were dipped in sodium hydroxide solution (about 5 percent) for 30 seconds at 160 to 180°F, and then were rinsed with cold water. This was followed by a dip in 60 percent nitric acid solution for 30 seconds at room temperature, followed by a cold water rinse. The panels were then anodized in 15 percent sulfuric acid solution at 78 to 80°F. The voltage was raised to 18 volts over 5 minutes and maintained at 18 volts for 30 minutes, with a current density of 12 to 15 amperes per square foot. The anodized panels were rinsed with cold water, dried, and stored in a desiccator until used. The electrical anodizing was done by the Contract Plating Company of Strafford, Connecticut.

A number of metal-surface primers prepared by the Linde Air Products Company were evaluated, as indicated in Tables IX and X, as well as in the following Glass Tape section. The GS-1 and X-31 Primers were diluted to 0.1 and 0.05 percent solids with toluene, and were used as indicated in Table IX.

The solvent for the VTS primer (vinyltriethoxysilane) was prepared by dissolving 0.08 percent by weight of sodium hydroxide in ethanol. The VTS was dissolved in that solvent to the indicated concentration by weight.

Aluminum panels were sent to the Linde Air Products Company where they were cleaned by the standard method, and their primers were applied and cured, as indicated in Table X. The primed panels were sealed in a polyethylene bag and were returned to this laboratory where they were immediately used for the preparation of lap joints bonded with CHR-122 silicone resin.

The effect of treating the aluminum surface with reducing agents is noted in Table XI. In the first set, the aluminum panels were immersed in a 10 percent ether solution of lithium aluminum hydride until the bubbling ceased (about five minutes). They were removed from the solution, wiped with a dry cloth, and dipped into DC-2103 silicone resin, the panels thus being exposed to the air for only one or two seconds. A check on this test was run by treating a sample of DC-2103 resin with the 10 percent lithium aluminum hydride solution. The solution was added until no further bubbling was evident. The resin solution was used to prepare lap joints. In the second set in Table XI, the aluminum panels were immersed in a 10 percent ether solution of lithium aluminum hydride, or 10 percent aqueous solutions of ammonium hydroxide, ferrous ammonium sulfate or sodium thiosulfate. The panels treated with lithium aluminum hydride were wiped and dipped in resin, as before. The others were wiped dry, rinsed in distilled water, wiped dry again, and placed in a desiccator filled with dry nitrogen gas. When thoroughly dried, they were brushed with the silicone resin, and lap joints were prepared.

3. Glass Tapes

The effects of using various types of glass fabric as reinforcement and as a carrier for the silicone resins are shown in Tables XII through XVII. Various treatments of the glass tapes and of the surfaces of the aluminum test panels were also evaluated.

The styles of glass fabrics are described in Table XXIX. While either No. 116 or No. 128 glass tape was used almost exclusively in this study, a comparison of the effectiveness of the various tapes may be found in Table XIII. The shear strength values of selected commercial and experimental silicone

resins and organo-modified silicone resins with glass tape
reinforcement are listed in Table XII.

Almost all of the resin-impregnated tape samples were
prepared by a standard dip-coating procedure, although several
samples listed in Table XII, as indicated there, were prepared
on a laboratory coating tower. In all cases, the glass fabric
or tape was heat-cleaned prior to use, by heating for four
hours at 1000°F to burn out all of the oils and starch. In
the standard procedure, strips of glass fabric, cut parallel
to the selvage of the cloth, were dipped in a solution of the
silicone resin, as received from the manufacturer (usually 40,
50 or 60 percent solids). The excess resin was allowed to drip
off, and the solvent was allowed to evaporate at room temperature
until the resin was tack-free (usually about 16 hours). A
piece of the impregnated tape was cut one inch wide and from
three-quarters to one inch long and was placed in the overlap
area (one inch wide by one-half inch long) between the aluminum
test panels. The lap joints were assembled in the usual manner
and were cured as in Method B-1 or B-2, as noted in the tables.

In several cases, as indicated, a Volan finish was applied
to the glass tapes before they were impregnated with the resin.
The Volan (methacrylato-chromic chloride) solution was obtained
from E. I. DuPont de Nemours Co., Inc., and was applied accord-
ing to directions (ammoniacal solution, dried at 200°F).

In other cases, as indicated, the heat-cleaned tape was
treated with the Linde primers or with aqueous solutions of
reducing agents by the procedure previously described. Also,
as indicated in the tables in a number of cases, the surfaces
of the aluminum test panelswere primed with a thin layer of
the resin solution and air-dried prior to assembly of the lap
joints.

As indicated above, several of the resin-impregnated tapes
described in Table XII were prepared on a pilot-scale coating
tower. This equipment (Figure 6), already in existence as part
of the general laboratory facilities, is essentially a continuous
dip-coating device with doctor blades for removal of the solvent
and precuring of the resin. The glass tape to be impregnated
was fed from a spindle (1) into a pan of resin solution (2) and
was held submerged by the guiding wheel cylinder (3) at the
base of the tower. The coated tape passed upward between doctor
blades (4) and through the heated tower (5) containing obser-
vation ports (7). The dried and cured tape was guided by the
idler rolls (8) at the top of the tower and was rewound on a

TAPE [REF.]
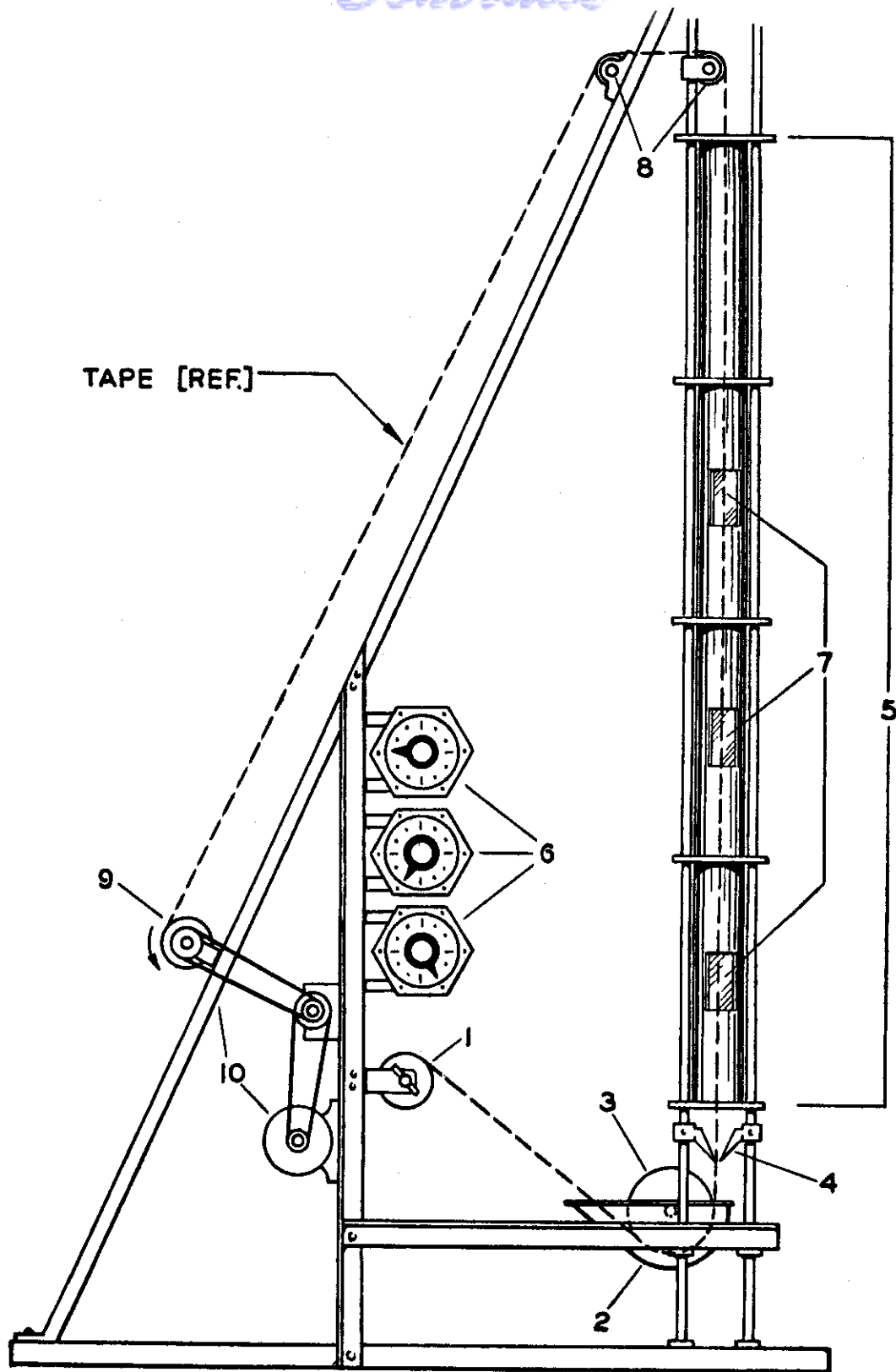
FIGURE 6 - PILOT SCALE COATING TOWER

removable drum (9) with a variable speed drive (10). The
tape speed was set at a rate of 16 yards per hour, giving a
total heating period of 10 minutes. The temperature in the
tower was controlled by variable transformers (6) to range
from about 200°F at the bottom to about 300°F at the top of
the tower. Under these conditions, the solvent was removed
and the resin was very slightly cured. Tapes prepared by this
method were tested in lap joints by the standard procedure
described earlier.

4. Fillers

The effect of various inorganic fillers in a commercial
silicone resin (DC-2103) and in three commercial organo-modi-
fied silicone resins (DC-1360, XR-807, X-2608) is shown in
Table XVIII. In order to obtain proper wetting of the fillers
with the resin solutions, it was found that the two materials
had to be ground together in a small mortar. A small quantity
of the resin solution, as received, was placed in a mortar,
the indicated amount of the filler was added and the materials
were ground until they appeared to be thoroughly blended. The
mixtures of experimental organo-modified silicone resins and
fillers listed in Table XX were prepared in this same way.

5. Blends

The results of a simple compatibility study of a series
of Dow Corning silicone resins are shown in Table XXI. Each
of the resin solutions was diluted with xylene to approximately
33 percent solids. Equal parts of two of the resin solutions,
as indicated in the table, were placed in a glass bottle and
were blended thoroughly. The mixtures were allowed to stand
for 24 hours at room temperature, and any separation, cloudiness
or gelling was noted. After this length of time, the solution
mixtures were stirred again and poured into aluminum-foil cups.
The solvent was removed by heating for 1 hour at 150°F, and
the resin films were oven-cured for 1 hour at 300°F, followed
by 16 hours at 480°F. Separation of the solution blend or
separation or appreciable cloudiness in the cured films were
interpreted as indications of incompatibility.

The silicone resins found to be compatible were blended
in the proportions indicated in Table XXII, and the lap joints
were prepared by the standard procedure (Method B-1).

6. Aging Studies

High-temperature aging studies were made of a group of commercial and experimental silicone and organosilicone resins. The results are listed in Tables XXIII, XXIV and XXV. In every case, the 16 hour cure was made at elevated temperatures, lap joints were prepared by Method B-1, except when as indicated in Table XXIII. The lap joints were removed from the jigs before high-temperature aging was initiated in air-circulating ovens. In order to minimize any effect of variations in the curing process, each of the four lap joints used for test at 70° and at 500°F after any given period of aging was taken from a different jig.

High-temperature aging studies were also run on silicone and organo-modified silicone resins (Table XXV) containing a filler or reinforced with glass tape. The Asbestine X was carefully ground into the resin solutions in order to disperse and wet the inorganic fibers uniformly. The No. 128 glass tapes were impregnated by the standard procedure described earlier, and the aluminum panels were primed with a thin layer of the same resin solution with which the tape was impregnated.

7. Special Bonding and Testing Techniques

The aluminum panels used in this work (4 x 1 x 0.064 inch) were shear-cut to size by means of large bed-type sheet-metal shears. The shear-cutting operation, however, leaves the edge of the panel with a slight bevel, which, depending on the handling of the pieces during the shearing process, may appear on different edges of the panels. Following a suggestion that the slight bevel might cause inconsistencies in the shear strength values, arrangements were made to have the edges of the test panels machined square. A comparison of the shear strengths of lap joints made with DC-2103 silicone resin, using either shear-cut panels selected to have beveled edges within the glued area or machined-edge panels, may be found in the first half of Table XXVI. The second half of Table XXVI shows the results of a similar series of tests, using one commercial silicone resin and one experimental silicone resin and using shear-cut panels chosen at random as well as machined-edge panels, but using Method B-2 for preparation of the lap joints instead of Method B-1 used in the first half of this table.

In the standard preparation of lap joints, described at the beginning of this portion of the experimental section,

a shim 0.003 inch in thickness, is normally used in the bonding jig (Figure 5). To determine the effect of varying the shim thickness, and thus the glue line thickness, the series of tests indicated in Table XXVII was run. A complete jig of eight lap joints (4 to be tested at room temperature and 4 at 500°F) was prepared from DC-2103 silicone resin and cured. The thickness of the glue lines was measured accurately before shear strengths were determined.

II. DISCUSSION

A. Synthesis of Resins and Resin Blends

Silicone Resin Chemistry

Discussions of the chemistry of the silicones can be found in several books (3,4) and in a number of articles. Only a brief, general picture of silicone resins is presented here. Specific details will be noted later in the discussion of the experimental work.

Silicone resins have a structure quite similar to that of quartz except that a number of the oxygen linkages in quartz are replaced by organic groups. These structures may be represented:

```
     |       |                                |
  -O-Si-O-Si-O-                            O     R
     |       |                             |     |
     O       O                          -O-Si-O-Si-O-
     |       |     |                        |     |
       -O-Si-O-Si-                          R     O
                                                  |       R
       Quartz                                  -O-Si-O-Si-O-
                                                  |     |
                                                        O
                                                        |
```
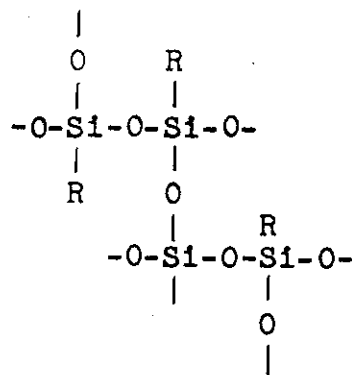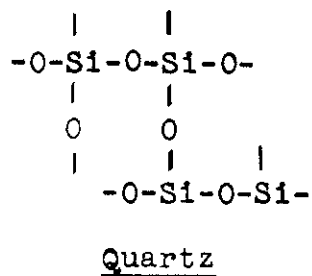
Silicone Resin

The R groups attached to the silicon have a tremendous effect on the physical and chemical properties of the polymer, depending on their type and number. The R groups used in the present work were almost entirely limited to methyl or phenyl, and the R/Si ratio ranged from 1.0 to about 1.8. An R/Si ratio of 1.0 represents one R group for every silicon atom, leaving three oxygen linkages, as indicated in the structure above. An R/Si of 2.0 would result in a linear polymer which has a structure such as shown below:

```
     R     R     R
     |     |     |
  -Si-O-Si-O-Si-O--
     |     |     |
     R     R     R
```
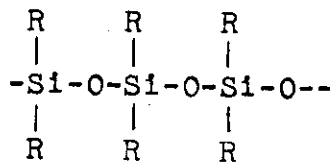
This structure is typical of the silicone elastomer polymer.

The silicone resins are prepared indirectly from quartz or silica. The silica is first converted to metallic silicon by reduction with carbon, or reacted directly with chlorine to produce silicon tetrachloride. The silicon or silicon tetrachloride is reacted further with organic chlorides either directly, or indirectly such as by the Grignard method, to prepare the organochlorosilane monomers used in this work. The organochlorosilanes can be converted further by reaction with alcohol to form the organoethoxysilane monomers.

As described in the experimental section of this report, the organochlorosilane or organoethoxysilane monomers were hydrolyzed to produce the intermediate silanols which condensed, with the elimination of water, to produce the siloxane polymer structure, as indicated:

$$RSiCl_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HCl$$

$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl$$

$$\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{HO-Si-OH}} + \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{HO-Si-OH}} \longrightarrow \underset{\underset{O}{|}}{\overset{\overset{R}{|}}{-Si-}} O \underset{R}{\overset{\overset{R}{|}}{-Si-}} O- \quad + H_2O$$
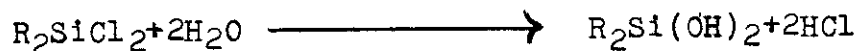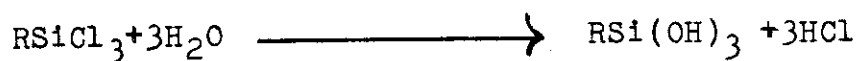
The outstanding resistance of the silicone resins to high-temperature oxidation and thermaldegradation led to their evaluation in the present program as high-temperature-resistant structural adhesives.

Synthesis of Silicone Resins

The purpose of thisdevelopment program was to evaluate commercial silicone resins as structural adhesives, and, if existing compositions were not suitable, to develop a high-temperature-resistant structural adhesive based on a silicone resin. A large number of commercially available silicone resin compositions were evaluated as high-temperature-resistant adhesives. The results of this evaluation are discussed in some detail later. For the most part, the actual compositions of the commercial resins were not revealed by the manufacturers, and thus no correlation could be made of the chemical composition and the

adhesive strength of these silicone resins. In order to provide such a correlation, a program of silicone resin synthesis was initiated as an important part of the second half of this contract.

A search of the literature (mainly patents) revealed two general methods for the preparation of silicone resins. The two methods are related, one method employing the organohalosilanes, the other the organoethoxysilanes. Both methods consist generally in mixing the monomers with water to hydrolyze them to the silanols, followed by heating to effect the polymerization of the silanols formed. The polymer is extracted or separated from the aqueous phase with a suitable solvent. The resin is then refluxed with the solvent for a period of time to remove residual water and acid, and to effect additional condensation.

After considerable experimentation, the standard procedure described in the Experimental Section of this report was developed, which was initially based on a process described in a patent by Welsh and Holdstock (5). It was soon evident that the technique of preparing the resins was an important factor in the adhesive strength of the product. A large excess of water and the proper selection of solvent, as well as the type of mechanical agitation, were important in the hydrolysis reaction and in the control of the hydrochloric acid produced by the hydrolysis. The bell-shaped agitator shown in Figure 1 was selected to provide efficient intermixing of the two phases without the formation of a very troublesome emulsion. Trichloroethylene was selected as the best solvent for general use.

The location of the monomer inlet tube in the hydrolysis apparatus was found to be quite important. Dropping the monomer mixture from above directly into the water phase caused premature gelling of the polymer. Locating the monomer inlet tube so that the monomers were delivered into the water phase also caused gelling and clogging of the inlet tube. Location of the inlet tube as low as possible in the trichloroethylene layer provided a uniform reaction and produced the best resin products on the basis of color, clarity, shelf-life and shear strength.

Maintaining the temperature of the reaction mixture at a point below room temperature effected a lower high-temperature shear strength in one case (compare CHR-136 with CHR-137) and a better high-temperature shear strength in another case (CHR-139 and CHR-140). In neither case was the product outstanding.

As mentioned above, hydrochloric acid is generated in the hydrolysis of the chlorosilanes. Addition of sodium hydroxide

solution or excess solid sodium bicarbonate into the reaction mixture, to control the pH, caused reduction of the shear strengths of the resins (CHR-122D and CHR-138).

The question of contamination of the silicone resin products was studied briefly. Silicone stopcock grease used in the apparatus is soluble in the monomeric organohalosilanes and was considered a possible source of contamination. Resin A-1 was deliberately contaminated with a small quantity of silicone grease, and a second resin (A-2) was prepared in clean apparatus assembled without grease. This contamination had comparatively little effect on the shear strength of the products.

At the completion of the resin preparation, the product is filtered through glass wool when it is poured into the storage bottle. In order to determine the effect of this step, a resin was prepared and filtered once through glass wool (A-3). A portion of this resin was taken for test, and the remainder (A-4) was filtered three more times through glass wool. Again, a portion was set aside for test, and the remainder (A-5) was passed through very fine filter paper. The additional filtrations through glass wool showed no improvement in high-temperature shear strength, and the final filtration through filter paper caused a noticeable decrease in shear strength at both room temperature and at 500°F.

Resin 151B was chosen for further study of the effects of purification. This resin solution was particularly cloudy and was brown in color. The resin solution was mixed with activated charcoal, and was agitated for twenty minutes. The slurry was then filtered through Celite, an absorbent diatomaceous earth. The filtrate was clear and almost water-white. The room-temperature shear strength of this resin was almost double that of the original 151B, and considerable improvement in high-temperature shear strength was noted. As an extension of this work, a quantity of CHR-179 resin was diluted with toluene, and the solution was passed through a Celite-packed filter. The resin filtrate obtained was a clear, yellow solution (179A). The filter cake was dispersed in methyl ethyl ketone, and the slurry was filtered. The fraction which was soluble in methyl ethyl ketone (179B) was also clear, but was much darker in color than the toluene fraction. The high-temperature shear strength of neither 179A nor 179B was significantly different from that of the original 179 resin, but the room-temperature shear strength of the methyl ethyl ketone fraction (179B) was considerably less than those of the other two. Further work should be done on the question of purification.

Resins prepared from all-ethoxy silane monomers used in place of chlorosilane monomers were, in general, somewhat better in appearance, but, in almost every case, showed lower shear strength values than resins of the same composition prepared from chlorosilane monomers.

The individual monomers used in the preparation of the silicone resins showed tremendously different rates of polymerization. For example, the polymerization rate of hydrolyzed methyltrichlorosilane is probably more than 1000 times that of hydrolyzed diphenyldichlorosilane (6). (The diphenylsilanediol is, in fact, quite stable.) An attempt to copolymerize these two monomers would be expected to produce a heterogeneous mixture of the two polymers. For this reason, diphenyldichlorosilane was not used in these preparations when it could be avoided, either phenyltrichlorosilane or methylphenyldichlorosilane being used to supply the phenyl portion of the mixture. Also, methyltrichlorosilane was converted to methylethoxydichlorosilane as a means of decreasing the reactivity of the monomer. In particular, the preparation of CHR-122 with the use of methylethoxydichlorosilane resulted in greatly increased shear strength in comparison with that of the original resin batch prepared with methyltrichlorosilane. CHR-182 resin prepared with methylphenyldichlorosilane showed a significant improvement in high-temperature shear strength in comparison with that of CHR-141 resin prepared with phenyltrichlorosilane.

Incremental addition of the monomers was tried as a further means of improving the homogeneity of the resin product. Here, the least reactive monomers were added to the hydrolysis medium first, followed slowly by the more reactive monomers. This method was particularly advantageous in the case of resins which were predominantly trifunctional and which contained high percentages of phenyl constituents. Resin CHR-128, prepared by the standard method, broke in the bonding jig. When it was prepared by incremental addition of the monomers, the resin (CHR-128A) showed good high-temperature shear strength and fair room-temperature shear strength. It is felt that further work should also be done on improving the homogeneity of the resin products by incremental addition and by other means.

Organo-Modified Silicone Resins

A limited number of silicone-organic resins are available commercially. In almost every instance, however, these resins are manufactured as coating resins and are considered to be silicone-modified organic resins rather than organo-modified silicone resins. The properties of these resins will be considered later in this discussion (see Evaluation of Adhesives).

It was felt that a chemical modification or copolymerization of a silicone resin with a smaller amount of organic resin would impart higher shear strength both at room temperature and at 500°F, would improve adhesion to metals, and would result in a faster initial cure, characteristic of the organic resins. In the preparation of the silicone resins, the monomers (organochlorosilanes or organoethoxysilanes) were hydrolyzed to the corresponding silanols which condensed under the influence of heat and acid catalyst to yield a cross-linked polymer of intermediate molecular weight. In the solution stage, ready for application as an adhesive, the silicone resin contains a number of residual -OH groups attached to silicon, as indicated by the Karl Fischer titration results in Table IV. These residual -OH groups are available for reaction with the residual -OH groups of alkyd and phenolic resins and with the residual -OH groups and epoxide groups of epoxy resins. It is also possible that a polyurethane-type addition may take place with an isocyanate or diisocyanate. Most of such reactions would eliminate water, which would provide an easy method of following the progress of the reaction. The polyurethane-type reaction might provide the outstanding adhesive properties of the isocyanate. In addition, a curing reaction might result which would proceed without the formation of water, which is a possible source of trouble in adhesive joints.

Terephthalic acid, tolylene diisocyanate, and triallyl cyanurate were used in initial attempts to modify silicone resins, the thought being that these relatively heat-stable materials would form organic links between portions of the silicone resin and thus reduce thermoplasticity at high temperatures and improve adhesion. The DC-804 resin was included in this series particularly because the Karl Fischer titration values indicated that this resin has an unusually high concentration of unreacted -OH groups. Noticeable improvement in shear strength resulted in several cases; in many cases, however, a decrease in shear strength was found. The shear strength of these modified resins will be considered in more detail later.

The modification procedure involved a considerable amount of heating and removal of water. This procedure was used in a control experiment which was run on DC-804 resin, alone, to determine the effect of advancing the extent of polymerization, or condensation, of the resin. This treatment resulted in a considerable increase in the room-temperature shear strength and a definite decrease in the high-temperature shear strength of the resin.

The X-14 series of silicone polymers, which are predominantly linear and contain a rather large percentage of residual, active ethoxy groups, were supplied by the Linde Air Products Company specifically for use in reactions with a variety of organic functional groups. Modifications of these resins with alkyd, epoxy and phenolic resins apparently proceeded satisfactorily, although elevated reaction-temperatures were required in order to produce homogeneous products from the higher epoxy resins and the phenolic resin.

DC-803 was selected as a soft, slow-curing resin thought to contain a relatively large amount of residual silanol end-groups, and modification of this resin with a large series of epoxy resins was made. Modifications of the resin appeared to proceed readily except in cases where large amounts of the high-molecular-weight Epon 1001 epoxy resin was used. Here, the addition of a small amount of diethylcarbitol apparently increased solubility sufficiently to permit modification.

Three further series of epoxy-modified silicone resins were prepared with the use of DC-2103, DC-2105 and DC-996 silicone resins. Although some difficulty was encountered with the use of the hard DC-2103 and DC-2105 resins, satisfactory modifications of these resins were prepared by the addition of diethylcarbitol.

A number of attempts to prepare silicone resins modified with commercial phenolic resins were unsuccessful. Although physical mixtures of the two resin solutions could be made at ordinary temperatures, the phenolic resin separated and gelled quickly as the temperature was raised in the reaction flask. A series of relatively stable solution blends of several of the epoxy-modified silicones with a phenolic resin (Plyophen 5023) was prepared at room temperature. A series of room-temperature solution blends of the epoxy-modified silicone resins with a polyamide resin (Polyamide 100, General Mills Inc.) was prepared.

The desired chemical modification of silicone resins with the various organic resins discussed above is dependent upon the presence of silanol groups in the silicone resin polymers. The actual number of these groups in commercially available silicone resins is unknown. A knowledge of the residual silanol groups in the various silicone resins would allow a more intelligent selection of the silicone resin and better control of the modification procedure. For this reason, a method of determining this information was sought. The use of the Karl Fischer reagent for the determination of the silanol group in monomers and in low polymers has been described in the literature (7). It is felt that the application of this method to the resin polymers, with proper modification, indicates comparative amounts of the silanol group in the resins. In future work, this method will be used to evaluate the ability of resins to react with other (modifying) resins.

Calibration tests of the Karl Fischer titrations with crystallized diphenylsilanediol produced results within three percent of the theoretical value. The initial tests on resins were made with DC-804 silicone resin which was thought to contain a relatively large number of residual silanol groups. A series of samples containing the Karl Fischer reagent was allowed to stand for varying lengths of time. Titration results showed that a relatively long period of time was required before the reaction was completed. A period of three hours was arbitrarily selected, and the series of relative values shown in Table IV was obtained

on eight silicone resins. Thus, a useful tool for evaluating silicone resins after preparation and before application as adhesives or before modification with other resins has been made available. This tool also gives one a measure of the amount of water to be expected during further condensation reactions.

Silicone-Isocyanate Copolymers

A series of experiments was run in an attempt to form a true copolymeric organo-silicone resin from the monomers. Diphenylsilanediol, which is a comparatively stable material and which can be purified by recrystallization, was selected for these experiments. Repeated early attempts to copolymerize the silanediol with terephthalic acid, low-molecular-weight terephthalate polyesters, and triallyl cyanurate met with no apparent success. Reaction of the silanediol with diisocyanates, however, apparently produced an addition product. Because of the outstanding adhesive properties of the organic polyurethanes, this work was followed with considerable interest.

The product of the reaction between diphenylsilanediol and 2,4-tolylene diisocyanate was found to have unusual thermal stability, decomposing gradually without melting at temperatures in excess of 325°C. The material, however, was insoluble in common organic solvents.

Further attempts to prepare a soluble or fusible product were not successful. It is felt, however, that further work may produce a useful product having good high-temperature resistance, and unusual adhesive strength. This opinion is based on the outstanding thermal stability noted above and on the shear strength of lap joints prepared from the dry monomer mixtures.

Data were presented in the Experimental Section on a brief study of the kinetics of the reaction of diphenylsilanediol and tolylene diisocyanate. The data, designating an essentially linear relationship as shown in Figure 4, indicate that the reaction is of second order; the reaction is therefore dependent on the concentration of both reactants. It appears that dioxane enhanced the reaction by increasing the solubility of the reactants. At the same time, however, dilution of the reaction mixture with more solvent decreased the reaction rate. It would appear, then, that the reaction can be slowed down at any given point by sufficient dilution of the reaction mixture. Such a technique would be promising in any further attempts to prepare the desired low molecular-weight copolymer. (A low molecular-weight product which will be soluble or fusible at a low temperature (50 to 150°F)

is needed in order to apply the resin in bonding applications.)

B. Evaluation of Adhesives

Standard Procedure

1. Commercial Silicone Resins

Data obtained in the evaluation of seventy-seven commercial silicone and modified silicone resins by the standard procedure described earlier are reported in Table I. Of these resins, the best shear strength values at 500°F were displayed by DC-2103 resin and especially by a low-viscosity modification of the same resin, DC-2103 LV, which had a shear strength at 500°F of 560 psi. Only a few other commercial silicone resins displayed shear strengths at 500°F greater than 300 psi. A Dow-Corning phenolic-modified silicone resin, XR-379, also displayed shear strengths at 500° greater than 300 psi. Other commercial organo-modified silicone resins displayed relatively poor bond strength at 500°F. Most of the commercial organo-modified silicone resins, however, showed high room-temperature shear strength values, the most outstanding being DC-1360, a silicone-terephthalate resin, having a shear strength of 2275 psi.

These values, while considerably below the high-temperature target shear strength of 1000 psi, were considered sufficiently promising to encourage extensive modifications, directed specifically toward the reduction of high-temperature thermoplasticity and the improvement of adhesion to metal surfaces. This target shear strength has now been realized with the epoxy-modified silicone resins synthesized in this laboratory.

2. CHR Silicone Resins (see Table II)

About two hundred silicone resins were prepared in this laboratory, in which the R/Si ratio varied from 1.0 to 1.5 and the organic composition varied from 0 methyl - 100 percent phenyl to 100 methyl - 0 percent phenyl. Resins having an R/Si ratio of less than 1.2 were difficult to prepare because of premature gelation, and were, in general, brittle and weak. Resins with an R/Si ratio greater than 1.5 were found to be more elastomeric than resinous and generally showed low shear strength values at high temperatures, due primarily to thermoplasticity. Most of the resins were prepared to have R/Si ratios ranging from 1.2 to 1.4, with the organic constituents ranging from 20 to 60 percent methyl and the remainder phenyl.

It was found that the difference between room-temperature and high-temperature shear strengths varied generally with chemical composition. A large difference between room-temperature and high-temperature shear strength can be considered an indication of thermoplasticity in the resin. This difference was found to increase generally as the R/Si ratio was increased, i.e., as the ability of the resin to cross-link was decreased. The best high-temperature shear strength values were generally found in resins with R/Si ratios from 1.10 to 1.30 and methyl contents from 30 to 60 percent.

It appears that failure of silicone resins on being aged at high temperature is due to a slow increase in the state of cure, or brittleness. On this basis, it would be reasonable to select as a structural adhesive a resin having comparatively low initial brittleness and relatively good high-temperature stability. These criteria would indicate that a resin having an R/Si ratio of 1.2 to 1.3 and a methyl-phenyl ratio of about 50:50 should yield a good initial high-temperature shear strength and should withstand aging at elevated temperatures for a considerable period of time without excessive embrittlement.

Further efforts to improve the homogeneity of the resins, as discussed earlier, would be expected to be an important factor in the reduction of thermoplasticity in the resins and should be important in improving high-temperature shear strength values obtained with these resins. It is felt that this factor is second only to improvement in the adhesion of resins to metal. The problem of adhesion to metal is discussed under Primers and Surface Treatments.

3. Organo-Modified Silicone Resins (see Table III)

With the use of selected commercial silicone resins and commercial alkyd, epoxy, phenolic, and polyamine resins, almost one hundred organo-modified silicone resins have been prepared in this laboratory. Three organic compounds were also evaluated as modifying agents.

Terephthalic acid, tolylene diisocyanate, and triallyl cyanurate were used in the first modifications of silicone resins. Modifications of DC-804 (M-40 and M-41) with tolylene diisocyanate and with terephthalic acid showed some promise. The tolylene diisocyanate modification displayed shear strength values slightly higher than those of the unmodified resin (Table I).

In a control run (M-39) where DC-804 was run through the same modification procedure in order to advance its state of polymerization, a room-temperature shear strength value considerably higher than that of the original resin (Table I) resulted; the 500°F shear strength value, however, was considerably reduced. It may be noted here that the water removed from the DC-804 in this experiment (M-39) was equivalent to about one OH group for every eight silicon atoms, or about two and one-half times as much as was indicated by the Karl Fischer titration value. The high-temperature shear strength value obtained by modification of DC-804 with tolylene diisocyanate was better than that of this control run M-39.

Modification of the Linde Y-1044 resin with triallyl cyanurate also effected considerable improvement over the original value for that resin. The high-temperature shear strength, however, was still quite low.

A series of modifications was made in which alkyd, epoxy, and phenolic resins were used with the Linde X-14 silicone polymers (later designated X-821). These polymers are stated to be predominantly linear, and contain a rather large percentage of residual active epoxy groups. They should be particularly suitable for copolymerization with alkyds, epoxies, and phenolics, intra-condensation or cross-linking being limited by the presence of the epoxy groups. Although the room-temperature shear strength values of some members of this group were good, notably the epoxy modifications, none showed good high-temperature shear strength. It is felt that the modifications effected insufficient cross-linking in these linear polymers, resulting in a product with relatively high thermoplasticity.

A change was made to the standard silicone resins, and DC-803, a soft, slow-curing resin, was selected for a fairly complete series of epoxy modifications. As little as 5 percent of Epon 834 (an epoxy resin of medium molecular weight) caused a noticeable increase in the room-temperature shear strength, while 80 percent of Epon 834 produced a room-temperature shear strength value of 3100 psi. Throughout the series, however, the high-temperature shear strength values were somewhat lower than the value for the unmodified DC-803 and were comparatively unaffected by changes in percentage or type of the epoxy resin.

Another series of epoxy-modified resins was prepared with the use of the best commercial silicone resin, DC-2103, a harder, faster curing resin than DC-803. This series produced the best modified silicone resins, those containing DC-2103 and 5 to 20 parts of Epon 834. Each of these resins showed room-temperature

and high-temperature shear strength values considerably above those for the unmodified silicone resin, one reaching 63 percent of the 1000 psi target at 500°F. It should be noted here that later batches of M-60 containing 20 percent Epon 834 showed high-temperature shear strengths higher than 900 psi and a high-temperature shear strength of 1035 psi (average of eight tests) when 15 percent Asbestine X filler was incorporated. The room-temperature shear strength of this filled resin was 1100 psi. In this same DC-2103 series, 10 percent of Epon 828 also provided shear strength values better than those for the unmodified resin.

Epoxy modification of DC-2105 resin resulted in improved room-temperature shear strength values but the high-temperature shear strength values were generally decreased. The room-temperature shear strength of DC-996 was improved only slightly by epoxy modification. The modified resins had no high-temperature shear strength.

A series of room temperature solution blends of a polyamine resin with epoxy-modified silicone resins displayed very poor shear strength values at 500°F.

Attempts to prepare copolymers of phenolic resins with silicone resins were unsuccessful because of lack of compatibility and premature gelling of the phenolic resin. An exception was the modification of DC-803 with phenolic resin, GJQ-11943, especially recommended for modification use. While this resin showed fair shear strength values, it was found to have very poor shelf-life. Room-temperature solution blends of epoxy-modified silicone resins with the Plyophen 5023 phenolic resin showed comparatively low room-temperature shear strength values. The high-temperature shear strength values, although not particularly high, showed the most promise of any of the phenolic blends.

4. Silicone-Isocyanate Copolymers

The difficulties in preparing a soluble or fusible product from the silicone-diisocyanate copolymerization experiments have been discussed earlier. The lap joints prepared from a dry mixture of the solid silanediol and the solid TDI dimer showed shear strength values of 820 psi at room temperature and 420 psi at 500°F. These results, while not exceptionally high, are considered unusual for a simple, dry mixture of the monomeric materials. It is felt that more work should be done to develop the ultimate properties of this adhesive system.

1. Special Curing and Catalyst Requirements

It will be noted that a relatively long high temperature cure (16 hours at 480°F) was used in the standard evaluation procedure. Such a rigorous curing requirement obviously is not desirable in the actual application of a structural adhesive. In the selection of the standard cure for this experimental work, however, two special factors were considered. First, it is known that many silicone resins require such a rigorous cure to develop optimum strength and flexibility. Secondly, in developing an adhesive capable of withstanding long aging periods at 500°F, a resin which would not withstand an initial aging of 16 hours at 480°F would be of little utility.

In many cases, the cures recommended by the manufacturer differed considerably from the standard evaluation cure. It should be noted, however, that most of the resins were developed and recommended for coatings and uses other than as structural adhesives.

A number of the commercial silicone resins were selected, and their curing requirements were compared by preparing lap joints in the standard manner and oven-curing for 2, 4, 8, 12 and 16 hours (Table V). With few exceptions, the resins increased in shear strength both at room temperature and at 500°F during the extended cure period from two hours to 16 hours. A notable exception was DC-1089, a silicone wire-varnish resin. The room-temperature shear strength of DC-804 decreased, but the high-temperature shear strength increased as a result of the extended cure. Although several of the silicone-organic commercial resins showed increased room-temperature shear strength after the extended cure at 480°F, all but two showed decreased high-temperature shear strength. Although the high-temperature shear strength of the two exceptions, DC-1360 and DC-807, increased, they were still quite low. DC-2103 developed its strength slowly and required an extended high-temperature cure.

In view of the long high-temperature cure required by most of the high-strength silicone resins, a series of catalysts were tested as a means of reducing this cure requirement (Table VI). The effects of a series of amines, octylene glycol titanates and two Dow-Corning catalysts (XY-15 and XY-24) high-temperature shear strength were compared (Table VI). It will be noticed that in almost every case the amine catalysts produced some improvement in the high-temperature shear strength but caused little or no change in the room-temperature shear strength. The

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octylene glycol titanates (du Pont) are classified as titanium chelates. These materials caused slight increases in the shear strength of a few resins, but considerably reduced the shear strength of others. The Dow-Corning XY-15 catalyst resulted in some improvement in the shear strength of DC-2106HV. In other cases, however, the Dow-Corning catalysts showed no improvement.

The effect of triethanolamine in DC-2103 resin was tested further, and the results are listed in Table VII. The catalyst showed a remarkable effect on the high-temperature shear strength, producing in four hours almost the full strength obtainable in the normal uncatalyzed 16-hour cure. The catalyst, however, had practically no effect on the room-temperature shear strength over curing periods ranging from 4 hours to 30 hours. This catalyst should be of considerable interest as a means of shortening the silicone resin cure.

Zinc Octasol, a curing catalyst recommended by Dow-Corning for use with silicone resins, was tested in three of the Dow Corning silicone resins (Table VIII). Increasing amounts of the catalyst (from 0.01 to 0.1 percent) decreased the room-temperature shear strengths to one-third the values obtained with the uncatalyzed resins.

2. Primers and Surface Treatments

It has been noted that in almost every case lap joints prepared with the silicone resins showed adhesive rather than cohesive failure, i.e., the failure occurred between the metal surface and the resin rather than internal failure to the resin itself. In view of this fact, a considerable amount of work was done in an attempt to find a suitable metal-surface priming material or surface treating technique which would increase the strength of the adhesive bond up to the cohesive strength of the resin itself. Data obtained in these tests are listed in Tables IX, X and XI. The results of further surface treatments and priming techniques on glass fabric are listed in Tables XIV, XV, XVI and XVII.

The degreasing and chromic acid-cleaning of the surface of the aluminum test panels is considered necessary. Unfortunately, none of the primers or surface treatments provided a significant improvement in shear strength either at room temperature or at 500°F, over the standard treatment.

3. Glass Tapes

In the actual application of structural adhesives, an adhesive

in tape form is generally preferred over a solution or hot-melt adhesive. In many cases, this tape form is obtained either by solution or hot-melt impregnation of the fabric with resin, followed by a slight precure if necessary. The fabric often adds the further advantage of acting as a reinforcement. A number of tests were made with glass fabric as a carrier or reinforcement of the silicone and organo-modified silicone resins.

The use of glass fabric as a carrier was found to be quite practical for the silicone resins, although a thin prime coating of the silicone resin applied to the test panels was found necessary to obtain satisfactory adhesion between the resin-impregnated glass tape and the metal surface. The use of glass fabric with the organo-modified resins causes a reduction in the shear strength values in almost every case. Little if any significant reinforcement of silicone or organo-silicone resins by the glass fabric, with or without various glass fabric and metal surface treatments, was noted. In a few isolated instances when heavier grades of glass fabrics were used, some increase in shear strength was noted.

It was found that glass fabric decreased the resistance of silicone resins to high-temperature aging. It is possible that at the high temperature the glass acted as an alkaline catalyst to increase the rate of hardening and caused premature embrittle-ment of the silicone resin.

4. Fillers

In general, both the cohesive and the adhesive strength of polymeric materials frequently can be increased tremendously by the addition of fillers of fine particle size. A number of inorganic fillers were tested in selected silicone resins, and the results are listed in Tables XVIII and XX. Some further evaluation of Asbestine X filler in high-temperature aging tests is shown in Table XXV.

In the initial test (Table XVIII) with DC-2103 silicone resin, only one filler, titanium dioxide, effected an improvement in the high-temperature shear strength values. All of the fillers tried in this series, including titanium dioxide, decreased the room-temperature shear strength values. The same series of fillers were tested in three silicone-organic resins, DC-1360 (silicone-terephthalate), XR-807 (silicone-alkyd) and X-2608 (silicone-alkyd). With DC-1360 resin, titanium dioxide showed considerable improvement in the high-temperature shear strength values and some improvement in the room-temperature shear strength. Two other fillers which improved the high-temperature shear strength of this resin were Santocel C and aluminum dust. With the other two silicone-organic resins, titanium dioxide again improved the

high-temperature shear strength as did Santocel C, mica and
Celite in the X-2608 resin. It should be noted that zinc oxide
and the magnesium oxide fillers caused a considerable reduction
in the shear strength of each of the silicone resins in which
they were tested.

Titanium dioxide, Asbestine X and aluminum dust were tested
in several loadings in four epoxy-modified silicone resins pre-
pared in this laboratory, and the results are listed in Table XX.
The Asbestine X was the most effective of the three fillers,
titanium dioxide being almost as good in most instances. The
aluminum dust in all cases showed higher room-temperature shear
strength values, but lower high-temperature shear strength values
than the other two fillers. It should be noted here that later
work with Asbestine X in CHR-M-60 resin (Table XXV), where the
filler was more thoroughly ground in the resin solution, produced
shear strength values at 500°F greater than 1000 psi.

It is felt that considerably more work should be done with
filler reinforcement of the silicone and organo-modified silicone
resins.

5. Blends

Tests were made to determine the effect of blending different
silicone resins found to be compatible with each other (Table XXI).
The results of shear strength tests of resin blends (Table XXII)
showed that in almost every case the shear strengths were averages
of the shear strengths of the individual resins. Blends of
experimental silicone resins prepared in this laboratory, CHR-122
and CHR-141, showed the same result; in fact, the shear strength
values of these blends were found to correspond roughly to the
shear strengths of individual resins having compositions comparable
to that of the blends (from data in Table II).

6. Aging Studies

An important feature of testing a high-temperature
structural adhesive involves aging a lap joint prepared with
the adhesive for an extended period of time at 500°F. Resistance
to shorter exposures at temperatures of 700°F and higher is
also desirable.

The initial aging studies (Table XXIII) were made on
selected commercial organo-modified silicone resins. These
resins were cured and aged at temperatures ranging from 480°F
up to 600°F, and the effect on shear strength was determined

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after periods of 100, 200 and 300 hours. In general, the silicone resins withstood aging up to 300 hours at 550°F, but broke after 200 hours at 600°F. The exception was DC-805 which did not break until 300 hours at 600°F; its high-temperature shear strength, however, was quite low. In this series, the high-temperature shear strength was upheld best by DC-803, although DC-2103 was almost as good. Of the three silicone-organic resins tested, DC-1360, 160-30-D, and X-2720, the latter withstood no aging at 500°F or higher. DC-1360 withstood 100 hours at 500°F but failed rapidly at 600°F.

In the next aging studies (Table XXIV), a group of epoxy-modified silicone resins synthesized in this laboratory, as well as their separate silicone and epoxy resin components, were aged at 500°F for periods up to 500 hours. The aging results of the epoxy resins alone did not agree entirely with the aging results of the corresponding epoxy-silicone resins. The shear strength at 500°F of Epon 562 was slightly better after 100 hours at 500°F than the others of the series. The corresponding epoxy-silicone resin, however, showed extremely poor resistance to aging. The epoxy-silicone resin which was comprised of DC-803 and Epon 834 showed the best resistance to aging in the group, the high-temperature shear strength (310 psi) after 500 hours of aging at 500°F being almost the same as the initial high-temperature shear strength. The addition of aluminum dust apparently decreased the aging resistance of three of the epoxy-silicone resins, but somewhat improved the aging resistance of the fourth (DC-803 and Epon 864).

The results of aging several silicone and epoxy-silicone resins at 600°F are shown in Table XV   CHR-122 silicone resin showed unusually high shear strength values at 500°F (600 psi), and 100 psi higher with No. 128 glass tape reinforcement. The resin withstood 120 hours accelerated aging at 600°F, and broke only after 190 hours. CHR-141 resin (R/Si 1.40, 55 percent methyl) initially showed a somewhat lower shear strength value at 500°F (450 psi) but withstood the full 240 hours of aging at 600°F, with, however, a decrease in shear strength at 500°F to 100 psi. With both of the silicone resins , the No. 128 glass tape caused a noticeable reduction in the high-temperature aging resistance of the resins.

Samples of CHR-M-60 epoxy-silicone resin (DC-2103 and 20 percent Epon 834) showed unusually high shear strength values (830 psi) at 500°F. The addition of 30 percent of Asbestine X filler to this resin increased the high-temperature shear strength to almost 1000 psi. CHR-M-61 (DC-2103 and 50 percent

Epon 834) showed much lower high-temperature shear strength
values, which were also increased considerably by the addition
of Asbestine X. These epoxy-silicone resins failed after
being aged for 70 hours at 600°F. Proper compounding of a
similar modification containing less epoxy resin, however,
should produce a relatively fast-curing high-temperature-
resistant structural adhesive.

It is felt that considerably more work should be done to
calibrate the 600°F aging so that a much shorter period of
time at that temperature may be used as a preliminary screening
test equivalent to 1000 hours of aging at 500°F (Target
Specification)

7. Special Bonding and Testing Techniques

It was noticed that in the shear-cutting of the aluminum
test panels a slight bevel was left on the edges of the panels.
This condition raised the question of what effect the slight
bevel, in one direction or the other, might cause. Data in
Table XXVI show the comparative effects of the panels with
slightly beveled edges, and panels in which the edges were
machined square, on the shear strength of DC-2103 silicone resin.
In the first set of lap joints, prepared by Method B-1, the
beveled-edge panels produced an average room-temperature shear
strength only 7 percent lower than that obtained with the use
of machined-edge panels. The precision with the machined-edge
panels was considerably better, however, a mean deviation of
5 percent and a maximum deviation of 10 percent being obtained,
as compared with a mean deviation of 9 percent and a maximum
deviation of 27 percent for the beveled-edge panels.

In the second half of Table XXVI, which lists the results
obtained on DC-2103 silicone resin prepared by Method B-2,
somewhat better precision was shown with both shear-cut panels
and machined-edge panels. The beveled-edge panels at room
temperature produced an average deviation of 8 percent and a
maximum deviation of 12 percent; at 500°F, the precision was
nearly the same, an average deviation of 8 percent and a
maximum deviation of 14 percent. The average shear strength
values, both at room temperature and at 500°F, were almost
identical for the beveled-edge panels and for the machined-edge
panels. With the machined-edge panels, the precision was quite
good, with an average deviation of only 1 percent and a maximum
deviation of 3 percent at room temperature and an average devia-
tion of 5 percent and a maximum deviation of 10 percent at 500°F.

An identical series of tests run at the same time on CHR-122
silicone resin showed results quite similar to those obtained
with the DC-2103 resin.

It appears that the slight bevel on the shear-cut panels
produced nearly the same average shear strength values as those
obtained in using machined-edge panels. The results with shear-
cut panels, however, were considerably less precise than those
obtained with machined-edge panels. The use of machined-edge
panels was initiated about halfway through this project, and
about half of the results in this report were obtained with
the use of these panels. On the basis of this study, however,
it is not felt that the use of shear-cut panels significantly
affected the results obtained in the earlier work. A similar
opinion is held concerning the use of Method B-1 and Method
B-2, which are also compared in Table XXVI. It is felt that
the precision obtained with Method B-1 is not sufficiently
less than that obtained with Method B-2 to affect the compar-
isons made from the results of the early screening tests. Method
B-2 was used in about the last quarter of the work on this
project, as indicated in the footnotes to the tables.

An experiment was run on DC-2103 silicone resin to determine
the effect of glue line thickness on shear strength. Little
or no variation was obtained either in the room-temperature or
high-temperature shear strength with variation of the glue line
thickness over the range 1 mil to 3 mils (0.001 to 0.003 inch).
It was found, however, that there was a considerable discrepancy
between the shim thickness and the thickness of the actual
glue line. Preliminary attempts to correct this discrepancy
showed it to have little or no effect on the shear strength
values.

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IV. SUMMARY AND CONCLUSIONS

1. An epoxy-modified silicone resin structural adhesive, prepared from 20 percent Epon 834 ard 80 percent DC-2103 resin (by weight of solids) and compounded with 30 percent Asbestine X filler, has produced unaged shear strength values at 500°F better than the target requirements of 1000 psi. The room-temperature shear strength of this composition, CHR M-60, is about 1100 psi.

2. DC-2103 silicone resin showed the highest shear strength values at 500°F in an evaluation of seventy-seven commercial silicone and organo-modified silicone resins. Of the commercial organo-modified silicone resins, DC-1360 displayed unusually high shear strength at room temperature (average, 2300 psi) but low shear strength at 500°F (average, less than 100 psi).

3. Silicone resin adhesives which have been synthesized in this laboratory show consistently higher shear strength values than the best available commercial silicone resins (greater than 1100 psi at room temperature and 600 psi at 500°F). The best high-temperature shear strength values were found in resins having an R/Si ratio from 1.10 to 1.30 and a methyl content from 30 to 60 percent.

4. About one hundred organo-modified silicone resins have been prepared in this laboratory, in which commercial silicone resins were combined with commercial alkyd, epoxy, phenolic, and polyamine resins, and with several organic compounds. Of these, the epoxy-modified silicone resins showed the most promise of yielding a satisfactory high-temperature-resistant structural adhesive composition.

5. The Karl Fischer reagent has been adapted for deter-mination of silanol groups in silicone resins. Hydroxyl values obtained are useful in the characterization of silicone resins and in the control of silicone modification reactions.

6. Silicone-isocyanate copolymerization work, while not producing a practical product, resulted in thermally stable materials and adhesive results of considerable interest.

7. Amine catalysts were found to be of considerable promise in reducing the cure requirements of silicone resin adhesive compositions. In DC-2103, 90 percent of the high-temperature shear strength (average about 500 psi) normally developed after sixteen hours at 480°F was developed in about four hours at 480°F.

8. Primers and surface treatments, beyond the initial degreasing and chromic acid treatment, provided no significant improvement in the adhesion of silicone or organo-modified silicone resins to an aluminum surface.

9. Glass fabric may be used as a carrier for a silicone resin adhesive. Little or no reinforcement, however, was added by the fabric. There were indications that glass fabric decreased the resistance of silicone resins to high-temperature aging.

10. Asbestine X (a fibrous magnesium silicate) and titanium dioxide were found to be of value as fillers for reinforcement in silicone and organo-modified silicone resins. Zinc oxide and magnesium oxide fillers reduced the shear strength of the silicone and organo-modified silicone resins in which they were tested.

11. Blends of compatible silicone resins produced shear strength values which were approximate averages of the shear strengths of the individual resins.

12. Several epoxy-modified silicone resins which were synthesized in this laboratory showed little or no change in shear strength at 500°F after being aged for 500 hours at 500°F. Several commercial silicone resins withstood aging for 300 hours at 550°F, with, however, a 50 to 60 percent reduction in shear strength at 500°F. A silicone resin synthesized in this laboratory withstood 240 hours of aging at 600°F, with, however, considerable reduction in shear strength at 500°F.

13. Silicone resin shear strength values obtained from lap joints prepared with machined-edge panels showed an average deviation of only one percent and a maximum deviation of three percent at room temperature, and an average deviation of five percent and a maximum deviation of ten percent at 500°F.

V. RECOMMENDATIONS

It is recommended that:

1. The investigation of epoxy-modified silicone resins be continued. This would include a brief study of copolymerization and solution-blend methods, further modifications, over a limited range, of commercial silicone resins with additional commercial epoxy resins, and more detailed work as indicated below.

2. A more detailed investigation be made of the composition used in CHR-M-60 epoxy-silicone resin, including studies of composition, filler, catalyst, and thermal stabilizers.

3. Modifications be made of commercial and experimental silicone resins and epoxy-silicone resins with phenolic resins.

4. Complete aging studies with aluminum and stainless steel be made on selected silicone and epoxy-silicone resins, with concurrent calibration of aging at 600°F in order that such a test may be used for accelerated screening.

5. Further improvements be made in the synthesis of silicone resins for use as high-temperature-resistant adhesives by the development of practical purification procedures and by the use of incremental addition of monomers or other techniques for improving the homogeneity of the polymers.

6. Soluble or fusible copolymers of silicone and isocyanate monomers be developed for evaluation as high-temperature structural adhesives.

TABLE I

COMMERCIAL SILICONE RESINS

Resin	Organic Modifier[2]	Shear Strength[1], Cumulative Average			
		Room Temperature		500°F	
		psi	No. of Tests[3]	psi	No. of Tests[3]
Dow Corning Corp.					
DC-801		1483	3	183	3
DC-802		1488	2	122	2
DC-803		1390	2	282	2
DC-804		861	8	316	8
DC-805		1555	1	250	1
DC-935		462	1	70	1
DC-935 HV		640	1	110	1
DC-993		1420	4	130	2
DC-994		1142	2	62	2
DC-996		1354	8	88	5
DC-1088		950	1	75	1
DC-1089		1033	3	60	3
DC-1360	Terephthalate	2275	13	91	13
DC-2103		1175	13	385	15
DC-2103 HV		925	1	390	1
DC-2103 LV		875	1	560	1
DC-2104		783	3	268	3
DC-2105		940	5	225	5
DC-2106		745	5	255	5
DC-2106 HV		450	1	230	1
XR-100		1156	6	317	6
XR-379	Phenolic	1140	1	310	1
XR-398	Alkyd	1454	5	73	3
XR-513		800	1	155	1
XR-537		1250	1	80	1
XR-538		955	1	110	1
XR-543		1043	3	242	3
XR-544		846	5	284	5
XR-551		0	1	0	1
XR-807	Alkyd	1612	3	78	3
XR-859	Phenolic	905	1	95	1
XR-875	"	690	1	180	1
XR-878	Alkyd	1050	1	175	1
XR-880	"	1580	1	0	1
XR-928		0	1	0	1
XR-1024		0	1	0	1
XR-4007		525	1	275	1

TABLE I (Cont'd.)

Resin	Organic Modifier[2]	Shear Strength[1], Cumulative Average			
		Room Temperature		500°F	
		psi	No. of Tests[3]	psi	No. of Tests[3]
General Electric Co.					
SR-32		952	2	(none)	
SR-17		970	1	115	1
SR-53		765	1	80	1
SR-82		830	1	120	1
SR-98		650	1	65	1
SR-02		390	1	30	1
SR-111		750[4]	1	125[4]	1
191-14-631		550	1	210	1
81390		1222	3	(none)	
81397		1023	3	268	3
Linde Air Products Co.					
X-62		1160	1	120	1
X-63		837	3	195	3
Y-1027		800	2	35	2
Y-1043	Styrene	980	1	20	1
Y-1044	"	750	3	10	2
Y-1054		750	1	0	1
Y-1166		830	2	0	2
Y-1167		860	2	0	2
Y-1203		1712[4]	4	180[4]	4
Y-1247		1770[4]	1	205[4]	1
Midland Ind. Finishes Co.					
160-29-H		1030	6	207	5
160-30-D	Alkyd	1633	2	35	1
X-2608	"	1694	4	62	3
X-2720	Epoxy	1640	3	118	2
RS-513	Alkyd	1265	3	64	3
RS-556	"	1327	2	160	1
Bakelite Corp.					
BRQ-12427		1250	1	40	1
BRQ-12431		890	1	10	1
ORQ-12554		560	1	0	1
ORQ-12555		590	1	8	1

1. The lap joints were prepared from the resins in accordance with the standard procedure (Method B-1, except as noted below in footnote 4) described in the Experimental Section, and were cured for 16 hours at 480°F.
2. Where disclosed by the manufacturer.
3. Each test consisted of shear tests on two lap joints, prepared, cured and tested in the same batch.
4. Prepared in accordance with Method B-2.

TABLE II

CHR-SYNTHESIZED SILICONE RESINS

R/Si Ratio	% Methyl	Resin CHR No.	R.T. Shear Strength, psi Aver.	High	Low	500°F Shear Strength, psi Aver.	High	Low
1.00	20	128A	475	500	450	480	490	470
1.10	(10)[1]	132	700	750	650	450	460	440
1.17	44	178	620	640	600	485	510	460
1.20	30	147	175	200	150	0	0	0
1.20	30	155	250	300	200	525	710	370
1.20	30	155E[3]	685	730	640	462	490	440
1.20	34	133	650	700	600	470	490	450
1.20	40	136[6]	875	900	850	270	280	260
1.20	40	137	800	850	750	515	520	510
1.20	(20)[2]	138[4]	400	400	400	147	165	130
1.20	45	139	575	650	500	107	185	160
1.20	50	28[3]	685	775	600	255	350	160
1.20	50	122C	615	660	580	432	490	380
1.20	50	122D[5]	780	800	740	275	300	260
1.20	50	122E[3]	605	680	560	347	370	300
1.20	50	122-1	590	600	575	420	425	400
1.20	50	122-2	760	800	700	630	650	610
1.20	50	135	775	800	750	530	540	520
1.20	60	151A	710	750	650	422	450	400
1.20	60	151B	710	860	600	375	430	300
1.20	60	151B[7]	1450	1480	1390	525	540	510
1.20	65	23A[3]	685	700	675	170	190	150
1.20	65	28A[3]	525	550	500	160	170	150
1.20	66	170	870	900	840	460	480	440
1.20	67	159E[3]	535	650	380	147	180	90
1.20	40	181	635	650	620	425	460	390
1.20	50	179	900	900	900	405	460	390
1.20	50	179A[7]	915	930	900	390	410	370
1.20	50	179B	590	600	580	400	400	400
1.20	60	180	820	880	760	397	410	385
1.20	33	194	455	460	450	210	240	180
1.20	37	193	490	510	470	190	190	190
1.20	42	192	590	590	590	325	330	320
1.20	46	191	610	640	580	325	360	290
1.20	54	189	920	940	900	300	310	290
1.20	58	188	990	1000	980	265	290	240

TABLE II (Cont'd.)

R/Si Ratio	% Methyl	Resin, CHR No.	R.T. Shear Strength, psi			500°F Shear Strength, psi		
			Aver.	High	Low	Aver.	High	Low
1.20	62	187	720	730	710	300	300	300
1.20	66	186	720	730	710	310	330	290
1.20	70	185	905	920	890	355	370	340
1.20	75	184	855	910	800	300	310	290
1.25	35	157	412	450	400	365	400	320
1.20	45	140[6]	475	500	450	360	370	350
1.25	50	163C	655	690	600	472	510	420
1.25	50	163D[5]	295	320	280	430	460	400
1.25	50	164	880	920	840	300	310	290
1.25	55	156	632	650	600	480	520	410
1.25	55	156E[3]	905	1000	720	315	340	300
1.25	64	173	710	720	700	280	310	250
1.25	65	158E[3]	347	400	300	67	80	50
1.25	65	171	844	900	780	380	390	370
1.30	40	154E[3]	515	540	500	120	160	100
1.30	45	183	1105	1120	1090	610	620	600
1.30	40	154	587	650	500	415	450	400
1.30	50	153	612	650	600	427	460	400
1.30	60	152	650	700	600	382	410	350
1.30	60	152E[3]	1065	1100	1000	220	260	200
1.30	60	150	800	900	700	405	510	290
1.30	63	172	780	820	740	495	510	480
1.40	40	A-1[8]	900	--	--	290	--	--
1.40	40	A-2	925	--	--	100	--	--
1.40	40	A-3	800	--	--	480	--	--
1.40	40	A-4	850	--	--	390	--	--
1.40	40	A-5	700	--	--	330	--	--
1.40	55	141	960	1080	900	300	330	250
1.40	55	141A	850	900	800	177	185	170
1.40	55	141B	587	675	550	302	310	295
1.40	55	141C	875	960	800	375	400	340
1.40	55	141D[5]	835	900	800	325	340	300
1.40	55	141E[3]	760	810	750	67	80	50
1.40	57	182	935	1000	870	485	510	460

TABLE II (Cont'd.)

1. 10 mole % methyl, 30 mole % vinyl, 60 mole % phenyl
2. 20 mole % methyl, 20 mole % vinyl, 60 mole % phenyl
3. Ethoxy-silane monomers used in place of the usual chloro-silane monomers
4. Sodium hydroxide solution added during hydrolysis to control pH
5. Excess of sodium bicarbonate present during hydrolysis to control pH
6. Temperature of hydrolysis reaction mixture maintained below 10°C
7. Purified (See Discussion Section)
8. See Discussion Section

TABLE III

ORGANO-MODIFIED COMMERCIAL SILICONE RESINS

Resin CHR No.	Silicone Portion Resin	Silicone Portion Supplier	Organic Modifier Portion Resin, or Compound	Type	Supplier	%	Reaction Temperature °C	Shear Strength, psi R.T.	Shear Strength, psi 500°F
M-1	X-14A	Linde	Terephthalic acid			10	120	20	0
M-2	X-14A	"	Tolylene diisocyanate			10	"	320	0
M-8	Y-1043	"	Triallyl cyanurate			10	"	1100	10
M-9	Y-1044	"	"			10	"	1375	100
M-3	DC-2103	Dow Corning	Tolylene diisocyanate			10	"	50	0
M-4	DC-2103	"	Tolylene diisocyanate (Dimer)			10	"	100	0
M-5	DC-2103	"	Triallyl cyanurate			10	"	800	80
M-6	DC-804	"	Tolylene diisocyanate (Dimer)			10	"	680	0
M-7	DC-804	"	Triallyl cyanurate			10	"	840	70
M-39	DC-804	"	---3			--	"	1275	1152
M-40	DC-804	"	Tolylene diisocyanate			10	"	1000	390
M-41	DC-804	"	Terephthalic acid			10	"	725	2301
M-20	X-14A	Linde	Rezyl X-315	Alkyd	Am.Cyanamid	10	200	480	195
M-21	X-14A	"	"	"	"	25	"	680	230
M-11	X-14A	"	"	"	"	50	"	0	0
M-13	X-14A	"	"	"	"	50	120	0	0
M-14	X-14A	"	X-869	"	"	50	"	0	0
M-19	X-14B	"	" X-315	"	"	10	200	920	220
M-18	X-14C	"	" X-315	"	"	10	120	560	15
M-23	X-14A	"	Epon 562	Epoxy	Shell	10	200	545	2101
M-22A	X-14A	"	"	"	"	20	230	435	0
M-12	X-14A	"	"	"	"	50	140	950	0

TABLE III (Cont'd.)

Resin CHR No.	Silicone Portion		Organic Modifier Portion					Reaction Temperature °C	Shear Strength, psi	
	Resin	Supplier	Resin, or Compound	Type	Supplier	%			R.T.	500°F
M-22	X-14B	Linde	Epon 562	Epoxy	Shell	10	200		590	80
M-24	"	"	Epoxy 562	"	"	10	"		1350	190
M-10	X-14C	"	Epon 562	"	"	50	"		200	0
M-17	X-14C	"	"	"	"	10	120		455	80
M-33	X-14B	"	Epon 834	"	"	20	270		1915	120
M-27	X-14A	"	Epon 864	"	"	10	"		1960	--
M-34	X-821	"	Hysol 6000 PR	"	Houghton	20	"		485	0
M-35	"	"	Hysol 6020	"	"	20	"		700	0
M-37	"	"	GJQ 11943	Phenolic	Bakelite	20	"		590	0
M-46	DC-803	Dow Corning	GJQ 11943	"	"	20	130		1375	245
M-43	"	"	Epon 562	Epoxy	Shell	20	"		1200	205
M-44	"	"	Epon 828	"	"	20	"		1725	100
M-49	"	"	Epon 834	"	"	5	"		1800	150
M-42	"	"	"	"	"	20	"		1550	175
M-55	"	"	"	"	"	33	"		1750	155
M-56	"	"	"	"	"	66	"		2010	100
M-57	"	"	"	"	"	80	"		3090	185
M-45	"	"	Epon 864	"	"	20	"		2050	95
M-50	"	"	Epon 1001	"	"	10	"		1490	175
M-50A	"	"	"	"	"	20	"		1100	40
M-51	"	"	"	"	"	33	"		2075	122
M-52	"	"	"	"	"	66	150		2240	150
M-53	"	"	"	"	"	80	"		2225	175
M-28	"	"	Epon 1007	"	"	20	130		1450	195
M-48	"	"	Hysol 6000 PR	"	Houghton	20	135		1800	225
M-47	"	"	Hysol 6020	"	Shell	20	"		2050	50
M-58	DC-2103	"	Epon 834	"	"	5	130		1135	618
M-59	"	"	"	"	"	10	"		1210	625
M-60	"	"	"	"	"	20	"		1425	450
M-61	"	"	"	"	"	50	"		1350	310

TABLE III (Cont'd.)

Resin CHR No.	Silicone Portion Resin	Silicone Portion Supplier	Organic Modifier Portion Resin, or Compound	Type	Supplier	%	Reaction Temperature °C	Shear Strength, psi R.T.	Shear Strength, psi 500°F
M-70	DC-2103	Dow Corning	Epon 562	Epoxy	Shell	10	170	775	110
M-71	"	"	Epon 828	"	"	10	"	1585	390
M-72	"	"	Epon 834	"	"	10	"	1725	220
M-73	"	"	Epon 864	"	"	10	"	1700	180
M-74	"	"	Epon 1001	"	"	10	"	1725	225
M-54	"	"	Epon 1001	"	"	20	110	760	300
M-75	"	"	Epon 1004	"	"	10	170	1490	145
M-76	"	"	Hysol 6000 PR	"	Houghton	10	"	1435	320
M-77	"	"	Hysol 6020	"	"	10	"	1630	230
M-62	DC-2105	"	Epon 562	"	Shell	10	110	460	80
M-63	"	"	Epon 828	"	"	10	120	1285	140
M-64	"	"	Epon 834	"	"	10	"	1315	180
M-65	"	"	Epon 864	"	"	10	"	1460	185
M-66	"	"	Epon 1001	"	"	10	"	1520	75
M-67	"	"	Epon 1004	"	"	10	"	1420	180
M-68	"	"	Epon 1007	"	"	10	"	1175	275
M-69	"	"	Epon 1009	"	"	10	"	1250	230
M-78	DC-996	"	Epon 562	"	"	10	140	920	75
M-79	"	"	Epon 828	"	"	10	"	1250	0
M-80	"	"	Epon 834	"	"	10	"	1600	0
M-81	"	"	Epon 864	"	"	10	"	1615	0
M-82	"	"	Epon 1001	"	"	10	"	1300	0
M-83	"	"	Epon 1007	"	"	10	"	1960	0
M-84	DC-2105-85% XR-543--15%	"	Epon 1001	"	"	10	120	1785	0
M-85	M-59	Comm.Hard Rubber	Polyamide #100	Polyamide	Gen. Mills	15	R.T.	485	125
M-86	M-61	"	"	"	"	15	"	975	45
M-87	M-71	"	"	"	"	15	"	105	65
M-88	M-83	"	"	"	"	15	"	0	0
M-89	M-58	"	Plyophen 5023	Phenolic	Reichhold	50	"	660	365

TABLE III (Cont'd.)

Resin CHR No.	Silicone Portion Resin	Supplier	Organic Modifier Portion Resin, or Compound	Type	Supplier	%	Reaction Temperature °C	Shear Strength, psi R.T.	500°F
M-90	M-58	Conn.Hard Rubber	Plyophen 5023	Phenolic	Reichhold	25	R.T.	780	390
M-91	M-59	"	"	"	"	50	"	540	285
M-92	M-59	"	"	"	"	25	"	580	245
M-93	M-60	"	"	"	"	50	"	570	380
M-94	M-60	"	"	"	"	25	"	730	320
M-95	M-61	"	"	"	"	50	"	600	0
M-96	M-61	"	"	"	"	25	"	170	55

1. Average of two tests
2. Average of three tests
3. Degree of polymerization advanced by cooking the silicone resin alone in the same way as in preparing the organo-silicone blends (see Experimental Section).

TABLE IV

KARL FISCHER SILANOL END-GROUP TITRATIONS OF
COMMERCIAL SILICONE RESINS

	Wt. of Resin (solids) gms	K.F. Reagent, cc.	mg. H_2O	mg. H_2O/ gm. resin
DC-801	2.86	1.35	4.4	1.52
DC-803	2.03	2.45	8.1	3.92
DC-804	2.80	9.15	29.5	10.40
DC-993	0.92	1.01	3.25	3.61
DC-996	1.52	0.90	2.94	1.94
DC-2103	3.14	1.00	3.20	1.01
DC-2104	3.04	3.7	12.0	3.90
DC-2106	3.12	1.45	4.72	1.51

Standardization: 1 cc of K.F. reagent equivalent to 3.31 mg H_2O
Time allowed for K.F. reaction: three hours

TABLE V

EFFECT OF TIME OF CURE AT 480°F ON COMMERCIAL SILICONE RESINS

Resin	R.T. Shear Strength, psi, after Curing at 480°F for (hours):					500°F Shear Strength, psi, after Curing at 480°F for (hours):				
	2	4	8	12	16	2	4	8	12	16
DC-801	1060				1715	10				190
DC-802	500				1520	0				145
DC-803	1380				1330	0				295
DC-804	1245	545	230	525	880	220	200	195	210	310
DC-993	840				1550	10				205
DC-994	385				1115	0				25
DC-996	1130				1220	15				115
DC-1089	1760	980	260	745	880	165	5	95	10	0
DC-2103	285	105	830	1010	1280	35	0	5	10	410
DC-2104	940				910	235				245
DC-2105	1390	720	700	45	1440	75	0	25	0	305
DC-2106	740				700	60				195
DC-1360	745				2645	0				80
XR-100	1130	1060	850	820	1200	40	20	10	455	335
XR-398	1375	1440	865	1585	1140	60	0	40	10	175
XR-543	1330	830	965	745	1090	45	70	0	195	255
XR-544	755	855	820	590	930	10	185	75	155	295
XR-807	395				1855	0				105
XR-880	1580				0	95				0
SR-17	440				970	10				115
SR-32	340				960	0				0
SR-53	630				765	55				80
SR-82	300				830	0				120
SR-98	375				650	0				65
SR-02	235				390	30				30

TABLE V (Cont'd.)

Resin	R.T. Shear Strength, psi, after Curing at 480°F for (hours):				
	2	4	8	12	16
GE-81397	1120				1050
I-62	460				1160
I-63	1550				650
Y-1043	895				1140
Y-1044	1370				750
160-29-H	870	250	770	670	710
160-30-D	1650				1990
X-2608	810				1600
RS-513	760				1195
RS-556	820				1525

Resin	500°F Shear Strength, psi, after Curing at 480°F for (hours):				
	2	4	8	12	16
GE-81397	40				60
I-62	0				120
I-63	130				85
Y-1043	20				20
Y-1044	185				0
160-29-H	0	0	20	0	65
160-30-D	125				35
X-2608	20				105
RS-513	10				110
RS-556	40				160

TABLE VI

CATALYSTS WITH SILICONE RESINS

(Shear Strength in Psi at Room Temperature/500°F)

Resin	Control	Triethanolamine 0.15%	Triethanolamine 0.35%	Diethanol-amine 0.1%	Octyl Glycol Titanate (1%) 2.2l	2l	3l	XY-15 0.15%	XY-15 0.22%	XY-24 0.05%
DC-804	1040/225				1105/265	670/225	450/330			
DC-993	1280/55				1520/110	1580/10	1600/75			
DC-2103	920/495	955/450			500/195	885/245	1035/325			
DC-2103 HV	925/390	940/525								
DC-2103 LV	875/560		910/535							
DC-2105	1009/219									
DC-2106	759/264									
DC-2106 HV	450/230									
XR-859	905/95							570/0	490/110	0/0
XR-875	690/180								525/375	985/100
XR-4007	525/275		588/405		3060/20	2560/20	1810/0			
DC-1360	2175/10				600/0	890/5	700/0			
XR-398	960/10				510/15	500/0	480/20			
X-2720	1700/55									
CBR-122	705/440	780/470[1]		590/415						
CBR-123	525/310			650/450						
CBR-132	700/460			525/525						
CBR-135	740/445	745/420[1]								
CBR-141	990/260	1110/250[1]								

1. Cured 8 hours at 480°F. (All others standard 16-hour cure at 480°F)

TABLE VII

EFFECT OF TIME OF CURE AT 480°F ON CATALYZED DC-2103

Cure, Hours	Catalyst	Glue Line, Mils	R.T. Shear Strength, Psi Aver.	High	Low	500°F Shear Strength, Psi Aver.	High	Low
2	(none)	1-1	525	550	500	95	100	90
2	0.1% Triethanolamine	9-9	535	550	520	470	490	450
4	(none)	1-1	775	800	750	280	290	270
4	0.1% Triethanolamine	5-5	550	600	500	480	490	470
6	(none)	1-1	725	750	700	335	350	320
6	0.1% Triethanolamine	3-3	925	950	900	360	370	350
8	(none)	1-1	885	900	870	420	430	410
8	0.1% Triethanolamine	3-3	775	800	750	600	620	580
12	(none)	3-3	425	450	400	440	450	430
12	0.1% Triethanolamine		980[1]	980[1]	840[1]	390[1]	430[1]	360[1]
16	(none)	14-14	410	420	400	360	380	340
16	0.1% Triethanolamine		750[1]	790[1]	710[1]	500[1]	610[1]	490[1]
20	(none)	1-1	900	900	900	500	510	490
20	0.1% Triethanolamine	6-6	750	800	700	530	540	520
30	(none)	1-1	900	900	900	550	570	530
30	0.1% Triethanolamine	6-6	725	750	700	575	650	500

Note (500°F Shear Strength): Broke when removed from jig.

1. These values represent a retest due to the poor results originally obtained.

TABLE VIII

ZINC OCTASOL CATALYST WITH SILICONE RESINS

	Room Temperature Shear Strengths, psi, After Curing and Aging at 480°F			
	8 hrs.	16 hrs.	100 hrs.	200 hrs.
DC-804				
1.0% Zn Octasol	425	250	475	375
0.2% "	625	550	575	475
0.1% "	600	700	625	575
0.01% "	725	575	575	300
DC-996				
1.0% Zn Octasol	375	350	525	610
0.2% "	700	525	875	830
0.1% "	975	550	950	975
0.01% "	1250	825	1150	1090
DC-2103				
1.0% Zn Octasol	490	450	650	755
0.2% "	900	825	825	790
0.1% "	875	875	875	898
0.01% "	875	875	775	525

TABLE IX

EVALUATION OF PRIMERS AND SURFACE TREATMENTS

Aluminum Test Panels[1]	Primer[2]	Resin	Glue Line, Mils	Room Temperature Shear Strength, psi
E-la anodized	Control	160-29-H[3]	3.5	530
"	0.1% GS-1	"	5	710
"	0.1% X-31	"	5	810
"	0.1% VTS	"	6	745
A-1;C-1 cleaned	Control	"	5	715
"	0.1% GS-1	"	5	775
"	0.1% X-31	"	6	760
"	0.1% VTS	"	6	675
E-1A anodized	0.05% GS-1	"	6	720
"	0.05% X-31	"	6	865
"	0.05% VTS	"	6	910
A-1;C-1 cleaned	0.05% GS-1	"	6	1040
"	0.05% X-31	"	5	1065
"	0.05% VTS	"	6	980
E-la anodized	Control	CHR-M-8[4]	5	520
"	0.1% GS-1	"	4.5	440
"	0.1% X-31	"	5	455
"	0.1% VTS	"	5	550
A-1;C-1 cleaned	Control	"	5	280
"	0.1% GS-1	"	5	205
"	0.1% X-31	"	6	235
"	0.1% VTS	"	6	285
E-la anodized	0.05% GS-1	"	6	535
"	0.05% X-31	"	5	415
"	0.05% VTS	"	1	480
A-1;C-1 cleaned	0.05% GS-1	"	1	195
"	0.05% X-31	"	1	185
"	0.05% VTS	"	1	200

TABLE IX (Cont'd.)

1. A-1 metal is 24S-T3 clad aluminum. Anodized panels were not cleaned after anodizing. C-1 and E-1a Procedures are described in Experimental section.

2. The primers are products of the Linde Air Products Company:
   GS-1 is a vinyl resin emulsion
   X-31 is vinylpolysiloxane
   VTS is vinyltriethoxysilane (see special preparation procedure in Experimental section)

   Primers were applied to panels from toluene solution (except the VTS). The solvent was evaporated at room temperature, and the treated panels were heated 5 minutes at 575°F prior to application of resin adhesive.

3. Midland Industrial Finishes, see Table I.

4. Synthesized in this laboratory, see Table III.

TABLE X

EVALUATION OF PRIMERS[1]

Panel Primer[2]	Resin	Glue Line, Mils	R.T. Shear Strength, psi			No. Tests	500°F Shear Strength, psi			No. Tests
			Avg.	High	Low		Avg.	High	Low	
None	CHR-122	1-1	750	800	700	4	630	650	610	4
1% Y-1059	"	1-1	460			1	480	500	460	2
.01% Y-1059	"	1-1	580			1	535	560	520	2
1% X-31	"	2-2	580	580	580	2	435	450	420	2
.01% X-31	"	2-2	650	660	640	2	490	500	480	2
1% X-172	"	1-1	720	740	700	2	410	420	400	2
.01% X-172	"	1-1	500	500	500	2	510	520	500	2
1% VTS	"	2-2	610	620	600	2	455	460	450	2
.01% VTS	"	2-2	655	660	650	2	460	470	450	2

1. The lap joints were prepared in accordance with Method B-2, Experimental Section.

2. The primers are products of the Linde Air Products Co., and the primed panels were prepared by that company:
   Y-1059 is a water-soluble silicone, cured 1 hour at 250°F.
   X-31 is vinylpolysiloxane, cured 30 minutes at 525°F.
   X-172 is a water-soluble vinylpolysiloxane resin, cured 45 minutes at 250°F.
   VTS is vinyltriethoxysilane, cured 1 hour at 250°F.

TABLE XI

REDUCING AGENT ALUMINUM SURFACE TREATMENT

Resin	Panel Treatment[1]	Glue Line, Mils	R.T. Shear Strength, psi			No. Tests	500°F Shear Strength, psi			No. Tests
			Aver.	High	Low		Aver.	High	Low	
DC-2103	None	1-1	1360			2				
"	Lithium Aluminum Hydride	1-1	0			2				
"	None[2]	3-3	965			2				
DC-2103	None	1-1	1025	1050	1000	2	450	460	440	2
"	Lithium Aluminum Hydride	1-1	250	450	100	4	266	290	240	4
"	Ammonium Hydroxide	1-1	770	1000	600	4	186	200	170	4
"	Ferrous Ammonium Sulfate	1-1	931	1000	900	4	509	610	410	4
"	Sodium Thiosulfate	1-1	900	1000	750	4	545	590	500	4

1. Lithium aluminum hydride used as a 10 percent solution ether; all others as 10 percent aqueous solutions.

2. The DC-2103 resin was treated with lithium aluminum hydride (see Experimental section).

TABLE XII

GLASS TAPES IMPREGNATED WITH SILICONE RESINS

Resin	Shear Strength, psi, Control (No Tape)		Shear Strength, psi, Metal Unprimed		Shear Strength, psi, Metal Primed[1]	
	R.T.	500°F	R.T.	500°F	R.T.	500°F
116 Glass Tape						
DC-804	950	255	760	560	950	525
DC-805[2]	1555	250	290	0	500	0
DC-996	1490	27	880	82	1035	130
DC-1360	1940	42	1750	155	1800	102
DC-2103	1340	440	1040	225	975	385
DC-2105[2]	940	225	600	0	1170	40
DC-2106[2]	745	255	480	55	1060	370
XR-100	1330	380	1125	255	1025	250
XR-398[2]	1454	73	200	0	845	15
XR-544	835	225	900	305	845	320
XR-807	1540	60	1300	27	1225	53
160-29-H	940	270	820	250	735	255
160-30-D	1600	25	970	5	1110	200
RS-513	1190	82	320	42	830	45
X-2608	1710	10	1060	5	1040	8
CHR-140	690	480			910	420
CHR-150	800	405			1040	220
CHR-151A	710	422			940	355
CHR-151B	710	375			850	180
CHR-M-48	1790	150			1590	150
CHR-M-49	725	300			900	185
CHR-122E	605	350	1005	570	940[3]	600[3]
CHR-141E	760	70	950	365	930[3]	415[3]
128 Glass Tape						
DC-804	950	255	690	315	800	390
DC-805[2]	1535	250	860	0	750	0
DC-996	1490	27	725	70	520	25
DC-1360	1940	42	1800	250	1560	120
DC-2103	1340	440	875	535	675	735
DC-2105[2]	940	225	755	0	1010	140
DC-2106[2]	745	255	865	220	950	325
XR-100	1330	380	870	215	760	220
XR-398[2]	1454	73	370	0	1110	0
XR-544	835	225	740	375	770	450

TABLE XII (Cont'd.)

Resin	Shear Strength, psi, Control (No Tape)		Shear Strength, psi, Metal Unprimed		Shear Strength, psi, Metal Primed[1]	
	R.T.	500°F	R.T.	500°F	R.T.	500°F
160-29-H	940	270	770	305	885	295
160-30-D	1600	25	890	17	970	215
RS-513	1190	82	795	42	500	57
X-2608	1710	10	410	0	920	35
CHR-152	735	335			670	160
CHR-153	670	385			600	70
CHR-154	650	215			540	215
CHR-156	580	260			800	165

1. Metal surface primed with a thin layer of the same resin used to impregnate tape
2. Tape impregnated and pre-cured on laboratory tower (see Experimental Section)
3. Volan-treated tape (see Experimental Section)

EVALUATION OF DIFFERENT TYPES OF GLASS TAPES

	Average Percentage Difference from Control (No Tape)					
Glass Tape No.	Panels Unprimed R.T.	500° F	No Tests	Panels Primed[1] R.T.	500° F	No Tests
Impregnated with Silicone Resins[2]						
116	-20	-23	16	-1	-10	36
128	-23	-17	14	-6	-8	48
108	-18	+1	2	-8	+4	4
D-94	-39	+8	2	-31	+8	4
126	+19	+8	2	+9	-5	2
162	No Test	+13	2	+38	+17	2
164	-3	-39	2	+1	-28	4
184	-32	+80	2	+12	-31	2
1000	+3	+7	2	+26	-47	2
112				-24	+16	2
143				+3	+5	2
Impregnated with Organo-Silicone Resins[3]						
116	-26	-33	14	-28	+11	18
128	-43	-9	14	-27	+4	14
108	-28	+58	2	-29	+40	4
D-94	-57	+55	2	-54	-14	4
126	-51	+47	2	-39	+19	4
162	No Test	+64	2	-62	-9	4
164	-67	+8	2	-67	+3	4
184	-75	+67	2	-90	-14	4
1000	-41	+19	2	-54	+14	4

1. Metal surface primed with a thin layer of the same resin used to impregnate the glass tape.

2. Various silicone resins, but the majority using DC-2103.

3. Various organo-silicone resins, but the majority using DC-1360.

TABLE XIV

EFFECT OF PRE-CURING SILICONE RESIN-IMPREGNATED TAPES

Resin	Panel Primer	Tape Treatment	Glass Bond Tape No.	Bond Cure, Hours[1]	Glue Line, Mils	R.T. Shear Strength, psi			No. Tests	500°F Shear Strength, psi			No. Tests
						Aver.	High	Low		Aver.	High	Low	
DC-2103	None	Air-dried	128	4	8-8	1010	1020	1000	2	190	230	150	2
"	20% DC-2103	"	128	4	8-8	960	1130	790	2	120	140	100	2
"	None	Precured 2 hrs@480°F	128	4	8-8	(Broke)	--	--	2	(Broke)	--	--	2
"	20% DC-2103	"	128	4	10-10	675	690	660	2	190	200	180	2
20% CHR-122[2]	C-260; 20% CHR-122[3]	Both dips precured, as above	116	16	8-8	(Broke)	--	--	2	210	240	180	2
"	"	(1st dips air-dried (2nd dip precured	116	16	8-8	805	900	710	2	245	270	220	2
"	"	(1st dip precured (2nd dip air-dried	116	16	7-7	370	380	360	2	85	90	80	2
"	"	Both dips air-dried	116	16	7-7	1210	1240	1180	2	555	550	550	2
DC-2103 with .1% TEA[4]	20% DC-2103	Air-Dried	116	6	3-3	1202	1260	1100	4	185	200	170	4
"	" with .1% TEA	"	116	6	3-3	1225	1300	1100	4	202	220	180	4
DC-2103 with .2% TEA	DC-2103 with .2% TEA[5]	No tape	--	8	2-2	790	820	730	4	280	330	200	4
"	"	"	--	8	2-2	850	960	790	4	445	570	350	4
"	"	Air dried	116	8	12-12	490	640	320	4	205	220	180	4
"	"	Precured 1 hr@300°F[6]	116	8	12-12	662	800	530	4	325	350	300	4
"	"	" @ 300°F	116	8	20-20	530	620	410	4	260	270	240	4
"	"	" @300°F[5]	116	8	15-15	65	100	30	4	310	410	260	4

1. Method B-1, oven-cured for the indicated number of hours at 480°F
2. 20 percent CHR-122 resin solution was applied to the tape in two coats.
3. A 20 percent solution of CHR-122 containing 0.1 percent triethanolamine was applied to the panels which had previously been primed with a 20 percent solution of Cohrlastic 260 (a silane primer).
4. TEA is triethanolamine.
5. Panels previously primed with a 10 percent solution of C-260
6. The glass tape was primed with a 10 percent solution of Cohrlastic 260 before being impregnated with resin.

TABLE XV

METAL SURFACE PRIMERS WITH SILICONE RESIN IMPREGNATED GLASS TAPES
(No. 128 Glass Tape)

Resin	Panel Primer[1]	Tape Primer	Glue Line, Mils	Shear Strength, psi R.T.	500° F
DC-2103	None	--2	1	1290	165
"	0.5% X-172	None	6	1000	155
"	0.05% X-31	"	6	780	355
"	0.05% GS-1	"	6	620	140
"	0.13% VTS	"	6	590	75
"	None	0.05% X-172	4	1120	170
"	"	0.05% X-31	5	1345	220
"	"	0.05% GS-1	4	1240	250
"	"	1.3% VTS	4	1180	350
"	0.05% X-172	0.05% X-172	4	985	190
"	0.05% X-31	0.05% X-31	4	1110	85
"	0.05% GS-1	0.05% GS-1	5	1120	150
"	0.13% VTS	1.3% VTS	4	940	70
"	None	--2	1	1000	405
"	"	None	7	1350	525
"	0.1% X-172	"	7	1025	245
"	" "	0.1% X-31	7	1200	400
"	" "	0.1% GS-1	7	1050	485
"	" "	1.3% VTS	7	850	410
XR-100	None	--2	1	1050	295
"	"	None	7	950	305
"	0.1% X-172	"	7	1000	250
"	" "	0.1% X-31	5	1100	60
"	" "	0.1% GS-1	6	850	125
"	" "	1.3% VTS	7	825	155
XR-544	None	--2	1	600	230
"	"	None	7	1075	215
"	0.1% X-172	"	7	1000	255
"	" "	0.1% X-31	7	750	375
"	" "	0.1% GS-1	7	750	450
"	" "	1.3% VTS	7	800	380
160-29-H	None	--2	1	700	210
"	"	None	7	900	180
"	0.1% X-172	"	7	850	210
"	" "	0.1% X-31	7	800	260
"	" "	0.1% GS-1	7	850	245
"	" "	1.3% VTS	7	900	165

1. The primers are products of the Linde Air Products Company. VTS is vinyltriethoxysilane, X-31 is vinylpolysiloxane, GS-1 is a vinyl resin emulsion, and X-172 is a water-soluble vinyl-polysiloxane resin.

2. Resin alone; no glass tape.

TABLE XVI

REDUCING AGENT ALUMINUM SURFACE TREATMENT WITH SILICONE RESIN IMPREGNATED GLASS TAPES

(No. 128 Glass Tape)

Resin	Panel Treatment	Tape Treatment	Glue Line, Mils	R.T. Shear Strength, psi			No. Tests	500°F Shear Strength, psi			No. Tests
				Aver.	High	Low		Aver.	High	Low	
CHR-122	None	No Tape	1-1	757	800	700	4	627	650	610	4
=	"	None	8-8	740	780	700	4	505	630	450	4
=	"	Ferrous Ammonium Sulfate	8-8	720	820	650	4	470	490	450	4
=	Ferrous Ammonium Sulfate	None	8-8	900	920	880	4	442	460	420	4
*	" " "	Ferrous Ammonium Sulfate	8-8	782	820	700	4	507	520	500	4
=	None	Sodium Thiosulfate	8-8	820	900	780	4	452	560	500	4
*	Sodium Thiosulfate	None	8-8	817	900	660	4	407	440	380	4
*	*	Sodium Thiosulfate	8-8	832	920	780	4	510	530	500	4

TABLE XVII

COMPARISON OF GLASS TAPE-REINFORCED AND GLASS FIBER-REINFORCED SILICONE RESIN ADHESIVES[1]

Resin	Glass Treatment	Glue Line, Mils	R.T. Shear Strength, psi Aver.	High	Low	No. Tests	500°F Shear Strength, psi Aver.	High	Low	No. Tests	Failure Adh%	Coh%
Chopped Glass Fibers[2]												
CHR-122E	None	8-8	680	720	600	4	405	440	380	4	90	10
*	Volan[2]	8-8	625	700	580	4	(Broke)	---	---	4	100	
CHR-141E	None	2-2	725	840	600	4	160	200	120	4	90	10
*	Volan[2]	7-7	920	940	900	4	155	200	120	4	100	
#116 Glass Tape[3]												
CHR-122E	None	4-4	1005	1020	980	4	570	600	520	4	100	
*	Volan	4-4	940	1000	880	4	600	620	580	4	100	
CHR-141E	None	4-4	950	960	920	4	365	400	340	4	100	
*	Volan	4-4	930	980	820	4	412	440	400	4	100	

1. Lap joints were prepared in accordance with Method B-2, Experimental Section.

2. See Experimental Section.

3. Metal surface primed with a thin layer (20 percent solution) of the same resin used to impregnate tape.

INORGANIC FILLERS IN SILICONE RESINS

Filler, %[1]	Reinforcing Fabric	Shear Strength, psi			
		R.T.	300°F	500°F	700°F
DC-2103					
None		1450		365	175
10 Mica				260	70
10 Santocel C		640		385	90
10 Valron (SiO$_2$)				315	50
10 Celite		760		355	110
10 TiO$_2$ [2]				375	160
10 Agerite Alba		650	430	340	
10 Agerite Alba				340	155
20 Al Dust		510		260	
20 Al Dust		850		260	
20 MgO		400		110	
20 ZnO		965		150	
10 TiO$_2$+10 ZnO		1100		325	
20 TiO$_2$ 3		800		400	
20 ZrO$_2$		750		140	
20 CaTiO$_3$		800		180	
20 CaZrO$_3$		580		210	
50 Al Dust		870		80	
20 Al Dust	D-94 Glass	770		360	
None	Dacron	800		105	
20 Al Dust	"	515		140	
DC-1360					
None		2100	90	70	
10 Mica		1525	130	80	
10 Santocel C		2505	170	95	
10 Valron (SiO$_2$)		2330	200	40	
10 Celite		2050	190	90	
10 Agerite Alba		2295	190	85	
10 TiO$_2$		2400	430	75	
20 Al Dust		1500		120	
20 Mica		1525	410	80	
20 Santocel C		2700	760	165	

TABLE XVIII (Cont'd.)

Filler, %[1]	Reinforcing Fabric	Shear Strength, psi			
		R.T.	300°F	500°F	700°F
20 Valron (SiO$_2$)		1270	440	60	
20 Celite		2200	650	90	
20 Agerite Alba		1840	500	95	
20 MgO		720		0	
20 TiO$_2$		1925	1450	310	165
20 ZnO		350		10	
10 TiO$_2$+10 ZnO		1100		90	
20 TiO$_2$3		1575		300	
20 ZrO$_2$		1400		75	
20 CaTiO$_3$		1050		110	
20 CaZrO$_3$		1200		70	
30 TiO$_2$		2400		245	
None	116 Glass	1250		45	
20 TiO$_2$	" "	1500		135	
None	" "	2100		125	
30 TiO$_2$	" "	2125		400	

XR-807

Filler, %[1]	Reinforcing Fabric	R.T.	300°F	500°F	700°F
None		2150		0	
20 TiO$_2$		1650		95	
None	116 Glass	1550		55	
20 TiO$_2$	" "	1650		145	

X-2608

Filler, %[1]	Reinforcing Fabric	R.T.	300°F	500°F	700°F
None		1955	170	70	
10 Mica		1945	70	110	
10 Santocel C		1295	190	110	
10 Valron (SiO$_2$)		1380	50	70	
10 Celite		1640	70	130	
10 Agerite Alba		2060	40	60	
10 TiO$_2$		1720	180	270	
20 TiO$_2$		1975		180	
None	116 Glass	1100		0	
20 TiO$_2$	" "	550		55	

1. Percentage by weight in the filled resin mixture.

2. Except where footnoted (3), the TiO$_2$ is Titanox RA.

3. Ticon T (see Table XIX).

TABLE XIX

DESCRIPTION AND SOURCE OF FILLERS

Filler	Name	Description	Source
Mica	Mica Dust	Ground white muscovite mica	Mineralite Sales Corp.
Santocel C	--	Aerogel silica	Monsanto Chemical Co.
Celite	--	Finely divided diatomaceous earth	Johns-Manville Corp.
Valron	--	Coated hydrophobic silica	E.I. duPont de Nemours & Co.
TiO_2	Titanox RA	Rutile titanium dioxide, 1% aluminum oxide	Titanium Pigment Corp.
TiO_2	Ticon T	Heavy, rutile titanium dioxide	Titanium-Alloy Manufacturing Co.
Agerite Alba	--	Hydroquinone monobenzyl ether	R.T. Vanderbilt Co.
Al Dust	--	Atomized aluminum dust 101	Aluminum Corp. of America
MgO	K.&M. Light Magnesium Oxide	Pigment grade magnesium oxide	Calco Chemical Division
ZnO	Black Label No. 20	Pigment grade zinc oxide	St. Joseph Lead Co.
ZrO_2	C.P. Zirconium Oxide	Less than 5 microns average	Titanium-Alloy Manufacturing Co.
$CaTiO_2$	Ticon C	0.5 to 3.0 microns average	" " "
$CaZrO_3$	Ticon CZ	0.5 to 3.0 microns average	" " "

TABLE XX

EVALUATION OF INORGANIC FILLERS[1]

Filler, %[2]	Glue Line, Mils	R.T. Shear Strength, psi Aver.	High	Low	No. Tests	500°F Shear Strength, psi Aver.	High	Low	No. Tests	Failure Adh.%	Coh.%
Adhesive No. CHR-M-58 (95% DC-2103, 5% Epon 834)											
None	1-1	1135	1150	1120	4	618	660	570	4	100	
15 Titanium Dioxide	3-3	1190	1200	1180	2	590	660	520	2	90	10
30 " "	2-2	1310	1320	1300	2	520	520	520	2	90	*
45 " "	3-3	950	980	920	2	660	720	600	2	*	*
15 Asbestine X	1-1	1280	1300	1260	2	445	450	440	2	*	*
30 " "	2-2	1140	1180	1100	2	505	510	500	2	*	*
45 " "	1-1	1120	1140	1100	2	570	580	560	2	70	30
15 Aluminum Dust	1-1	1600	1620	1580	2	380	390	370	2	90	10
30 " "	2-2	1310	1340	1280	2	295	310	280	2	*	*
45 " "	3-3	1620	1700	1540	2	290	300	280	2	*	*
Adhesive No. CHR-M-59 (90% DC-2103, 10% Epon 834)											
None	1-1	1210	1350	1060	4	625	640	600	4	100	
15 Titanium Dioxide	1-1	1160	1240	1080	2	385	400	370	2	100	
30 " "	2-2	1240	1280	1200	2	350	400	300	2	*	*
45 " "	5-5	940	960	920	2	470	500	440	2	*	*
15 Asbestine X[3]	1-1	1250	1260	1240	2	395	400	390	2	*	*
30 " "	2-2	1290	1300	1280	2	645	720	570	2	*	*
45 " "	3-3	1290	1340	1240	2	440	540	340	2	70	30
15 Aluminum Dust	3-3	1490	1500	1480	2	370	380	360	2	100	
30 " "	2-2	1620	1680	1560	2	190	200	180	2	*	*
45 " "	3-3	1790	1800	1780	2	270	300	240	2	*	*
Adhesive No. CHR-M-60 (80% DC-2103, 20% Epon 834)											
None	1-1	1425	1500	1300	4	447	480	400	4	100	
15 Titanium Dioxide	1-1	960	1020	900	2	345	360	330	2	90	10
30 " "	2-2	1410	1480	1340	2	465	580	350	2	*	*
45 " "	3-3	1170	1200	1140	2	340	380	300	2	*	*
15 Asbestine X	1-1	1170	1240	1100	2	510	540	480	2	100	
30 " "	2-2	1280	1300	1260	2	585	620	550	2	90	10
45 " "	1-1	1255	1260	1250	2	580	600	560	2	70	30
15 Aluminum Dust	3-3	1480	1500	1460	2	425	450	400	2	90	10
30 " "	2-2	1760	1780	1740	2	365	400	330	2	*	*
45 " "	3-3	1720	1740	1700	2	190	200	180	2	*	*

TABLE XX (Cont'd.)

Filler, %[2]	Glue Line, Mils	R.T. Shear Strength, psi Aver.	High	Low	No. Tests	500°F Shear Strength, psi Aver.	High	Low	No. Tests	Failure Adh.%	Coh.%
Adhesive No. CHR-M-61 (50% DC-2103, 50% Epon 834)											
None	1-1	1350	1500	1050	4	310	330	300	4	100	
15 Titanium Dioxide	3-3	1120	1180	1060	2	180	210	150	2	"	
30 "	1-1	1700	1720	1680	2	235	250	220	2	"	
45 "	10-10	980	980	980	2	210	250	170	2	"	
15 Asbestine X	1-1	1110	1120	1100	2	390	400	380	2	100	100
30 "	9-9	730	760	700	2	255	280	230	2	70	30
45 "	7-7	1030	1060	1000	2	400	420	380	2	90	10
15 Aluminum Dust	6-6	1800	2100	1500	2	220	240	200	2	100	
30 "	9-9	1430	1460	1400	2	135	150	120	2	100	10
45 "	8-8	1520	1560	1480	2	210	220	200	2	90	10

1. The lap joints were prepared in accordance with Method B-2 (Experimental Section).

2. Percentage by weight in the filled resin mixture.

3. Magnesium silicate, International Talc Co.

TABLE XXI

COMPATIBILITY OF MIXTURES OF SILICONE RESINS[1]

	DC-801	DC-802	DC-804	DC-935	DC-993	DC-994	DC-996	DC-997	DC-1088	DC-1089	DC-1360	DC-2103	DC-2104	DC-2105	DC-2106	XR-100	XR-261	XR-398	XR-543	XR-544	XR-807	XR-856	XR-928
DC-801																							
802	C																						
804	C	X																					
935	X	X	C																				
993	C	X	C	X																			
994	C	X	X	X	C																		
996	C	C	C	X	C	C																	
997	X	X	C	X	X	X	X																
1088	X	X	X	X	X	X	X	X															
1089	X	X	X	X	X	X	X	X	C														
1360	X	X	X	X	X	X	X	X	C	C													
2103	C	X	C	C	C	C	C	C	X	X	X												
2104	C	C	C	C	C	X	C	C	X	X	X	C											
2105	C	C	C	X	C	C	C	X	X	X	X	C	C										
2106	C	C	C	X	X	C	C	X	C	X	X	X	C	C									
XR-100	C	X	X	C	C	C	X	C	C	X	X	C	C	C	X								
261	X	X	X	X	C	X	C	X	C	C	X	C	X	C	C	C							
398	X	C	X	X	X	C	C	X	C	C	X	X	X	C	X	C	X						
543	C	C	C	C	C	C	C	X	X	X	X	X	X	C	C	C	C	X					
544	C	X	C	C	C	C	X	C	C	C	X	X	C	X	C	C	C	X	C				
807	X	C	X	X	X	X	C	X	X	X	X	X	X	X	X	X	X	C	X	X			
856	C	C	C	X	C	X	C	C	X	X	X	X	C	C	C	C	C	X	C	C	X		
928	-	-	-	-	-	-	-	-	-	-	X	-	X	-	-	-	-	-	-	-	-	-	

C – Compatible

X – Incompatible

- – No Test. (XR-928 resin set up in the bottle before tests were completed)

1. Dow Corning silicone resins were used in this experiment.

TABLE **XXII**

SILICONE RESIN BLENDS

Blend Composition			Shear Strength, psi	
Resin A	Resin B	Wt. % of B	R.T.	500° F
DC-2103	(none)	---	1062	612
"	DC-804	25	862	420
"	"	75	700	400
"	"	100	757	347
"	DC-935	50	600	0
"	"	100	462	70
"	DC-993	50	250	0
"	"	100	1420	130
"	DC-994	50	1680	200
"	"	100	1142	62
"	DC-996	50	550	0
"	"	100	1850	88
"	DC-1360	50	1755	200
"	"	100	2275	91
"	160-29-H	50	1080	415
"	"	100	1030	207
DC-2103[1]	(none)	---	1160	422
"	DC-804	25	917	412
"	"	75	822	337
"	"	100	695	305
DC-2103[2]	(none)	---	1087	392
"	DC-804	25	1162	372
"	"	75	1000	352
"	"	100	912	357
DC-804	(none)	---	860	320
"	DC-2104	50	0	0
"	"	100	783	268
"	DC-2105	50	550	30
"	"	100	940	225
"	DC-2106	50	610	0
"	"	100	745	255
"	XR-544	50	625	0
"	"	100	846	284
"	XR-856	50	0	0
"	"	100	905	95

TABLE **XXII** (Cont'd.)

| Blend Composition | | | Shear Strength, psi | |
Resin A	Resin B	Wt. % of B	R.T.	500°F
CHR-122	(none)	--	740	510
"	CHR-141	25	675	500
"	"	75	805	410
"	"	100	1100	300
CHR-122[2]	(none)	--	1025	620
"	CHR-141	25	1000	525
"	"	75	925	472
"	"	100	951	300

1. Resin or resin blend impregnated in No. 128 glass tape. Panels primed with same resin.

2. Resin or resin blend impregnated in No. 116 glass tape. Panels primed with same resin.

TABLE XXIII

HIGH-TEMPERATURE (480–600°F) AGING OF COMMERCIAL SILICONE RESINS

Resin	Glue Line, Mils	R.T. Shear Strength, psi Initial	Aged, Hours[1] 100	200	300	500°F Shear Strength, psi Initial	Aged, Hours[1] 100	200	300
Cured and Aged at 480°F									
DC-804	2	715	400	Broke	360	75	10	Broke	130
DC-2103	2	665	970	885	865	210	140	130	425
DC-2105	2	505	1025	760	905	40	115	55	265
XR-100	3	955	925	925	900	235	240	210	410
XR-544	3	795	780	755	720	270	145	95	190
160-29-H	3	885	955	910	740				
Cured and Aged at 500°F									
DC-803	1	1410	940	940	810	300	230	250	210
DC-805	1	870	1360	1490	1450	30	50	30	75
DC-2103	2	990	810	730	790	180	340	310	230
DC-1360	1	1990	1400	1390	1390	30	65	0	0
160-30-D	1	1300	Broke during aging			0	Broke during Aging		
X-2720	1	1430	*	*	*		*	*	*
Cured and Aged at 550°F									
DC-803	2	1150	890	800	880	330	200	110	160
DC-805	2	1560	1450	1500	1245	0	0	35	75
DC-2103	1	970	790	650	650	395	85	70	185
DC-1360	1	2135	720	Broke	Broke	70	75	Broke	Broke
160-30-D	1	Broke during cure				Broke during cure			
X-2720	2	830	Broke during aging			25	Broke during aging		
Cured and Aged at 600°F									
DC-803	3	805	650	Broke	Broke	165	220	Broke	Broke
DC-805	3	720	1100	1200	Broke	0	30	40	*
DC-2103	4	820	450	Broke	*	210	140	Broke	*
DC-1360	4	490	Broke during aging			0	Broke during aging		
160-30-D	3	Broke during cure				Broke during cure			
X-2720	3	*	*	*	*	*	*	*	*

1. The "initial" time is after a 16-hour cure at the indicated temperature; the aging periods are in addition to the initial 16-hour cure.

TABLE XXIV

HIGH-TEMPERATURE (500°F) AGING OF SILICONE AND ORGANO-SILICONE RESINS

Resin	Glue Line, Mils	R.T. Shear Strength, psi, Aged, Hours						500°F Shear Strength, psi, Aged, Hours					
		Initial	100	200	300	400	500	Initial	100	200	300	400	500
DC-803	2-2-2-1-2-2	1100	790	620	770	880	950	340	350	250	280	170	180
"	2-2-2-1-2-2	1250	850	650	750	850	970	360	370	280	300	180	160
DC-804	3-1-1-1-2-1	700	480	500	550	450	660	280	220	200	150	120	120
"	3-1-1-1-2-1	650	550	480	600	500	660	300	260	140	190	110	100
Epon 562	2-1-3-3	1650	880	Broke	Broke	Broke	Broke	240	200	Broke	Broke	Broke	Broke
"	2-1-3-3	1800	800	"	"	"	"	260	180	"	"	"	"
Epon 828	4-4-3-3	1700		Broke during aging				160		Broke during aging			
"	4-4-3-3	1750		"				200		"			
Epon 834	3-3-3-3-3	2600	900	Broke	Broke	Broke	850	240	160	Broke	Broke	Broke	Broke
"	3-3-3-3-3	2500	700	"	"	"	800	270	150	"	"	"	"
Epon 864	2-4-3-3-3	2600	400	"	"	"	1000	150	70	"	"	"	"
"	2-4-3-3-3	2000	400	"	"	"	950	170	90	"	"	"	"
CHR-M-43[1] (562)	2-1-2-2-1	900		Broke during aging				190		Broke during aging			
"	2-1-2-2-1	1100		"				180		"			
CHR-M-44[1] (828)	2-2-2-2-2-2	1900	970	300	300	950	820	200	440	180	110	90	120
"	2-2-2-2-2-2	1900	1000	350	350	800	800	250	320	250	150	120	140
CHR-M-42[1] (834)	2-2-2-1-2-2	1450	850	550	900	800	720	300	290	220	340	290	320
"	2-2-2-1-2-2	1530	900	620	800	750	760	340	320	250	330	330	300
CHR-M-45[1] (864)	3-3-3-3-3-3	2300	1050	520	Broke	Broke	940	140	340	230	Broke	Broke	Broke
"	3-3-3-3-3-3	2100	1100	500	"	"	900	140	200	200	"	"	"
CHR-M-43[1,2] (562)	7-7-6-7	1100		Broke during aging				200		Broke during aging			
"	7-7-6-7	1050		"				210		"			
CHR-M-44[1,2] (828)	7-6-6-6	1700	600	400	Broke	Broke	Broke	350	250	250	Broke	Broke	Broke
"	7-6-6-6	1700	900	500	"	"	"	330	290	220	"	"	"
CHR-M-42[1,2] (834)	6-4-5-2	1650	650	600	400	"	"	230	460	330	200	"	"
"	6-4-5-2	1850	700	620	500	"	"	250	490	350	250	"	"
CHR-M-45[1,2] (864)	7-7-7-2-2	1400	800	800	600	480	"	340	615	350	220	200	"
"	7-7-7-2-2	1300	900	700	700	500	"	350	350	520	240	170	"

1. This resin is DC-803 modified with an Epoxy resin (20 percent by weight) supplied by the Shell Chemical Corporation. The Epon number appears below the resin number

2. This organo-modified silicone resin was mixed (50 percent by weight) with Atomized Aluminum Dust 101 (see Table XII).

TABLE XXV

HIGH-TEMPERATURE (600°F) AGING OF SILICONE AND ORGANO-SILICONE RESINS[1]

Resin	Glue Line, Mils	Variation	Hours Aged at 600°F	R.T. Shear Strength, psi			500°F Shear Strength, psi		
				Aver.	High	Low	Aver.	High	Low
CHR-M-60[2]	1-1	30% Asbestine X	0	1080	1160	1000	950	1040	860
"	-	"	70	Broke during aging			Broke during aging		
"	-	"	120	" " "			" " "		
"	-	"	190	" " "			" " "		
"	-	"	240	" " "			" " "		
CHR-M-60	1-1	None	0	1130	1140	1120	830	980	680
"	-	"	70	Broke during aging			Broke during aging		
"	-	"	120	" " "			" " "		
"	-	"	190	" " "			" " "		
"	-	"	240	" " "			" " "		
CHR-M-61[3]	1-1	30% Asbestine X	0	950	960	940	580	580	580
"	-	"	70	Broke during aging			Broke during aging		
"	-	"	120	" " "			" " "		
"	-	"	190	" " "			" " "		
"	-	"	240	" " "			" " "		
CHR-M-61	1-1	None	0	1220	1240	1200	240	300	180
"	-	"	70	Broke during aging			Broke during aging		
"	-	"	120	" " "			" " "		
"	-	"	190	" " "			" " "		
"	-	"	240	" " "			" " "		

TABLE XXV (Cont'd.)

Resin	Glue Line, Mils	Variation	Hours Aged at 600°F	R.T. Shear Strength, psi Aver.	High	Low	500°F Shear Strength, psi Aver.	High	Low
CHR-122	5-5	#128 Glass Tape	0	960	1020	900	700	740	660
"	5-5	"	70	520	540	500	200	220	180
"	5-5	"	120	350	400	300	110	120	100
"	-	"	190	Broke during aging	"	"	Broke during aging	"	"
"	-	"	240	"	"	"	"	"	"
"	1-1	None	0	820	840	800	600	640	580
"	1-1	"	70	630	640	620	285	300	270
"	1-1	"	120	390	420	360	120	140	100
"	1-1	"	190	375	390	360	--	120	--
"	-	"	240	Broke during aging	"	"	Broke during aging	"	"
CHR-141	5-5	#128 Glass Tape	0	910	920	900	420	420	420
"	5-5	"	70	250	300	200	105	110	100
"	5-5	"	120	160	200	120	50	60	40
"	-	"	190	Broke during aging	"	"	Broke during aging	"	"
"	-	"	240	"	"	"	"	"	"
"	1-1	None	0	910	920	900	450	460	440
"	1-1	"	70	390	400	380	190	200	180
"	1-1	"	120	380	400	360	100	100	100
"	1-1	"	190	305	360	290	105	110	100
"	1-1	"	240	325	340	310	97.5	105	90

1. Method B-2 (see Experimental Section)
2. Blend of 80 percent DC-2103, 20 percent Epon 834
3. Blend of 50 percent DC-2103, 50 percent Epon 834

TABLE XXVI

COMPARISON OF SHEAR CUT AND MACHINED EDGE ALUMINUM PANELS

	Room Temperature Shear Strength, psi	
	Shear Cut Panels, Selected Beveled Edges Within Glued Area	Machined Panels, Square Edges Only In Glued Area
Resin DC-2103[1]		
1.	950	1220
2.	950	1110
3.	1440	1350
4.	1200	1300
5.	950	1180
6.	1150	1300
7.	1220	1200
8.	1200	1150
Average Shear Strength	1133	1223
Range	490	250
Maximum Deviation	308	128

- -

	Shear Strength, psi			
	Shear Cut Panels, Random Choice		Machined Panels	
	R.T.	500°F	R.T.	500°F
Resin DC-2103[2]				
1.	1180	430	1100	450
2.	950	510	1100	500
3.	1000	570	1100	520
4.	1100	500	1050	540
Average Shear Strength	1058	503	1088	503
Range	230	140	50	90
Maximum Deviation	123	73	38	53
Resin CHR-122[2]				
1.	800	540	650	550
2.	800	650	700	530
3.	700	350	680	420
4.	650	490	750	510
Average Shear Strength	738	507	695	503
Range	150	300	100	130
Maximum Deviation	83	157	55	83

1. Method B-1 (see Experimental Section); glue lines 2 mils, average
2. Method B-2 (see Experimental Section); glue lines 1 mil, average

TABLE XXVII

EFFECT OF GLUE LINE THICKNESS ON THE SHEAR STRENGTH OF DC-2103 SILICONE RESIN[1,2]

Shim Thickness, Mils[3]	Glue Line, Mils[4]	R.T. Shear Strength, psi Aver.	High	Low	No. Tests	500°F Shear Strength, psi Aver.	High	Low	No. Tests
1	1-1	875	950	800	4	515	550	480	4
2	1-1	850	870	830	4	450	520	340	4
3	1-1	800	900	600	4	490	560	430	4
4	1½-1½	920	950	900	4	378	680	270	4
5	2-2	838	880	800	4	350	370	330	4
6	2-2	843	900	750	4	385	430	350	4
7	2-2	950	1000	900	4	390	410	350	4
8	2½-2½	900	920	880	4	493	520	450	4
9	3-3	918	950	900	4	453	480	430	4
10	3-3	900	950	850	4	405	430	390	4

1. The lap joints were prepared in accordance with Method B-1, (see Experimental Section).
2. All bond failures were 100 percent adhesive.
3. Shim thicknesses are in excess of panel thickness. (See page 14.)
4. Glue line thicknesses are the average thicknesses of the respective 4 R.T. and 500°F Shear Strength test specimens.

TABLE XXVIII

DESCRIPTION OF COMMERCIAL MATERIALS[1]

Dow-Corning Corporation

DC-801	Silicone Protective Coating Resin
DC-802	" " " "
DC-803	" " " "
DC-804	" " " "
DC-805	" " " "
DC-935	" Electrical Insulating Varnish Resin
DC-993	" " " " "
DC-994	" " " " "
DC-996	" " " " "
DC-1088	" Insulating Wire Varnish Resin
DC-1089	" " " "
DC-1360	" Wire Enamel Insulating Varnish-Silicone-Terephthalate Resin
DC-2103	" Bonding Resin
DC-2104	" " "
DC-2105	" " "
DC-2106	" Laminating Resin
XR-100	Experimental Silicone Resin
XR-379	" " " (Phenolic Modified)
XR-398	" " " (Alkyd Modified)
XR-513	" " "
XR-537	" " "
XR-538	" " " (Similar to DC-935)
XR-543	" " "
XR-544	" " "
XR-551	" " " (Similar to DC-2103, but more brittle)
XR-807	" " " (Alkyd Modified)
XR-859	" " " (Phenolic Modified)
XR-875	" " " (" ")
XR-878	" " " (Alkyd Modified)
XR-880	" " " (Alkyd Modified)
XR-928	" " "
XR-1024	" " " (Similar to XR-928)
XR-4007	" " " (Similar to DC-2103, but more flexible)
XY-15	Curing Catalyst for Silicone Resin
XY-24	" " " " "

General Electric Co.

SR-17	Silicone Flexible Insulating Resin for Extreme Hot or Cold
SR-32	Silicone Resin
SR-53	" " for water repellency
SR-82	" "

1. See Table XIX for inorganic fillers.

TABLE XXVIII (Cont'd.)

General Electric Co. (Cont'd.)

SR-98	Silicone Varnish, High Temperature Hard Flexible Film Resin
SR-02	Silicone Resin
SR-111	Experimental Silicone Resin
191-14-631	Silicone Resin
81390	Experimental Silicone Resin (Class H Insulation)
81397	" " "

Linde Air Products Co.

GS-1	Vinyl Silicone Resin
VTS	Vinyltriethoxysilane
X-14A	Low-Molecular-Weight Linear Polysiloxane Containing Some Residual Ethoxy Groups
X-14B	Low-Molecular-Weight Linear Polysiloxane Containing Some Residual Ethoxy Groups
X-14C	Low-Molecular-Weight Linear Polysiloxane Containing some Residual Ethoxy Groups
X-31	Vinylpolysiloxane
X-62	Silicone Resin
X-63	" "
Y-1027	" Coating Resin
Y-1043	Silicone-Styrene Copolymer - Experimental Potting Compound
Y-1044	" " " " " "
Y-1054	Silicone Wire Enamel
Y-1166	" " "
Y-1167	" Protective Coating Resin
Y-1203	" Adhesive Resin
Y-1247	" " "

Midland Industrial Finishes Co.

160-29-H	Clear Silicone
160-30-D	Silicone Alkyd, Oil Modified
RS-513	" "
RS-556	" " Oil Modified
X-2608	" "
X-2720	" Epoxy

Bakelite Corp.

BRQ-12427	Silicone Molding Resin (Phenolic Modified)
BRQ-12431	" " " " "
GRQ-12554	" " "
GRQ-12555	" " "
GJQ-11943	Phenolic Resin

TABLE XXVIII(Cont'd.)

The Connecticut Hard Rubber Co.

Cohrlastic 260 Silicone-Metal Surface Primer

Shell Chemical Co.

Epon 562	Epoxy Resin
" 828	" "
" 834	" "
" 864	" "
" 1001	" "
" 1004	" "
" 1007	" "
" 1009	" "

American Cyanamid Co.

PDL-7669	A Polyester: Partially polymerized triallyl cyanurate
Rezyl X-315	Alkyd Resin
Rezyl X-869	" "

Houghton Chemical Co.

| Hysol 6000 PR | Epoxy Resin |
| Hysol 6020 | " " |

General Mills, Inc.

| Polyamide Resin | |
| 100 | Polyamide Resin |

Reichhold Chemicals, Inc.

Plyophen 5023 Phenolic Resin

E. I. Du Pont de Nemours & Co.

OGT-21	Octylene Glycol Titanate, 2 moles R:1 mole Ti
OGT-2.21	" " " , 2.2" " " "
OGT-31	" " " , 3 " " " "
TPT	Tetra isopropyl titanate, titanium ester from Pigment Dept.
TBT	Tetra n-butyl " " " " " "
Volan	Methacrylato·chromic chloride solution in isopropanol

TABLE XXIX

DESCRIPTION OF GLASS FABRICS

Style	Oz/sq.yd.	Thickness, mils	Count - Ends and Picks	Breaking Strength, lbs/in. Warp	Fill	Weave	Finish
106	.85	1.5	56 x 56	46	52	Plain	
108	1.43	2	60 x 47	70	40	"	
116	3.16	4	60 x 58	150	140	"	
126	5.37	6.5	34 x 42	225	195	"	
128	6.00	7	42 x 32	250	200	"	
162	12.20	15	28 x 16	450	350	"	
164	12.60	14.5	20 x 18	500	450	"	
184	25.90	27	42 x 36	950	800	8 H. Sat.	
1000	10.1	13	--	463	426	Plain	
D-94[1]	2.1	4	20 x 28			Leno Marquisette	114[2]

1. Hess Goldsmith Company
2. 114 Finish - Heat-cleaned to completely desize. Treated with Methacrylate chromic-chloride to improve adhesion.