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# ROOM-TEMPERATURE-VULCANIZING SILICONE ADHESIVE

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UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

*Contracts*  
FOREWORD

This report was prepared by The Connecticut Hard Rubber Company, New Haven, Connecticut, under USAF Contract No. AF 33(616)-2542. The contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials," Task No. 73405, "Compounding of Elastomers," formerly RDO No. 617-12, "Compounding of Elastomers," and was administered under the direction of the Rubber and Plastics Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt J. M. Kelble acting as project engineer.

The period covered by this report is from June 1954 to March 1955.

WADC TR 55-289

All commercially available adhesives recommended for bonding silicone rubber to aluminum and to itself without the use of heat and pressure have been evaluated. Dow Corning A-4000, a two-component adhesive, fulfilled nearly all target requirements. Two catalysts, Dow Corning XY-22 and XY-27, were tested with A-4000; of the two, XY-27 is recommended. It is suggested that the 24-hour peel strength requirement be lowered from ten pounds per inch to eight pounds per inch, which would enable the A-4000:XY-27 combination to meet all the specifications of the contract.

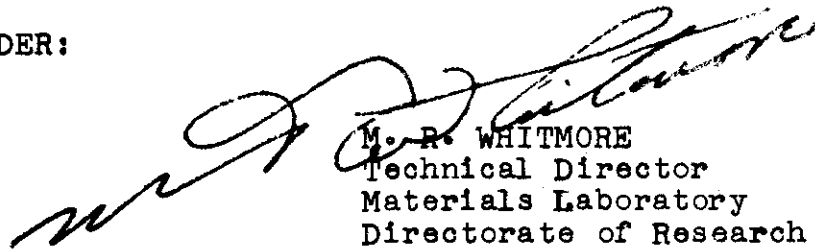
A study of other room-temperature-curing systems with various modified siloxanes is reported. With the use of several curing systems which were developed during the course of the work, materials were prepared for bonding silicone rubber to aluminum and to itself. Poor bonds were obtained to aluminum. Good bonds were obtained to silicone rubber with the use of a cement compounded from Linde Y-1170, a hydrogenmethyl silicone fluid.

A literature survey of silicone adhesives and room-temperature curing systems is also included in this report.

#### PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE  
Technical Director  
Materials Laboratory  
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*Continued*  
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## INTRODUCTION

Commercially available adhesives which will bond silicone rubber to metal or to itself require curing with the use of high heat and pressure. These adhesives are silicone-base materials. Organic adhesives, which can usually be adjusted to cure at room temperature as well as at high temperatures, do not adhere to the inert surface of silicone rubber.

There is then a need for a compound, probably of silicone base, which will bond silicone without the use of heat and prolonged pressure. This type of material would make it simple to combine a silicone part into an assembled product, especially an intricate assembly with curved surfaces. The aircraft industry with its considerable need for silicone rubber should find this adhesive a most convenient tool.

The object of this contract was to carry out research leading to the development of a method or an adhesive which would satisfactorily bond silicone rubbers to aircraft metal and themselves without the use of heat and pressure.

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## EXPERIMENTAL PROGRAM

The general program for the work on this contract has been as follows:

- A. Evaluation of Commercially Available Adhesives (silicones and nonsilicones)
- B. Evaluation of Dow Corning A-4000 RTV Adhesive
- C. Development of a New RTV Adhesive
  1. Study of curing agents and activators for a basic recipe using a low-molecular-weight silicone polymer
  2. Study of fast-curing silicone resins
    - a. Evaluation of certain resins on which data have been obtained by this laboratory during the course of Air Force Contract No. AF 33(616)-427
    - b. Modifications of the above resins with silicone rubber, plasticizer, etc.
  3. Curing of modified siloxane polymers
    - a. Various molecular weight siloxanes
    - b. Methylhydrogen siloxanes
    - c. Methylvinyl (or allyl) siloxanes
    - d. Chlorinated methyl siloxanes
    - e. Glycerol-stabilized, depolymerized methyl siloxanes
  4. Preparation of other modified siloxane polymers
  5. Testing materials developed as adhesives
- D. Literature Survey



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EXPERIMENTAL WORK

A. Evaluation of Commercially Available Adhesives

Objective: A number of commercially available materials were obtained from suppliers for possible use in bonding silicone rubber to aluminum or to itself. The bond strength, as required by the Contract, was to be in accordance with Table I. If the adhesives failed to approach the target properties, they were rejected and no further testing was done with this material.

TABLE I

TARGET PROPERTIES

<u>Type of Bond</u>	<u>Peel Strength in lbs/inch</u>	
	<u>4-hr cure at R.T.</u>	<u>24-hr cure at R.T.</u>
Silicone to Silicone	3 lbs minimum	10 lbs minimum
Silicone to Aluminum	3 lbs minimum	10 lbs minimum

---

Five different adhesives, Epon VI, Bond Master M654, DuPont 4678, Thiokol T-120-1 and Dow Corning A-4000, were tested with the use of the method described below.

Procedure for Testing Peel Strength: The peel test specimens were prepared from a 2 x 12 x 0.125 inch strip of silicone rubber (Dow Corning Silastic 250) and a 2 x 6 x .063 inch panel of aluminum (Alclad 24S-T3). Before bonding, the rubber was cleaned by brushing the surface with perchloroethylene or methyl ethyl ketone. The aluminum panels were degreased with the same solvent before being cleaned with a sodium dichromate-sulfuric acid solution. (Fifty grams of sodium dichromate was dissolved in 1500 cc of water, to which 272 cc of concentrated sulfuric acid was added.) The degreased aluminum sheets were placed in the above cleaning solution for ten minutes at 150°-160°F. The plates were then removed from the bath, washed with water, and dried with a clean paper towel.

The adhesive was applied to both rubber and aluminum by means of a spreading machine (Fig. 1), unless other instructions were specified by the manufacturer. After being allowed to stand for the prescribed drying time, the two coated surfaces were brought into intimate contact, a roller being used to insure uniformity

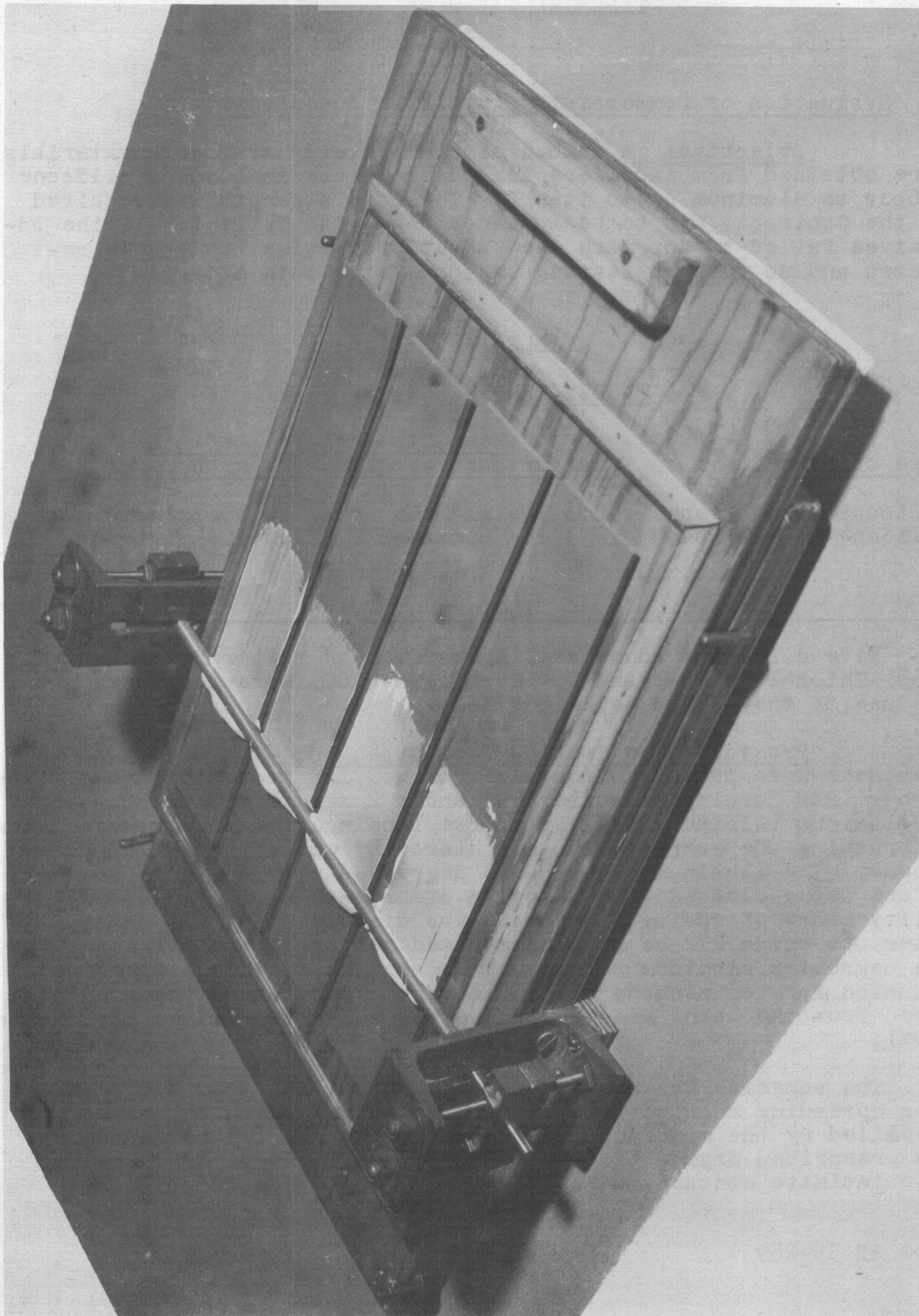


FIG 1-ADHESIVE SPREADING MACHINE

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of contact.

After the bond had been cured for the specified time, the samples were cut in strips, one inch wide, in such a way that the center inch of the two-inch width was used. It was important to cut through the adhesive, although it was not necessary to cut the aluminum plate.

Materials being tested for adhesion were peeled (or stripped) back at an angle of 180 degrees to the clad aluminum sheet on a Scott Tester having a jaw separation rate of two inches per minute (Fig. 2). The first and last inch of the specimen were not used, and all readings are the numerical average of the peak loads. In all peel tests, four samples were tested for each material. All results were recorded electrically on calibrated sheets.

Results: Dow Corning A-4000 gave results which approached the target properties, and further tests were then conducted with it (see Section B). The remaining four adhesives were rejected (Table II).

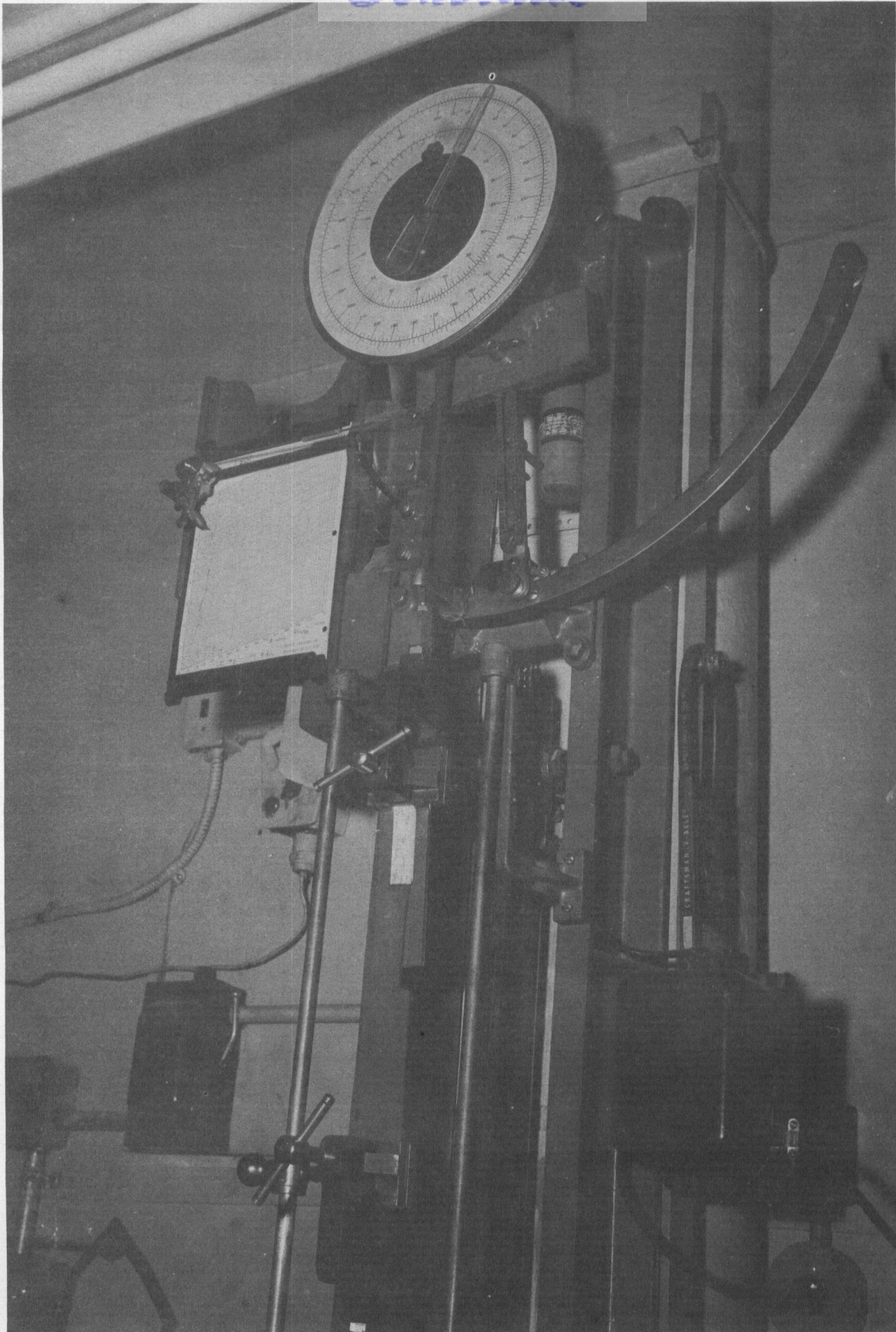


FIG 2-PEEL STRENGTH TEST

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EVALUATION OF COMMERCIALY AVAILABLE ADHESIVES

<u>Adhesive</u>	<u>Cleaning Method<sup>1</sup></u>	<u>Time of Cure, hrs</u>	<u>Peel Strength<sup>2</sup>, lbs/in.</u>	<u>Cause of Failure</u>
Epon VI + Catalyst A	A B	4	None	Cohesive
Epon VI + Catalyst A	A B	24	<0.25	Adhesive (Rubber) <sup>3</sup>
Epon VI + Diethylene- triamine	A B	4	None	Cohesive
Epon VI + Diethylene- triamine	A B	24	<0.25	Adhesive (Rubber) <sup>3</sup>
Bond Master M654 + CH-8 Catalyst	A B	4	<0.25	Adhesive (Rubber) <sup>3</sup>
Bond Master M654 + CH-8 Catalyst	A B	24	0.25	Adhesive (Rubber) <sup>3</sup>
DuPont 4678 Cement	C B	4	<0.25	Adhesive (Rubber) <sup>3</sup>
DuPont 4678 Cement	C B	24	<0.25	Adhesive (Rubber) <sup>3</sup>
Thiokol T-120-1	C B	4	<0.25	Cohesive
Thiokol T-120-1	C B	24	0.25	Adhesive (Rubber) <sup>3</sup>

Dow Corning-See Section B, Page 9.  
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## Notes:

1. Cleaning Methods: A-- Perchloroethylene  
B-- Sodium dichromate-sulfuric acid  
cleaning solution  
C-- Methyl ethyl ketone
2. All data are the average of four samples.
3. The major point of failure was at the interface between the adhesive and the rubber.

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## B. Evaluation of Dow Corning A-4000 RTV Adhesive

Objective: Dow Corning A-4000 is an air-drying adhesive consisting of a 75 percent dispersion of silicone polymer in xylene. With the addition of catalyst, this adhesive will set up in 24 hours at room temperature. Dow Corning A-4000 Adhesive was fully evaluated at first, with Dow Corning XY-22 as the catalyst. Later Dow Corning XY-27 was used.

The target properties for this adhesive, as outlined in the contract, are shown below:

1. **Bond Strength** - The bond strength to be developed shall be as follows:

<u>Type of Bond</u>	<u>Peel Strength in lbs/inch</u>	
	<u>4-hr cure at R.T.</u>	<u>24-hr cure R.T.</u>
Silicone to Silicone	3 lbs minimum	10 lbs minimum
Silicone to Aluminum	3 lbs minimum	10 lbs minimum

2. **Water-Resistance** - The adhesive properties of silicone to clad aluminum samples when peel-tested after 24 hours' water-immersion shall not decrease more than 15 percent of the original adhesion value.

3. **Oil-Resistance** - The adhesive properties of the silicone to aluminum test specimens when peel-tested after 24 hours' immersion in MIL-L-6082, Grade 1100 Oil (ASTM No. 1) at 212°F shall not decrease more than 25 percent of the original adhesion value.

4. **Temperature Properties** - The bonded specimen shall be placed in a dry-air oven and aged for 24 hours at a temperature of 212°F. A two-pound weight shall then be placed on the silicone at 90 degrees to the aluminum and shall be allowed to remain in place for 24 hours at the testing temperature. The sample shall show no separation.

5. **Storage Stability** - Any adhesives or primer coatings developed shall show no signs of deterioration or gelling after 4 weeks' aging at 120°F.

Procedure for Testing Peel Strength: The procedure is that described previously (page 3) except that the adhesive, unless otherwise noted, was applied with a brush and was allowed

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to air-dry for 15-30 minutes until tacky.

Preliminary Investigation of Dow Corning A-4000 Adhesive:  
Dow Corning A-4000 Adhesive, containing 2.5 percent of XY-22, was applied to the aluminum panels and to Silastic 250 sheets in the manner recommended by the manufacturer.

Results: Dow Corning A-4000 Adhesive gave bond strengths of approximately half the target requirements, which were many times greater than any other commercial adhesive tested.

Table III

## INVESTIGATION OF DOW CORNING A-4000 ADHESIVE WITH CATALYST XY-22

<u>Bond No.</u>	<u>Adherends</u>	<u>Peel Strength lbs/in. 4 hours</u>	<u>Peel Strength lbs/in. 24 hours</u>	<u>Major Point of Failure</u>
6	Silastic 250 to Alclad Al	3.50	---	Cohesive
12	"	2.00	---	"
7	"	--	5.75	Adhesive (R) <sup>1</sup>
13	"	--	3.00	"

Note 1: The major point of failure was at the interface between the adhesive and the rubber.

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Effect of Initial Pressure: The effect of initial pressure was determined by using a 2-pound and a 10-pound roller to press together the aluminum and silicone rubber test specimens.

Results: The amount of pressure applied made no significant difference in bond strength, as long as it was enough to press the two surfaces together uniformly.



A-4000 WITH XY-22: EFFECT OF INITIAL PRESSURE

<u>Bond No.</u>	<u>Weight of Roller, lbs</u>	<u>Peel Strength lbs/in. 4 hours</u>	<u>Peel Strength lbs/in. 24 hours</u>	<u>Major Point of Failure</u>
24	2.0	3.00	---	Cohesive
25	2.0	--	2.25	"
26	10.0	1.50	---	"
27	10.0	--	3.00	Adhesive(R)

Variations in Drying Time: After application of the catalyzed A-4000 to the aluminum and silicone rubber, the adhesive should show an aggressive tackiness before the two surfaces are brought together. In order to determine the optimum length of time on which to attain this tackiness, variations in drying time were studied.

Results: At the particularly warm room-temperature of 27°C (summer season), optimum tackiness of the adhesive was achieved in 10 minutes.

Table V

A-4000 WITH XY-22: VARIATIONS IN DRYING TIME

<u>Bond No.</u>	<u>Average R.T., °C</u>	<u>Drying Time, minutes</u>	<u>Peel Strength lbs/in. 24 hours</u>	<u>Major Point of Failure</u>
14	27	10	3.75	Adhesive(R)
15	27	20	3.50	"
16	27	30	3.00	"
17	27	40	2.50	"

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Molding and Cleaning Silastic 250: After 24 hours, the major point of failure was almost always in adhesion to the rubber. Changes in the mold release agent during the molding operation, as well as changes in the method of cleaning the molded sheet, were studied.

Results: The condition of the surface of the rubber made a considerable difference in the degree of adhesion. The use of mica dust as a mold release agent or as a dusting powder definitely hinders adhesion. Soap is recommended as a mold release agent, and the use of water followed by toluene is preferred for cleaning the rubber sheets.

Table VI

A-4000 WITH XY-22: MOLDING AND CLEANING SILASTIC 250

<u>Bond. No.</u>	<u>Mold Release Agent</u>	<u>Cleaning Method for Silastic 250</u>	<u>Peel Str. lbs/in. 4 hrs</u>	<u>Peel Str. lbs/in. 24 hrs</u>	<u>Major Point of Failure</u>
26	Mica Dust	Toluene	1.50	---	Cohesive
27	"	"	--	3.00	Adhesive (R)
28	Soapine	"	2.50	---	Cohesive
30	"	"	3.00	---	"
29	"	"	--	6.00	Adhesive (R)
31	"	"	--	6.25	Adhesive (M) <sup>1</sup>
32	"	Water & Toluene	3.00	---	Cohesive
34	"	"	3.25	---	"
36	"	"	3.25	---	"
33	"	"	--	6.75	"
35	"	"	--	9.00	"
37	"	"	--	6.50	"

*Conclusions*

Note: 1 The major point of failure was at the interface between the adhesive and the metal.

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Variation in Glue Line Thickness: The changes in technique described above did not provide the radical increase in bond strength needed for achieving the target requirements. However, the major point of failure did change from adhesion to cohesion when soap was used as the mold release agent in the molding of Silastic 250. It was then thought that a change in the amount of adhesive applied might increase the bond strength.

Results: The target requirements of the contract can be reached by using a generous amount of adhesive. A glue line of 15-25 mils is needed to provide the required bond strength.

Table VII

A-4000 WITH XY-22: VARIATION IN GLUE LINE THICKNESS

<u>Bond No.</u>	<u>Method of Application</u>	<u>No. of Coats on Each Surface</u>	<u>Avg. Glue Line, mils</u>	<u>Peel Str., lbs/in. 24 hours</u>	<u>Major Point of Failure</u>
38	Spreader	---	8	6.00	Cohesive
39	"	---	9	6.00	"
40	"	---	13	7.75	"
41	"	---	19	8.25	"
43	Brush	1 (regular)	7	7.50	"
42	"	2 (regular)	17	11.50	"
44	"	1 (thick)	18	11.00	"
45	"	"	13	3.25 <sup>1</sup>	"
46	"	"	13	9.50	"

Note 1: Peel Strength after 4 hours instead of 24 hours

Variation in Catalyst Concentration: Although it was found that Dow Corning A-4000 Adhesive could meet the required target properties for bond strength, the concentration of catalyst, Dow Corning XY-22, was varied to determine whether an optimum amount was being used.

Results: Increasing the concentration of XY-22 resulted in some improvement in the bond strength of the adhesive, but this treatment was contraindicated by a decrease in the pot-life of the catalyzed adhesive.

Table VIII

A-4000 WITH XY-22: VARIATION IN CATALYST CONCENTRATION

<u>Bond No.</u>	<u>Percent Concentration of XY-22</u>	<u>Pot-Life, hours</u>	<u>Peel Str., lbs/in. 24 hours</u>	<u>Major Point of Failure</u>
47	2.0	6	6.25	Cohesive
48	2.5	5	9.00	"
49	3.0	4	9.25	Adhesive(R)
50	3.5	3	10.35	"

Priming of Silastic 250: The major point of failure when the adhesive was applied properly was now almost always cohesive, but there still were occasional adhesive failures to the rubber. The effect on bond strength of primers applied to Silastic 250 was studied.

Results: Priming the rubber with various materials considerably decreased rather than increased the adhesion to the rubber. There was one exception, a two percent solution

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of tetra-n-butyl titanate, which caused neither a significant increase nor decrease in bond strength.

Table IX

A-4000 WITH XY-22: PRIMING OF SILASTIC 250

<u>Bond No.</u>	<u>Primer</u>	<u>Avg. Glue Line, mils</u>	<u>Peel Str., lbs/in. 24 hours</u>	<u>Major Point of Failure</u>
56	Dow Corning 260	10	3.75	Adhesive (R)
57	Dow Corning XA-4004	12	6.00	"
64	50% Methylene bis (4-phenyl isocyanate)	22	0.75	"
65	50% Naphthalene-1,5-diisocyanate	17	6.00	"
66	2% Tetrabutyl Titanate	17	8.50	"

Preparation of Aluminum for Bonding: An air-drying adhesive is normally used because it is a quick and convenient tool. Since acid-cleaning of aluminum is not a convenient method for preparing a surface, easier cleaning methods were studied.

Results: There was little difference in bond strength, whichever method was used. It is therefore not necessary to use an acid cleaning solution for preparing the aluminum surface for bonding.

A-4000 WITH XY-22: PREPARATION OF ALUMINUM FOR BONDING

<u>Bond No.</u>	<u>Preparation of Aluminum Surface</u>	<u>Avg. Glue Line, mils</u>	<u>Peel Str., lbs/in. 24 hours</u>	<u>Major Point of Failure</u>
55	Sulfuric Acid-Sodium Dichromate Cleaning Solution & Toluene	16	10.50	Cohesive
51	Perchloroethylene & Toluene	14	8.00	Adhesive(R)
52	Steel Wool & Toluene	15	8.50	"
53	Detergent & Toluene	14	7.75	"
54	Detergent, Steel Wool & Toluene	13	9.75	"

Specification Testing of A-4000 Adhesive With Catalyst XY-22:

The contract calls for adhesive properties meeting the specifications listed on page 9.

Results: The data show that A-4000 Adhesive with XY-22 Catalyst gave bond strengths in excess of the target requirements when silicone was bonded to aluminum. At room temperature, water-immersion slightly increased bond strength, and oil-immersion only slightly reduced the original value, the bond strength remaining within a 25 percent leeway. Temperatures of 212°F, however, made a considerable difference in both air-aging and oil-immersion. The resinous adhesive was very weak and brittle after 24 hours' exposure to air at this temperature. A silicone-to-silicone bond failed to pass the ten pounds per inch requirement after 24 hours of cure. Neither Dow Corning A-4000 Adhesive nor Catalyst XY-22 showed any signs of deterioration or gelling after 4 weeks' aging at 120°F.

A-4000 WITH XY-22: SPECIFICATION TESTING

<u>Bond No.</u>	<u>Test</u>	<u>Passed or Failed</u>	<u>Peel Str., lbs/in. 24 hours</u>	<u>Major Point of Failure</u>	<u>Condition of Adhesive After test</u>
58	Silicone to Aluminum	Passed	12.00	Cohesive	Elastomeric
67	Silicone to Silicone	Failed	5.75	Adhesive(R)	"
59	Water-Immersion at R.T.	Passed	13.25	"	"
60	Oil-Immersion at 212°F	Failed	1.75	"	Weak
62	Air-Aging at 212°F	Failed	---	"	Weak, brittle
63	Oil-Immersion at R.T.	No Specification	8.00	"	Elastomeric
--	Storage Stability	Passed	---		

Comparison of Catalysts XY-22 and XY-27: In the evaluation of Dow Corning A-4000 Adhesive catalyzed with XY-22, it was found that the adhesive meets all the target properties except the heat-aging specification in air or oil at 212°F for 24 hours. Dow Corning has since replaced XY-22 with a new catalyst, XY-27, which is supposed to improve the high-temperature properties of the adhesive. The concentration of XY-27 used with A-4000 was 4.5 percent by weight compared with 2.5 percent of XY-22.

It was the purpose of this experiment to compare the performance of the new Dow Corning catalyst, XY-27, with that of the old Dow Corning catalyst, XY-22, when used in conjunction with Dow Corning Adhesive A-4000. Special attention was directed toward the high-temperature aging specification which the older combination failed to meet.

Results: The data indicate that Catalyst XY-27 is superior to Catalyst XY-22 as far as aging at 212°F is concerned. The bond strength of an aged sample was such that it was very difficult to pull the adherends apart with the hands. However,

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Catalyst XY-27, when mixed with the A-4000, did not achieve the bond strength at room temperature obtained with the use of XY-22. The adhesive catalyzed with XY-27 displayed an average bond strength of 9.09 pounds per inch after one day at room temperature, as compared with 12.00 pounds per inch displayed by the adhesive catalyzed with XY-22. This inability to meet the 10 pounds per inch requirement at room temperature, however, is not nearly as important as passing the high-temperature specification, which the adhesive catalyzed with XY-22 failed to do.

Table XII

A-4000 ADHESIVE: COMPARISON OF  
CATALYSTS XY-22 AND XY-27

<u>Bond No.</u>	<u>Catalyst</u>	<u>Test</u>	<u>Curing Time, Days @ R.T.</u>	<u>Peel Str., lbs/in.</u>	<u>Passed or Failed</u>	<u>Major Point of Failure</u>
58	XY-22	Silicone to Aluminum	1	12.00	Passed	Cohesive
77	XY-27	"	1	9.09	Failed	"
79	"	"	3	9.57	+	"
80	"	"	7	9.69	+	"
62	XY-22	Aging in Air at 212°F	*	---	Failed	Adhesive(R)
73	XY-27	"	*	---	Passed	None

Notes: \*Cured and aged according to specification  
+No specification



*Continued*

C. Development of a New RTV Adhesive

1. Curing Agents and Activators

Objective: A number of curing peroxidic agents and activators were obtained from suppliers. Combinations of the curing agents and activators have been evaluated for room-temperature activity to determine whether the activator reduces the temperature of cure.

Each of the activators listed in Table XIII, Column B, was mixed with General Electric Viscasil 30,000 silicone fluid, and then one of the peroxides listed in Column A was added to the mixture. These samples were examined for curing activity at various temperatures.

Table XIII

LIST OF PEROXIDES AND ACTIVATORS

Column A - Peroxides

Benzoyl Peroxide  
2,4-Dichlorobenzoyl Peroxide  
Tert-Butyl Perbenzoate  
Cumene Hydroperoxide  
Acetyl Peroxide

Column B - Activators

Lead Uversol (Napthenate), 24%  
Lead Octasol (Octoate), 24%  
Iron Uversol (Napthenate), 6%  
Iron Octasol (Octoate), 6%  
Zinc Uversol (Napthenate), 8%  
Zinc Octasol (Octoate), 8%  
Dow Corning XY-15(Metal Salt), 20%  
Octylene Glycol Titanate (2.21)  
Tetraisopropyl Titanate  
Tetra-2-ethylhexyl Titanate  
Tetra-n-butyl Titanate  
Triethylenetetramine  
Triethanolamine  
Diethanolamine  
Ethanolamine  
Sequestrene NA-2  
Sequestrene Fe-2  
Ethylenediamine, 76%  
Diethylenetriamine

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Procedure: One hundred parts (5.0 grams) of Viscasil 30,000 fluid were mixed with 1,2,4 and 8 parts of each activator. Four parts of one of the peroxides were then added to each activator-fluid sample just prior to the curing cycle. Each sample was examined for curing activity at the end of  $\frac{1}{2}$ , 1, and 24 hours at a temperature of 75°C. Those that looked promising were then tested at 50°C and down to 25°C.

Extent of cure is indicated by an arbitrary number code having the following key:

- 1 - no cure
- 2 - partial cure (some elasticity)
- 3 - semicure (elastic but soft)
- 4 - full cure (tight and firm)

Results: At a temperature of 25°C, only tetraisopropyl titanate and tetra-n-butyl titanate activated the curing action of benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butyl perbenzoate, and cumene hydroperoxide in Viscasil 30,000. The curing action, however, started before the peroxide was added. This would indicate that the titanate is doing the curing and that the peroxide is not really activated. These titanates become deactivated in some way by acetyl peroxide, for even at 75°C titanate-acetyl peroxide combinations showed no signs of curing the silicone fluid.

Of course the above strong titanate esters cured the Viscasil at 50°C. Also the less active ester, tetra-2-ethylhexyl titanate, and the titanium chelate, octylene glycol titanate, partially cured Viscasil 30,000 at 50°C but only in the presence of tertbutyl perbenzoate. This was also true of the organometallic drying agents, Iron Octasol, Zinc Uversol and Zinc Octasol.

Table XIV

THE ACTION OF VARIOUS ACTIVATORS ON SEVERAL PEROXIDES

Activator	Parts/100 Parts Viscasil 30,000	A. 75°C						After 24 Hours								
		After 1/2 Hour			After 1 Hour			After 1 Hour			After 24 Hours					
		BP	CLBP	TBP	CHP	AP	BP	CLBP	TBP	CHP	AP	BP	CLBP	TBP	CHP	AP
No Activator		1	1	1	1	1	1	1	1	1	1	2	2	1	1	1
No Peroxide or Activator		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Lead Uversol	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Lead Octasol	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
Iron Uversol	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Iron Octasol	1.0	1	1	1	1	1	1	1	1	1	1	4	1	2	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	4	1	3	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	4	1	3	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	2	1	1	1	1
Zinc Uversol	1.0	1	1	1	1	1	1	1	1	1	1	2	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	4	1	2	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	3	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	2	1	1	1	1
Zinc Octasol	1.0	1	1	1	1	1	1	1	1	1	1	2	1	2	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	4	1	2	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	3	1	3	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	3	1	3	1	1

Table XIV (Contd.)

THE ACTION OF VARIOUS ACTIVATORS ON SEVERAL PEROXIDES

Activator	Parts/100 Parts Viscasil 30,000	After 1/2 Hour			After 1 Hour			After 2 1/2 Hours					
		BP	CLBP	TBP	CHP	AP	BP	CLBP	TBP	CHP	AP		
DC XY-15	1.0	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1
Octylene Glycol	1.0	1	1	1	1	1	1	1	1	1	3	1	1
	2.0	1	1	1	1	1	1	1	1	1	3	1	1
	4.0	1	1	1	1	1	1	1	1	1	2	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1
Tetraisopropyl Titanate	1.0	1	1	1	1	1	1	1	1	1	2	3	1
	2.0	1	1	1	1	1	1	1	1	1	4	3	1
	4.0	1	2	1	2	1	2	1	2	1	3	3	1
	8.0	2	2	1	2	1	2	1	2	1	3	3	1
Tetra-2-ethylhexyl Titanate	1.0	1	1	1	1	1	1	1	1	1	2	1	1
	2.0	1	1	1	1	1	1	1	1	1	4	2	1
	4.0	1	1	1	1	1	1	1	1	1	3	3	1
	8.0	1	1	1	1	1	1	1	1	1	2	2	1
Tetra-n-butyl Titanate	1.0	1	1	1	1	1	1	1	1	1	2	2	1
	2.0	1	1	1	1	1	1	1	1	1	3	2	1
	4.0	1	1	1	1	1	1	1	1	1	3	2	1
	8.0	1	1	1	1	1	1	1	1	1	2	1	1
Triethylenetetramine	1.0	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1
Triethanolamine	1.0	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1

*Contrails*

Table XIV (Contd.)

THE ACTION OF VARIOUS ACTIVATORS ON SEVERAL PEROXIDES

Activator	Parts/100 Parts Viscasil 30,000	After 1/2 Hour				After 1 Hour				After 24 Hours						
		BP	CLBP	TBP	CHP	AP	BP	CLBP	TBP	CHP	AP	BP	CLBP	TBP	CHP	AP
Diethanolamine	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Ethanolamine	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Sequestrene NA-2	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Sequestrene Fe-2	1.0	1	1	*	1	1	1	1	1	1	1	1	1	*	1	1
	2.0	1	1	*	1	1	1	1	1	1	1	1	*	1	1	1
	4.0	1	1	*	1	1	1	1	1	1	1	1	*	1	1	1
	8.0	1	1	*	1	1	1	1	1	1	1	1	*	1	1	1
Ethylenediamine	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Diethylenetriamine	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

*Controls*

Table XIV (Contd.)

THE ACTION OF VARIOUS ACTIVATORS ON SEVERAL PEROXIDES

B. 50°C

Activator	Parts/100 Parts Viscasil 30,000	After 1/2 Hour				After 1 Hour				After 2 1/2 Hours						
		BP	CLBP	TBP	CHP	AP	BP	CLBP	TBP	CHP	AP	BP	CLBP	TBP	CHP	AP
No Activator		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
No Peroxide or Activator		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Iron Octasol	1.0	1	-	1	-	1	-	1	-	1	-	1	-	1	-	1
	2.0	1	-	1	-	1	-	1	-	1	-	1	-	1	-	1
	4.0	1	-	1	-	1	-	1	-	1	-	1	-	1	-	1
	8.0	1	-	1	-	1	-	1	-	1	-	1	-	2	-	1
Zinc Uversol	1.0	1	-	1	-	1	-	1	-	1	-	1	-	1	-	1
	2.0	1	-	1	-	1	-	1	-	1	-	1	-	2	-	1
	4.0	1	-	1	-	1	-	1	-	1	-	1	-	2	-	1
	8.0	1	-	1	-	1	-	1	-	1	-	1	-	2	-	1
Zinc Octasol	1.0	1	-	1	-	1	-	1	-	1	-	1	-	1	-	1
	2.0	1	-	1	-	1	-	1	-	1	-	1	-	1	-	1
	4.0	1	-	1	-	1	-	1	-	1	-	1	-	1	-	1
	8.0	1	-	1	-	1	-	1	-	1	-	1	-	2	-	1
Octylene Glycol Titanate	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Tetraisopropyl Titanate	1.0	2	2	2	1	2	2	2	2	2	2	2	2	2	1	3
	2.0	2	2	2	1	2	2	2	2	2	2	2	2	2	1	3
	4.0	2	2	2	1	2	2	2	2	2	2	2	2	2	3	3
	8.0	1	2	2	1	2	2	2	2	2	2	2	2	3	3	3
Tetra-2-ethylhexyl Titanate	1.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

*Contrails*

Table XIV (Contd.)

THE ACTION OF VARIOUS ACTIVATORS ON SEVERAL PEROXIDES

Activator	Parts/100 Parts Viscasil 30,000	After 1 Hour				After 24 Hours			
		BP	CLBP	TBP	CHP	BP	CLBP	TBP	CHP
Tetra-n-butyl Titanate	1.0	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1
Sequestrene NA-2	1.0	1	1	-	1	1	-	-	-
	2.0	1	1	-	1	1	-	-	-
	4.0	1	1	-	1	1	-	-	-
	8.0	1	1	-	1	1	-	-	-
Sequestrene Fe-2	1.0	1	*	*	*	*	*	*	*
	2.0	1	*	*	*	*	*	*	*
	4.0	1	*	*	*	*	*	*	*
	8.0	1	*	*	*	*	*	*	*
No Activator		1	1	1	1	1	1	1	1
No Peroxide or Activator		1	1	1	1	1	1	1	1
Tetraisopropyl Titanate	1.0	2	2	2	2	2	2	2	2
	2.0	2	2	2	2	2	2	2	2
	4.0	1	2	2	2	2	2	2	2
	8.0	2	2	2	2	2	2	2	2
Tetra-n-butyl Titanate	1.0	1	1	1	1	1	1	1	1
	2.0	1	1	1	1	1	1	1	1
	4.0	1	1	1	1	1	1	1	1
	8.0	1	1	1	1	1	1	1	1

C. 25°C

Notes:

- BP - Benzoyl Peroxide
- CLBP - 2,4-Dichlorobenzoyl Peroxide
- TBP - Tert-Butyl Perbenzoate
- CHP - Cumene Hydroperoxide
- AP - Acetyl Peroxide
- \* - No Activator available
- - No further testing required for this peroxide

*Contrails*

## 2. Study of Fast-Curing Silicone Resins

Comments: Although a large number of resins were available for investigation, lack of time prevented their being tested as air-drying adhesives for bonding silicone rubber to metal or to itself.

However, some aspects of silicone resin chemistry were investigated, and the results of these experiments can be found below under "Curing of Modified Siloxane Polymers."

## 3. Curing of Modified Siloxane Polymers

Objective: A number of modified siloxanes containing organic groups other than the usual methyl groups were obtained for this study. The first point of attack was to develop a system which would cure the silicone at the modifying group at room temperature. A number of different compounds, most of which were difunctional, were mixed with the modified siloxanes, and the mixtures were examined for curing activity within different periods of time at various temperatures.

The modified siloxanes used for this experiment were: Dow Corning A-4000 Adhesive which is possibly a methylhydrogen siloxane containing some trifunctional material; General Electric Viscasil 30,000, a methyl siloxane fluid having a viscosity of 30,000 centistokes; Linde Silicone Y-1170, a methylhydrogen siloxane fluid having a 15:1 ratio of methyl to hydrogen groups; Linde Silicone Y-1169, a methylhydrogen siloxane fluid having a 50:1 ratio of methyl to hydrogen groups; Dow Corning 410, a methylvinyl siloxane gum containing approximately 4 mole percent of vinyl groups; Linde W-96, a modified siloxane gum, possibly containing a very small amount of olefinic groups; Connecticut Hard Rubber G-2, a glycerol-stabilized, depolymerized silicone gum; and Cl-Viscasil 30,000, a chlorinated silicone fluid containing 0.5 chlorine atom per silicon atom. (Details concerning the preparation of this latter polymer are located in the appendix to this report.)

The compounds used as prospective curing agents were: Dow Corning XY-22, one of the catalysts for the A-4000 Adhesive; benzoyl peroxide, a free-radical generating compound, normally used for curing methyl siloxanes; ethylenediamine; methylene-bis (4-phenylisocyanate); tetraisopropyl titanate; dibromobutane; azo-bis (isobutyronitrile); a combination of sulfur, zinc oxide, tetramethylthiuram disulfide and Accelerator 808 (a butyraldehyde-aniline condensation product), which is normally used for accelerating cures of double bond-containing polymers; a combination



*Continued*

of p-quinone dioxime and lead dioxide, which is also used for curing double bond-containing polymers; and a combination of lead oxide and Accelerator 808, which is frequently used for accelerating cures of neoprene-type polymers.

Procedure: One hundred parts (5.0 grams) of silicone polymer were placed in aluminum dishes, to which were added 1, 2, 4 and 8 parts of curing agent, unless otherwise noted. Sometimes the curing agents were not used over the entire range of concentration. The reason was that only a minimum amount of the particular curing agent or siloxane was available. The mixed products were examined for curing activity at the end of 0,  $\frac{1}{2}$ , 1 and 24 hours at a temperature of 100°C. Those that looked promising were then tested at 75°C and down to 50°C and 25°C.

The results of this study are listed in Table XV. Because of the large amount of data, only the 24-hour observations, which are the most significant, are presented.

The key to the number code used for extent of cure is the same as that on page 20.

Results: The data for 25°C show the following clear-cut results: (1) Dow Corning XY-22 cured not only the A-4000 Adhesive but also the hydrogen-modified siloxanes, Linde Y-1169 and Y-1170; (2) ethylenediamine cured Cl-Viscasil 30,000; (3) tetraisopropyl titanate cured all of the siloxanes tried; and (4) dibromobutane partially cured the A-4000 Adhesive.

VULCANIZATION OF SILOXANE POLYMERS

Parts	Curing Agent	A-4000				Viscasil 30,000				Linde Y-1170 15:1				Linde Y-1169 50:1			
		Extent of Cure After 24 Hours at Temperatures °C															
		100	75	50	25	100	75	50	25	100	75	50	25	100	75	50	25
No Curing Agent		4	4	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1.0	Dow Corning XY-22	4	4	4	4	1	-	-	-					4			
2.0		4	4	4	4	1	-	-	-					4			
4.0		4	4	4	4	1	-	-	-					4			
8.0		4	4	4	4	1	-	-	-	4	4	4	4	4	4	4	4
1.0	Benzoyl Peroxide	4	4	4	1	2	3	1	-					2			
2.0		4	4	3	1	3	3	1	-					3			
4.0		4	4	3	1	3	3	1	-					4			
8.0		4	4	3	1	3	3	1	-	4	4	1	-	4	4	1	-
1.0	Ethylenediamine	3	4	2	-	1	-	-	-					1			
2.0		3	4	2	-	1	-	-	-					1			
4.0		3	4	3	-	1	-	-	-					1			
8.0		3	4	2	-	1	-	-	-	1	-	-	-	1	-	-	-
1.0	Methylene-bis(4-phenylisocyanate)	1	-	-	-	1	-	-	-					1			
2.0		1	-	-	-	1	-	-	-					1			
4.0		2	-	-	-	1	-	-	-					1			
8.0		2	-	-	-	1	-	-	-	1	-	-	-	1	-	-	-
1.0	Tetraisopropyl Titanate	4	4	4	4	1	2	2	2					3			
2.0		4	4	4	4	2	2	2	2					3			
4.0		4	4	4	4	2	2	2	2					3			
8.0		4	4	4	4	2	2	2	2	4	4	4	4	4		4	3
1.0	Dibromobutane	4	4	3	2	1	-	-	-								
2.0		4	4	3	2	1	-	-	-								
4.0		4	4	3	2	1	-	-	-								
8.0		4	4	3	2	1	-	-	-	1	-	-	-	1	-	-	-
1.0	Azo-bis(isobutyronitrile)	4	3	1	-	1	-	-	-								
2.0		4	3	1	-	1	-	-	-								
4.0		4	3	1	-	1	-	-	-								
8.0		4	3	1	-	1	-	-	-	2	3	2	2	2	3	2	2
2.5	Sulfur																
5.0	Zinc Oxide	4	4	3	1	1	-	-	-	1	-	-	-	1	-	-	-
1.0	Tetramethylthiuram Disulfide																
1.0	Accelerator 808																
2.0	p-Quinone Dioxime	4	4	4	1	1	-	-	-	4	3	2	1	3	1	1	-
10.0	Lead Dioxide																
10.0	Lead Oxide	4	4	1	-	1	-	-	-	4	4	3	1	4	4	1	-
5.0	Accelerator 808																

VULCANIZATION OF SILOXANE POLYMERS

Parts Curing Agent	50% DC-410				50% Linde W-96				G-2				Cl. Viscasil 30,000			
	Extent of Cure After 24 Hours at Temperature °C															
	100	75	50	25	100	75	50	25	100	75	50	25	100	75	50	25
No Curing Agent	1	1	1	1	1	1	1	1	1	1	1	1	2	2	1	1
1.0 Dow Corning XY-22	1	-	-	-	1	-	-	-	2	2	1	1				
2.0	1	-	-	-	1	-	-	-	4	3	1	1				
4.0	1	-	-	-	1	-	-	-	4	3	2	1				
8.0	1	-	-	-	1	-	-	-	4	4	3	1	3	1	-	-
1.0 Benzoyl Peroxide	4	4	3	1	4	4	3	1	2	1	-	-				
2.0	4	4	3	1	4	4	3	1	2	1	-	-				
4.0	4	4	3	1	4	4	3	1	3	2	-	-				
8.0	4	4	3	1	4	4	3	1	4	1	-	-	4	4	3	2
1.0 Ethylenediamine	1	-	-	-	1	-	-	-	1	-	-	-				
2.0	1	-	-	-	1	-	-	-	1	-	-	-				
4.0	1	-	-	-	1	-	-	-	1	-	-	-				
8.0	1	-	-	-	1	-	-	-	1	-	-	-	4	4	4	4
1.0 Methylene-bis(4-phenylisocyanate)	1	-	-	-	1	-	-	-	2	1	-	-				
2.0	1	-	-	-	1	-	-	-	2	1	-	-				
4.0	2	-	-	-	1	-	-	-	3	1	-	-				
8.0	2	-	-	-	1	-	-	-	4	1	-	-	1	-	-	-
1.0 Tetraisopropyl Titanate	4	4	4	3	4	4	4	3	2	2	2	3				
2.0	4	4	4	4	4	4	4	4	4	2	2	3				
4.0	4	4	4	4	4	4	4	4	4	4	4	4				
8.0	4	4	4	4	4	4	4	4	4	4	4	4	2	2	3	3
1.0 Dibromobutane	1	1	-	-	1	-	-	-	1	-	-	-				
2.0	1	1	-	-	1	-	-	-	1	-	-	-				
4.0	2	1	-	-	1	-	-	-	1	-	-	-				
8.0	1	1	-	-	1	-	-	-	1	-	-	-	2	1	-	-
1.0 Azo-bis(isobutyronitrile)	4	4	1	-	4	4	3	1	1	-	-	-				
2.0	4	4	2	-	4	4	3	1	1	-	-	-				
4.0	4	4	2	-	4	4	3	1	1	-	-	-				
8.0	4	4	2	-	4	4	3	1	1	-	-	-	3	3	2	1
2.5 Sulfur																
5.0 Zinc Oxide	4	2	1	-	1	-	-	-	1	-	-	-	1	-	-	-
1.0 Tetramethylthiuram Disulfide Accelerator 808																
2.0 p-Quinone Dioxime	1	-	-	-	1	-	-	-	1	-	-	-	1	-	-	-
10.0 Lead Dioxide																
10.0 Lead Oxide	1	-	-	-	1	-	-	-	4	3	2	1	3	2	-	-
5.0 Accelerator 808																

Curing Hydrogen-Modified Siloxanes with Organometallic Salts:

It is known that Si-H groups react easily with strong alkalies such as sodium hydroxide. The action on Si-H groups of organometallic salts, which are slightly basic compounds, was studied in this experiment. Because of the limited amount of hydrogen-containing polymer (Linde Y-1170) available, preliminary screening was done by adding various metal salts to Dow Corning A-4000 Adhesive which is believed to contain hydrogen groups.

The tests were conducted in aluminum cups. Eight parts of catalyst were used in each case. The extent of cure was recorded according to the code on page 20.

Results: Lead or Zinc Octasol are fast-curing catalysts for this system. Therefore, Lead and Zinc Octasol proved to be proper compounds for use in determining whether metal salts are basic enough for removing the hydrogen from Si-H groups.

Table XVI

CURING A-4000 ADHESIVE WITH ORGANOMETALLIC SALTS

<u>Catalyst</u>	<u>0</u>	<u>Extent of Cure at 25°C</u>		
		<u>After 1/2 Hour</u>	<u>After 1 Hour</u>	<u>After 2 1/2 Hours</u>
None	1	1	1	1
DC XY-15	1	2	2	3
DC XY-22	1	2	2	4
Lead Uversol	1	1	1	4
Lead Octasol	1	1	2	4
Iron Uversol	1	1	1	2
Iron Octasol	1	1	1	2
Zinc Uversol	1	1	1	2
Zinc Octasol	1	1	2	4

In the next experiment, Lead Octasol was added to several different siloxanes, these being General Electric Viscasil 30,000 silicone fluid; Linde W-96 gum; Dow Corning 410 gum; Dow Corning 2103 resin, a methyl phenyl resin (approximately 40 percent phenyl) having an R/Si ratio of approximately 1.25; General Electric SF-69, a polymerizable light silicone fluid; Connecticut Hard Rubber CHR-VIII, a methyl phenyl resin (approximately 4.5 percent phenyl) having an R/Si ratio of 1.7; Dow Corning A-4000 Adhesive; and Linde Y-1170 fluid, a methyl-

*Continued*

hydrogen siloxane having a 15:1 ratio of methyl to hydrogen groups.

Results: Lead Octasol not only acted as a catalyst for thermosetting, through the OH groups, the resins, DC-2103, CHR-VIII, A-4000, and the polymerizable fluid, SF-69, but also catalyzed the removal of hydrogen from the Si-H groups on A-4000 and Linde Y-1170. Bubbling was noted in the hydrogen-modified siloxanes for a few hours after the Lead Octasol was added, indicating that two hydrogens were removed in the form of hydrogen gas. Cross-linking then took place, probably at the site of this cleavage, as evidenced by the full cure of these polymers after 24 hours at 25°C.

Table XVII

EFFECT OF LEAD OCTASOL ON SILOXANE POLYMERS

Polymer	Parts		Extent of Cure at 25°C			
	Lead	Octasol	0	After ½ Hr	After 1 Hr	After 24 Hrs
G.E. Viscasil 30,000	0	1	1	1	1	1
"	8	1	1	1	1	1
Linde W-96 (50%)	0	1	1	1	1	1
"	8	1	1	1	1	1
DC-410 (50%)	0	1	1	1	1	1
"	8	1	1	1	1	1
G.E. SR-69	0	1	1	1	1	1
"	8	1	1	1	1	2
DC-2103	0	1	1	1	1	1
"	8	1	3	3	4	4
CHR-VIII	0	1	1	1	1	1
"	8	1	2	2	4	4
DC A-4000	0	1	1	1	1	1
"	8	1	1	4	4	4
Linde Y-1170	0	1	1	1	1	1
"	8	1	1	1	1	4

*Continued*

Curing Hydrogen-Modified Siloxanes With Boron Trifluoride-Piperidine Complex: Another basic compound, boron trifluoride-piperidine complex, was mixed with Linde Y-1170 and Dow Corning A-4000 Adhesive to determine whether this material also catalyzes the removal of hydrogen from the Si-H groups.

Results: Boron trifluoride-piperidine complex also catalyzed the cure of hydrogen-modified siloxanes.

Table XVIII

EFFECT OF BORON TRIFLUORIDE-PIPERIDINE  
COMPLEX ON SILOXANE POLYMERS

Polymer	Parts of BF <sub>3</sub> - Piperidine	Extent of Cure at 25°C			
		0	After ½ Hr	After 1 Hr	After 24 Hrs
DC A-4000	0	1	1	1	1
"	8	1	2	2	3
Linde Y-1170	0	1	1	1	1
"	8	2	2	3	3

4. Preparation of Other Modified Siloxane Polymers

Objective: This research has established the ease of curing compounds containing Si-H groups at room temperature. It was the purpose of this experiment to evaluate compounds of this type as air-drying adhesives. Linde Y-1170, a straight-chain fluid (R/Si ratio = 2.0), was obtained from the Linde Air Products Company. Various resins containing Si-H groups, having different R/Si ratios (1.9 to 1.5), were prepared.

Procedure: The polymerization of the resins was carried out in a reaction flask equipped with a high-speed glass agitator, a reflux condenser, and an inlet tube for the monomer mixture. The reaction flask contained 200 cc of trichloroethylene and 600 cc of distilled water. The end of the inlet tube was touching the bottom of the flask and was well immersed in the trichloroethylene layer. The blend of monomers (dimethyldichlorosilane, hydrogenmethyldiethoxysilane, and phenyltrichlorosilane) was dissolved in 50 cc of trichloroethylene. The solution of monomers was added to the mixture

in the flask, with rapid stirring, over a period of 30 minutes. The temperature was maintained as close to room temperature as possible by keeping the reaction flask in a continuous cold water bath. After the addition of monomers was completed, the mixture was stirred for an additional five minutes. The layers were allowed to separate, the resinous layer sinking to the bottom of the flask and the acidic aqueous layer floating at the top. The aqueous layer was decanted, and the lower layer was washed overnight with a continuous flow of water. The resin mixture was then stripped of any residual water and trichloroethylene by distillation. The resulting resin was dark in color and was purified by filtering with a diatomaceous earth. The final product was a clear, straw-colored, viscous fluid.

Table XIX shows the monomer charge of each of the resins prepared.

Results: The resins P-3, P-4, P-6, P-10, and P-11 were tested for Si-H groups by adding Lead Octasol and noting whether any evolution of gas occurred. There was gas in the case of every resin except P-3 which contained none of the hydrogenmethyl monomer.

Table XIX

PREPARATION OF HYDROGENMETHYLPHENYL SILOXANE RESINS

<u>Polymer No.</u>	<u>R/Si Ratio</u>	<u>Monomers</u>	<u>Molecular Weight</u>	<u>Monomer Charge Ratio</u>	<u>Monomer Charge Grams</u>
P-3	1.75	C <sub>6</sub> H <sub>5</sub> SiCl <sub>3</sub>	212	2.50	53.0
		(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	129	7.50	89.5
P-4	1.90	C <sub>6</sub> H <sub>5</sub> SiCl <sub>3</sub>	212	1.0	21.2
		(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	129	7.875	101.0
		HCH <sub>3</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	134	1.125	15.1
P-6	1.75	C <sub>6</sub> H <sub>5</sub> SiCl <sub>3</sub>	212	2.50	53.0
		(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	129	6.56	84.5
		HCH <sub>3</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	134	0.94	12.6
P-10	1.60	C <sub>6</sub> H <sub>5</sub> SiCl <sub>3</sub>	212	4.00	84.5
		(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	129	5.00	64.7
		HCH <sub>3</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	134	1.00	13.4
P-11	1.50	C <sub>6</sub> H <sub>5</sub> SiCl <sub>3</sub>	212	5.00	106.0
		(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	129	4.00	51.8
		HCH <sub>3</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	134	1.00	13.4

5. Testing Materials Developed as Adhesives

Objective: Previous work has indicated several possible methods of obtaining an air-curing adhesive for bonding silicone rubber to metal or to itself. The object of this experiment was to test the materials obtained by these methods to determine if the materials could meet the specifications outlined in the contract. Four different types of material were tested: (1) modified Dow Corning A-4000 Adhesive, (2) various compounded silicone rubbers, (3) a compounded silicone fluid containing Si-H groups (Linde Y-1170), and (4) hydrogenmethylphenyl siloxane resins. The procedure for testing peel strength can be found on page 3.



# Contrails

**Results:** The data in these experiments reveal that Dow Corning Adhesive A-4000 catalyzed with XY-22 adheres to rubber and aluminum better than any of the materials developed during the course of this research. Compound #4741 catalyzed with Lead Octasol (Bond No. 89b) shows exceptional promise as an air-drying, rubber-to-rubber adhesive, as evidenced by a peel strength value of 18.0 pounds per inch.

Table XXa

TESTING OF MODIFIED DOW CORNING A-4000 ADHESIVE

<u>Bond No.</u>	<u>Adherends</u>	<u>Adhesive</u>	<u>Parts Catalyst</u>	<u>Curing Time, Days@R.T.</u>	<u>Peel Str., lbs/in.</u>	<u>Major Point of Failure</u>	<u>Cond. of Adhesive After test</u>
72a	M <sup>1</sup> to R <sup>2</sup>	A-4000	2.5 XY-22	1	7.35	Cohesive	Elastomeric, soft
72b	"	"	"	2	9.95	"	Elastomeric, tough
73a	"	A-4000+ 20 pts Asbestine	"	1	3.20	Adhesive(M)	"
73b	"	"	"	2	8.55	Cohesive	"
81	"	"	4.5 XY-27	1	5.12	"	Wet, soft
71	"	A-4000 <sup>3</sup>	2.5 XY-22	4	6.47	Adhesive(R)	Brittle, tough
74a	"	A-4000	4.0 TPT <sup>4</sup>	1	0.84	"	soft
74b	"	"	"	2	1.10	"	Elastomeric, tough
82	"	A-4000+ 20 pts Asbestine	4.5 XY-27	Air-Aging Failed Test @ 212°F		Cohesive	Brittle

# Contrails

Table XXb

## TESTING OF COMPOUNDED SILICONE RUBBERS

Recipe #4734

G.E. SE-81477	100.0 parts
Santocel CS	15.0 "
Titanox RA	50.0 "
Iron Oxide	5.0 "

<u>Bond No.</u>	<u>Adherends</u>	<u>Adhesive</u>	<u>Parts Catalyst</u>	<u>Curing Time, Days@R.T.</u>	<u>Peel Str., lbs/in.</u>	<u>Major Point of Failure</u>	<u>Cond. of Adhesive After Test</u>
75a	M to R	Silastic 6-128	4.0 TPT	1	0	Adhesive (M&R)	Gummy
75b	"	"	"	2	0	Adhesive(M)	"
76a	"	#4734	"	1	1.33	"	Elastomeric
76b	"	"	"	2	0.44	"	"

TESTING OF COMPOUNDED LINDE Y-1170

Recipe #4741

Linde Y-1170	100.0 parts
Santocel CS	15.0 "
Titanox RA	50.0 "
Iron Oxide	5.0 "

<u>Bond No.</u>	<u>Adherends</u>	<u>Adhesive</u>	<u>Parts Catalyst</u>	<u>Curing Time, Days@R.T.</u>	<u>Peel Str., lbs/in.</u>	<u>Major Point of Failure</u>	<u>Cond. of Adhesive After Test</u>
83a <sup>5</sup>	M to R	#4741	4.0 Lead Octasol	1	0	Adhesive (M)	Pasty
83b <sup>5</sup>	"	"	"	3	0	"	Elastomeric
89a <sup>5</sup>	R to R	"	8.0 Lead Octasol	2	0.70	Cohesive	"
89b <sup>5</sup>	"	"	"	5	18.0 <sup>6</sup>	"	"
89c <sup>5</sup>	"	"	"	5	7.68 <sup>7</sup>	Adhesive(R)	"

Table XXd

TESTING OF HYDROGENMETHYLPHENYL SILOXANE RESINS

<u>Bond No.</u>	<u>Adherends</u>	<u>Adhesive</u>	<u>Parts Catalyst</u>	<u>Curing Time, Days@R.T.</u>	<u>Peel Str., lbs/in.</u>	<u>Major Point of Failure</u>	<u>Cond. of Adhesive After test</u>
84 <sup>5</sup>	M to R	P-3 <sup>8</sup>	4.0 Lead Octasol	1	0	Adhesive (M&R)	Weak, dry
85 <sup>5</sup>	"	P-4	"	1	0	"	"
86 <sup>5</sup>	"	P-6	"	1	0	"	"
87 <sup>5</sup>	"	P-10	"	1	0	"	"
88 <sup>5</sup>	"	P-11	"	1	0.20	Adhesive(R)	Brittle

WADC TR 55-289

# Contrails

## Notes:

1. M= Metal (Clad Aluminum 24S-T3)
  2. R= Rubber (Silastic 250)
  3. Linde W-96, containing forty parts of Valron (a DuPont silica) and cured with 4.0 parts of tetraisopropyl titanate (50 percent toluene solution), was used as a metal primer.
  4. TPT= Tetraisopropyl titanate
  5. Each value represents only one test. Normally, each value is the average of quadruplicate tests.
  6. The rubber broke during test, and the value may have been slightly higher.
  7. The adhesive layer was very uneven because of the fact that the adhesive had set up slightly, this being the last bond prepared in the series.
  8. P-3 Resin contains no Si-H groups.
-

## DISCUSSION AND CONCLUSIONS

### Evaluation of Commercially Available Adhesives

Commercially available adhesives were tested according to the procedures outlined in this report. None of the adhesives except Dow Corning A-4000 came near the requirements of the contract.

Epon VI was tested with two different activators, Catalyst A and diethylenetriamine. No readings were taken in either case at four hours because the adhesive was not completely cured. After 24 hours at room temperature, both mixtures gave peel strengths of less than 0.25 pounds per inch.

The peel strengths of Bond Master M-1654 with CH-8 Catalyst after 24 hours at room temperature showed only a slight increase over the pull recorded after 4 hours' curing time which was less than 0.25 pounds per inch.

Solvent-activated, DuPont 4678 Cement showed an actual decrease in peel strength from the results at 4 hours to those at 24 hours. Both were less than 0.25 pounds, however, and the difference was insignificant.

Thiokol T-120-1 gave a poor cure at 4 hours and showed cohesive failure at less than 0.25 pounds per inch. After 24 hours, the cure was good, but the peel strength had only increased to 0.25 pounds per inch.

Dow Corning A-4000 Adhesive gave bond strengths of approximately half the target requirements, which were many times greater than any other commercially available adhesive tested. Further tests were then conducted with it. The peel strengths of all of the other adhesives tested were in the vicinity of 0.25 pounds per inch, so no further investigation of their possible use as the target was warranted.

Of all the adhesives tested the major cause of poor peel strength was the failure of the bond at the adhesive silicone rubber interface. This would indicate the necessity of having a silicone-base adhesive for successful bonding.

### Evaluation of Dow Corning A-4000 RTV Adhesive

The peel strengths after a four-hour cure at room temperature were quite close to the minimum of 3 pounds per inch required by

the contract. The peel strengths for a 24-hour cure were approximately half of the required 10 pounds per inch.

In order to improve these promising results, several variations in the method of applying the adhesive were tried. One variation, the effect of initial pressure, was determined by using a two-pound and a ten-pound roller to press together the aluminum and silicone rubber test specimens. It was found that the amount of pressure applied made no significant difference in bond strength, as long as it was enough to press the two surfaces together uniformly. Another experiment was conducted in which the drying time was varied (10, 20, 30, and 40 minutes). The peel strengths decreased from 3.75 to 2.50 pounds per inch as the drying time was extended. This would seem to indicate that if the coated panels were allowed to dry too long before they were brought into contact, the adhesive would start to set and the bond strength would thus be lessened.

It was noticed that the major point of failure was usually in adhesion to the silicone rubber surface. On close observation of the samples, there appeared to be specks of mica dust on the rubber surface even after it was cleaned with solvent. The operation of molding the Silastic 250 rubber was changed in that Soapine was used as the mold release agent instead of mica dust. This seemed to be the answer; the condition of the surface of the rubber made a considerable difference in the degree of adhesion since results showed that the major point of failure was now generally in cohesion and less frequently in adhesion to the rubber. Therefore, soap is recommended as a mold release agent, and the use of water followed by toluene is preferred for cleaning the rubber sheets.

The variations in technique described above did not provide the radical increase in bond strength needed for achieving the target requirements. Because the failure was cohesive, it was thought that a change in the amount of adhesive applied might increase the bond strength. It was found that the amount of adhesive applied made a great deal of difference. Results showed that a minimum glue line of 15 mils is necessary to achieve the required bond strength of 10 pounds per inch.

Either two thin coats (each coat being allowed to dry for 10 to 15 minutes) or one thick coat will do a satisfactory job. With this generous coating, the drying time, that is the interval between the time when the adhesive is applied and the time that the two adherends are brought together, should be governed by the tackiness of the adhesive.

*Conrails*

One observation about the Dow Corning A-4000 Adhesive which should be mentioned is the effect of its solvent, xylene, on the silicone rubber. A generous amount of adhesive is needed for good bond strength. A longer drying time is therefore required, which means a longer time that the solvent is in contact with the rubber. Some swelling and warping of the rubber results. This condition, along with the added effect of hydrogen evolving during cure, might reduce bond contact unless some prolonged, or possibly intermittent, pressure is applied. It was also noticed after the peel strength test that the solvent or the adhesive seemed to embrittle and deteriorate the rubber at the bond interface. Perhaps multiple coatings would be preferable to one thick coat.

Although Dow Corning A-4000 Adhesive can meet the target requirements of the contract as described above, the concentration of catalyst, Dow Corning XY-22, was varied to determine whether an optimum amount was being used. It was shown that an increase in the concentration of XY-22 resulted in some improvement in the bond strength of the adhesive. This increased bond strength was probably derived from the increased state of cure, after twenty-four hours. However, the rate of cure increased with more catalyst, which correspondingly reduced the pot-life of the catalyzed adhesive. Therefore, the use of larger amounts of catalyst to increase the bond strength of the A-4000 Adhesive is not advisable.

The major point of failure when the adhesive was applied properly was now almost always cohesive, but there still were occasional adhesive failures to the rubber. The effect on bond strength of primers applied to Silastic 250 was studied. All of the primers used to improve adhesion to the rubber decreased the bond strength considerably. In fact, all failures were in adhesion to the rubber. The only exception was a two percent solution of tetra-n-butyl titanate which neither significantly increased nor decreased the bond strength obtainable without a primer.

The value of an air-drying adhesive is its convenience. Since it is not convenient to acid-clean all metal parts before applying the adhesive, easier cleaning methods were sought in an effort to simplify the entire method of application. Results indicated that the adhesive sticks very well to the aluminum, regardless of the cleaning method used. Differences in bond strength obtained by the use of these cleaning methods are more properly attributed to variations in glue lines, since none of the variations showed adhesive failure to the metal. It is therefore not necessary to use an acid cleaning solution for preparing the aluminum surface for bonding.

*Contract*

A complete evaluation of the A-4000 Adhesive was carried out to determine whether it could meet all of the specifications listed in the contract. Neither Dow Corning A-4000 Adhesive nor the Catalyst XY-22 showed any signs of deterioration or gelling after four weeks' aging at 120°F. The A-4000 Adhesive, catalyzed with XY-22, gives bond strengths in excess of the target requirements when silicone is bonded to aluminum. At room temperature, water-immersion made no significant difference in bond strength. Oil-immersion only slightly reduced the original value, the bond strength still remaining within a twenty-five percent leeway. Temperatures of 212°F, however, made a considerable difference in both air-aging and oil-immersion. The resinous adhesive was very weak and brittle after 24 hours' exposure to air at this temperature. A silicone-to-silicone bond failed to pass the ten pounds per inch requirement after 24 hours of cure. This latter result was not completely unexpected since the A-4000 Adhesive is a resinous material; probably a more elastomeric type of material is needed for bonding silicone rubber to silicone rubber. In this respect, the A-4000 Adhesive may possibly be made more elastomeric by using less than the normal amount (2.5 percent) of catalyst.

The A-4000 Adhesive, when catalyzed with Dow Corning Catalyst XY-22, met all of the specifications outlined in the contract except the silicone-to-silicone bond and high-temperature aging (212°F) in air or oil. Dow Corning has since replaced Catalyst XY-22 with the new XY-27 which is supposed to improve the high-temperature properties of the adhesive. An experiment was conducted to compare the performance of the new Dow Corning catalyst, XY-27, with that of the old Dow Corning catalyst, XY-22, when used in conjunction with Dow Corning Adhesive A-4000. Special attention was directed toward the high-temperature aging specification which the older combination failed to meet.

It was found that Catalyst XY-27 is superior to Catalyst XY-22 as far as aging at 212°F is concerned. Bonds prepared with the A-4000 Adhesive catalyzed with XY-27 satisfactorily met the high-temperature aging requirement by exhibiting no creep after 24 hours at 212°F when a two-pound weight was placed at a ninety-degree angle to the aluminum. The bond strength of an aged sample was such that it was very difficult to pull the adherends apart with the hands.

Catalyst XY-27 is a slower curing catalyst than XY-22, as evidenced by an average peel strength after 24 hours at room temperature of slightly less than 10 pounds per inch when the former is used and more than 10 pounds per inch when the



latter is used. Inasmuch as the performance of this adhesive at high temperature is more important than the peel strength at room temperature (as long as it is close to the target requirements), the desirable catalyst for use with the A-4000 Adhesive is XY-27. It is therefore recommended that the specification calling for a minimum peel strength of 10 pounds per inch after 24 hours at room temperature be changed to a minimum of 8 pounds per inch.

### Development of a New RTV Adhesive

The study of peroxide-activator systems for curing General Electric Viscasil 30,000 silicone fluid was not very fruitful since none of the peroxides was influenced by various activators at room temperature. At a temperature of 25°C, only tetraisopropyl-titanate and tetra-n-butyl titanate effected a cure. However, the curing action started before the peroxide was added signifying that the titanate was doing the curing and that the peroxide was not really activated. For some reason, these titanates become deactivated by acetyl peroxide, for even at 75°C titanate-acetyl peroxide combinations showed no signs of curing the silicone fluid.

At 50°C, the above titanate esters cured the Viscasil silicone fluid. The less active ester, tetra-2-ethylhexyl titanate, and the titanium chelate, octylene glycol titanate, partially cured Viscasil 30,000, but only in the presence of tert-butyl perbenzoate. This was also true of the organometallic drying agents, Iron Octasol, Zinc Uversol and Zinc Octasol. Of the five peroxides tested, it would seem that tert-butyl perbenzoate is the most easily activated.

A number of modified siloxanes containing organic groups other than the usual methyl groups were obtained and several curing systems were developed in an attempt to cross-link the polymers at the modifying group at room temperature. The modified siloxanes which were used were: Dow Corning A-4000 Adhesive which is possibly a methylhydrogen siloxane containing a small amount of trifunctional material; General Electric Viscasil 30,000, a methyl siloxane fluid having a viscosity of 30,000 centistokes; Linde Silicone Y-1170, a methylhydrogen siloxane fluid having a 15:1 ratio of methyl to hydrogen groups; Linde Silicone Y-1169, a methylhydrogen siloxane fluid having a 50:1 ratio of methyl to hydrogen groups; Dow Corning 410, a methylvinyl siloxane gum containing approximately 4 mole percent of vinyl groups; Linde W-96, a modified siloxane gum, possibly containing a very small amount of olefinic groups;

*Continued*

Connecticut Hard Rubber G-2, a glycerol-stabilized, depolymerized silicone gum; and Cl-Viscasil 30,000, a chlorinated silicone fluid containing 0.5 chlorine atom per silicon atom.

The compounds used as curing agents were: Dow Corning XY-22, one of the catalysts for the A-4000 Adhesive; benzoyl peroxide, a free-radical generating compound, normally used for curing methyl siloxanes; ethylenediamine; methylene-bis(4-phenylisocyanate); tetraisopropyl titanate; dibromobutane; azo-bis(isobutyronitrile); a combination of sulfur, zinc oxide, tetra-methylthiuram disulfide and Accelerator 808, (a butyraldehyde-aniline condensation product), which is normally used for accelerating cures of double bond-containing polymers; and a combination of lead oxide and Accelerator 808, which is usually for accelerating cures of neoprene-type polymers.

At 25°C it was found that tetraisopropyl titanate cured all of the siloxanes tried. Dow Corning XY-22 cured not only the A-4000 Adhesive, but also the Linde methylhydrogen siloxanes, Y-1170 and Y-1169. Ethylenediamine cured chlorinated Viscasil 30,000. Dibromobutane partially cured the A-4000 Adhesive. A disadvantage of both the titanate and diamine cures is that curing activity starts immediately. This, of course, is not desirable, for the polymer sets up before it can be applied to the aluminum or rubber specimen.

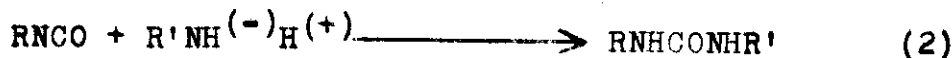
Of interest in this research is the curing activity of tetraisopropyl titanate. The curing action of this compound on various siloxanes is not clear. Possible ways that this curing reaction may take place are: 1) the titanate reacts with the free hydroxyl groups (for example, at the end of each polymer chain) to form supermolecules, 2) the titanate breaks the Si-O bonds, enters into a Meerwein-Ponndorf reaction, rearranges the polymer, and forms a siloxane resin.

One of the original ideas for solving the problem of developing a room-temperature-vulcanizing adhesive was to react a diisocyanate with the hydrogen on a silicone polymer having occasional Si-H groups along the chain. This hydrogen is very reactive, and diisocyanates are known to react with most active hydrogens.

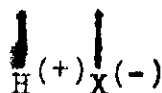
An observation made during this study of modified siloxanes and curing agents was that the diisocyanate compound, methylene-bis(4-phenylisocyanate), did not seem to react with the siloxanes containing the Si-H groups. Some known reactions were studied to determine the theoretical reason why the compounds did not react.

# Contrails

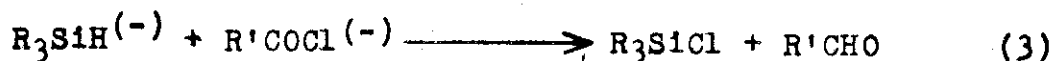
One probability was that the hydrogen in the Si-H group was a negative entity and not at all positive, as required in the isocyanate reaction. For example, reactions of isocyanates with hydroxy and amino compounds, both of which contain positive hydrogens, are well known.



or in more graphic form,  $\text{R} - \text{N} - \text{C} = \text{O}$

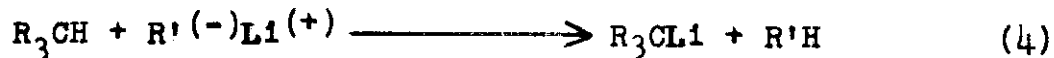


An example of the negativity of the hydrogen in the Si-H group is shown by the following known reaction:



The definitely negative chlorine shifts easily into the silicon compound, manifesting the apparent negativity of that position.

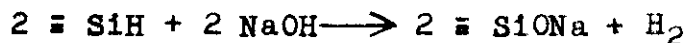
Other examples of known reactions show a difference in the Si-H and the C-H groups:



In Equation No. 4, the positive lithium replaces the hydrogen on the hydrocarbon, while in Equation No. 5, the negative alkyl group replaces the hydrogen in the silicon compound.

The above reactions point to the fact that the hydrogen of the Si-H group is negative. Isocyanate compounds react only with active positive hydrogens, and therefore no reaction takes place between the hydrogen silane and an isocyanate.

It is known that Si-H groups react easily with basic compounds such as sodium hydroxide:



Organometallic salts, normally used as drying agents, are basic compounds. The action on Si-H groups of several of these salts

# Conclusions

was studied. Dow Corning A-4000 Adhesive was selected for use because of the limited amount of Linde Y-1170 available. Fast-curing action was obtained with Lead and Zinc Octasol.

Lead Octasol was then added to several siloxanes to discover whether the silicon-hydrogen bond is the reactive site. The experiment showed that Lead Octasol not only acts as a catalyst for thermosetting, through the OH groups, the resins, DC-2103, CHR-VIII, A-4000, and the polymerizable General Electric fluid SF-69, but also catalyzes the removal of hydrogen from the Si-H groups on A-4000 and Linde Y-1170. Bubbling was noted in the A-4000 and Linde Y-1170, the removal of hydrogen in the form of hydrogen gas indicating that Lead Octasol definitely acted on the Si-H groups. Cross-linking then took place at the site of this cleavage, as evidenced by the full cure of Linde Y-1170 after 24 hours at 25°C.

Another basic compound, a complex of boron trifluoride and piperidine, also cleaved the hydrogen from the Si-H groups of A-4000 Adhesive and Linde Y-1170, resulting in a cross-linked polymer.

These experiments reveal that silicone polymers containing intermittent Si-H groups can be cured at room temperature with several kinds of basic compounds. The introduction of Si-H groups into the silicone polymer is therefore an essential prerequisite for any investigation of adhesive properties.

## Preparation of Other Modified Siloxane Polymers

This research has established the ease of curing at room temperature, compounds containing Si-H groups. A straight-chain fluid (Linde Y-1170) having a 15:1 ratio of methyl to hydrogen groups was obtained from the Linde Air Products Company. Various resins containing Si-H groups, having different R/Si ratios (1.9 to 1.5), were prepared. The method used in polymerizing these resins, that of Welsh and Holdstock (General Electric Company), is described in the section of this report covering the experimental work. Care was taken to keep the reaction flask cool so that the temperature of the reaction would remain close to room temperature to prevent thermal cleavage of the Si-H bond. All of the resins prepared with hydrogenmethyldiethoxysilane as one of the monomers were tested for Si-H groups by adding Lead Octasol and noting whether any evolution of gas occurred. There was gas in every case, indicating that the silane monomer had been incorporated into the polymer without thermal or chemical breakdown of the Si-H groups.

## Testing Materials Developed as Adhesives

Work throughout this project has indicated several possible methods of obtaining an air-curing adhesive for bonding silicone rubber to metal or to itself. The materials obtained by four of these methods have been tested, these being modified Dow Corning A-4000 Adhesive, various compounded silicone rubbers, a compounded silicone fluid containing Si-H groups (Linde Y-1170), and hydrogenmethylphenyl siloxane resins.

It was found that the filler, Asbestine, used to modify the Dow Corning A-4000 Adhesive, reduced peel strength instead of improving it. This was true after 24 hours at room temperature and after 24 hours at 212°F. In both cases, the bonds failed to meet specifications. When the A-4000 Adhesive was cured with the titanate ester, tetraisopropyl titanate, the curing action was too fast. This was also evident when tetraisopropyl titanate was used to cure Silastic 6-128 and a compounded stock (CHR #4734) having as a base General Electric methylphenyl silicone gum, SE 81477. The compound seemed elastomeric enough, but because of the premature "set" of the polymer before application, there was no significant adhesion.

Adhesives having a base of Linde hydrogenmethyl silicone fluid, Y-1170, were compounded, Lead Octasol being used as the curing agent. The adhesives cured well, as was expected. These materials were used in bonding silicone rubber to aluminum and to itself. The adhesion of silicone rubber to aluminum was nil, but adhesion of the silicone rubber to itself was exceptionally promising, bonds up to 18 pounds per inch being obtained after 5 days at room temperature. This development is interesting and should be pursued further.

The last phase of this research involved the evaluation of siloxane resins containing Si-H groups, as air-curing adhesives. The resins had R/Si ratios ranging from 1.9 to 1.5. None of the resins adhered either to aluminum or to silicone rubber. While Lead Octasol cured the resins, the cured products were weak and dry, and, in one case, somewhat brittle. Two explanations for these poor results are possible, one of these being the apparent lack of high-molecular-weight polymer, due mainly to the acidic polymerization. (Basic polymerization was out of the question because of the susceptibility to cleavage of the Si-H bond in the presence of a basic medium). A second reason might be the existence of too many free -OH groups to interfere in the cure, since the curing agent, Lead Octasol, is not selective in its choice of reacting with Si-OH or Si-H groups.

## *Conclusions*

Chlorinated Viscasil 30,000 silicone fluid, cured with a diamine, is another material discovered during the course of this research, which cures at room temperature. This was not investigated as an adhesive, since, like compounds cured with tetraisopropyl titanate, the curing action is so immediate that the adhesive is not too practical for use. However, a siloxane containing fewer chlorine atoms in relation to silicon atoms than the chlorinated siloxane used in this research, and a diamine less reactive than ethylenediamine, may very well be a practical combination.

## LITERATURE SURVEY

A survey of the literature is presented which will provide the reader with enough background information to understand the scope of the contract better.

The purpose of this survey was to conduct a search of trade journals, periodicals, patent literature and chemical journals in an effort to find references to any available materials which might be useful in the development of a method suitable for bonding silicone rubber to metal or to itself at room temperature. There is a great deal of literature on adhesives, and there are numerous methods of classification. In keeping with the aims of this project, the following outline of topics was followed in preparing this survey.

- A. Adhesives which can be cured at room temperature.
- B. Adhesives which bond silicone to metal or to itself.
- C. Primers which aid in the bonding of silicone to metal.
- D. Curing agents and curing mechanisms for silicones.

### A. Adhesives Which Can Be Cured at Room Temperature

A waterproof siloxane cement has been developed by P. J. Chevalier (1) which is said to set at room temperature. No mention is made specifically as to its use with silicone and/or aluminum, but it is said to adhere to the most varied materials. The best cements are those comprised of methylpolysiloxane, a filler and lead acetate--also, lead stearate, lead phenate, lithium stearate, lithium phenate or lithium acetate. The fillers used are lead monoxide, beryllium sulfate, calcium carbonate, silica and asbestos powder. The maximum number of methyl groups per silicon atom in the methylpolysiloxanes is 1.4, and there are only 8-20 silicon atoms per molecule.

Another adhesive which is known to set at room temperature is a mixture of natural rubber (or GR-S), trichlorosilane and benzene, which are reacted to give viscous liquids (2). These fluids set up to clear, tack-free films after standing in air at room temperature for 15 minutes to 1.5 hours. The films adhere strongly to the glass on which they dry.

A method of making siliceous resinous products which harden on standing and are suitable for adhesives is described in a patent by White (3). The products produced by the invention are, in general, prepared from colloidal dispersions of silica in organic solvents, particularly anhydrous solvents of the type which are miscible with water. When these colloidal dispersions of anhydrous organosols are diluted with water, the silica

contained therein is precipitated in a resinous state. The resulting precipitate may be removed from the sol or solution by filtration, washed to remove impurities and then mechanically dried, as by pressing between sheets of absorptive material. The final product which is gummy or plastic in character, but hardens on standing for 8 to 10 hours, may be used to cement surfaces together.

An adhesive, setting at room temperature, suitable for bonding metal to metal, resin to resin, wood to wood, or any combination thereof, may be prepared from glycidyl ethers of polyhydric phenols to which are added fluid control agents and hardening agents (4). Glycidyl ethers of polyhydric phenols are prepared by causing one, two, or more moles of epichlorohydrin to react with one mole of a dihydric phenol in the presence of 1.1 to 1.3 equivalents of base (such as NaOH per mole of epichlorohydrin). Various dihydric phenols are suitable, including mononuclear phenols like resorcinol and polynuclear phenols like bis-phenol. Fluid control agents include polyglycidyl ethers of polyhydric alcohols or other monoepoxy compounds. These polyglycidyl ethers are prepared by causing a suitable polyhydric alcohol or monohydroxy compound to react with epichlorohydrin in the presence of 0.1 to 2.0 percent of acid-forming compounds like  $\text{BF}_3$ . Suitable monoepoxy compounds include 2,3-hexylene oxide, decylene oxide, and, as a preferred group, methyl, allyl and phenyl glycidol ethers. Hardening agents include alkalies, alkali phenoxides, carboxylic acids or anhydrides, metal halides, phosphoric acids and partial esters, but preferably amino compounds like diethylenetriamine and triethylamine.

The addition of an organic diisocyanate to cements prepared from alkylene polysulfide elastomer (compounded or not) imparts adhesive properties which make the products useful for adhering various materials to each other, including rubber, synthetic elastomers and metals (5). Any aliphatic or aromatic diisocyanate is effective, but that recommended most highly is methylene-bis(4-phenylisocyanate). The proportion of diisocyanate depends on the particular derivative, the nature of the adhesive, the material to which it is applied, and the method of application.

The adhesives can be used in a two-step process (a solution of the diisocyanate is applied first), or a cement containing the olefin polysulfide elastomer and diisocyanate can be applied in a single operation. If the diisocyanate is mixed with the cement for the single-step method, the cement must be used promptly because of a tendency to set.



## B. Adhesives Which Bond Silicone to Metal or to Itself

The fundamental inertness of silicone rubber makes special adhesives necessary to bond this material to itself or to other materials (6). Effective silicone bonds and joints can be made with the appropriate commercial products.

General Electric produces a paste, known as SS-64, for bonding silicone to metal, which requires curing at elevated temperatures (7), (8). A versatile silicone paste called SS-15 can be used as a bonding material when applied in conjunction with General Electric Primer SS-67. General Electric SE-76 gum may also be compounded by fabricators to produce a range of materials similar to SS-15. General Electric SE-100, or SE-100S which is a 35 percent solution of SE-100 in xylene, can be used in place of SS-15, with the added advantage that no primer is needed. It will produce a bond equal in strength to that obtained with SS-15 and can be handled in the same manner as that prescribed for SS-15. The bond must be cured at 260°F for 20 minutes.

Dow Corning XC-269 and XC-271 are pressure-sensitive silicone adhesives (9). They require elevated temperatures for curing. Three other materials which are used to bond silicone rubber to other surfaces are silicone rubber compounds themselves. Silastic 6-127 is an orange tan, high-strength silicone rubber that produces a very strong bond between silicone rubber and adjoining surfaces. It has a heavy paste-like consistency. To produce optimum bond strength, it must be freshly milled prior to use. Silastic 6-128 is similar to Silastic 6-127 except that it is translucent. The method of application is the same. Silastic 110 Adhesive is a low-consistency, tacky, white paste which can be applied with a knife or spatula. It does not change consistency or dry out at room temperature.

## C. Primers Which Aid in the Bonding of Silicone to Metal

Normally, it is very difficult to bond silicones because they present a surface of inert methyl groups, closely packed together (8). Primers, though, react chemically when applied to rubber and set up a surface which is more conducive to bonding.

Dow Corning 796 Primer improves the bond obtained between silicone rubber and the metal surface (9). It contains ethyl orthosilicate which requires moist air to effect hydrolysis and give the desired film. It can easily be applied by dipping, spraying or brushing. Hydrolysis can be accelerated through the use of a humidity chamber, provided that the excess moisture is completely removed by heating at about 250°F for several minutes before further steps in the bonding procedure are taken.

If desired, Dow Corning 796 Primer may be diluted with absolute alcohol.

General Electric has developed a primer known as SS-67, which, when used with the cement, SS-15, will bond vulcanized silicone rubber to a variety of materials including aluminum (6), (7). Another General Electric primer is GE-81267 (10). The above primers are applied to the cleaned metal surface by dipping, spraying, etc., and then are allowed to dry for twenty minutes. The rubber is pressed to the surface at 125°F for 10-20 minutes.

Disilanes (e.g., dimethyltetrachlorodisilane) are primers for the adhesion of silicone cements to glass and metal (11), (12). A 1-5 percent solution of disilane in a nonhydrolyzing solvent (i.e., toluene, carbon tetrachloride, etc.) is brushed or sprayed on the surface and is allowed to dry in air. The surface is then washed with water to remove hydrochloric acid from the polymerized film, and is dried again, this time in an oven. The silicone rubber cement or resin is then applied to this surface.

Vinyltrichlorosilane is used as a sizing agent for heat-cleaned glass cloth. It is possible that it can be used as a metal primer in the same manner as the disilanes described above.

Siliceous surfaces become organophilic when treated with organosilicon compounds, usually organosilicon halides (13), (14). General effectiveness of priming treatment is improved if the material is heated after treatment at a temperature below the boiling point or decomposition temperature of the compound employed. The adhesion of organic resins to the organophilic surfaces thus provided is substantially greater than it would be on the original untreated surface.

Well-known methods for treating surfaces to be bonded (not necessarily silicone) are described below.

(a) Natural or synthetic rubber is bonded to metal or glass (15) by applying a primer coat containing a finely divided metal having an average particle size of 2-10 microns, and then applying a second primer coat containing a finely divided metal oxide or other hard material having a particle size of 0.1-15 microns. The primer coats generally also contain a rubber derivative, such as chlorinated rubber. In addition, a step-off cement made of the elastomer to be bonded is usually applied.

# Contrails

(b) Vulcanized rubber is adhered to metal or glass (16) by applying to the rubber surface a layer of chlorinated rubber, coating this layer with a layer of synthetic rubber (e.g., GR-S,) coating the synthetic rubber with another layer of chlorinated rubber, and this multi-coated rubber is pressed into intimate contact with the metal or glass. Heat and pressure are not required. The middle synthetic rubber layer materially aids adhesion.

(c) Natural rubber is prepared for bonding to metals by washing the surface with concentrated sulfuric acid for four minutes and then washing in running water (17). This causes cracks which increase the strength of the bond, and is called "cyclizing."

The preparation of metal surfaces for bonding is extremely important. Contrary to the case of rubber where efforts are made to increase the roughness of the surface, the metal surface is made as smooth as possible for better adhesion. One method which is commonly used is sandblasting with a metal abrasive (18). Dipping in a warm sulfuric-chromic acid bath may also be done (19). Many other chemical means have been used, depending on the particular metal surface and on the type of adhesive employed.

## D. Curing Agents and Curing Mechanisms for Silicones

Silicone resins will air-dry to a tack-free film, but the best properties are obtained after the film has been heat-cured (20). Liquid, soluble polysiloxane resinous compounds may be heat-hardened at lower temperatures and in shorter periods of time by incorporating in the mixture small amounts of catalyst, such as quaternary ammonium bases or their derivatives (21).

The curing process, for example, can be speeded up by the use of driers (acting as catalysts) of the type commonly used with drying oils (20). These include the compounds of lead and cobalt, such as oxides, naphthenates, carbonates, borates and resinates (22). Zinc, calcium and manganese naphthenates and resinates may also be used (23). When a resin containing a metallic salt stands at room temperature for 1-2 days, the resin tends to advance to the insoluble and infusible state. Thus, the shelf-life of such a mixture is only a few hours. Despite the tendency of the resin to gel at room temperature, rather long molding times are required to harden the resin-organometallic salt mixture at high temperature.

# Conclusions

Small amounts of lead tetraphenyl catalyze the cure of heat-hardenable polysiloxane resins. Resins containing this catalyst can be cured to a solid state in a much shorter time and at lower temperatures than uncatalyzed resins (24). The cure time and temperature are even lower than those used for resins containing the metal salts listed above, although at room temperature the lead naphthenate sample gelled much faster than the tetraphenyl sample.

Treatment with alkali of a liquid organopolysiloxane, previously bodied by heating, results in the production of a heat-hardenable resinous polymer. This compound has a shorter life than can be achieved by resinifying the polymer either by heat-bodding alone or by the presence of an alkaline reacting agent throughout the entire bodying process (25).

Silicone rubber is generally vulcanized with some type of peroxide, such as benzoyl peroxide (20). The most satisfactory explanation of the vulcanization reaction is that benzoyl peroxide forms free radicals on being heated and that these intermediate products remove hydrogen from methyl groups of the polymer. These latter groups then become free radicals ( $\text{CH}_2$ ) which react with one another, bringing about cross-linking.

The useful peroxide vulcanizing agents are stable at ordinary temperatures, but at elevated temperatures they decompose and react as described above. Where it is desirable not to use heat in activating the peroxide, it is necessary to find a chemical means of promoting reaction.

Peroxides stable at room temperature include benzoyl peroxide, tert-butyl peroxide, ethyl peroxide, 1-phenylethyl-tert-butyl peroxide, hydrogen peroxide, tert-butyl perbenzoate, p-toluyyl peroxide, o-bromobenzoyl peroxide,  $\alpha$ -thenoylperoxide, o-chlorobenzoyl peroxide, trimolecular acetone peroxide, various other aromatic and acyl peroxides, and aldehydic and acidic superoxides (26).

Disintegration of organic peroxides in solvents can be accelerated by such materials as triphenylmethyl or molecular oxygen, but the extent of decomposition is dependent on the solvent. There is thought to be a reaction of the peroxide with the solvent (27). By the choice of a proper solvent-peroxide combination, it might be possible to effect a room-temperature cure by adding the peroxide to the silicone rubber dispersion shortly before use as a cement.

# Contrails

The decomposition of tertiary butyl peroxide, trimolecular acetone and ethyl peroxide at 80° to 100°C is catalyzed by aniline, amyl nitrile, lead tetraethyl,  $\alpha$ -naphthol,  $\beta$ -naphthol, manganese naphthenate,  $\alpha$ -naphthyl amine, phenyl-p-aminophenol, phenyl-p-naphthylamine, hydroquinone, and triphenyl thiophosphite (28). Antiknock compound (lead tetraethyl and aniline) increases the reactivity of ethyl peroxide and benzoyl peroxide from two to ten times. Benzaldehyde also increases the activity coefficient of benzoyl peroxide severalfold (29). A solution of 1-phenyl-ethyl-tert-butyl peroxide in 0.4 mole of piperidine gives 100 percent decomposition in 80 hours (30).

In sufficiently polar media, decomposition of peroxide is effected by an ionic mechanism. For example, manganese dioxide when activated by the addition of electrolytes will catalyze decomposition with or without platinum black (31). Hydrogen peroxide decomposition is catalyzed by chromic acid and dichromates in various solvents (32). Metal salts and oxides also have a catalytic effect. Heavy metal salts react with hydrogen peroxide to form unstable peroxides. Catalysis by means of salts and oxides of such metals as Cu, Fe, Pb, Hg, Co, Ni and Mn is restricted by increasing the hydrogen ion concentration (33), (34). Cupric hydroxide has a catalytic action on both hydrogen peroxide and peracetic acid in alkaline solution (35). This suggests the possibility of a room-temperature cure by adding a base to an adhesive containing a peroxide and a heavy metal salt or oxide in acid media. The base not only would neutralize the acid, allowing the catalyst to be activated, but might also liberate heat which would, in itself, help effect a cure.

Stabilizers of metal peroxides are magnesium, cobalt, and stannous or stannic compounds such as phosphates (34). For example, magnesium hydroxide will remove copper from solution, thus stabilizing an alkaline solution of hydrogen peroxide. Organic stabilizers include alcohols, ketones, urethanes, silicates, etc. (33). If one of these compounds were present in an otherwise very active adhesive mixture, the peroxide could be activated by removing the stabilizer chemically.

Cold rubber (such as GR-S cold rubber) is polymerized at low temperatures (-10° to 50°C) by means of a combination of peroxide-type catalyst plus a reducing agent. An analogous catalyst system perhaps may be applied to the room-temperature vulcanization of a silicone adhesive. A typical combination for this redox system is ferrous ion-peroxide (or hydroperoxide). In more complicated systems, the reducing agent (or activator) is employed in conjunction with another reducing compound (co-

## Contrails

activator), such as a sugar, as well as the peroxide catalyst. Under ideal conditions, the activator, having been converted to its oxidized state by reaction with peroxide, is continuously converted back to its reduced state by the co-activator, which, by the nature of its chemical structure, cannot interact with the peroxide catalyst.

The best co-activators for this peroxide-ion system are polyhydroxy ketones (sugars, such as inose, sorbose and fructose) (36). Polyhydroxy aldehydes, glycerol and ascorbic acid give lower conversions, while polymeric polyhydroxy compositions are of no value. Caprylyl peroxide, lauroyl peroxide and cumene hydroperoxide can be used without iron (37). Aliphatic, acetyl and succinic peroxides are not effective in metal-free systems.

Polyamines are effective activators, but the effectiveness of polyamines reaches a maximum in tetraethylenepentamine and gradually decreases in higher homologs (38).

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List of Commercial Adhesive Suppliers

<u>Adhesive</u>	<u>Supplier</u>
Epon VI	Shell Chemical Company 500 Fifth Avenue New York 36, New York
Bond Master M654	Rubber and Asbestos Corporation 225 Belleville Avenue Bloomfield, New Jersey
DuPont 4678 Cement	E. I. DuPont de Nemours & Company, Inc. Wilmington, Delaware
Thiokol T-120-1	Thiokol Chemical Corporation Trenton 7, New Jersey
Dow Corning A-4000	Dow Corning Corporation Midland, Michigan

Aluminum

Due to the fact that a slow delivery (6 weeks or more) of Alclad 24S-T86 would greatly delay the room-temperature-adhesive project (AF 33(616)-2542), Lt. Kelble of Wright Field was contacted by telephone on June 16, 1954 to obtain permission to change the specification to Alclad 24S-T3. The difference in the two materials is only a slight variation in the tempering method. Lt. Kelble told Dr. F. L. Kilbourne, Jr., that it would be permissible to proceed with Alclad 24S-T3.

## Preparation of Chlorinated Silicone Fluid

Four hundred grams of General Electric Viscasil 30,000 silicone fluid were dissolved in four hundred grams of carbon tetrachloride (50 percent solution) in a one-liter flask, equipped with a high-speed glass agitator. A short length of perforated Kel-F tubing, curved below the agitator, was used for the dispersion of gas into the solution. The outlet tube was placed just beneath the surface of a water bath. Cooling was accomplished by streaming water over the outer surface of the flask.

The reaction was carried out in the presence of ultraviolet light. The solution of silicone gum was thoroughly flushed with nitrogen for four hours, to remove dissolved oxygen. The ultraviolet lamp was turned on, and the chlorination was immediately initiated by passing through the solution approximately equal parts by volume of nitrogen and chlorine. The temperature rose fairly rapidly to 50°-55°C and deviated little throughout the remainder of the reaction period.

The progress of the reaction was followed by means of rapid determinations of the density of the gum. A small sample of the solution was removed from the reaction flask, dried rapidly over a boiling isopropanol bath, sprinkled with talc, rolled into a ball between the fingers, and floated in carbon tetrachloride, toluene being added until the ball was just suspended in the mixture. The density of the carbon tetrachloride-toluene mixture was measured, with a hydrometer. This value indicates the density of the gum sample. Figure 3 shows the relationship of chlorine content to gum density as determined by this method.<sup>1</sup>

At the end of four hours, the density of the gum was 1.12 which corresponds to a Cl/Si ratio of approximately 0.50. The reaction was stopped by turning off the ultraviolet lamp and immediately shutting off the flow of chlorine. Nitrogen was passed through the solution for four additional hours. The solvent was removed from the product by evaporation under forced, filtered air. The material was then ready for testing.

Note 1: This relationship was determined earlier in this laboratory under Navy Contract NOas 51-766c, Bureau of Aeronautics.

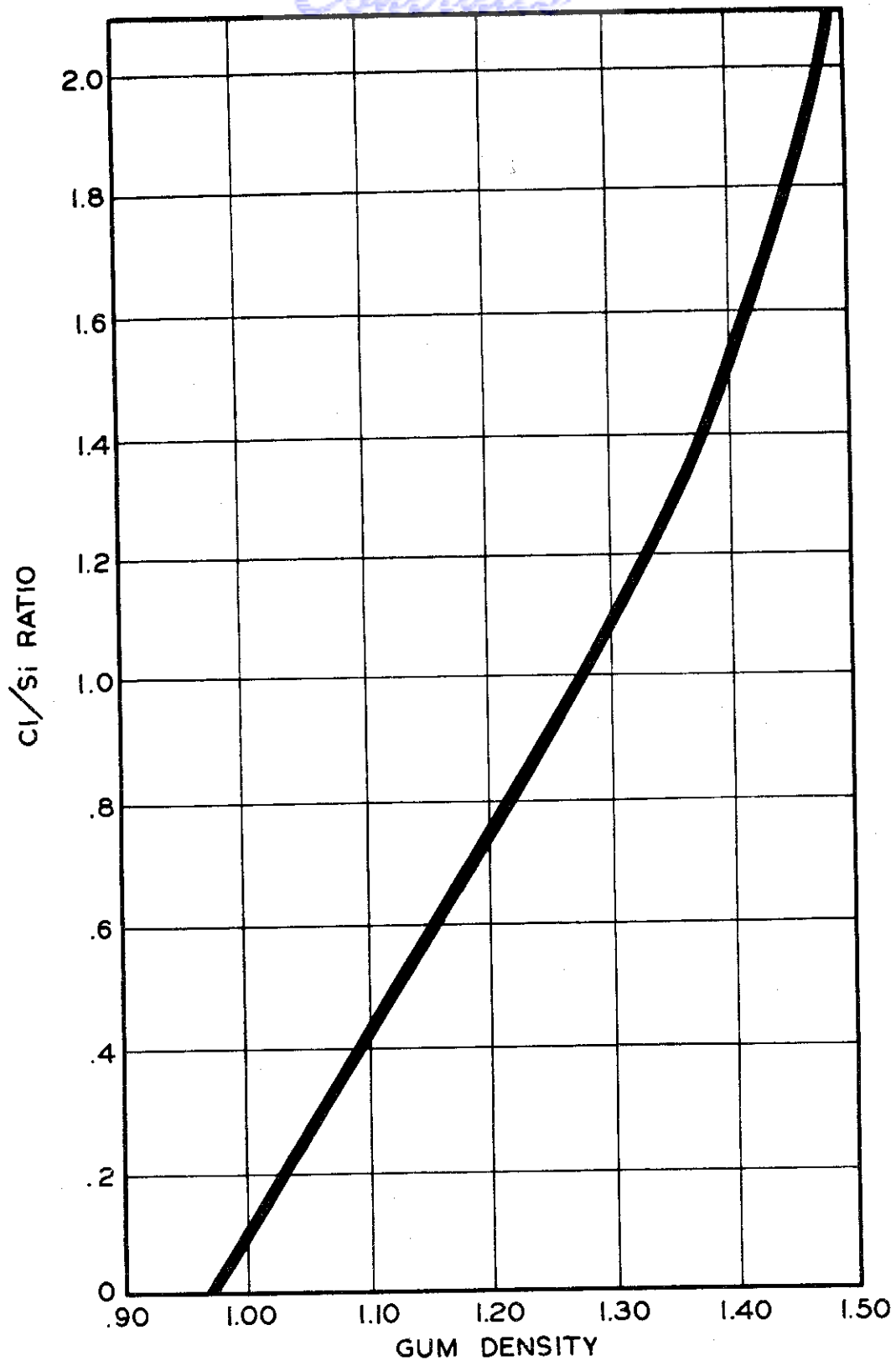


FIG. 3 - THE RELATIONSHIP OF CHLORINE CONTENT TO GUM DENSITY IN CHLORINATED SILICONE RUBBER.