NRL REPORT 3994

PREPARATION OF SILICONE COMPOUNDS FOR USE IN HIGH-TEMPERATURE ORGANIC FINISHES-II

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ABSTRACT

The investigation of silicone polymer systems for use in high-temperature resistant coatings has been extended. The effect of meta- and para-fluorophenyl and of meta-trifluoromethylphenyl groups on silicone resins containing them has been determined. These single substituents failed to improve the heat resistance of the resins. Silicones prepared directly from Grignard reaction mixtures were shown to be inferior to those prepared from pure chlorosilanes at the same charge ratios. A silicone resin prepared by a process developed under contract to the U. S. Army Signal Corps was equivalent in heat resistance to commercially available silicone protective coating resins.

The results have been discussed in the light of currently accepted theories of silicone resin preparation and performance, and recommendations made accordingly.

PROBLEM STATUS

This is a final report; no further work on this problem is contemplated and the problem may be considered closed.

AUTHORIZATION

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PREPARATION OF SILICONE COMPOUNDS FOR USE IN HIGH-TEMPERATURE ORGANIC FINISHES - II*

INTRODUCTION

Designers of equipment for use under conditions of relatively high temperatures have long been handicapped because of a lack of suitable surface coatings, that is, easily applicable, adherent, resinous materials which do not undergo detrimental chemical or physical changes in the environment involved. Such coatings must prevent chemical or physical deterioration of the substrate which often functions structurally in service equipment such as high-speed aircraft, guided missiles, projectiles, and numerous electrical devices. The substrate is usually metallic, but in some instances surfaces of glass, plastic, fiber, graphite, rubber, or other material need high-temperature protection.

As has been pointed out previously (1), some of the properties of the ideal finish may be compromised depending on the end use; thus a single criteria—heat stability—is the most important in evaluation of these surface coatings. Were an organic resinous material of sufficiently good heat stability available it would probably be suitable for one of the substances or uses mentioned. Accordingly, this project has been concerned with attempts to synthesize resins possessing heat stability to a greater degree than do commercially available products.

Modifications of silicone resins were sought which might be expected to possess the desired increased heat stability. This course of action is justified by the traditional function of this activity as an organic coatings development group, and by the limited applicability of ceramics, metallic frits, electrolytic deposits, and other possible methods of attaining the desired protection.

The current work, and that previously described (1), comprise syntheses of silicone polymers and their evaluation as clear, unpigmented coating materials.

BACKGROUND ON SILICONES

The silicones are compounds of silicon, oxygen, and organic radicals in which the silicon atoms are joined into chains, rings, or net structures by oxygen bridges, and some or all of the remaining silicon valences are satisfied by organic radicals in which a carbon atom is linked to silicon. The silicon valences which are not satisfied by bridge oxygen or by organic radical (the so-called end groups or hindered positions in polymers) may be satisfied by chlorine, hydroxyl, or alkoxy groups. A hypothetical compound illustrating these structures is reproduced on page 2.

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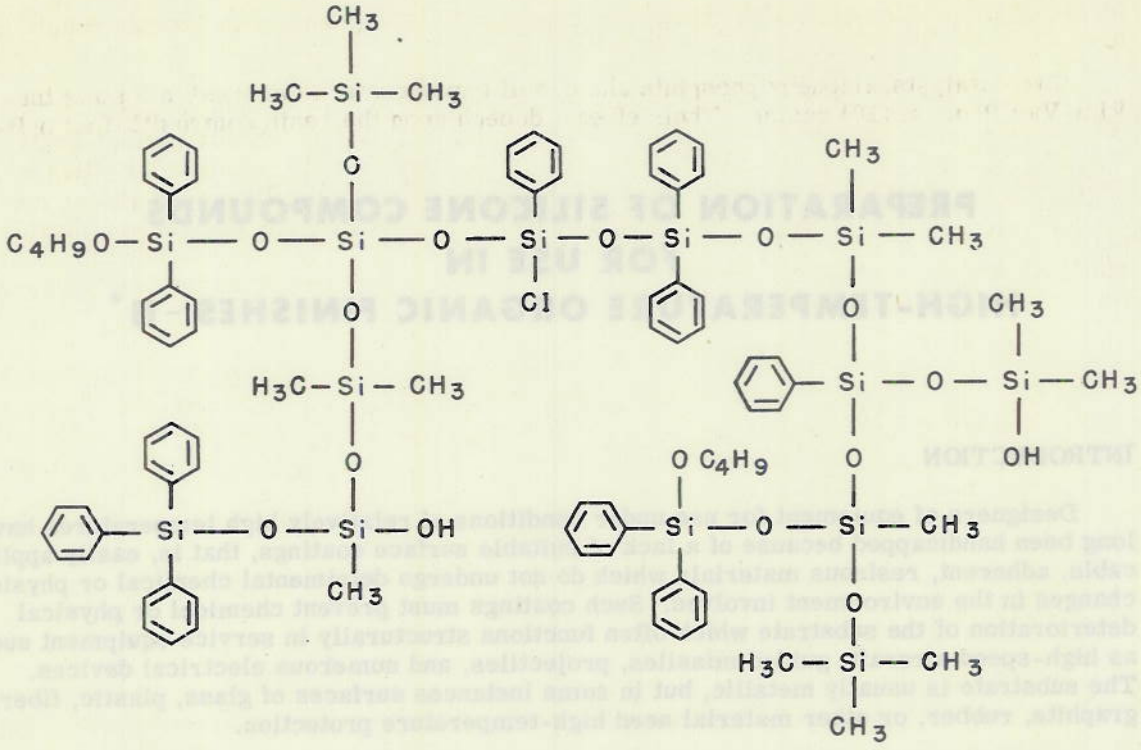
* The first report in this series was published as NRL Report 3870. See Reference (1).



An examination of the structure reveals an additional manner of chain termination, the triradical substituted silicon atom. The chemistry of the silicones has been discussed in several excellent texts (2,3), and has been summarized in sufficient scope by Weaver (1). Only a very brief review suffices for this report.

Silicone resins are produced by the controlled hydrolysis of organochlorosilanes (e.g., CH_3SiCl_3, $(CH_3)_2SiCl_2$, $(C_6H_5)_2SiCl_2$, and many others) followed by condensation, either spontaneous or induced, of the low molecular weight silicones thus formed. The properties obtainable range from low freezing point oils through viscous oils and thermoplastic solids, to cross-linked infusible resins. This wide range of properties is made possible because of the different functionalities (up to 4 in $SiCl_4$) of the organochlorosilanes which may be used.

The properties of aryl silicones are such that they are unsuited for use in surface coatings. The polymers are weak and brittle at ordinary temperatures. Chlorination of the aromatic nucleus is reported to improve the heat stability of the aryl silicones, but the other physical properties are not improved. In particular the following sentence is pertinent, "The fluorophenyl silicones are particularly interesting as stable flameproof resins for service at elevated temperatures" (4).

The properties of methyl silicone resins vary depending upon the composition and method of preparation, but they are not as heat resistant as the aryl silicones. Under the influence of temperatures ranging from 350°C (662° F) to 450° C (842° F), the methyl silicones depolymerize to yield volatile compounds of simpler structure which distil out of the resin (5).

Aryl-alkyl silicone copolymers have been found to possess properties intermediate between those of the aryl silicones and the alkyl silicones, and, in fact, some have mechanical strength and toughness exceeding those of the pure types. "Methyl phenyl silicone—develops a good balance of flexibility, strength, and infusibility when the molar proportions of methyl and phenyl groups are almost equal and the total (R + Ar)/Si) ratio is about 1.8. Compositions

higher in proportion of methyl groups are preferred to those higher in phenyl groups, in order to avoid brittleness" (6).

Silicone resins and their copolymers with alkyd, phenol-formaldehyde, urea-formaldehyde, or other organic resins have been studied extensively for surface coating use. "It may be assumed (without much justification) that the commercial silicone resins now being used in enamels are methyl and methyl phenyl silicones of rather low R/Si ratio" (7). Lead oxide, and organic compounds of iron, cobalt, manganese, nickel, and zinc have been used as curing catalysts. An alkyd primer is recommended for best adhesion of silicone resins to metals. Aluminum powder is considered the best pigment for heat-resistant silicone paints (7).

In view of the properties expected from silicone resins as set forth in the preceding paragraphs the present problem is concerned with the preparation and evaluation of some silicone resins containing fluorine. Weaver (1) made several attempts to synthesize trifluoromethylchlorosilanes by the following method.

$$CF_3Cl \xrightarrow[320 \pm 20^\circ C]{Si\text{--}Cu} (CF_3)_n SiCl_{(4-n)}$$

This approach was not successful.

In December 1950, Haszeldine reported the preparation of a Grignard reagent from trifluoromethyliodide (8) and, in September 1951, released some important details of the process (9):

1. Extremely anhydrous conditions.
2. Very low temperature at start.
3. Spectroscopically pure magnesium necessary.

At the same time, Haszeldine reported the isolation of ditrifluoromethyldichlorosilane according to the reaction:

$$2CF_3MgI + SiCl_4 \longrightarrow (CF_3)_2SiCl_2 + \text{others.}$$

The mono- and trifunctional compounds had not been positively identified at the time of this revelation. Surprisingly, simple hydrolysis of these substances failed to produce resinous materials. For this reason and because of the preparational difficulties, NRL has made no further attempts to produce trifluoromethylchlorosilanes.

The Vita-Var Corporation (10) under contract to the U. S. Army Signal Corps developed a silicone resin for use in impregnating transformer coils. Included were specific directions for hydrolysis which are reproduced in the experimental section of this report. The resins were said to have excellent heat-resistant properties at 260° C (500° F), and accordingly several equivalent preparations have been made. The Vita-Var report also introduced the compound triphenylphosphite as a curing catalyst for silicone resins. The catalyst was found to improve the heat-stability of the resins.

EXPERIMENTAL PROCEDURE

Preparation of Chlorosilanes

A. Intermediates

The preparation of p-fluorobromobenzene, m-fluorobromobenzene, and m-trifluoromethylbromobenzene has been reported by Weaver (1). Additional quantities of m-fluorobromobenzene were required for this work.

The reaction sequence was exactly similar to that previously described (1):

1. Bromination of nitrobenzene to yield m-bromonitrobenzene.
2. Reduction of m-bromonitrobenzene to yield m-bromoaniline.
3. Diazotization of m-bromoaniline in the presence of fluoboric acid to yield m-bromophenyldiazoniumfluoborate.
4. Pyrolysis of m-bromophenyldiazoniumfluoborate to yield m-fluorobromobenzene.

The first two steps were carried out precisely as before, but several modifications were made in steps 3 and 4. The detailed procedures, therefore, are described in the following paragraphs.

m-bromophenyldiazoniumborofluoborate — Eighty-four grams (0.50 mole) of m-bromoaniline was dissolved in 200 ml of 45% HBF_4 solution in a 1500-ml beaker. A slush of the amine-fluoborate salt resulted. The mixture was cooled to 0 °C; then 200 gm of crushed ice was added and stirred in. The temperature fell to -7°C. The beaker was placed in an ice-water bath and addition of a cooled (0°C) solution of 35 gm (0.50 mole) of sodium nitrite in 70 ml of water was started immediately. Vigorous stirring of the reaction mixture was required since the mass was extremely pasty, especially in the initial stages of the reaction. The addition required 15-20 minutes. The temperature was not allowed to exceed +5°C. The reaction mixture was then allowed to stand in the cold bath for 0.5 hour with occasional stirring. The product was collected on sintered glass and drained by suction. The tan solid was washed successively with two 100-ml portions of cold 10% HBF_4 solution, two 75-ml portions of cold methanol, and finally four 100-ml portions of cold ether. The product, after drying in a desiccator over concentrated H_2SO_4, was a pure white powder. The yield of 204-210 gm was slightly lower than that obtained by Weaver (1), but the purity of the product was superior.

m-fluorobromobenzene — Two hundred grams of the pure, dry diazonium salt was suspended in 400 ml of light petrolatum in a one-liter, three-necked flask equipped with agitator, thermometer, and an efficient reflux condenser. The top of the condenser was joined via a glass tube to a water trap in a hood. The flask was heated by a Glas-Col hemisperical mantle controlled by a Variac, set initially at 50 volts. When the temperature of the reaction mixture reached 113°C, the voltage was reduced to zero. Decomposition began and the internal temperature rose to 118°-120°C. When the temperature had fallen to 115°C, the heating was continued, and the voltage was increased gradually until the temperature reached 180°C.

The mixture was allowed to cool to 90°C before addition of 200 ml of water. The aqueous suspension was then poured into a two-liter flask arranged for steam distillation. About 1500 ml of distillate were collected, and the organic layer was taken up in ether. The ether solution was washed with two 100-ml portions of 5% NaOH solution and three 100-ml portions of water, then dried by anhydrous $MgSO_4$, filtered, and heated on the steam bath to evaporate most of the ether.

The residual solutions from seven batches were mixed and distilled. A 72% yield of m-fluorobromobenzene, bp 144°-146°C, was obtained.

B. Grignard Reagents

The usual techniques were employed in preparing Grignard reagents from m-fluorobromobenzene, p-fluorobromobenzene, m-trifluoromethylbromobenzene, and bromobenzene.

The halogen compounds were added dropwise to a stirred mixture of magnesium and ether. Reflux temperature was maintained and external cooling was used to allow a reasonably rapid addition rate. Iodine catalysis was required to initiate the reactions. The reagents were prepared, transferred, and stored under nitrogen.

C. Fluoroarylchlorosilanes

The Grignard reagents were reacted with silicon tetrachloride to yield mixtures of fluoroarylchlorosilanes from which several individual compounds were isolated by fractional distillation. The boiling ranges are listed in Table 1.

TABLE 1
Boiling Ranges of Fluoroarylchlorosilanes

Compound	bp (°C)	Pressure (mm)
p-fluorophenyltrichlorosilane	62-74	0.5
di-p-fluorophenyldichlorosilane	100-105	0.7
m-fluorophenyltrichlorosilane	100-103	38
di-m-fluorophenyldichlorosilane	131-133	2.8
tri-m-fluorophenylchlorosilane	188-190	2.6
m-trifluoromethylphenyltrichlorosilane	74-82	2-3
di-m-trifluoromethylphenyldichlorosilane	148-152	3
tri-m-trifluoromethylphenylchlorosilane	175-179	2.9

p-fluorophenylchlorosilanes — The Grignard reagent from 51.0 gm (2.1 moles) of magnesium and 368 gm (2.1 moles) of p-fluorobromobenzene, in 900 ml of dry ether, was dropped into 172 gm (1.0 mole) of silicon tetrachloride and 500 ml of dry ether in a three-liter flask equipped with agitator, reflux condenser, and dropping funnel. The rate of addition was sufficient to maintain gentle reflux. Three hours were required for addition and the mixture was stirred under reflux for another three hours.

The mixture was allowed to settle overnight; then the supernatant fluid was poured into another flask for distillation. The residual salts were washed with three 200-ml portions of ether which were added to the distilling flask. The ether was distilled off at atmospheric pressure. When the volume was reduced to about 1/3 the original, the settling, decantation, and salt washing procedure were repeated. The ether solution was distilled at atmospheric pressure and finally at 20 mm until all the ether and unreacted silicon tetrachloride were removed.

The remainder was distilled at lower pressures through a simple Claisen distilling head. Two fractions were collected:

52°-66°C at 0.3 mm—45.6 gm
103°-120°C at 0.6 mm—129 gm

The residue was 66 gm.

The corresponding fractions from several runs were combined and redistilled. The p-fluorophenyltrichlorosilane was collected at 62°-74°C at 0.5 mm, the di-p-fluorophenyldichlorosilane at 100°-105°C at 0.7 mm. No purity check was made on these substances, but they are believed to be as pure as the technical grade organochlorosilanes which have been used in all the resin syntheses herein described.

m-fluorophenylchlorosilanes — The Grignard reagent from 47.0 gm (1.96 moles) of magnesium and 330 gm (1.875 moles) of m-fluorobromobenzene in 900 ml of dry ether was added slowly to 241 gm (1.4 moles) of silicone tetrachloride and 500 ml of dry ether, maintained at 5°-10°C. The mixture was allowed to warm to room temperature and settle overnight.

The decantation and washing procedure used was similar to that described for the synthesis of the p-fluorophenylchlorosilanes. The distillation procedures were carried out after mixing the ether solutions from two batches. Final distillation was made through a 30 inch glass-helix-packed, jacketed column with a total reflux partial takeoff head. After careful removal of low boilers, the following fractions were collected at 3 mm pressure:

40°-60°C	24 gm
60°-70°C	161 gm
70°-130°C	35 gm
130°-150°C	254 gm

No attempt was made to recover higher boiling products. The second and fourth fractions were used directly as m-fluorophenyltrichlorosilane and di-m-fluorophenyldichlorosilane, respectively.

From previous runs the boiling points obtained for doubly fractionated m-fluorophenylchlorosilanes were:

m-fluorophenyltrichlorosilane	100°-103°C at 38 mm
di-m-fluorophenyldichlorosilane	131°-133°C at 2.8 mm
tri-m-fluorophenylchlorosilane	188°-190°C at 2.6 mm

m-trifluoromethylphenylchlorosilanes — The Grignard reagent from 24.3 gm (1.00 mole) of magnesium and 225 gm (1.00 mole) of m-trifluoromethylbromobenzene in 900 ml of dry ether was dropped into 344 gm (2.00 moles) of silicon tetrachloride cooled at -20°C. The addition required one hour. The mixture was allowed to warm slowly to room temperature and settle overnight. The decantation, washing, and concentration steps were carried out as previously described and the initial distillation through a simple Claisen head yielded:

RT to 90°C at 45 mm	25 gm
90° to 124°C at 45 mm	68 gm
121° to 141°C at 25 mm	53 gm

The residue was 30 gm.

In another preparation only 172 gm (1.00 mole) of silicon tetrachloride was used. The fractions of product collected were:

RT to 90°C at 45 mm	17 gm
90° to 115°C at 45 mm	33 gm
70° to 149°C at 3.0 mm	71 gm

The residue was 43 gm.

The separation seemed rather poor; so the second and third fractions from each of the runs were all combined and distilled through the column described in the preceding section. Mechanical difficulties plagued the entire operation, but the following separation was achieved:

RT to 67° C at 3.5 mm
68° to 80° C at 3.5 - 6 mm - - - 76.2 gm
125° to 135° C at 2.5 - 4.0 mm - - 73 gm
175° to 179° C at 2.9 mm - - - - - 19 gm

The first fraction above was combined with the first fractions from the initial distillations and the mixture distilled through the column at 38 mm. The fraction collected at 88° - 98°C was added to the second fraction (bp 68° -80° C at 3.5-6 mm) of the first distillation through the column. These combined fractions were then distilled through the column. The m-trifluoromethylphenyltrichlorosilane distilled at 74° -82° C at 2-3 mm. To the residue form this fractionation was added the third fraction (bp 125° -135° C at 2.5-4 mm) of the first distillation through the column, and the di-m-trifluoromethylphenyldichlorosilane was collected at 148° -152 °C at 3 mm.

Synthesis of Silicone Resins

Grignard Method — A Grignard reagent was prepared from an aryl halide and added to appropriate mixtures of silicone tetrachloride and methyl trichlorosilane. The resulting mixed aryl-alkylchlorosilanes were hydrolyzed by pouring the reaction mixture onto an excess of chipped ice. The ether layer was separated, washed free of acid, dried over magnesium sulfate, then warmed on the steam bath until most of the ether had distilled off. Further condensation was effected simply by heating on the steam bath, heating in an oil bath with catalysts, or by heating with catalysts and passing a stream of air through.

The resins prepared in this manner are listed in Table 2.

Direct Method — Alkyl and arylchlorosilanes, obtained by purchase or synthesis, were dissolved in ether and the resulting solution poured onto ice. The resins were worked up as described in the preceding paragraphs.

These silicones are described in Table 3.

The Vita-Var Process (10) — The Vita-Var corporation, under an army contract, developed a silicone resin, which was reported to have a film life in excess of 500 hours at 260° C (500° F). Explicit directions were given for all stages of the preparation.

1. The organochlorosilanes,

   CH_3SiCl_3 0.16 mole

   $(CH_3)_2 SiCl_2$ 0.41 mole

   $C_6H_5SiCl_3$ 0.24 mole

   $(C_6H_5)_3SiCl_2$ 0.21 mole

were dissolved in twice the volume of dry toluene.

2. A mixture of three parts toluene to one of water was used as the hydrolyzing solution. Four times the theoretical quantity of water required to hydrolyze all the Si—Cl bonds was used.

TABLE 2
Charge Composition of Silicones — Grignard Method

No.	Moles C_6H_5Br	Moles CH_3SiCl_3	Moles $SiCl_4$	$\frac{R + Ar}{Si}$	$\frac{Ar}{R}$	Condensation	Solvent	Remarks
S-3	0.50	0.167	0.167	2.0	3.0	4 hrs on steam bath	Methyl Cellosolve	Charge equivalent to No. 220 (1)
S-4	0.50	0.20	0.20	1.75	2.5	4 hrs on steam bath	Methyl Cellosolve	Charge equivalent to No. 195 (1)
S-5[a]	0.45	0.50	- --	1.95	1.05	4 hrs on steam bath	None	Charge equivalent to No. 210 (1)
S-6	0.525[b]	0.50	0.025[b]	1.95	1.05	8 hrs on steam bath	None	Charge equivalent to No. 210 (1)
S-7	0.50	0.40	- --	2.25	1.25	(A) 12 hrs on steam bath (B) - (A) + 12 hrs at 125°C with air bubbled through + 6 hrs at 160°-70°C	None Xylene	Charge equivalent to No. 210 (1)
S-8	0.80	- --	0.40	2.0	- --	3 hrs at 180°C with $FeCl_3$ catalyst	Xylene	Charge equivalent to No. 197 (1)
S-9	0.80	- --	0.40	2.0	- --	4 hrs at 180°C	Methyl n-amyl ketone	Charge equivalent to No. 197 (1)
S-22	0.50	0.55	- --	1.91	0.91	2 hrs at 180°C with $FeCl_3$ catalyst	Methyl n-amyl ketone	Considerable gel formed and was filtered off
S-23	0.50	0.45	- --	2.11	1.11	2 hrs at 150°C + 3 hrs at 150°C with $FeCl_3$ catalyst	None	
S-24	0.50	0.52	- --	1.97	0.97	3 hrs at 180°C	Methyl n-amyl ketone	
S-25	0.80	0.40	- --	2.0	- --	4 hrs on steam bath	None	Considerable solid filtered off

[a] 0.025 mole of $(C_6H_5)_3SiCl$ was added after completion of the Grignard reaction and before hydrolysis.

[b] The Grignard reagent from 0.075 mole of C_6H_5Br was reacted with 0.025 mole of $SiCl_4$, the CH_3SiCl_3 was added, and then the Grignard reagent from 0.45 mole of C_6H_5Br.

TABLE 3
Charge Composition of Silicones — Direct Method

No.	CH_3SiCl_3	$(CH_3)_2SiCl_2$	$C_6H_5SiCl_3$	$(C_6H_5)_2SiCl_2$	$(C_6H_5)_3SiCl$	$(CH_3)_3SiCl$	$\frac{R+Ar}{Si}$	$\frac{Ar}{R}$	Condensation	Solvent	Remarks
S-26	---	1.0	0.20	0.80	0.10	- ---	1.95	1.05	4 hrs on steam bath	None	Charge exactly similar to No. 210 (1)
S-27	---	0.167	0.033 p-fluoro	0.133 p-fluoro	0.017	- ---	1.95	1.05	4 hrs on steam bath	Xylene	Charge equivalent to No. 210 (1)
S-29	---	0.10	0.10 p-fluoro	0.20 p-fluoro	- ---	- ---	1.75	2.5	2 hrs at 150°C	Methyl n-amyl ketone	Charge equivalent to No. 195 (1)
S-37	---	- --	- ---	0.20 p-fluoro	- ---	- ---	2.00	- ---	2 hrs at 180°C catalyzed by $FeCl_3$	Methyl n-amyl ketone	Charge equivalent to No. 197 (1)
S-38	---	0.1	- ---	0.20 p-fluoro	0.033	0.067	2.25	1.25	8 hrs on steam bath + 1 hr at 190°C	Methyl n-amyl ketone	Charge equivalent to No. 217 (1)
S-39	---	0.083	- ---	0.25 p-fluoro	- ---	- ---	2.00	3.0	1 hr at 200°C	Methyl Cellosolve	Charge equivalent to No. 220 (1)
S-45	---	0.475	0.20	0.325	- ---	- ---	1.8	0.895	Reflux in toluene until all H_2O is removed	Toluene	Product half solid half liquid before reflux with toluene
S-46	0.2	0.375	- ---	0.425	- ---	- ---	1.8	0.895	Reflux in toluene until all H_2O is removed	Toluene	Product insoluble in ether before reflux with toluene
S-48	---	0.475	0.20 p-fluoro	0.325 p-fluoro	- ---	- ---	1.8	0.895	Reflux in toluene until all H_2O is removed	Toluene	Product ether soluble before reflux with toluene
S-64	---	0.475	0.20 m-fluoro	0.325 m-fluoro	- ---	- ---	1.8	0.895	Reflux in toluene until all H_2O is removed	Toluene	Product ether soluble before reflux with toluene
S-65	---	0.475	0.20 m-trifluoro methyl	0.325 m-trifluoro methyl	- ---	- ---	1.8	0.895	Reflux in toluene until all H_2O is removed	Toluene	Product ether soluble before reflux with toluene

3. The organochlorosilane solution was added to the vigorously stirred hydrolysis mixture maintained at 40° -70° C.

4. After addition the mixture was stirred and held at 80°-95° C for 30-150 minutes (usually 60).

5. The toluene layer was separated and washed to remove acid, then dried either azeotropically or by use of solid disiccants.

6. The toluene was removed by distilling at reduced pressure.

7. Resin viscosity was adjusted with toluene.

The preparations made by this procedure are listed in Table 4.

TABLE 4
Charge Composition of Silicones — Vita-Var Process

No.	CH_3SiCl_3	$(CH_3)_2SiCl_2$	$C_6H_5SiCl_3$	$(C_6H_5)_2SiCl_2$	$\frac{R + Ar}{Si}$	$\frac{Ar}{R}$	Remarks
S-90	0.16	0.41	0.24	0.21	1.61	0.675	
S-110	0.16	0.41	0.24 m-trifluoro-methyl	0.21 m-trifluoro-methyl	1.61	0.675	84.1% solids
S-111	0.16	0.41	0.24	0.21	1.61	0.675	72.4% solids
S-112	0.16	0.41	0.24 p-fluoro	0.21 p-fluoro	1.61	0.675	81.6% solids
S-147	0.16	0.41	0.24 m-fluoro	0.21 p-fluoro	1.61	0.675	81.4% solids

In the preparations there was a difficulty caused by emulsification during the neutralization and washing procedure, although the report claims easy separation in these operations.

Modification of Silicone Resins — Many of the silicone resins reported here and by Weaver (1) were poor resins for use in surface coatings. Most of these seemed to be either very difficult or impossible to cure. A few attempts were made to modify the resin properties.

For example, S-7 (A) and S-7 (B) (see Table 2) were mixed and heated with $FeCl_3$ for 6 hours at 140° C and 6 hours at 180° C, dissolved in xylene and methyl n-amyl ketone, and the former solvent distilled out. The resulting resin was labelled S-10.

Modifications of a series of direct method resins (see Table 3) are recorded in Table 5.

TABLE 5
Modifications of Silicone Resins

No.	Original No.	Wt. Resin (gm)	ml Conc. H_2SO_4	ml H_2O	Reflux Time
S-45-T	S-45	192	6	150	1 hour
S-46-T	S-46	152	5	125	1 hour
S-48-T	S-48	171	5	150	1 hour
S-64-T	S-64	93.5	3	75	3 hours
S-65-T	S-65	51.0	2	50	3 hours

After refluxing the resins were separated, neutralized, washed, and dried.

Evaluation of Silicone Resins

Screening Tests on Weaver's Resins (1) — The resins were poured onto 2- x 6-inch anodized aluminum panels, air dried several hours, then placed into a muffle furnace held at 371°C (700°F) for 16 hours. After this time the furance door was opened, the heat shut off, and the panels allowed to cool in the open furnace. When cool, the panels were examined and the relative integrity and appearance of the remaining coating was estimated.

During the heating period large quantities of dense white vapors were seen to issue from the muffle furnace. This phenomenon has been observed in all the heat tests conducted on silicone resins in this Laboratory.

Five resins were selected for further study on the basis of their heat resistance in this test. Their compositions are listed in Table 6, and in the column marked "Remarks" the results of some baking tests are included.

TABLE 6
Charge Composition of Selected Silicones (1)

No.	$\frac{R + Ar}{Si}$	$\frac{Ar}{R}$	Remarks
195	1.75	2.5	1 hour at 190°C - soft, brittle, nontacky
197	2.00	- -	1 hour at 190°C - soft, very brittle, nontacky
210	1.95	1.05	16 hours at 190°C - liquid
217	2.25	1.25	16 hours at 190°C - tacky
220	2.00	3.0	16 hours at 190°C - tacky

Screening Test on Grignard Method Silicones — The silicones prepared by the Grignard method were screen-tested exactly as described in the preceding paragraphs. The evaluation, where possible, was made by comparison with the resins listed in Table 6. The observations are summarized in Table 7.

TABLE 7
Screening Tests — Grignard Method Silicones

No.	Results
S-3	More decomposition than 220 (1)
S-4	Less decomposition than 195 (1), but poorer adhesion
S-5	More decomposition than 210 (1)
S-6	More decomposition than 210 (1), better than S-5
S-7	Very inferior to 217 (1)
S-8	Approximately equivalent to 197 (1)
S-9	Inferior to S-8
S-10	Very inferior to 217 (1)
S-22	Fair protection and heat resistance
S-23	Broke into large flakes
S-24	Very poor

Screening Tests on Fluorine-Containing Silicones — Five of the fluorine-containing silicones (see Table 3) were examined in a curing test at 190° C (374° F). They were treated with 1 percent by weight of phosphoric acid and baked at 190° C (374° F) and also at 300° C (572° F). The results are summarized in Table 8. These resins had poor adhesion when cured. The coatings designated "soft" in the table were readily scratched with the fingernail.

TABLE 8
Curing Studies on Fluorine-Containing Silicones

No.		1 percent added H_3PO_4			
	1 hour at 190° C	1 hour at 190° C	4 hours at 190° C	64 hours at 190° C	5 hours at 300° C
S-27				tacky	dry, soft
S-29	very tacky	dry, soft	dry, soft	dry, soft	dry, soft
S-37	tacky	dry, soft	dry, soft	hard, brittle	soft, brittle
S-38	very tacky	tacky	tacky	tacky	tacky
S-39	very tacky	dry, soft	dry, soft	dry, soft	hard, brittle

Heat Tests on Silicone Resins — The group of resins characterized by the charge ratios (R + Ar)/Si = 1.8 and Ar/R = 0.895 (see Table 3) were brushed onto weighed aluminum panels. They were allowed to air-dry 16 hours; then were baked for one hour at 260°C

(500°F) to eliminate solvent and to promote cure. The panels were cooled and weighed. The heating was continued, with occasional removal and weighing, until the total time at 260°C (500°F) reached 135 hours. These tests were started in triplicate. Two panels of the three were removed from the 260°C (500°F) test after 69 hours and continued in test at 315°C (600°F) for 71 hours.

The heat losses are tabulated in Table 9.

TABLE 9
Percent Heat Losses of Silicones

No.	Hours at 500°F							
	3	9	25	47	69	135	69 + 5 at 600°F	69 + 71 at 600°F
S-45	7	11	17	21	24	41	39	67
S-46	11	12	17	22	26	31	33	55
S-48	6	10	12	15	19	32	29	59
S-64	4	6	9	11	13	15	16	28
S-65	28	48	62	69	73	74	75	78

The same group of resins was tested in a similar type of exposure at 315°C (600°F) for a total of 157 hours. The commercial silicone resins DC 801 and DC 803 were included in this group. The base weight of the resin for the heat-loss values was taken on the basis of one hour at 315°C (600°F). The results are tabulated in Table 10. Comments on appearance of the coatings at the conclusion of the test are included.

TABLE 10
Percent Heat Losses of Silicones

No.	Hours at 600°F							Appearance after 157 hours
	3	6	11	27	48	69	157	
S-45	9	14	23	38	48	56	66	Shrunk, very rough
S-46	7	11	15	24	32	38	47	Rough, brittle
S-48	7	12	17	31	39	44	48	Brittle, bad adhesion
S-64	6	9	13	16	20	21	24	Checks, brittle, fair adhesion
S-65	28	34	39	44	47	48	52	Scaled, rubs off readily
DC 801	3	5	7	11	15	17	19	Hard, checks, brittle
DC 803	2	4	6	9	12	13	15	Slight checks, brittle

This series of resins was also tested at 371°C (700°F), along with commercial resins GE 81061 and GE 81129 and the modified resins (see Table 5). The resin solutions were

brushed onto aluminum panels, air-dried 16 hours, baked one hour at 260°C (500° F) to cure and determine the weight of the resin, then heated at 371°C (700°F) and weighed after one and two hours heating. This determination was also made on a number of resins prepared by Weaver (1) and by the writer. The results are collected in Table 11.

TABLE 11
Percent Heat Losses of Silicones

No.	1 hour at 700° F	2 hours at 700° F	Appearance after 1 hour at 700°F
S-45	42	44	Checks
S-46	40	44	Long cracks, poor adhesion
S-48	43	50	Rough, checks in thick sections
S-64	27	31	Rough, checks
S-65	80	82	Scales, discolors
DC 801	11	17	Good (cracks in 2 hours)
GE 81061	7	9	Cracks, loses adhesion
GE 81129	40	46	Rough (cracks in 2 hours)
S-45-T	31	37	Good
S-46-T	27	32	Slightly tacky
S-48-T	28	37	Tacky
S-64-T	31	41	Good
S-65-T	82	83	Evaporated from surface
217 (1)	41	48	Tacky (dry in 2 hours)
S-38	45	51	Dry (slight cracks in 2 hours)
220 (1)	66	76	Dry (bare patches in 2 hours)
S-39	38	45	Good (slight cracks in 2 hours)
195 (1)	18	25	Bare patches, shrinkage
S-29	25	30	Smooth, no shrinkage
197 (1)	15	17	Good, darkens
S-37	24	30	Slight cracking
210 (1)	28	34	Evaporated patches
S-27	36	44	Smooth, darkens
S-90[a]	12	14	Cracks

[a] S-90 was prepared by the Vita-Var Process (10)

The resins prepared by the Vita-Var Process were tested in similar fashion. Triphenylphosphite (7% by weight of the silicone) and cobalt naphthenate (0.1% cobalt by weight of the silicone) were tried as curing catalysts and heat stabilizers for these resins, and in addition for DC 801 and S-45 (see Table 3). The heat losses are listed in Table 12.

TABLE 12
Percent Heat Losses of Silicones Prepared by the Vita-Var Process

No.	1 hour at 700° F	2 hours at 700° F	Curing Catalyst	Remarks
S-110	64	67	No catalyst	Rough, dull
S-111	26	32	No catalyst	Soft, rough
S-112	26	35	No catalyst	Soft, rough
S-147	45	72	No catalyst	Slightly tacky, dull
DC 801	16	22	No catalyst	Hard
S-45	30	37	No catalyst	Nonadherent
S-110	36	44	7 percent TPP	Soft
S-111	22	27	7 percent TPP	Hard
S-112	26	31	7 percent TPP	Hard, glossy
S-147	29	34	7 percent TPP	Soft, glossy
DC 801	16	19	7 percent TPP	Hard, glossy
S-45	38	43	7 percent TPP	Soft
S-110	47	52	0.1 percent Co	Checks
S-111	13	19	0.1 percent Co	Soft
S-112	21	26	0.1 percent Co	Soft, dull
S-147	27	37	0.1 percent Co	Slightly tacky
DC 801	12	15	0.1 percent Co	Hard, glossy
S-45	27	33	0.1 percent Co	Soft

Another set of the TPP-catalyzed resins was baked 18 hours at 150°C (302°F), then placed in the muffle furnace at 371°C (700°F) for 16 hours, and finally cooled slowly. They all cracked and peeled badly.

Cobalt naphthenate caused darkening of the resin solutions and films. Triphenylphosphite caused gelation of S-111 and S-112 in three weeks, and viscosity increases in the other resins to which it was added.

DISCUSSION

Preparation of Intermediates

The fluorine-substituted arylchlorosilanes required in addition to those synthesized by Weaver (1) were synthesized by the same series of reactions which he employed. The details have been described in the EXPERIMENTAL section. Modifications were developed which made the syntheses more convenient in the laboratory and, at the same time, produced products of greater purity.

The method used for decomposing the diazonium fluoborates, while not novel in principle (11), represents a seldom-used departure from the ordinary techniques of the Schiemann reaction. By conducting the decomposition in an inert liquid medium with good agitation, the temperature can be controlled at the minimum necessary to give a reasonable reaction rate. The rather slow evolution of the by-product gases reduces the entrainment of product to such a degree that an elaborate system of recovery traps is unnecessary, a good reflux condenser being sufficient. In addition, there is no carbonization, no difficulty in cleaning the equipment after reaction.

Only the fluorine-containing arylchlorosilanes were prepared in this Laboratory; methyl- and phenylchlorosilanes were commercially available. The tedious process of fractionating the fluorine-substituted arylchlorosilanes was justified by the failure of the silicones prepared directly from Grignard reaction mixtures to equal those prepared by hydrolysis of mixtures of relatively pure arylchlorosilanes. The only alternative would have been the preparation of a large number of experimental silicones by hydrolysis of Grignard reaction mixtures in order to determine the charge ratios necessary to reproduce the direct-method silicones.

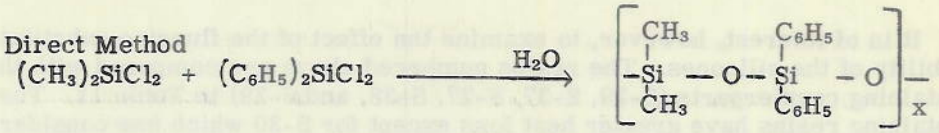
A Comparison of the Properties of Silicone Resins Prepared by the Grignard Method and by the Direct Method

For laboratory synthesis, the Grignard method is simpler for preparing resins containing substituted aryl radicals bonded to silicone because the appropriate substituted arylchlorosilanes are not commercially available. This was recognized by Weaver (1), who suggested that the Grignard method be used.

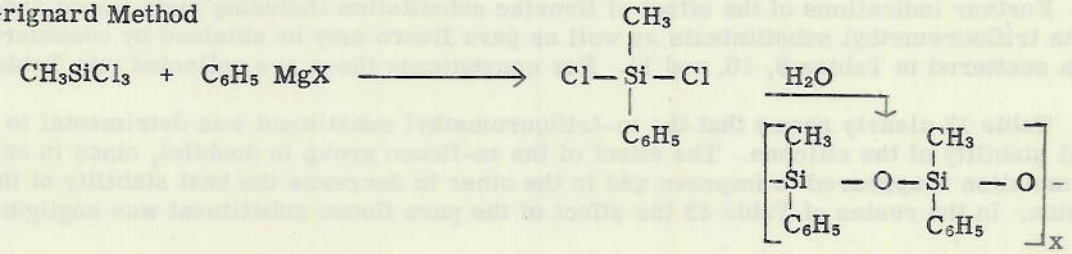
An examination of Table 7 reveals that with the exception of S-8 and 197 (1), the resins prepared by the Grignard method are inferior to those prepared by the direct method. It is perhaps unfortunate that the resins selected from Reference (1) on the basis of a heat-resistance test exhibited such poor surface coating qualities (see Table 6). However, the comparison of the methods should be valid despite this annoyance. The compositions indicate that the ratio (R + Ar)/Si is considerably higher than recommended by Rochow (6), as are the Ar/R ratios. Resin No. 195 (1) is an exception. These departures from the accepted practice may account for the poor coatings properties of the resins under discussion. It is significant that S-22, which approaches more closely to Rochow's recommendations than the others in Table 7, is the best in this group.

Since the Grignard method has in this instance proved inferior to the direct, it is of interest to consider a probable reason for this behavior. One of the differences is the nature of the groups bonded to a single silicon atom. The following equations will clearly illustrate this difference:

Direct Method



Grignard Method



Such a subtle difference would not be expected to make much difference in the properties of the silicone, but in addition, must be considered the nonspecificity of the first step in the Grignard reaction. The substitution of the chlorine atoms of CH_3SiCl_3 follows a statistical rather than a stepwise course; so the reaction mixture may contain unreacted CH_3SiCl_3, $CH_3(C_6H_5)_2SiCl$, and $CH_3Si(C_6H_5)_3$ as well as the desired $CH_3(C_6H_5)SiCl_2$. With these groups of from 0 to 3 functions present at hydrolysis, differences between resins from Grignard and direct methods do not seem incongruous.

These differences resulted in abandonment of the Grignard method and made necessary the preparation of the fluorine-substituted chlorosilanes as described in the experimental procedure.

Comparison of Ordinary and Fluorine-Containing Methylarylsilicones

The analogs of Nos. 195, 197, 210, 217, and 220 (1) were prepared in which the phenyl groups were para substituted by fluorine. Examination of Table 8 shows these resins to be poorly constituted for surface coatings as, indeed, were the forerunners.

TABLE 13
Effect of Fluorine Substitution on Heat Loss

No.	Substituent	$\frac{R+Ar}{Si}$	$\frac{Ar}{R}$	Percent Heat Loss		
				69 hours[a] 500°F	157 hours[b] 600°F	2 hours[a] 700°F
S-45	None	1.8	0.895	24	66	44
S-46	None	1.8	0.895	26	47	44
S-48	p-fluoro	1.8	0.895	19	48	50
S-64	m-fluoro	1.8	0.895	13	24	31
S-65	m-trifluoromethyl	1.8	0.895	73	52	82
S-90	None	1.61	0.675	--	--	14
S-110	m-trifluoromethyl	1.61	0.675	--	--	67
S-111	None	1.61	0.675	--	--	32
S-112	p-fluoro	1.61	0.675	--	--	35
S-147	m-fluoro	1.61	0.675	--	--	72

[a] 1 hour 500°F to obtain resin weight

[b] 1 hour 600°F to obtain resin weight

It is of interest, however, to examine the effect of the fluorine substitution on the heat stability of the silicones. The resins numbered above are compared with their fluorine-containing counterparts (S-29, S-37, S-27, S-38, and S-39) in Table 11. The fluorine-containing resins have greater heat loss except for S-39 which has considerably less than 220 (1). No reason can be advanced for this anamoly.

Further indications of the effect of fluorine substitution including meta fluoro and meta trifluoromethyl substitutents as well as para fluoro may be obtained by considering data scattered in Tables 9, 10, and 11. For convenience these are collected into Table 13.

Table 13 clearly shows that the m-trifluoromethyl substituent was detrimental to the heat stability of the silicone. The effect of the m-fluoro group is doubtful, since in one formulation it appeared to improve and in the other to decrease the heat stability of the resins. In the resins of Table 13 the effect of the para fluoro substituent was negligible.

The data have not established, and indeed it would be prohibitively difficult to establish, whether the effects of fluorine substituents are caused by their actual presence in the resin or by a change in the course of the condensation reaction. It is the personal opinion of the author that the latter effect predominates, at least in these instances where only single substituents are involved.

Effect of Charge Ratios on Heat Stability

The silicone resins 197, 217, and 220 (1) have charge ratios which are undoubtedly not representative of the ratios in the cured polymer and, accordingly, are not considered in this discussion. Table 14 is a collection of charge ratios and heat stability data of a number of resins selected from other tables in this report. Commercial resins of unknown composition are included for comparison.

TABLE 14
Effect of Charge Ratio on Heat Losses of Silicones

No.	$\frac{R + Ar}{Si}$	$\frac{Ar}{R}$	Percent Heat Loss 2 hours 700°F
210 (1)	1.95	1.05	34
S-45	1.80	0.895	44,37
S-46	1.80	0.895	44
195 (1)	1.75	2.50	25
S-90	1.61	0.675	14
S-111	1.61	0.675	32
DC 801	- --	- ---	17,22
GE 81061	- --	- ---	9
GE 81129	- --	- ---	46

Only S-90, a Vita-Var Process (10) resin approaches the heat resistance of commercial resins DC 801 and GE 81061. This lends strong support to the opinion of Rochow that commercial silicones have low (R + Ar)/Si ratios (7). There is a slight suggestion that higher Ar/R ratios improve heat stability and this is not inconsistent with theory. The best heat stability, therefore, would be expected from a phenyl silicone of low (R + Ar)/Si ratio. Unfortunately these are too weak and brittle for practical use (4).

Effect of Curing Catalysts on Heat Resistance

Two catalysts, triphenylphosphite and cobalt naphthenate, were used in testing the Vita-Var Process (10) resins. Their effects depend upon the resin composition as indicated in Table 12, but both improve the heat resistance of the resins. The effect is presumed to be caused by an increase of cross linkages and chain length in the cured films. Neither was completely satisfactory from the coatings standpoint; triphenylphosphite caused gelation of the resins in three weeks, cobalt naphthenate caused discoloration of the coating.

The Effects of Heat on Silicone Resins

During the course of the various heat-loss tests reported, particularly those at 371°C (700°F), thick, white fumes were evolved from the resins. The majority of this decomposition took place during the first hour of test. The failure of the resins as coatings was observed to follow two courses.

Resins which proved to have high heat loss appeared to have distilled from the panel, in many instances leaving rough surfaces or bare patches. Finally the remaining resin cracked and lost adhesion. Resins of low heat loss, including the commercial resins, failed only by cracking and loss of adhesion. These phenomena are consistent with the reported properties of silicones (2,3).

The distillation phenomena of the high-heat-loss resins indicates that a large portion of the molecules are either of low molecular weight or are chains in which alkyl groups are present with relatively few aryl groups. The latter would indicate heteropolymerization as opposed to copolymerization. Whatever the reason for this initial distillation or evaporation of the high heat loss resins, their action after that reaction is complete is similar to that observed for the low-heat-loss resins, that is, failure by cracking and loss of adhesion. Such failure is usually attributed to an increase in cross linking until the polymer structure becomes so rigid that further cross linking becomes geometrically impossible without a radical change in the gross structure, in this case the cracking or the separation of resin from the substrate. Since Hyde and DeLong (12) have observed benzene among the products of decomposition of aryl silicones, it appears that the cross linkings are established through scission of silicon-aryl group bonds and formation of new silicon-oxygen-silicon bonds with the aid of atmospheric oxygen.

CONCLUSIONS

1. Silicone resins made by directly hydrolyzing Grignard mixtures were inferior to those made by hydrolyzing prepared mixtures of pure organochlorosilanes at the same charge ratios.

2. Silicone resins containing m-trifluoromethylphenyl groups were inferior in heat resistance to those containing unsubstituted phenyl groups.

3. Silicone resins containing m- and p-fluorophenyl groups were approximately equivalent in heat resistance to those containing unsubstituted phenyl groups.

4. A silicone resin with heat loss equivalent to some commercially available silicon resins has been prepared by the Vita-Var Process.

5. No silicone resins available were satisfactory as coatings for exposure at 371° C (700°F), when tested in unpigmented form.

RECOMMENDATIONS

1. For best possible heat resistance, silicone resins should be formulated according to the following principles, keeping in mind that a practical coating must be obtained:

   (a) Lowest possible ratio of (R + Ar)/Si

   (b) Highest possible ratio of Ar/R

   (c) Hydrolysis in a hydrocarbon-water mixture under rigidly controlled conditions

   (d) Use of a curing catalyst which develops the toughness and flexibility required of the polymer, and at the same time increases its heat stability

2. In view of the failure of the fluorine-containing silicones prepared here to enhance the heat resistance of the resins, further work should be held in abeyance, at least until a thorough evaluation of the newer commercial materials can be made. Therefore this is a final report on NRL Problem No. 32C03-20.

ACKNOWLEDGMENTS

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