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UNIVERSITY OF LOUISVILLE

// AIRCRAFT FINISHES FOR ELEVATED TEMPERATURES

A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Wilbur Louis Hayne, Jr.
//

December, 1947

AIRCRAFT FINISHES FOR ELEVATED TEMPERATURES

Wilbur Louis Hayne, Jr.

Approved by the Examining Committee.

Director	R. H. Williams
	G. C. Williams
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December, 1947

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ABSTRACT

This thesis presents formulations of heat resistant finishes to withstand a temperature of 750°F. The methods of preparation and testing of the various coatings are given together with a tabulation and discussion of results. Included in this investigation is the laboratory preparation and testing of phenyl silicone.

Best results were obtained with a two coat system; the primer coat consisting of a heat reactive organic vehicle pigmented with a mixture of aluminum, zinc, and cadmium, and a top coat of a silicone-glyceryl phthalate vehicle pigmented with aluminum.

INTRODUCTION

The production of protective organic coatings is lately emerging as an industrial science after having been primarily a development of the arts. Surface coatings are used for one or more of five main purposes: the protection of structural and technical materials, decoration, sanitation, better light distribution or greater illumination of objects, and surface smoothness.

The most important function of surface coatings is the protection of structural and technical materials. The necessity for protection is emphasized by the estimation (1) that up to 2 percent of the world's tonnage of iron must be replaced yearly because of corrosion. Since production of iron and steel amounts to well over several billion tons per year, these losses correspond to approximately a billion dollars annually.

Modern aircraft present a difficult problem for surface protection, and aircraft design has been extensively studied and altered so as to increase the resistance to corrosion from galvanic and chemical actions wherever possible. However, the optimum surface protection may not be attainable because of the unique requirements. In some cases, corrosion resistance is subordinated to strength or other design criteria and the assembly therefore demands the use of protective coatings to the final piece.

Wartime experience demonstrated that existing organic coatings were barely sufficient for the services

intended (2), and it was imperative that heat resistance, hardness, smoothness, and adhesion be increased to meet the more rigorous conditions of new and improved Naval aircraft.

Engine exhaust assemblies, jet propulsion engine parts, etc., are normally of ferrous metals and corrode very rapidly at the high operating temperatures. Since present heat resistant coatings are not satisfactory above 600°F, a coating is necessary for the higher temperatures.

These considerations resulted in the Navy Department Bureau of Aeronautics making preliminary investigations in the field of heat resistant finishes. To supplement and advance these investigations, the Bureau of Aeronautics contracted with the University of Louisville Institute of Industrial Research to develop a heat resistant aircraft finish for metal surfaces. The finish is to have the following characteristics:

1. It shall withstand exposure to a temperature of 750°F for a period of several hundred hours.
2. It shall appreciably retard corrosion of the base metal.
3. It shall adhere when subjected to vibrations of the amplitude and frequency encountered in aircraft.
4. It shall pass a bend test over a 1/2 inch mandrel after subjection to 750°F.
5. It shall possess acceptable application

properties which will result in a smooth, thin, and continuous film.

6. It shall be capable of being cured at a maximum temperature of 300°F.

7. It shall have a blue color if possible.

In the development of heat resistant finishes, coatings based on the following types of vehicles were to be investigated;

- (a) Silicones
- (b) Fluorinated silicones
- (c) Chlorinated silicones
- (d) Fluorinated hydrocarbons.

The contract excluded investigation in the ceramic and porcelain fields, since these programs were underway elsewhere.

A literature survey indicated two different approaches to the problem: (1) an investigation of commercially available materials, and (2) the laboratory preparation and evaluation of theoretically satisfactory materials including types of silicones not now commercially available. The differences in these approaches to the problem necessitated the subdivision of the project into two sections; the first pertaining to those products available commercially, and the second relating to the laboratory preparations. These topics are separately treated in this thesis.

I PREPARATION AND TESTING OF HEAT RESISTANT FINISHES

HISTORICAL

The first protective coating, as such, was the pitch that the Egyptians used for waterproofing ships (3). The Chinese and Japanese about 400 A.D. developed much better coatings by pigmenting the sap tapped from the "Rhus vericifera" (varnish tree). Improvements were slow as the production of coatings remained an art until the twentieth century, when many innovations and new materials were developed by engineers and chemists. However, the problem of producing a satisfactory heat resistant coating remained unsolved.

Many attempts have been made to develop suitable protective coatings that will withstand elevated temperatures for prolonged periods, and a number of patents have been obtained by investigators who claimed moderate success for the various formulations. One of the earliest was for a process outlined by Princess Demidoff (4), who claimed magnesium carbonate as the basis for a finish to resist the temperature corrosion of metallic surfaces such as furnaces and chimneys.

Other patents (see Literature Cited) described various pigments, such as aluminum, graphite, powdered camphor, talc, titanium, and metallic oxides (5, 6, 7, 8), and vehicles including glue binders, melted lard, linseed oil, and Japanese varnish (9). Several investigators have claimed good results with alkali silicates, and several coatings of this type have been patented. The chief differences in this latter type are in the materials used for settling, and the pigments used in the mixture.

All these formulations failed to meet modern requirements satisfactorily and research was intensified during the war in an effort to meet increasing and more severe demands. As presented by the Houston Production Club, "All investigators concurred in stating that films composed of organic binders began to decompose below 600°F and disintegrate to an extent that rendered them valueless between 600°F and 800°F under prolonged heating." (10)

Previous work under this same research program has produced protective coatings capable of withstanding the temperature of 750°F (11). Three vehicles were satisfactory, namely; (a) a high grade phenolic spar varnish, (b) a silicone resin, (c) and a mixture of glyceryl phthalate varnish and a silicone resin. Numerous pigments in a large range of varying proportions were tested in these vehicles with mixtures of aluminum, zinc, and cadmium providing the most satisfactory results. However, adhesion, weathering, and flexibility, either singly or in combination, proved to be a serious factor in conjunction with the heat resistance and warranted further investigation.

THEORETICAL

General Coating Behavior

Coatings and related organic finishing materials consist essentially of a continuous, film-forming phase in which is dispersed a pigment or combination of pigments. The ability to convert this film from a mobile heterogeneous liquid to a solid phase is essential, because it is designed for the initial purpose of applicability, and for the final development of an immobilized structure. This final structure must adhere to the base metal and should be inert to the chemical and physical effects of the surroundings. Paints and finishes protect metals by virtue of the interposition of this adherent film between the metal and the corroding agent, and the longer this film performs its protective function, the better is the coating.

Numerous factors are involved in the protective life of coating films. They should all have such characteristics as good adhesion, cohesion, flexibility, and hardness in addition to a reasonably attractive appearance. Undesirable characteristics such as blistering, brittleness, chalking, fading, cracking, and checking should be minimized or eliminated entirely.

Adhesion plays a very decisive role in the determination of the usefulness of a finish. Films themselves can be made which exhibit all other desirable characteristics referred to above, but serve no practical value because of their inability to remain attached to the metal surface.

Experimental investigations indicate that the primary requirement of good adhesion is that the coating medium come into direct contact with the base metal. According to some theories, this contact permits the electrical forces of the atoms in the metal surface to interact readily with electrical forces of the polar molecules of the finishing medium. Since the distance over which these attractive forces can act is very minute (not over more than a few molecular layers of the coating medium), the adhesive constituents must have a certain degree of mobility to permit proper alignment of the electrical forces. These short range forces seem to be fundamental to good adhesion, but may be influenced by other factors such as surface cleanliness.

Flexibility is an essential characteristic of a protective coating. Distensibility measurements on stripped films are of value and permit evaluation of these properties, but the drawback to this procedure is that a true appraisal of adhesion is impossible. A stripped film may show good flexibility, but have little value in application because of poor adhesion. Conversely, in practical applications, a film which shows good adhesion will probably exhibit satisfactory flexibility characteristics.

Blistering, cracking, flaking, easy removal by some external force, etc. are failures that may seem to suggest a simple cause for loss of adherence. However, these failures are only the final signs of loss of adherence and are the net

effect of a number of competing forces. Some of the factors to be considered in these failures are the nature and type of substrate, physical and chemical state of the metal surface, degree of water impermeability, and resistance of the coating to high temperatures.

Vehicles

The vehicle, irrespective of its chemical composition, must be able to be converted from a fluid to the immobile solid state of a "film", rather than to a crystalline or non-coherent amorphous condition. To accomplish this conversion, a resinous state must first be developed, either by virtue of resin molecules already dispersed in the solvent or by the development of resinous molecules by chemical reaction with components such as oxygen in the environment, and/or by heating. The large size of molecules is associated directly with a large molecular surface area, and molecular surface attractions such as van der Waal's forces group these surfaces into micellar structures. Thus large molecules, complexity of structure, and large surface areas characterize the resinous state and determine the solid film formation (12) (13).

The physical properties, such as elasticity and adhesion, are determined by the size and geometric structure of the molecules (14). The presence of dipole moments of polar atoms and radicals in the molecules effectively increases adhesive properties of the resin.

To obtain the most satisfactory film formation from any resin, sufficient air drying followed by proper curing treatment at higher temperatures is normal. Processing in an oven or baking under an infra-red lamp are the most widely used procedures for this purpose.

Pigments

Unpigmented organic films find limited use as protective coatings since the addition of pigments produces important changes in these coatings. The normal organic film is strengthened, hardened, and made more durable by pigmentation, since the rate of moisture penetration is greatly decreased and the destructive action of heat and ultraviolet rays is reduced. The particle type, size, shape, and distribution, as well as wettability of the pigment, are all fundamental factors in determining film life and its type of failure. Chalking, for example, is a failure resulting from improper wetting of a pigment by the vehicle.

The selection of pigments for elevated temperature protection is limited to those stable at the required temperature or capable of oxidation to a stable form. In addition to stability, the electrochemical relationships between the pigments and the coated surfaces merit consideration. Since passage of moisture will permit galvanic action to start, progress, and finally destroy the base metal, the coating should contain a pigment inhibiting this action. Metallic

pigments which meet these specifications are aluminum, zinc, cadmium, and tin, of which aluminum and zinc warrant special mention.

Metallic zinc dust and zinc oxide both impart an inhibitive character to a protective coating. The protective action of zinc dust when used on steel is due chiefly to the anodic character of the zinc metal with respect to iron. Zinc dust coatings also give excellent service over zinc surfaces since acidic components in the vehicle react preferentially with zinc dust rather than with the zinc at the base-metal interface (15). Zinc metal has the additional protective property of diffusing intergranularly into the metal surface at high temperatures (16).

Aluminum pigments are usually covered with an oxide film which prevents utilization of the inherent anodic character of this metal. For most exposures, then, aluminum pigments are used in top coats. These pigments possess additional useful properties. Due to the method of manufacture, the aluminum pigments are of a lamellar structure and are coated with an adherent organic film. The result of this combination of factors is that the pigment particles align themselves horizontally and concentrate in the outer part of the film. This "leafing" action lengthens materially the path which moisture must traverse to get through the film, and since exclusion of ultraviolet light by this metallic pigment is of a high order, the aluminum pigments give increased protection to the coatings.

Panel Preparation

The best metal panels for a standardized general test are cold-rolled automotive steel because of its availability, uniformity, and general use (17). For obtaining good initial adhesion, both the physical texture of this surface and its state of cleanliness are very important. A highly polished surface offers less opportunity for adhesion than a mechanically roughened surface, as the latter provides more actual surface area. Measurements indicate that certain roughening treatments increase surface area twentyfold (18), which improves the mechanical anchorage of the film. The most widely used methods of preparing the metal for testing may be classified as (19):

1. Methods which do not materially change the surface characteristics of the metal. This means of cleaning includes alkali, emulsion, and solvent cleaning.
2. Methods which mechanically or chemically alter the surface characteristics of the metal. The mechanical processes are those such as sanding, and shot or sand blasting. The chemical processes are ordinary pickling or the use of phosphoric acid and a grease solvent to clean and roughen the surface.
3. Methods which convert surfaces to a non-metallic coating adapted to inhibiting

corrosion and increasing the adhesion of the applied finish. This group includes treatments such as Parkerizing and Bonderizing.

Application

After proper panel preparation, the coating may be applied by many methods, including spraying, dipping, brushing, roller coating, tumbling, whirling, electronic spraying, etc. Differences in performance due to application procedure have been observed (20), and it is desirable to apply test finishes in a manner similar to that to be used in practice. The spraying procedure has the advantages of being more convenient and rapid, and was chosen for the preparation of test panels in this research.

The thickness of the applied film is a vital factor, as coatings differ greatly in their performance at different film thicknesses. For this reason, finishes should be tested at a controlled film thickness, preferably corresponding to the thickness to be used in service. That the importance of this factor cannot be overemphasized is indicated by Krumbhaar (21) as follows: "All data on mechanical film properties and indirectly on the performance and durability are dependent on the thickness of the film. The same finishing material at two different coating thicknesses may exhibit widely different behavior; the durability may vary and the type of failure may be completely changed."

As a general rule, a coating system consisting of two or more different coats should be considered for testing purposes as an entity rather than a combination of a primer and top coat with different sets of properties. Mattiello (22) states that experimental work indicates the primer provides certain fundamental properties, such as adhesion and water protection, while such features as abrasion and spotting resistance reside essentially in the top coat. Since the primer coat lies next to the metal, this coat must be considered as being more significant than the top coat.

Test Methods

Measurement of certain physical attributes of coatings as toughness, strength, distensibility, etc., and knowledge of these properties permits forecasting ultimate coating life. The ordinary means of evaluating coated panels include subjective evaluation by visual inspection, the knife edge test, and the fingernail test. Many attempts have been made to improve upon and eliminate these procedures by use of measuring instruments, but extensive work has indicated that at present the fingernail is superior to any testing instrument (23). Since reproducibility is difficult to obtain, it is common practice to run two or three sets of triplicate tests with appreciable time intervals between them (24).

Flexibility tests are widely used. The bending procedure is used to test this property and is ordinarily performed

over a conical mandrel. Several variables influence these test results (25). Those most important are mandrel radius, bending rate, and coating thickness. The results of this test indicate the performance to be expected from the coating with respect to adhesion, elasticity, hardness, and cohesion. Specifically, the bend test can be considered a severe test for adhesion.

Outdoor testing on coated panels is preferred, as it is the best method of determining probably service life of a coating. This test cannot be considered absolute however, due to variations in climatic conditions over a period of time. Because of the time required for such tests, it is not always practical to evaluate coatings in this manner, and for this reason accelerated weathering machines have been adopted. These units give only an approximate indication of the true protective value of the finish in service and are primarily used as relative standards.

Heat Resistant Finishes

The previous discussion applies to coatings in general. In the preparation of a heat resistant coating, the problem is more specific, as the number of materials which may be used is definitely limited because of oxidation and/or decomposition at the required temperature of 750°F. The pigments listed above have indicated their applicability (11), and the problem resolves itself mainly into utilizing these pigments correctly

in a suitable vehicle.

Materials that merit consideration for satisfactory vehicles are: (a) heat resistant substances such as polytetrafluorethane, coumarone-indene resins, and silicone resins; (b) a volatile material which will carbonize and leave the pigments fritted upon the surface of the metal. Polytetrafluorethane is difficultly soluble and has poor adhesion; therefore it was not studied in the present work. Coumarone-indene resins and silicone resins are thermally stable but oxidize at high temperatures in the presence of air. The possibility exists that a suitable antioxidantizing or plasticizing material may be found to prevent or retard this type of failure, but work to date does not justify proceeding along these lines at present (11).

The most promising avenues for a solution to the problem appeared to lie in further investigation of the two systems reported by Lutz (11). The zinc-aluminum-cadmium pigmentation in a volatile spar varnish vehicle offered possibilities; and an aluminum pigmented silicone-glyceryl phthalate formulation also gave indication of being satisfactory. However, more research and testing of pigment combinations and further information on this latter vehicle itself are necessary.

Glyceryl phthalate was originally used in conjunction with silicones to promote more rapid drying, as the silicones remain tacky until cured at a minimum temperature

of 400°F. However, beside improving drying rates, glyceryl phthalate to the aluminum pigmented silicone also improved those characteristics evaluated by the bend test. In addition, glyceryl phthalate served as a thinner and offered the following advantages over a conventional thinner (11):

1. Better preheating protection;
2. Better suspension of the pigment in the can;
3. Faster curing of the film.

An explanation of the superior qualities exhibited by the silicone-glyceryl phthalate vehicle over the silicone itself may be that a copolymer is developed. Since each vehicle is known to polymerize by condensation, i.e., by removal of water, there is no apparent reason why these two materials should not be capable of co-condensation. This possibility is referred to in a recent publication (26), which states that this development has proved to give a coating which possesses the desirable properties of both components.

Possible theoretical structures of such a chemical combination appear to be these as shown:

or, reaction with the carboxyl group,

(b)

EXPERIMENTAL

With due consideration to the previous discussion and the recommendations of Lutz (11), this research was started with the program outlined below:

1. Extensive tests would be made on Lutz' formulation #208 to determine more specifically the characteristics of this formulation consisting of a silicone-glyceryl phthalate vehicle pigmented with aluminum and zinc.
2. Different metallic pigments in varying proportions would be tested in the same silicone-glyceryl phthalate vehicle used for #208 to attempt improvement.
3. Additional work would be carried out to determine the limitations of heat reactive organic vehicles.

Before presenting experimental results, the apparatus used, methods of coating and panel preparation, and testing methods will be discussed. In all formulations, the pigments and vehicles are commercially available.

The pigments comprising the formulations were weighed into a 1/2 pint can using a triple beam balance with an accuracy of .01 gram. A sufficient quantity of vehicle was added to form a paste, six steel balls approximately 1/4 inch in diameter added, the can sealed and placed on a rotating mixer. This appliance operated effectively as a pebble mill, grinding the contents of the can into a homogeneous mixture. After proper dispersion of the pigment, the remaining vehicle was added and

blended into the desired consistency for application.

Panels were prepared for coating by emery polishing and solvent cleaning with an acetone-toluene mixture. The panels were sprayed in a hood containing a stand for proper positioning of the samples. After a sixteen hour air drying period for each coat, the specimens were hung on a rack and placed under an infra-red lamp for a more intense drying and curing period. A picture of the arrangement of this equipment is shown in Figure 1.

A muffle furnace was used for testing the heat resistant characteristics of the paint. The rack supporting the panels was placed in this furnace and the temperature raised to and held at 750°F by a Micromax. A picture of the apparatus in operation with the furnace door open for inspection is shown in Figure 2.

After every seventeen hour heating period, the panels were inspected. If the appearance was still satisfactory, the panels were removed individually from the furnace interior and quenched in cold water. Coatings that withstood this test were dried and bent in a conical mandrel. This 8 inch mandrel, Figure 3, had a cone-shaped center bar that tapered from 1 1/2 inch to 1/4 inch and was fitted with a clamp that permitted bending over the desired radius. The panels were further examined with a low power magnifying glass. Subsequently, the panels were checked for erosion tendencies and corrosion resistance in an accelerated weathering apparatus. This machine had

Fig. 1 Infra-Red Lamp and Panel Arrangement
Used for Curing Coatings.

Fig. 2 Muffle Furnace with Micromax Control Used
for Testing Heat Resistant Finishes.

Fig. 3 Conical Mandrel Used for Bend Test.

a rotating drum to which the panels were fastened, and periodically the panels passed directly under a fine water spray. The entire chamber was under a blanket of mist from this spray, so that the panels were in a completely saturated air medium. All coatings were also given a scratch adhesion test.

A few of the superior coatings were tested on a heated pipe stand arrangement (27). The paint was applied on the exterior of a thoroughly cleaned 18 inch section of 1 1/2 inch standard steel pipe. The pipe was erected vertically with a section of 1 inch copper tubing mounted concentrically inside to serve as a radiating body and decrease the temperature gradient along the steel pipe. Thermocouple wells drilled along the length of the outer pipe permitted temperature readings during tests. The coated pipe was air dried 16 hours. A Meker burner placed under the pipes gave the desired temperature for curing and testing. Temperatures were read at hourly intervals, and water was sprayed frequently on the heated surface from a wash bottle. In this manner, the ability of the coating to withstand conditions corresponding to service applications was evaluated.

The first formulation corresponded to Lutz' #208, which was recommended (11) as his most satisfactory coating. Since this preparation contained DC* 802, and literature received from the Dow-Corning Company stated that DC 801 also gave heat resistant films, a sample containing the latter was

*Note: DC refers to Dow-Corning Silicone series.

also prepared. Compositions were as shown in Table I.

Table I - Composition of Preliminary Samples

Sample Number	Pigment	Vehicle	
H1	6 Al	10 DC 802	15 G. P.*
H2	6 Al	10 DC 801	15 G. P.

Note: Quantities are parts by weight.

The first group of these panels failed by blistering and peeling in the furnace. Measurement of film thickness showed that all films exceeded 1 mil, so more panels were sprayed with similar formulations in a thinner film. The second group of panels had film thicknesses approximately 0.5 mil and withstood the temperature of 750°F satisfactorily. Further preparation and testing of film thickness on panels indicated that this finish must be applied in a thin, smooth, continuous film not to exceed 0.7 mil in depth, with a thickness of 0.5 mil preferable.

This initial coat, while thin, protects the surface completely for an extended period of time at 750°F. Each of these formulations when held at this temperature for over 300 hours retained an appearance similar to that obtained after only a few hours heating. These panels also withstood repeated quenchings and passed the bend test satisfactorily. Because of the thin coating, the panels rusted after 50 hours exposure in

*Note: G. P. - Glyceryl Phthalate

a weathering machine. These coatings will withstand temperatures as high as 1120°F for a few hours.

The feasibility of a two coat application was tested, curing each coat four hours under an infra-red lamp. However, in a given group of panels, some failures always occurred by blistering. Those coatings which did not fail on heating exhibited decreased flexibility, and rusted after 100 hours weathering in the test machine. The failure by blistering of the two coat panels could be prevented by heating the first coat to 750°F before application of the second coat. Heating at this temperature was not desirable since it was a curing period for the first coat and exceeded the limiting curing temperature of 300°F. These panels also rusted rapidly (within 100 hours) in the weathering apparatus. Those coatings containing DC 802 exhibited slightly better bending characteristics and weathering ability than those containing DC 801. In addition to the blistering difficulty, H1 and H2 skinned rapidly when stored.

In an attempt to increase both adhesive and weathering characteristics of these coatings, addition of varying quantities of micronized mica was made as suggested in the literature (28, 29). The results obtained on single coat application are shown in Table II on page 30.

The coatings containing mica were a slight improvement over the previous group, and failures still resulted if the coatings were applied too heavily. Additional tests in both one and two coat applications indicated that mica may improve

Table II - Formulations Containing Aluminum and Mica with Comparative Results

Sample No.	Pigment Comp. (Grams)	Appearance After Heating To 750°F for 16 Hours	After Quench From 750°F	Bend Test	Appearance After 50 Hours in Weatherometer
H14	6.0 M	S. F.	Failed	----	-----
H15	5.5 Al .5 M	Good	Good	Good	Rust Spots
H16	4.8 Al 1.2 M	Good	Good	Good	Rust Spots
H17	4.0 Al 2.0 M	Good	Good	Fair	Rust Spots
H18	4.8 Al 1.2 M	Good	Good	Good	Rust Spots

Note: Glyceryl Phthalate (15 gms.) and DC 802 (10 gms.) were used in all formulations except H18 where DC 801 replaced DC 802.

S. F. - Slight Flaking

the weathering characteristics of the basic formulation, H1, if used in a quantity less than 20 per cent of the total pigment content.

A series of coatings was prepared containing various combinations of aluminum, zinc, cadmium, tin, and mica. The complete series is shown in Table III on page 31. The proportion of glyceryl phthalate to silicone (DC 802) was 15 to 10 (parts by weight) in all cases.

Results of the tests on these formulations indicated the following: (a) The combination of zinc with aluminum in the silicone-glyceryl phthalate vehicle increases rust preventive characteristics of the coating. However, above an optimum weight ratio of 1 part zinc to 2 parts aluminum, the chalking

Table III - Coatings Containing Aluminum, Zinc, Mica, Tin, and Cadmium in Various Combinations, and Comparative Results

Sample No.	Pigment Comp. (Grams)	21 Hours at 750°F	Quench Test	Bend Test	150 Hours in Weatherometer
H33	5.4 Al 0.6 M	Good	Good	Good	Rusty
H34	6 Al 0.7 Cd	Good	S. F.	Good	Rusty
H35	5 Al 0.5 Cd .5 M	S. F.	S. F.	Good	S. R.
H36	6 Al 0.5 Zn	Good	Good	Good	Rusty
H37	5 Al 0.5 Zn .5 M	S. F.	S. F.	Good	Rusty
H38	5 Al 1 Zn .5 M	S. F.	S. F.	Good	S. R.
H50	5 Al 1 Zn	Good	Good	Good	S. R.
H39	4 Al 2 Zn	Good	Good	Good	S. R.
H40	2 Al 4 Zn	Good	Good	Good	Chalking
H41	1 Al 5 Zn	Good	Good	Good	Exc. Ch.
H46	6 Sn	Failed	----	----	-----
H47	2 Al 4 Sn	Good	Good	Good	Rusty
H48	4 Al 2 Sn	Good	Good	Good	Rusty
H49	1 Al 5 Zn 2 Cd	Good	Good	Good	S. Ch.

Note: S. F. - Slight Flaking
 S. R. - Slightly Rusty
 Exc. Ch. - Excessive Chalking
 S. Ch. - Slight Chalking

becomes excessive. (b) Mica addition improves weathering characteristics of the coating to some extent. (c) The addition of tin offers no noticeable improvement in the finish. (d) The effect of cadmium on the weatherability is similar to that of zinc, in that rust preventive characteristics are increased.

Cadmium also serves to decrease chalking when used in combination with zinc.

Storage stability and other characteristics of these formulations were checked over a period of time. The coatings sprayed better when diluted with a small amount of toluene and did not thicken as rapidly on standing. Addition of a small amount of zinc to the basic coating, H1, also prevented skinning for a longer period of time. Conversely, those formulations containing mica skinned more rapidly than similar dispersions with no mica content. In conjunction with these tests, zinc oxide was also checked as recommended (30), but had no effect in preventing skinning. (See Table XI in Appendix.)

Several formulations of pigments in a heat reactive organic vehicle were prepared in order to evaluate and compare this type of coating with the others. The composition of each, and test results, are summarized in Table IV, on page 33.

All these formulations exhibited good heat resistant characteristics. Although H19 and H20 discolored slightly and had a brownish hue, their protective ability was unimpaired. None of the panels peeled or blistered when quenched from 750°F. The appearance of H19 was slightly inferior to the other formulations after bending, but a very slight powdering took place in other preparations that was not evident in H19. These coatings had rust preventive qualities superior to any previous groups when tested in the weathering machine. These finishes weather over 300 hours before any rusting is present, but they

Table IV - Varying Proportions of Aluminum, Zinc, Cadmium, and Mica in a Heat Reactive Organic Vehicle

Sample No.		16 Hours at 750°F	Quench	Bend Test
H19	5 Zn 1 Al	Slt. Discolored	Good	Good
H20	5 Zn 1 Al 0.5 Cd	Slt. Discolored	Good	Good
H21	5 Zn 1 Al 2 Cd	Good	Good	Good
H22	5 Zn 1 Al 7 Cd	Good	Good	Good
H23	5 Zn 1 Al 2 Cd 2 M	Good	Good	Good

Sample No.	5 Hours at 1120°F	Quench	Bend Test
H19	Satisfactory	Good	Failed
H20	Satisfactory	Good	Failed
H21	Satisfactory	Failed in Spots	Failed
H22	Satisfactory	Failed in Spots	Failed
H23	Satisfactory	Failed	Failed

Note: 30 grams of heat reactive phenolic spar varnish was used as the vehicle in all cases.

tend to chalk and wash excessively. Despite the fact that rusting is prevented for an extended period of time, this type of failure makes the coating of doubtful value. More extensive tests indicated that H21 was the most satisfactory formulation of the type containing a heat reactive organic vehicle.

Several factors are significant in a comparison of this type coating with silicone-glyceryl phthalate finishes. This formulation, H21, has no storage difficulties such as

skinning or thickening, and the film air dries completely. No failures were encountered because of film thickness and all test panels passed quench and bend tests satisfactorily.

To determine effects of varying zinc aluminum ratios in the previous group, a series of formulations ranging from 100 per cent aluminum to 50 per cent zinc-50 per cent aluminum were prepared as listed in Table V.

Table V - Effect of Varying Aluminum to Zinc Ratio

Sample No.	Pigment Comp. (Grams)	16 Hours at 750°F	Quench Test
H25	6 Al	Peeled	----
H26	5 Al 1 Zn	Peeled	----
H27	4 Al 2 Zn	Peeled Slightly	Failed
H28	3.5 Al 3.5 Zn	Good	Failed

Note: Heat reactive phenolic spar varnish (30 gms.) was used as the vehicle in all cases.

Formulation H25 was the poorest of the series and, although improvement was found through the series to H28, none was satisfactory. This series, when compared with the preceding group, showed that higher zinc concentrations give much better heat resistance and adhesion in the heat reactive phenolic spar varnish.

Other formulations were prepared to determine the effect of different pigment combinations in a heat reactive organic vehicle as shown in Table XII in the Appendix. None of these formulations were as satisfactory as the series H19

through H23, and H21, as stated previously, was the best coating of this type.

Analysis of results obtained on the two classes of coatings, namely, the silicone-glyceryl phthalate type and the heat reactive organic type, showed certain specific failures with each. Lack of adhesion and weatherability was found in the former case, and excessive chalking and washing was characteristic of the latter. Certain distinct advantages appeared possible if the coatings could be combined in a manner that would minimize or eliminate the shortcomings of the individual formulations. A solution seemed to be in a pigmented heat reactive organic vehicle serving as an undercoat, or primer, and covered with a top coat of the silicone-glyceryl phthalate finish.

The advantages that might be expected by using this two coat system are as follows:

1. The drying period could be shortened if the heat reactive organic vehicle was the undercoat.
2. Adhesive failures between the primer coat and substrate on heating or quenching could be minimized.
3. Chalking and washing of the primer coat should be minimized.
4. Weathering failures should be appreciably decreased.

Theoretically, adhesive difficulties might be

encountered between the two coats since the top coat contains an alkyd resin and the primer consists of a heat reactive phenolic resin vehicle. However, the first sample panels prepared with the two coat system, H21 topped with H38, showed definite promise and merited further investigation. Additional panels were therefore prepared to permit more exhaustive testing.

All two coat panels embodying the system outlined above had excellent heat resistant qualities. However, several failures occurred by flaking on quench test, and the bending characteristics were not too satisfactory. Cracking and loss of adhesion between the two coats was evident. Conversely, as expected, the weathering qualities were superior to any panels tested with either coatings separately. A series of formulations was therefore prepared in an attempt to improve adhesive and bending characteristics. Extensive tests were made on the best of the phenolic coatings, and on additional heat reactive organic coatings as listed in Table VI.

Table VI - Additional Pigmented Heat Reactive Organic Coatings Prepared as Primer Coats

Sample No.	Pigment Composition (Grams)	16 Hours at 750°F	Quench Test	Bend Test
H51	1 Al 5 Zn 2 Cd .9 Asb.*	Good	Good	Good
H52	1 Al 5 Zn 2 Cd .9 Mica	Good	Good	Good

Note: Vehicle was 30 grams of heat reactive phenolic spar varnish in all cases.

*Asb. - Asbestine

Additional top coats are listed in Table VII.

Table VII - Additional Silicone-Glyceryl Phthalate Formulations Prepared as Top Coats

Sample No.		16 Hours at 750°F	Quench Test	Bend Test
H53	5 Al 1 Zn	Good	Good	Very Good
H54	5 Al 1 Zn 0.5 Asb.	Good	Good	Good
H56	6 Al 0.5 Asb.	Good	Good	Good
H57	5 Al 1 Cd	Good	Good	Good
H58	6 Al 1 IB	Failed	Good	Good
H59	6 Al 0.1 Zn	Good	Good	Good
H60	6 Al 0.1 Zn 0.5 Asb.	Good	Good	Very Good
H61	5 Al 0.7 Zn 0.5 Cd	Good	Good	Good
H62	5 Zn 1 Al 2 Cd 1 UB	Good	Good	S. P.

Note: Vehicle was 10 grams DC 802 and 15 grams glyceryl phthalate in all cases.

Asb. - Asbestine
 IB - Iron Blue
 UB - Ultramarine Blue
 S. P. - Slightly Powdery

A summary of the results obtained by these tests is shown in Table VIII, page

The formulations listed in Tables VI and VII were tested as single coats before being used in conjunction as a two coat system. Iron blue was added in H58 and ultramarine blue in H62 in an effort to give the coating the blue appearance that is desired by the Navy. The ability of iron blue pigment to hide the aluminum pigment was negligible, and the

coating failed by peeling when raised to a temperature of 750°F. The ultramarine blue gave a lavender color to H62 when applied. This color gradually faded on continued exposure in the furnace because of oxidation and decomposition of the pigment. The coloring completely disappeared after 80 hours in the furnace.

Table VIII - Summary of Results Obtained on Various Two Coats Systems

Failure on Quench		Poor or Failed on Bend		Fair on Bend		Good on Bend	
Composition Coats		Composition Coats		Composition Coats		Composition Coats	
1st	2nd	1st	2nd	1st	2nd	1st	2nd
H52	H38	H52	H1	H21	H54	H21	H1
H52	H36	H51	H38	H21	H54	H21	H50
H52	H54	H51	H1				
H51	H36	H21	H36				
H21	H58	H21	H38				
H21	H59	H51	H54				
H21	H60	H19	H1				
		H19	H50				

The grouping or rating of all two coat systems in Table VIII is an average of results obtained by a series of the tests on each combination of coatings. Several important conclusions are deduced by rating the coatings in this manner:

- (a) Asbestine and mica in the undercoat and/or in the top lowers adhesion between the two coats; (b) The addition of

cadmium in the top coat also lowers the adhesion; (c) H21 is evidently the most satisfactory undercoat; (d) H1 and H50 are the two most satisfactory top coats.

Further tests on the two best coatings in Table VIII indicate that the thickness of the undercoat does not effect the adhesion of either H1 or H50 to it, but does materially increase the weathering properties. The thickness of the top coat is of vital importance however, as poor bending characteristics and failures on the thumbnail scratch test result if this second coat is over 0.7 mil in thickness.

The two coat system H21 and H1 was tested next on the pipe stand. This test indicated that the system would give good service up to a temperature of 900⁰F, but some blistering and flaking occurred above this temperature when water was sprayed on the hot surface.

SUMMARY AND CONCLUSIONS

Silicone (DC 802)-glyceryl phthalate coatings containing aluminum, aluminum-zinc, and aluminum-zinc-cadmium will withstand temperatures of 750°F in one and two coat applications. All coats must be applied in thicknesses of 0.5-0.7 mil, as above this thickness failure occurs in a few hours at test temperature. One coat applications satisfactorily pass a bend test over a 1/2 inch mandrel, but two coat applications have a tendency to crack and peel on bending. These coatings are essentially air drying, but require an initial curing period under an infra-red lamp or in an oven before exposure to 750°F.

Some rusting of the aluminum pigmented coating appears in pin point spots after 50 hours exposure in a mist chamber. Two coat application decreases this rusting to some extent. Addition of zinc and cadmium materially increases weatherability, and mica aids this property to a lesser extent.

In this type of coating, the optimum zinc - aluminum ratio to prevent excessive chalking is 1 part zinc to 2 parts aluminum. This ratio can vary to the extent of 5 parts zinc to 1 part aluminum when 2 parts cadmium are present. Zinc and toluene additions serve to decrease "skinning" of these formulations. The use of mica with aluminum up to 20 per cent of total pigment content increases weatherability to a limited extent, but mica has the disadvantage of causing the finish to "set up" rapidly. The use of tin offers no noticeable improvement.

Coatings formulated with a pigmentation of zinc-alum-

inum or zinc-aluminum-cadmium in a heat reactive organic vehicle (heat reactive phenolic varnish) have many good characteristics. These protective coatings, with pigment weight ratios of 5 parts Zn to 1 part Al and 5 parts Zn to 1 part Al and 2 parts Cd withstand the temperature very well and possess excellent bending characteristics. The heat resistance and adhesion of the coating are materially decreased if smaller amounts of zinc are used. Zinc and cadmium pigments provide good weathering characteristics, and aluminum pigment aids this property due to its "leafing" ability. In addition, aluminum assists in suspending the heavier pigments. Addition of mica and asbestine does not improve these formulations either when used alone or as primer coats. The substitution of iron for cadmium in these formulations decreases weatherability.

The only difficulty with these coatings is their tendency to chalk and wash. This type of failure is to be expected, however, whenever pigments are improperly wet by a vehicle, and this condition is present when using a heat reactive organic vehicle.

Either the silicone-glyceryl phthalate or the heat reactive organic formulations may be used in single or multiple coat applications for special conditions where good weathering characteristics are not of major importance. However, certain two coat systems are more satisfactory under any conditions. The best of these is a primer consisting of 5 zinc-1 aluminum-2 cadmium in 30 heat reactive phenolic varnish, topped with a

coating composed of 6 aluminum-10 silicone (DC 802)-15 glyceryl phthalate (all parts by weight). The advantages obtained by use of this two coat system in place of multiple coat application of either type finish separately may be enumerated as follows:

1. Shorter drying period (than in the case of silicone-glyceryl phthalate coatings);
2. Better flexibility and adhesion;
3. More desirable and better weathering characteristics.

This two coat system has passed all the laboratory tests satisfactorily and will be submitted as a solution for the problem.

II LABORATORY PREPARATION OF PHENYL SILICONE
HISTORICAL

During the past 80 years, organic compounds of silicon have been the subject of many academic studies (31). Since both carbon and silicon are elements in group IV of the periodic system having normal valences of four, replacement of the carbon with silicon in organic compounds is feasible. Theoretically, a compound of both materials would yield an organic-inorganic molecule possessing simultaneously the properties of an inorganic glass and of an organic resin.

Dr. F. S. Kipping, Professor of Chemistry, University of Nottingham, England, was responsible for most of the fundamental research in the field of organo-silicon compounds. Kipping and his associates experimented with these compounds for more than four decades. During this period, he and his associates prepared a large number of organo-silicon-oxygen compounds and laid the foundations for synthesis of more complex silicone molecules.

In the middle 1930's, scientists of the Corning Glass Works realized that one property of these compounds - polymerization to a permanent hardness - which troubled Kipping, might prove advantageous for use in high temperature electrical insulation. Their research, along with that of General Electric, had prolific results. Numerous products, all members of the silicone family, were prepared and tested.

The silicone family constitutes a large, new field of materials, and the silicones have become the basis for a new branch of plastics. The total possible number of silicones is

astronomical with the possible combinations of the several variables (32) in conjunction with temperature, rate, and degree of polymerization. To date, a large number of silicones have been made and investigated in various degrees; but research into the vast field of silicone chemistry has just begun.

THEORETICAL

The many necessary aspects of coating preparation and properties for finishes in general, and high resistance coatings in particular, have been discussed in a previous section. The property of thermal stability possessed by the silicones makes them promising for use in coatings to resist elevated temperatures. This property is derived basically from repeated silicon - oxygen linkages which are the structure of the silicones. This chain itself represents the stable oxidized structure common to such inert substances as silica and the silicates. The energy bonding the silicon to oxygen is 50 per cent greater than that of a carbon - carbon bond.

Commercial availability of theoretically desirable silicone resins is limited at present; therefore, a laboratory preparation of one or more particularly desirable resins (33) was necessary. Since there is more than basic bond structure to be considered in adapting these heat resistant molecules to specific purposes, a discussion of basic silicone chemistry will render succeeding remarks more understandable.

Sand, brine, air, and coal or oil are the raw materials from which the silicones are manufactured. Sand is heated with coke, forming silicon carbide. Under the influence of heat, this carbide reacts with chlorine obtained from salt water to form silicon tetrachloride. The compound selected to form the organic part of the silicone is treated with chlorine also to obtain an organic halide (34). This halide, when combined with magnesium, forms an addition product, the Grignard

reagent. Combination between silicon tetrachloride and the Grignard reagent (splitting out chlorine from the organic halide and from the silicon tetrachloride) permits a hydrocarbon group to replace a chlorine atom on the silicon tetrachloride. Successive replacements in this manner yield a series of organo-silicon chlorides. Those compounds represented by the formulas RSiCl_3 and R_2SiCl_2 are most important in building up of silicones.

Two more steps are necessary to obtain the silicones. The organo silicon chlorides, or chlorosilanes, are treated with water to form intermediate silanols, while hydrochloric acid is washed out. Condensation then proceeds between these various silanols to form the large, complex molecules that are built upon the silicon-oxygen-silicon skeleton. Reference to Figure 4, page 50, will give the general scheme of these reactions.

Methods other than the Grignard reaction are available for producing the carbon - silicon bonds. Two general reactions are applicable; the direct method and the substitution methods, of which the Grignard is one. Other substitution methods may be listed as (a) substitution by alkyls of zinc, mercury, and aluminum (35, 36); (b) sodium condensation (Wurtz reaction); and (c) absorption of hydrocarbons (37, 38). The direct synthesis method attaches both halogen atoms and organic groups to the silicon in one operation (39). The catalyst (40) and its initial distribution have much to do with the reaction

Fig. 4-Derivation of Silicones from Ultimate Sources

in early stages (41).

Hydrolysis of the organo silicon chlorides is accomplished by the addition of water and proceeds very rapidly. Variations may be made in the method of hydrolysis (42), but the reaction ordinarily takes place with little delay or difficulty.

The condensation of the hydrolysis products, the diols, is the factor which controls the final silicone network. Kipping has observed the stepwise condensation reactions in the phenyl compounds, and although the progress of other organo-silanediol reactions has not been followed, it may be assumed that their behavior is similar. The condensation proceeds at a rate dependent only upon the number of hydroxyl groups present at any given time, and a wide variety of molecular species is formed (43). Since the number of hydroxyl groups is rapidly depleted in this process, heat, dehydrating agents, or catalysts (44) may be employed to hasten the condensation; i.e., "cure" the polymeric mass to the required degree. As the size of the organic molecule attached to the silicon is increased, the heat required to obtain a siloxane molecule of given size is increased. With an organic group the size of the phenyl radical, approximately 100°C is required to initiate polymerization. The type of organic group present also influences the nature of the condensation product and its behavior towards reagents (45).

Since the condensation consists of elimination of an $(OH)^-$ group from one silicon and an H^+ from another, various

molecular arrangements may be obtained. The general types are (a) the linear polymer formed by a difunctional silicon atom; (b) the moderately cross linked organosiloxane chain formed by trifunctional silicon atoms at intervals along this chain; (c) the more highly cross linked three dimensional form created by tetrafunctional silicon. The functionality of the silicon is determined by the number of organic substituents per silicon atom. Thus a convenient measure of the degree of cross linking is the ratio of carbon to silicon atoms. This ratio is less than two when any cross linking has occurred, and is one when every silicon atom is trifunctional (46, 47). Schematic examples of each of the three types may be observed in Figure 5 on page 53.

The nature of the silicone resin to be prepared for a given problem can be controlled to a large extent by careful consideration of the above facts. Properties such as solubility, fusibility, etc., can be expected to depend principally on the degree of cross linking which in turn is a function of the degree of organic substitution. The mechanical and chemical properties change with kind and type of organic group used in the substitution on the silicon. The more carbon atoms there are present in the alkyl or aryl groups, the less the domination of the basic siloxane structure. The silicone field thus becomes as large and as broad in scope, comparatively, as the organic polymer chemistry.

After a study of the above theories and facts, the

Difunctional Silicon Atom

Trifunctional Silicon Atom

Tetrafunctional Silicon Atom

Fig. 5 Molecular Arrangements Formed By
Functional Silicon

decision was made to use one of the aryl silicones, the first to be phenyl silicone. This polymer was not available commercially and not much data, other than known heat stability, were reported.

Phenyl silicone offered several aspects to the solution of the heat resistant coating problem. The resistance of this silicone to oxidation is superior to that of methyl and ethyl silicones, since phenyl silicone decomposes in the neighborhood of 400°C to 500°C (48). The prospect of chlorinating or fluorinating the aromatic nucleus (49) to introduce even more thermal stability was also considered. Chlorinated phenyl silicones are thermally stable up to at least 450°C (50), and the fluorophenyl silicones presumably exhibit stability at even higher temperatures. Also the aromatic nucleus becomes flameproof if three or more chlorine atoms are introduced into this structure.

Although the compound was known to be weak and brittle when cold (51), alteration of the degree of cross linking by varying condensation procedure and curing temperature could improve this property as well as the aforementioned chlorination or fluorination. One other alternate procedure would be that of forming a copolymer between an aryl and an alkyl silicone.

Forming a copolymer offers a means of altering the properties of various classes of silicone resins and is accomplished by cocondensation of the respective silicols (52). This copolymer method has the advantage of permitting various

alkyl and aryl groups to be allotted in different ratios within a single polymeric structure. This method permits a wide range of properties to be obtained and makes allowances for a balance of flexibility, mechanical strength, and thermoplasticity. Experimentation has subsequently disclosed that both superior strength and toughness may be expected in the copolymer, rather than the copolymer being merely a compromise between the best properties of each of the pure compounds.

Methyl phenyl silicone is an example of a superior copolymer and offers another field of investigation from the phenyl silicone. A film in which the R/Si ratio was 1.8 (53), the molar proportions of phenyl and methyl being approximately equal, withstood an electrical power factor test for 640 hours at 300°C while being constantly flexed by hot and cold air. At the completion of the test, cracks in the film were not visible to the naked eye. Neither methyl nor phenyl silicone alone could equal the test. A theory is needed at present to explain the development of these superior mechanical properties not present in either of the compounds separately, so that a guide to future formulations will be available.

Phenyl silicone has been used in the above examples, but other aryl silicones that have been prepared all resemble this compound rather than the higher alkyl silicones. The xylyl and naphthylsiloxanes of the type $(RSiO_{1.5})_x$ are soluble glassy substances of polymeric character (54), and ditolyl silicone is a low melting sticky resin also brittle when cold (55).

Benzyl silicone, although containing an aromatic nucleus, behaves similarly to the alkyl silicones due to the fact that the phenyl group is attached to the silicon atom through the $-CH_2-$ group. The condensation product of dibenzyl silanediol is an oil and not a resin as is the case with all the alkyl silicones unless cross linking is promoted in some manner (56, 57). Similar possibilities may exist for this material that exist for the phenyl silicone as described previously.

"The job of silicone chemists and to no little extent, their art, is so to "tailor" the high polymeric organo-silicon oxide molecules that a variety of products, each designed to meet specific requirements, can be produced." (58)

This survey is the background with which experimental laboratory work was begun. The first two choices for preparation were the phenyl and benzyl substituted silicones. These compounds should serve as guides to future syntheses.

EXPERIMENTAL

The initial preparation of diphenyl dichlorosilane by the Grignard reaction was begun after a review of Kipping's procedure for synthesizing this material (59).

The necessary quantity of silicon tetrachloride was placed in a three-necked, round bottom flask, and diluted with benzene. This flask was fitted with an electric stirrer, a reflux condenser, and a dropping funnel connected to a similarly equipped flask in which the Grignard reagent was prepared. The dry ether and magnesium were placed in a second flask and the whole system flushed out with dry nitrogen. Bromobenzene was added in small amounts to the mixture of magnesium and ether and the reaction was started by any or all of the following methods as required; (a) the addition of a few crystals of iodine, (b) the addition of a small quantity of previously prepared Grignard reagent, (c) the application of heat at the bottom of the flask. When the reaction commenced, the flask was immersed in an ice bath and the reaction continued at 0°C. Upon completion of the reaction, it was necessary to transfer the Grignard reagent by nitrogen pressure into the dropping funnel of the first flask containing the silicon tetrachloride and benzene. The benzene-tetrachloride container was surrounded by an ice bath and the Grignard reagent was added slowly while the mixture was being constantly stirred. After addition was completed, the product was stirred for a further period of thirty minutes, after which as much ether as possible was distilled off. Two volumes of benzene

were added next and the magnesium salts were separated in an apparatus consisting of two large Buchner Funnels sealed together, one being inverted over the other. (The top funnel had a drying tube attached and the bottom one was connected to a filtration flask.) The magnesium salts were well washed with benzene and the combined filtrate and washings were repeatedly fractionated at 303°C and atmospheric pressure in a standard distillation flask.

Two separate preparations were made in this manner. The quantities used in each run are shown in Table IX on page 60. Run #1 was primarily a trial to test the technique, and approximately 3 grams of product were obtained. However, in Run #2, larger quantities of reactants were used and the yield was nearly 40 grams of diphenyl dichloro silane.

The hydrolysis of 20 grams of this product was attempted by solution in 8 ml of toluene with addition to a mixture consisting of 8 ml toluene, 17.5 ml of amyl alcohol and 72.5 ml of water (60, 61). No crystals of diphenyl silane diol appeared and therefore an attempt was made to recover the diphenyl dichloro silane by distillation. The mixture could not be separated, as a hard brittle mass formed in the flask upon application of heat. After repeated attempts failed to dissolve this material in boiling toluene, benzene, acetone, and ether, it was discarded.

The solution remaining was suspected to be diphenyl dichloro silane and it was desired to check this by some means

Table IX - Preparation of Diphenyl Dichloro Silane

Run #1

Materials Used	Volume	Grams	Moles
Magnesium		12	.5
Bromobenzene		78.5	.5
Silicon Tetrachloride		40	.235
Benzene	86 cc (as diluent for SiCl_4)		
Ether	350 cc (for preparation of Grignard reagent)		

Run #2

Magnesium		27	1.125
Bromobenzene		177	1.125
Silicon Tetrachloride		85	.5
Benzene	172.5 cc		
Ether	700.0 cc		

other than the boiling point; a titration procedure as recommended by Rochow (62) was used. Two portions of diphenyl dichloro silane, 1.7301 gm and .9770 gm were hydrolyzed by placing the samples in a mixture of ice, water, and ether. The hydrolysis product, diphenyl silane diol, dissolved in the ether leaving the chlorine ion to form hydrochloric acid which was titrated with a standard sodium hydroxide solution. Calculations indicated a chlorine content of 21.32 per cent by weight in the sample as compared to the formula value of

27.96 per cent. This result was considered to be fair agreement with theory, since the sample was over a month old and had undoubtedly hydrolyzed to some extent before analysis.

Warm ethyl alcohol and benzene were used to recrystallize the .6 gram of diphenyl silane diol from the titration procedure. These crystals had a melting point of 148°C , which corresponds to the melting point given in the literature (62).

Since the procedure of adding the diphenyl dichloro silane to ice, water, and ether gave good results, 15 grams of the remaining silane were also reacted to form the diol. However, recrystallization of this diol gave only approximately 5 grams of pure diphenyl silane diol.

The .6 gram diphenyl silane diol that was obtained initially was polymerized by heating to 440°F . The temperature was then permitted to drop to 380°F over a period of 15 minutes, and the sample then cooled to room temperature. The polymerized product was a hard, brownish mass.

This polymerization product, phenyl silicone, was dissolved in an equal weight of toluene and brushed on an emery polished and solvent cleaned panel for testing. The coating was air dried for 24 hours, cured at 140°C for 3 hours in an oven, and placed in a muffle furnace at 750°F for 20 hours. Upon examination, the coating had fine hair line cracks, but was otherwise apparently unaffected by the high temperature. The panel was given a bend test, and while the resinous film did not actually flake, it easily could be rubbed off. This

test indicated that the film was of a brittle nature and did not possess good adhesive characteristics.

The remaining diphenyl silane diol was polymerized at a lower temperature in an attempt to produce a less highly linked chain structure so that the film would have more flexibility. The maximum temperature used was 390°F for 15 minutes, after which the resin was cooled to 200°F before cooling to room temperature. This product was very viscous but not solid as in the previous polymerization. The change in weight resulting from the polymerization as well as the additions to and use of the phenyl silicone are shown in Table X.

Table X - Weight Loss During Polymerization at 390°F;
Additions to and Application of Resin.

	Weight of Crystals (Grams)	Weight Lost in Heating	Addition to Resin	Applied to Panel Number
Crucible #1	1.00	.21	Toluene - .79 gm	C-1
Crucible #2	1.00	.15	DC 801 - .85 gm	C-2
Crucible #3	1.09	.23	DC 802 - .86 gm	C-3

Sufficient toluene (a few drops) was added to the resinous materials applied to the C-2 and C-3 panels to permit brush application. Two panels were prepared from each formulation and sample panels of DC 801 and DC 802 were also prepared for comparison. All panels were air dried for 17 hours, and then placed under an infra-red lamp for drying. The panels were placed at such a distance from the lamp that the temperature was 75°C, and the phenyl silicone films did

not appear to dry to any extent. When cooled, these films were only slightly tacky, which indicates that these phenyl resin films are thermoplastic. All panels were removed from the infra-red lamp after 5 hours of intermittent heating and cooling, and placed in the muffle furnace where they remained for 19 hours at 750^o F.

Panels of the copolymerized diphenyl silane diol, phenyl silicone, were the best after heating, although displaying fine cracks and some tendency to rub off the panel. The panels of C-3, containing a mixture of phenyl silicone and DC 802, were of nearly the same appearance and properties. Panels of C-2 were much poorer than these two groups, and were almost as poor as the DC 801 and DC 802 by themselves. These last two were poorest, since both had oxidized and flaked off the panel almost completely during heating.

As a final test for the remaining phenyl silicone, one gram was dissolved in toluene, and aluminum pigment and glyceryl phthalate were added in the same weight proportions, 0.6 : 1.5, that proved successful with the DC 802. Two panels were brushed with this pigmented phenyl silicone, and these were cured under the infra-red lamp for four hours. These coated panels were essentially tack-free at the end of the curing period.

The panels withstood 750^oF in the muffle furnace for 20 hours and satisfactorily passed the quench test. These panels also had sufficient flexibility to pass the bend test with no evident loss of adhesion.

SUMMARY AND CONCLUSIONS

Phenyl silicone was prepared successfully by the method of Kipping. This product had good heat resistant characteristics and was superior to the silicones commercially available at the present time. This silicone gave evidence of being thermoplastic at low temperatures (150°F), but this property was eliminated by heating to the temperature of the problem, 750°F . Mixtures of this silicone with the DC Silicones 801 and 802 did not give as good a film as phenyl silicone alone.

Polymerizing of the diphenyl silane diol was performed at only two temperatures, 440°F and 390°F . The lower temperature gave a phenyl silicone that was viscous in nature rather than the solid mass obtained at the higher temperature. The slower polymerization seemed preferable as the product was more readily dissolved and gave a slightly better coating after heating to 750°F .

Tests of the phenyl silicone in the same manner that gave a good heat resistant coating with the commercial silicones, i.e., with aluminum pigment and glyceryl phthalate, showed the coating to have satisfactory heat resistant characteristics. The quench test and the flexibility test also indicated that this coating possesses satisfactory adhesion.

This investigation of the properties of phenyl silicone when used as a heat resistant protective coating was only preliminary in nature. The results indicate that a more extensive research is warranted.

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APPENDIX

Table XI - Formulations Containing Zinc Oxide Addition
to Test Effect on Skinning

Sample No.	Pigment Comp. (Grams)	16 Hours at 750°F	Bend Test	50 Hours in Weatherometer
H42	5.0 Al 1 Zn 0.7 ZnO	Good	Fair	Slt. Rusty
H43	4.5 Al 1 Zn 1.3 ZnO	Good	Fair	Slt. Rusty

Note: Vehicle was 10 Si 802 and 15 G.P. in all cases.

Table XII - Addition of Iron and Mica to Pigmented Heat
Reactive Organic Vehicle

Sample No.		16 Hours at 750°F	Quench Test	Bend Test	Weathering
H29	5.0 Zn 1.0 Al 0.7 Fe	Good	Good	Good	W.C.
H30	5.0 Zn 1.0 Al 2.0 Fe	Good	Good	Good	W.C.
H31	4.5 Zn 0.9 Al 1.8 Cd	Good	Good	Good	W.C.
H44	4.08 Zn 1.5 Al 0.5 M .5 Fe	S. D.	Good	Fair	W.C.

Note: Vehicle was 30 grams heat reactive phenolic clear spar varnish in all cases.

S. D. - Slightly Discolored

W. C. - Washing and chalking to an undesirable extent.

Commercial Materials Used and Their Manufacturers

1. Paste, Aluminum, Grade A, Army-Navy Aero. Spec. AN-TT-A-461a
Contractor: U. S. Bronze Powder Wks., Inc.
220 W. 42nd St., New York 18, N. Y.
2. Standard Zinc Dust - 22 (Horse Head Products)
New Jersey Zinc Sales Company, New York
3. MD 201 Cadmium Powder
Metals Disintegrating Co., Inc., Elizabeth, N. J.
4. Iron Powder (Reduced by Hydrogen)
General Chemical Company, New York
5. Ultramarine Blue #3155
C. J. Osborn Co., 132 Nassau St., New York, N. Y.
6. Micro-Mica
English Mica Company, Spruce Pine, North Carolina
7. Varnish, Spar, Glyceryl, Phthalate, Spec. AN-TT-V-116
Beckwith Chandler Co., Newark, N. J.
8. Varnish, Heat Reactive Phenolic Clear, VG-5293
E. I. duPont De Nemours and Co., (Inc.),
Wilmington, Del.
9. DC 801 and DC 802 Silicone Resins
Dow-Corning Corporation, Midland, Michigan

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VITA

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