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University of Louisville

High Temperature Coatings
//

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

Irvin Henry Lutz
//

June, 1947

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High Temperature Coatings

Irvin Henry Lutz

Approved by the Examining Committee.

Director R. A. Williams

G. C. Williams

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June, 1947

TABLE OF CONTENTS

List of Tables	iv
List of Figures.	vi
Acknowledgement to Director.	vii
Abstract	viii
Introduction	2
Historical	6
Theoretical.	10
Experimental	20
Summary and Conclusions.	43
Literature Cited.	46
Appendix	50
Acknowledgement.	60
Vita	62

LIST OF TABLES

Table Number	Title of Table	Page
I	Heat Resistant Properties of the 800 Series Silicones.	24
II	Effect of Reducing Pigments on Silicone Finishes.	25
III	Effect of Plasticizers on Silicone Coatings.	27
IV	Coatings Containing Aluminum, Zinc, Lead, and Mixtures of Lead with Aluminum	28
V	The Effect of Lead in High Temperature Coatings.	28
VI	Data on the Fusing of Metallic Powder Mixtures	30
VII	Data on Coatings Containing Tin.	31
VIII	Variation of the Properties of Aluminum-Zinc Coatings with Changing Aluminum-Zinc Ratios.	33
IX	Silicone-Glycerol Phthalate Coatings	35
X	Aluminum Pigmented Silicones	37
XI	Comparison of Glycerol Phthalate-Silicone Coatings with the Straight Silicones	38
XII	Non-Metallic Pigmented Silicones	39
XIII	Heavily Pigmented Silicones.	41
XIV	Proprietary Coatings	50
XV	Plasticized Silicones.	51
XVI	Coatings, Containing Lead.	53
XVII	Coatings, Containing Tin.	55
XVIII	Coatings, Containing Cadmium.	56
XIX	Coatings, Containing Iron.	57

LIST OF TABLES (Cont.)

Table Number	Title of Table	Page
XI	Silicone-Glycerol Phthalate.	58
XII	Silicone Varnish Heavily Pigmented with Zinc and Zinc Oxide.	59

LIST OF FIGURES

Fig. No.		Page
1	Apparatus used in Preparation of Samples.	21
2	Pipe Stand Used for Testing Coatings.	23
3	Constitution Diagram of the Zinc-Magnesium System	29

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ABSTRACT

This thesis is a report on coatings exclusive of the porcelain enamels which may be used at temperatures as high as 750° F., and also a description of the properties of the more heat resistant resins of commerce. The method of preparation and testing of the various coatings investigated in this research is given, and the results are tabulated and discussed.

Best results were obtained with Dow Corning silicones of the 800 series heavily pigmented with either zinc dust or aluminum bronze, and with glycerol phthalate -- silicone coatings pigmented with aluminum bronze.

INTRODUCTION

Surface coatings are used for one of five main purposes: for protection of materials of construction against corrosion, for decoration, for obtaining better illumination of objects, for sanitation, and for easily obtaining a desired surface condition -- the latter effect being especially important in aerodynamic considerations. However, the use of surface coatings for protection of materials of construction against corrosion is by far their most important use today.

Surface coatings have constantly demonstrated their importance in this protective function in modern everyday life. Many of the engineering advances of the modern age would be nullified to a great extent if the severe operating conditions of modern appliances and the deleterious effect of the elements were not offset by protective coatings. It has been estimated (1) that 2 percent of the world's tonnage of iron must be replaced yearly due to corrosion, and that the losses resulting from corrosion run over a billion dollars per year.

The protection of naval aircraft against corrosion is an especially difficult and important problem. The gravity with which the Bureau of Aeronautics considers the corrosion problem is illustrated by Lt. Commander A. M. Malloy when he states, "The small margin dividing victory and defeat in combat may often be determined by the film of protection which is afforded by organic coatings." Naval aircraft parts operate under extremes of weathering conditions. The exhaust pipe of the modern airplane is an example of a member of which is subjected to extreme conditions. It is exposed to the high temperature of the exhaust fumes, the frigid

temperatures of arctic airports, and the intensely corrosive salt spray encountered in naval operations.

Considerable effort has been expended in the design of aircraft, and the types of metals employed have been altered in order to increase the resistance to corrosion from various effects such as galvanic action, oxidation, etc. However, due to special requirements the best metals for corrosion resistance can not always be used. Structural strength can not be compromised in order to obtain corrosion resistance. The only alternative is to develop coatings which will satisfactorily protect the parts against corrosion.

The job of protecting aircraft parts against corrosion has been accomplished to a great extent (2). However, at the time when this research was begun no satisfactory protective coating had been developed to withstand temperatures in excess of 600° F. This deficiency was becoming increasingly important due to the increased use of jet-propelled aircraft, in some of which large sections of the fuselage are at high temperatures.

With these considerations in mind, the Bureau of Aeronautics contracted with the University of Louisville Institute of Industrial Research to investigate protective coatings for use at high temperatures. The particular criteria which were set for the coating at that time are the following:

"The coating is to withstand prolonged exposure to a temperature of 750° F. when used on steel surfaces. It is to have the application characteristics of conventional paint, and is to produce the desired

properties by air drying or baking at a maximum temperature of 300° F. In addition, the coating is to maintain the requisite durability, adhesion, flexibility, etc., that will be encountered in service."

It was requested at the start of this study that any investigations in the fields of ceramics and porcelain finishes be omitted, as a project of this type of application was under investigation elsewhere.

HISTORICAL

The earliest evidences of the use of surface coatings are the drawings found by archeologists in the caves of prehistoric man (3). The paints were composed of natural red oxides such as red ochre and were used solely for decorative purposes. Since the earliest recorded civilization existed in dry climates where there was little necessity for protective coatings, we find that here too the inhabitants of these early civilizations were concerned mainly with the artistic value of paints. The fact that Egyptian art treasures were sealed in tombs did not create a critical need for lasting paints as we know today.

Probably the earliest material used for an industrial protective coating was pitch. Pitch was used on the bottoms of ships during the Greek period mainly to make the vessels watertight, but doubtless it was discovered that these coatings preserved the hulls of the ships (4). There is no mention of varnishes in any writings of this period, except a bitumen coating material described by Pliny (5).

The orientals were far ahead of the occidentals of this period. The Chinese and Japanese employed the sap tapped from the Rhus Vernicifera (varnish tree) as a vehicle in preparing paints which are known as Japanese lacquers. This process of preparing lacquers was a highly developed art in Chinese life as early as several centuries before the time of Christ. As early as A.D. 400 the Japanese established a state department to govern the use of lac in preparing paints (6). The use of these Japanese lacquers developed into a fine art.

As late as the turn of the twentieth century the materials used for the manufacture of surface coatings were very small in number.

After the turn of the century, progress became rapid in order to meet the more exacting requirements of a modern civilization. As a result of this progress, a vast array of coatings have been designed to fulfill almost every color fancy, to give almost any surface effect, and to give protection under almost every weather condition. However, at the time this research was started, no coating had been designed which would perform satisfactorily under high temperature conditions, that is, above 600° F.

The need of a heat resisting coating had long been recognized. In the earliest chemical abstract, 1907, a French patent for a high temperature paint was obtained by Princess Demidoff (7). In this patent a process was outlined for preparing paints with a magnesium carbonate base which was said to provide a covering which resisted elevated temperatures on metallic surfaces such as chimneys.

In 1915 a United States patent was obtained by E. R. Stowell on a coating composition prepared from carborundum powder and sodium silicate. (8). This mixture was said to form a heat and acid resisting paint.

In 1928 F. T. Walker ran a series of tests on coatings for high temperature use in which the vehicles tested were: linseed oil; fish oil; bitumens, asphaltum, coal tar, and petroleum pitches; sodium silicate solution; portland cement wash; shellac solution; rosin, etc., and cellulose ester lacquer. Pigments tested were graphite; pure metals and alloys; and ordinary paint pigments. He found that the best results were obtained with aluminum bronze powder in one part of Japaners gold size and two parts of naphtha (9).

Numerous other patents of similar nature have been obtained on

materials of this type up to the present time. Most of them are patents on coatings in which the vehicle consists of an alkali silicate.

The patented silicate coatings are all very similar, the only difference being the materials added to aid in the setting of the silicate, the pigments used in the formulation, or the ratio of alkali oxide to silica used in forming the soluble silicate used as the binder. The patents abstracted below are typical of patents obtained on silicate mixtures to be used as heat resisting finishes.

Swiss 209,264 June, 1940 This material, which cannot be attacked by fire, contains water glass, bulk white, burnt lime, gypsum, and cement.

British 545,840 June, 1942 A fire resisting coating composed of an aqueous suspension of bentonite, asbestos powder, and sodium silicate.

Other mixtures patented (7-36) usually employed magnesium oxide, alkali borophosphates, silica sols, and other such materials as binders. However, none of these formulations were totally satisfactory.

A statement of existing problem is quoted in an article on the subject by the Houston Paint Club in the November, 1946 edition of the American Paint Journal.

"(1) Up to the time of the war, no satisfactory finishes for surfaces heated above 600°F. for any length of time had been developed or marketed, but each investigator claimed moderate success for his specific formula.

"(2) All investigators concurred in stating that films composed of organic binders began to decompose below 600°F., and disintegrated to an extent that rendered them valueless between 600°F., and 800°F. for prolonged periods of heating."

THEORETICAL

In general a satisfactory protective coating should be adherent, flexible, abrasion resistant, coherent, hard, and should offer protection against corrosion. These factors determine the acceptability of a coating, and consequently all formulations should be prepared with an insight into factors affecting these characteristics.

Adhesion is of prime importance in determining the acceptability of a coating (37). It is dependent upon the bond between the film and base metal. Factors which affect either the physical condition of the surface of the substrate or the specific adhesion of the coating to the substrate equally determine the adhesion of the coating.

The physical condition of the surface of the substrate can affect adhesion either through an interlocking of the coating and substrate, or through an increase or decrease of the surface of contact on which the forces of adhesion operate (38). With physical interlocking of the film and base as is possible when there is penetration of the coating material into the interstices of a porous material, adhesion is excellent. For example, in tests made on wood samples glued with a penetrating glue, it was found that failure was due either to a failure of the wood, a failure of the glue film, or a combination of the two, but failure was not due to a lack of adhesion. Interlocking is much more difficult in the case of clean metallic surfaces, due to the inability of the coating material to penetrate the surface. However, it has been found that artificial roughening of the surface by either physical or chemical means increases the surface, and hence the adherence of a coating to the surface. Besides roughening of the surface, the adherence of the coating may also be

increased by increasing the fluidity of the coating by either heat or by the use of solvents. Increasing the fluidity permits better penetration of the film-forming substance into the interstices, and hence better interlocking. Judicious use must be made of solvents and thinners, however, as the shrinkage stresses developed upon their evaporation are of such magnitude that actual rupture of the adhesive bond may result.

The specific adhesion of a system is dependent upon the chemical natures of the surface and film-forming substance. In general the chemical forces of specific adhesion exert their effect on layers of base material and film-forming substance through distances only a few molecules thick. This results in an orientation of molecules next to the film. Consequently the adhesion of a film is independent of the thickness of the film. Any factors which tend to increase these chemical forces, such as improving the wetting ability of the coating, or actual chemical combination of substrate and coating as occurs in the galvanizing of iron, greatly increase the adhesion of a coating to the base metal.

Contrary to the usually accepted view, good flexibility of a film is not necessarily connected with good adhesion although the converse appears to hold (39). Pigments have a specific effect on the adhesion of coatings of varying flexibility. Flexible coatings show improved adhesion on pigmentation, and brittle films show a decrease in adhesion on pigmentation.

In the design of coatings for the protection of steel surfaces, the selection of a coating system which will offer resistance to water penetration is a fundamental requisite. Resistance to water penetration is

not only a function of the vehicle, but it is also a function of the pigmentation employed. The resistance to water penetration can be greatly increased by the employment of leafing pigments (40). Fine aluminum powders are probably the best leafing pigments known, and the resistance to water penetration of coatings containing them is phenomenal. The vehicle however, must be sufficiently fluid to permit mobility of the pigment particles and thus allow the leafing characteristic of the pigment to assert itself. Also various thinners and resins appear to have specific effects on the leafing of the pigments.

Resistance to water penetration is not the only aspect to be considered however. It has long been recognized that basic pigments such as zinc yellow, basic lead chromate, and red lead, are especially valuable for use in surface primers. (41,42,43) Their action is thought to be due to the neutralizing effect obtained by their use. Cathodic protection of metallic surfaces has probably not been sufficiently stressed in the past. Recently it has been proposed that use be made of this phenomenon in a coating which contains mostly zinc dust and thinner, with very little resin (44). Laboratory tests show that such coatings on rusty steel give cathodic protection in sea water to metal exposed at scratch lines for over two years. Certainly any coating for surfaces which are to be in contact with moisture should be designed with cathodic protection in mind.

Flexibility, abrasion resistance, and hardness are all important properties of any satisfactory coating. Flexibility is usually a property of the coating determined largely by the vehicle employed.

However, improper pigmentation of a coating can result in poor flexibility. Improved flexibility of any resin may be obtained by proper plastizing.

The abrasion resistance of a film is really determined by the cohesion, hardness, and adherence of the film. Cohesion is almost completely determined by the vehicle employed, although this property, as in the case of flexibility, can be adversely affected by improper pigmentation. Factors determining hardness are self evident and require no explanation.

It is of primary importance in studying metal protective systems to realize that there are at least two factors more important than the composition of the coating applied in their effect on the life of the paint. They are: (1) The condition of the metallic surface being painted (2) the thickness of the film being applied. In comparing protective coatings it is essential that these two factors be held constant. A paint having all the desired characteristics mentioned above will perform poorly if applied to a poor surface and/or if applied incorrectly.

In the design of a heat resistant coating to withstand a temperature of 750°F. all the previously mentioned factors pertaining to coatings in general must be kept in mind. However, the problem becomes much more specific when we consider the very limited number of materials which may be used for such high temperature applications. Indeed, the problem evolves into a consideration of just what materials are available which have the ability to withstand a temperature of 750°F., and which have some promise of forming a film.

This problem is better emphasized if a review is made of the heat resisting ability of some of the resins which are considered heat

resistant.

Polytetrafluorethane, or "Teflon," probably the most heat resistant resin known at the present time, undergoes a solid-phase transition at 620°F., with a sharp drop in strength. In the neighborhood of 750°F., it decomposes slowly to yield gaseous products, and extremely small amounts of fluorine-containing gases are given off at temperatures as low as 400°F. Another difficulty encountered in the use of "Teflon" in a metal protective coating is that it is of non-sticky nature and its adherence to metals is poor (45).

Silicones are also very highly regarded for use in high temperature applications. Some methyl silicone resins suffer no decomposition or disintegration over a period of years at 400°F. and maintain their dielectric strength for long periods, even at 550°F. However, at temperatures above 550°F. the methyl silicones oxidize, leaving a residue of silica. The upper service limits of temperature of the silicone resins may be raised if oxygen is excluded, for it is oxidation of the methyl group that imposes the limit. Phenyl silicone has exceptional thermal stability, but it is thermoplastic and does not have the ductility and general desirable characteristics of the methyl silicones. However, a copolymer of methyl and phenyl silicone may be prepared which has a toughness and strength superior to methyl silicone. These materials have as their upper service temperature limit a temperature of approximately 500°F. but in the absence of air, these and other silicones are thermally stable at temperatures as high as 900°F. (46, 47).

Some chlorinated resins, particularly the chlorinated diphenyls, are highly regarded for their inertness and resistance to high temperatures. Chlorinated diphenyls are unaffected by boiling caustic solution, resist the action of dilute acids, and are stable to heat for long periods of time at temperatures as high as 600°F., and for short periods at much higher temperatures. They will not, however, withstand temperatures in excess of 600°F. for long periods of time, and are thermoplastic materials which soften or melt at high temperatures. Chlorinated diphenylbenzine and chlorinated naphthalene are materials with the same general properties as the chlorinated diphenyls (48, 49).

Other resins generally considered heat resisting are not nearly as good as the previously mentioned resins. In general, other resins are unsatisfactory for use at temperatures as high as 600°F. (50).

With these facts in mind, two approaches to a solution of the problem of obtaining a finish to withstand a temperature of 750°F. are evident: (1) the development or location of a vehicle that will withstand the desired temperature; (2) the formulation of a pigment-vehicle system in which the vehicle will volatilize at 750°F., leaving the pigment fritted on the surface.

The primary requisite of any vehicle to be used alone as a high temperature protective coating is that the vehicle will be resistant to the effects of oxygen at the desired temperature. From the previous statements it can be seen that Teflon is the only resin which even approaches this condition. It is stable and its resistance to oxygen up to temperatures as high as 700°F. is probably satisfactory for most coating uses.

The decomposition of Teflon above 750°F. probably is of the auto-catalytic type, and the addition of a retarder which will combine with the fluorine as it is liberated may reduce the decomposition tendencies. As yet no data are available on the use of Teflon as a resin in paint formulations. The main difficulty encountered in adapting it to the protective coating industry is that no solvents are known for this material. Latex solutions, such as are now being used with the chlorine homologue of Teflon, can undoubtedly be formed, and therefore, this difficulty may be circumvented. However, even though such solutions be obtained, it is anticipated that much work would be necessary in order to obtain a satisfactory coating — particularly since the adhesion characteristics are poor.

There are many resins which are thermally stable up to temperatures in excess of 750°F., but which oxidize on exposure to air. Two examples of resins of this type are the silicones, and the coumaroneindene resins. All resins of this general type, when used at temperatures as high as 750°F., require the addition of materials to act as antioxidants and protect the base resin from oxidation. The antioxidant can be a pigment or can be incorporated as part of the vehicle. Several pigments with antioxidizing characteristics are available: borax, cadmium sulfide, carbon black, and other sulfides and reducing substances. Only one class of materials appears plausible for use in the vehicle itself — chlorinated diphenyl. Compounds of the chlorinated diphenyl type have a tendency to impart oxidation resistance to other materials in solution, much as if the solution as a whole were chlorinated. A case familiar to many is the addition of

carbon tetrachloride to organic solvents, by which procedure, the mixed solvents may be made noncombustible. Chlorinated diphenyl is also attractive because it is a plasticizer and would be valuable in this respect, as most resins become brittle when exposed to high temperatures over any period of time.

It is evident that any materials which are to be inherently resistant to oxidation at high temperatures are of two types. They are either completely inorganic, or are organic in nature but contain atoms in their chemical structure which are not noticeably affected by oxygen — for example, chlorine, fluorine, or nitrogen. Teflon has been mentioned previously. It was anticipated that chlorinated and fluorinated silicones could be produced that would have comparable stability to Teflon. This is born out in a recent publication which states that fluorinated silicones are resistant up to temperatures as high as 800°F. Another class of compounds of this type is the phthalocyanines. The phthalocyanines, however, are not plastic in nature, and much research is necessary before phthalocyanine resins may be produced which are suitable for use as film-forming substances.

Particular impetus was given during the war to the adaptation of inorganic materials to coatings as a substitute for scarce organic materials. It is noted that these efforts were singularly unsuccessful as judged by the fact that such coatings are used only in very special applications, such as the coating of welding rods, where the necessary physical properties of the coating are of quite different nature.

A recent advance which may hold some promise is the use of

ethyl silicate for preparation of silica sols to be used as vehicles. A silica sol prepared by means other than the hydrolysis of ethyl silicate, that is, by neutralizing alkali silicate with acid, would be expected to have like applicability. Sols prepared in this manner, however, lack stability, and in solutions concentrated enough to be used as paint vehicles it has not yet been possible to obtain a stable sol. The same difficulty is encountered in the use of ethyl silicate; however, sols can be prepared from this material shortly before use with no difficulty and with no complicated apparatus, simply by mixing the ethyl silicate with water and a catalyst to accelerate hydrolysis. Gelling inhibitors have been used by other investigators with ethyl silicate and are reported to give stability for more than 250 days. Literature obtained from the manufacturers indicates that coatings formulated from ethyl silicate would have all the disadvantages of those formulated from silicones, plus the added inconvenience that they cannot be stored for long periods of time.

EXPERIMENTAL

Careful consideration of the facts discussed in the previous section led to the initiation of the following program:

1. Antioxidants and plasticizers would be used in an effort to improve the silicones.
2. Various metallic pigments would be formulated with carbonizing vehicles.
3. An attempt would be made to synthesize silicones containing aryl groups, followed by chlorination or fluorination to determine any improvement in properties.

Before going into a discussion of the experimental data, the method of preparation of the formulations, and the method used for evaluating the coatings will be described. In this phase of the problem commercial spar varnishes and blends thereof were used in all preparations. The pigments were commercial types which were readily available on the market.

The components comprising the formulations were weighed out on a triple beam balance and then mixed on a pebble mill. The procedure was as follows: The pigments to be used in the formulations were accurately weighed into a $\frac{1}{2}$ pint can using a triple beam balance which was accurate to 0.01 gram. Enough vehicle was then weighed into the can to form a stiff paste. Several steel balls $\frac{1}{2}$ inch in diameter and smaller were placed in the can, and the can was then set on a roll mixer. This device gave the effect of a small pebble mill when the cans were rotated on the mill. The formulations were ground on this miniature pebble mill for a period of 16 hours or until proper dispersion of the pigment was obtained. The

balance of the vehicle was then added to the formulation and properly incorporated into the finish, using the same device as above. A picture of the apparatus used in the various formulations is shown below.

Fig. No. 1 APPARATUS USED IN PREPARATION OF SAMPLES

The formulations were tested as follows: A one coat application of the coating was sprayed on a bonderized and/or solvent-cleaned and emery-polished steel panel. The panels, after spraying, were given a sixteen hour

air drying, and then heated in an electric furnace for two hours at 150°C. The temperature was then raised to 750°F. and held at this temperature for a period of from six to thirty-two hours, depending on the appearance of the panel after examination. The furnace was then turned off and the panels were allowed to cool in the furnace with the doors open. If the coatings still appeared satisfactory by visual inspection, they were given a bend test over a conical mandrel tapering from $1\frac{1}{2}$ " to $\frac{1}{4}$ ". Coatings which appeared satisfactory after bending were checked for washing tendencies, corrosion resistance, and resistance to thermal shock. The coatings were checked for washing tendencies and corrosion resistance by placing them in an accelerated weathering machine without the carbon arcs operating. This gave an effective mist chamber in which the panels periodically passed directly under a fine water spray. All panels were given a scratch test.

The coatings which appeared especially interesting were tested on a heated pipe stand, one of which is shown in illustration number two. The pipe stand is constructed from a section of $1\frac{1}{2}$ " standard steel pipe 18" long, inside of which is placed a section of 1" diameter copper tubing 20" long. The section of copper tubing acts as a radiating element and creates a more uniform temperature gradient on the pipe. This was necessary since the conductivity of the steel is so poor that too great a temperature gradient is obtained when steel alone is used. The temperature is measured by means of thermocouples placed in wells drilled partially through the steel pipe. Coatings to be tested on this apparatus were sprayed on the sanded surface of the steel pipe and allowed to dry for 24 hours. The pipe stand was then assembled and a Meker burner placed under

the assembly.

Fig. No. 2 PIPE STAND USED FOR TESTING COATINGS

The pipe was heated for 48 hours, or until failure was obtained. During the heating operation water was frequently sprayed from a wash bottle

onto the heated coating under test. In this manner the conditions which the coating would meet in service were simulated.

The first coatings were formulated using silicone varnish as the vehicle. These varnishes were formulated from alkyl silicones and solvent. Dow-Corning silicones were tested on an "as received" basis to become familiar with application technique and with the properties of the silicones. These materials showed very good heat resistance up to 500°F., but in most cases the films became brittle when heated to and held at 625°F. for relatively long periods of time. The resin designated "DC 802" appeared to be the best heat resistant material of the four silicones tested. In Table No. 1 are shown some of the results using the four silicone resins 801, 802, 803, 804, and blends thereof.

TABLE 1 - HEAT RESISTANT PROPERTIES OF THE 800 SERIES SILICONES

Coating Composition (parts by weight)	16 hrs. 500°F.	8 hrs. 625°F.	$\frac{1}{2}$ " Blend	8 hrs. 750°F.	$\frac{1}{2}$ " Blend
Dow-Corning #801	Very good	Cracked			
Dow-Corning #802	Very good	Good	Good	Fair	Peeled
Dow-Corning #803	Very good	Good	Peeled		
Dow-Corning #804	Very good	Cracked			
40% 801, 60% 803	Very good	Good	Good	Fail	
60% 801, 40% 803	Very good	Fail			
DC #802, 2lbs/gal Al	Very good	Good	Good	Good	Fine cracks

It can be seen from these results that aluminated "DC 802" is a satisfactory coating in some respects but it would not pass a bend test. Another important property not presented in Table No. 1 is the corrosion resistance of the films. It was found that the resistance to corrosion of

aluminated "DC 802" was excellent.

As stated in the preceding section, at the temperature of this problem, 750°F., the silicones oxidize, leaving a residue of silica which is very brittle. Because of this oxidation, attempts were made to incorporate in the silicone coatings certain antioxidants that would protect the silicone structure. Cadmium sulfide, which was recommended by several pigment authorities as a good reducing pigment, was thoroughly investigated, and it did not materially improve the resistance of silicones to oxidation. Other antioxidants that were evaluated were carbon black, borax, and sodium-cobalti-nitrate. On the basis of these tests, it appears that although reducing substances may for a short time prevent oxidation, they will not

TABLE II - EFFECT OF REDUCING PIGMENTS ON SILICONE FINISHES

Coating Composition (parts by weight)	12 Hours at 625° F.	16 Hours at 750° F.
*10 CdS, 30 #801		Fail
20 CdS, 30 #801		Fail
14 CdS, 2 Al, 30 #802		Fail
10 CdS, 30 #803		Fail
20 CdS, 30 #803		Fail
10 CdS, 30 #804		Fail
20 CdS, 30 #804		Fail
1 Carbon Black 30 #802	Good	Fail
* 2 T.C.P. 40 #801	Poor	
10 CdS, 2 T.C.P. 30 #801	Fair	Fail

*Note: Tri-Cresol-Phosphate is abbreviated T.C.P.
CdS - Cadmium sulphide yellow

protect at this temperature for extended periods of time. Representative data obtained using reducing pigments are shown in Table II.

Chlorinated diphenyls were used in silicone formulations primarily as plasticizers and secondarily as antioxidants. Various concentrations of the more completely chlorinated diphenyls were first tested at 625°F. in an effort to obtain a coating that would stand up at this lower temperature. It was found that the chlorinated diphenyls did improve the coating somewhat, but not enough improvement was noted to warrant further investigation. The results obtained using the chlorinated diphenyls are indicated in Table III. Indications are that the only way to prevent oxidation over a long period of time is to prevent oxygen contact by the use of inorganic top coats.

Consideration of the results above, and data obtained from interviews and correspondence with the manufacturers of silicone resins, indicated that silicone resins would not be satisfactory at the high temperature of this problem. Further investigation of the silicone resins was therefore deferred until later, in order to investigate the possibilities of coatings formulated from metallic pigments, and vehicles which carbonize at the temperature of this problem.

As mentioned earlier, in this type of coating an attempt was made to frit or melt a coating onto the surface. The first coatings were formulated with lead, zinc, or aluminum as pigments, and data obtained using these pigments is shown in Table IV. The vehicle used in these formulations was a thin-bodied heat-reactive clear phenolic varnish. Coatings with aluminum and lead pigments only, after heating to 750°F. were very powdery, the pure lead in particular having this disadvantage. In fact, it was found that the pure lead coating completely oxidized to red lead. These and other

TABLE III - EFFECT OF PLASTICIZERS ON SILICONE COATINGS

Composition (parts by weight)	Appearance After Heating for 16 Hours at 625°F.	Bend Test on Heated Panel 1/8" Mandrel
DC 804	Many cracks after 8 hours	Peeled
30 #804, 2 #1260	Many fine cracks after 24 hours	Peeled
30 #804, 4 #1260	Good after 8 hours, cracks after 24 hours	Peeled
30 #804, 8 #1260	Few fine cracks after 24 hours	Cracked -- did not peel
30 #804, 1 #1260	Many cracks after 8 hours	Peeled
30 #804, 2 #5460	Cracked after 8 hours	Peeled
30 #804, 2 #1268	Good after 8 hours, cracked after 24 hours	--
30 #804, 5 #1268	Badly cracked after 8 hours	Peeled
30 #804, 10 #1268	Fine cracks after 8 hours	Adhered
30 #801, Straight	Badly cracked after 8 hours	--
30 #801, 4 #1260	Several cracks after 8 hours	Peeled
30 #801, 8 #1260	Several cracks after 8 hours	Peeled

Note: Numbers 1260, 1268, and 5460 are company designations of "Aroclors" made by the Monsanto Chemical Company.

data obtained later indicate that metallic lead was completely unsatisfactory in formulations designed for high temperature due to its oxidation. The effects of the presence of lead in high temperature coatings is clearly shown by Table V.

TABLE IV - COATINGS USING ALUMINUM, ZINC, LEAD, AND MIXTURES OF LEAD WITH ALUMINUM AS PIGMENTS

Pigment Composition (parts by weight)	Appearance After Heating to 750°F. For 16 Hours	Results of Bending the Heat Tested Sample
Aluminum	Some Chalking	Powdered
Zinc	Good	Fair
Lead	Lead Oxidized to Red Lead	Very Poor
Lead 15, Aluminum 2	Discolored and Powdery	Very Poor
Lead 5, Aluminum 5	Powdery	Poor

NOTE: Heat reactive phenolic spar varnish was used on the vehicle.

TABLE V - THE EFFECT OF LEAD IN HIGH TEMPERATURE COATINGS

Composition (parts by weight)	Appearance After Heating	Bend Test
10 Pb 5 Zn 1 Al	Flaked, Powdery	Very Poor
7½ Pb 5 Zn 1 Al	Flaked, Powdery	Very Poor
5 Pb 5 Zn 1 Al	Powdery	Very Poor
2½ Pb 2 Zn 1 Al	Very slightly Powdery	Poor
1 Pb 5 Zn 1 Al	Very slightly Powdery	Fair
5 Sn 1 Al	Good	Good

NOTE: Heat reactive phenolic spar varnish was used on the vehicle.

The pure zinc coatings appeared to have some merit, but the investigation of them was delayed in order to study systems in which some melting of the pigment would take place. It was thought that the melting would give better adherence and a denser coating with subsequent improvement in the protective power of the coating.

The first work in this type of application was performed using systems of metals which form low melting eutectics. A typical temperature composition diagram of the desired type is shown below. Interest was centered on those two component systems in which a very small percentage of one component gave a eutectic composition. A test for fusing of the various systems was made by intimately mixing ground resin with the metallic powders comprising the system, and placing these in an oven held at 750°F. for an eight hour period.

Fig. No. 3 CONSTITUTION DIAGRAM OF THE ZINC-MAGNESIUM SYSTEM

Several different mixtures of metallic powders were investigated. Particular attention was focused on the eutectics formed by aluminum-zinc, magnesium-zinc, and copper-magnesium. An investigation of the data in Table VI however, discloses that the better fusing mixtures were not those in which a eutectic is formed, but were those which contained some tin. In these latter systems, a diffusion of one metal into the other was not a requisite for low temperature melting.

TABLE VI - DATA ON THE FUSING OF METALLIC POWDER MIXTURES

Composition (Parts by weight)	Extent of Fusing After 8 Hrs. At 750°F.
10 Zinc, 0.3 Magnesium	Slight, if any
10 Zinc, 0.6 Magnesium	Slight, if any
10 Zinc, 0.3 Magnesium, 0.5 Lead	Slight, if any
10 Zinc, 0.5 Aluminum	Slight, if any
2 Zinc, 1 Magnesium, 2 Lead, 5 Bronze	Slight, if any
1 Magnesium, 10 Lead	Fused
1 Tin, 10 Lead	Fused
1.5 Tin, 10 Zinc, 0.6 Aluminum	Fused

From the table it can be seen that metallic mixtures based on the formation of a eutectic showed very poor fusion. The poor fusion could be expected since oxygen again enters the picture. In order that the eutectic mixture melt at the temperature indicated from a constitution diagram, the metallic components must be in intimate contact with each other. Oxides formed on the surface of the metals would prevent this contact. Also with metals in a finely divided state, oxidation probably occurred before melting caused a fusion on the components.

After the study of the various eutectics mentioned above, attention was turned to systems consisting of aluminum, tin and another metal. The tin was introduced because of its low melting point. It was felt that the tin would also form a carrier for the other metals in the system. The aluminum was used to aid in keeping the heavier pigments suspended and to aid in corrosion resistance. Zinc was first studied as the third component, as indications were that the zinc would form a binding medium of zinc plus zinc-tin eutectic.

Various formulations were investigated in which the tin concentration was kept constant and the amounts of aluminum and zinc were varied.

TABLE VII - DATA ON COATINGS CONTAINING TIN

Composition (Parts by weight)	Appearance After 16 Hrs. At 750°F.	Bend on Heated Panel
2 Sn 2 Al 2 Zn	Good	Peeled
4 Sn 2 Al 2 Zn	Good	Slight Chalking
6 Sn 2 Al 2 Zn	Good	Slight Chalking
8 Sn 2 Al 2 Zn	Good	Slight Chalking
10 Sn 2 Al 2 Zn	Good	Slight Chalking
12 Sn 2 Al 2 Zn	Good	Slight Chalking
6 Sn 2 Al 3 Zn	Good	Slight Chalking
6 Sn 2 Al 1 Zn	Good	Some Chalking
6 Sn 1 Al 4 Zn	Good	Slight Chalking
6 Sn 1 Al 6 Zn	Good	Very Slight Chalking
6 Sn 1 Al 10 Zn	Good	Good
6 Sn 6 Zn	Good	Good
6 Sn 3 Al	Good	Chalking

Note: Vehicle used was heat reactive phenolic spar varnish.

A higher concentration of tin was used next and the concentrations of the other two components varied in the same manner as in the first procedure. In this way it was possible to study the effect of each of the constituents as the amounts were varied through five different tin concentrations. These results are shown in Table VII. It was very difficult to distinguish visually any difference in the coatings as the tin content was varied, but it was found that increasing the ratio of zinc to aluminum definitely lessened the chalking tendency of the coating.

The properties of the aluminum, tin, zinc type coatings are as follows: A coating of this type satisfactorily passes the temperature test. It also withstands the bend test, as it neither powders nor peels off, and although soft, has good adherence and appearance. A coating of this type has been given an accelerated weathering test for a period equivalent to outdoor exposure of over three months and there was no failure. However, in a spray chamber this type of coating washed to an undesired extent, but gave better protection than a coating composed only of aluminum powder. A microscopic examination of the coating at a 400 magnification showed the following:

1. The coating consists of metallic particles bonded together to a certain extent, although the continuous metallic phase could not be distinguished.
2. The vehicle has completely volatilized.
3. Iron-tin or iron-zinc compounds were not observed on the surface of the metal panel, although small amounts could have been present.

In the light of these results, a series of panels was prepared using the two components aluminum and zinc in varying ratios. The results are shown in Table VIII and verify the above conclusion in that the presence of aluminum appears to increase the chalking tendencies of the finish. Increasing the ratio of zinc to aluminum in the finishes did not, however, appear to decrease the washing tendencies of the films. Phenolic heat reactive varnish was used in all the above formulations as the vehicle.

TABLE VIII - VARIATION OF THE PROPERTIES OF ALUMINUM-ZINC COATINGS
WITH CHANGING ALUMINUM-ZINC RATIOS

Composition (weight ratios)	Chalking Tendency After 16 Hours At 750°F.	Degree of Washing in Mist After 300 Hours
1 Zn 2 Al	Increasing ↑	Some, No Rusting
1 Zn 1 Al		Some, No Rusting
2 Zn 1 Al		Some, No Rusting
3 Zn 1 Al	Decreasing ↓	Some, No Rusting
4 Zn 1 Al		Some, No Rusting
6 Zn 1 Al		Some, No Rusting
10 Zn 1 Al		Some, No Rusting

Besides the above formulations, two other metals were used in the formulations of paints in which the vehicle is used only as a convenient means of applying a metallic film. The other two metals were cadmium and iron, and data for these films may be obtained in the appendix. The use of these two metals in the formulations brought no improvement in the coatings. However, the data on these two materials are limited and no definite

conclusions can be made at this time.

From the data it can be seen that all the finishes prepared using vehicles which volatilize tend to wash when placed in the mist chamber. In an endeavor to improve the corrosion resistance of the metallic films, silicone resin was blended with air drying glycerol phthalate and used in the formulations. It will be remembered from the previous discussion that aluminated "DC 802" gave a very corrosion resistant film. It can be seen from Table IX that the addition of "DC 802" in amounts up to 50% of the glycerol phthalate resin resulted in a great improvement in the finish. Also, the presence of glycerol phthalate in the vehicle enables much less strenuous curing conditions of the film to be used than is necessary when the straight silicone alone is used. These finishes appeared to satisfactorily meet the requirements of a heat resistant finish as set by the Navy. An aluminum-zinc pigmented material of this type containing vehicle composed of 40% silicone (50% solids) and 60% glycerol phthalate was substantially air drying, withstood a maximum temperature of approximately 800°F., satisfactorily passed a bend test, and showed very little if any washing when placed in a spray chamber for a period of 300 hours.

In conjunction with the investigation of glycerol phthalate-silicone coatings an investigation was conducted of heavy pigmented silicones. It had been observed in several tests on aluminum pigmented silicones that peeling of the panels sometimes took place on cooling of the samples, but no failure of these finishes was observed while they were at the high temperature of the test. This peeling on cooling seemed to indicate that peeling was due to a difference in the expansion coefficients of the coating

TABLE IX - SILICONE-GLYCEROL PHTHALATE COATINGS

Composition of Vehicle (parts by weight)	Pigment	Coating Thickness (mils)	Appearance After 16 Hours At 750°F.	Bend on Heat Tested Panel	Washing In Spray
Glycerol Phthalate	Aluminum		Very poor		
23 G.P., 2 Silicone	Aluminum	0.5	Fair	Fair	Rusted 24 hrs.
21 G.P., 4 Silicone	Aluminum	0.6	Good	Good	Rusted 24 hrs.
18 G.P., 7 Silicone	Aluminum	0.6	Good	Good	Rusted 24 hrs.
15 G.P., 10 Silicone	Aluminum	0.7	Good	Good	Rusted 24 hrs.
10 G.P., 15 Silicone	Aluminum	0.7	Good	Fair	Rusted 48 hrs.
7 G.P., 18 Silicone	Aluminum	0.6	Good	Fair	Rusted 200 hrs.
4 G.P., 21 Silicone	Aluminum	0.7	Good	Failed	None
2 G.P., 23 Silicone	Aluminum	0.6	Good	Failed	
15 G.P., 10 Silicone	Aluminum	3 coats 1.5 total	Good	Good 1"	Good 300 hrs.

Note: All samples were between 0.5 mil. and 1.0 mil. in thickness. The silicone used was Dow Corning #802.

and substrate. It was thought that this difference could be decreased if the expansion coefficients of the coatings were varied through the use of various amounts of metallic pigments. With this in mind, a series of coatings was prepared using aluminum, and zinc dust pigments in greater amounts than had heretofore been used. The results of these tests are indicated in Table X on the following page. It can be seen that very heavy pigmentation of the silicones resulted in coatings which did not peel on cooling. This seems to confirm the opinion expressed above that failure was due to the difference in coefficients of expansion of the coating and substrate.

If the glycerol phthalate-silicone coatings are compared with the coatings of like pigment to silicone ratios, it appears that the addition of glycerol phthalate improves the nature of the heat resistant film in respect to those quantities tested by a bend test over a mandrel. The data are by no means conclusive, but this comparison is shown in Table XI.

Other advantages the addition of glycerol phthalate have over the addition of thinner are:

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

Silicones heavily pigmented with non-metallic pigments were also investigated. Data obtained on these finishes are by no means complete, but indicate that the plating effect of metallic pigments is not essential to the formation of a satisfactory film. These data are shown in Table XII. It appears from these results that the properties of the pigment definitely influence the characteristics of the heat tested film. It can

TABLE X - ALUMINUM PIGMENTED SILICONE VARNISHES

Coating Composition (parts by weight)	Thickness mils	Appearance After 16 Hrs. At 750°F.	Bend on Heated Panel
2.0 Al 25 Silicone	0.6	Failed	
4.0 Al 25 Silicone	0.5	Failed	
6.0 Al 25 Silicone	0.7	Failed	
8.0 Al 25 Silicone	1.0	Failed	
10 Al 25 Silicone	0.6	Fair	
12 Al 25 Silicone	1.0 & 0.5	Good	Failed
12 Al 20 Silicone	1.5 & 0.6	Good	Failed
15 Al 20 Silicone	3.0	Good	Failed
20 Al 20 Silicone	0.5, 1.0, & 1.5	Good	Failed
20 Al 16 Silicone	2.5	Good	Failed
25 Al 16 Silicone	1.5	Good	Failed
20 Al 10 Silicone	0.5 & 1.5	Good	Failed
20 Al 8 Silicone	1.5	Good	Failed

Note: Dow Corning silicone number 802 (50% solids) was used in all formulations. Reynolds Metals aluminum lining number 30 was used in all formulations.

TABLE XI

COMPARISON OF GLYCEROL PHTHALATE CONTAINING SILICONES
WITH SIMILAR COATINGS CONTAINING NO GLYCEROL PHTHALATE
ON A SILICONE TO PIGMENT RATIO BASIS.

Composition of Glycerol Phthalate Containing Coating	Bend on Heated Sample (24 Hrs. At 750°F.)	Composition of Straight Silicone	Bend on Heating (24 Hrs. At 750°F.)
8 Zinc 1 Al 2 Silicone 23 Gly. Phthal.	Good	8 Zinc 1 Al 2 Silicone	Failed
8 Zn 1 Al 21 Sil. 4 G.P.	Failed by Heating	8 Zn 1 Al 20 Sil.	Failed by Heating
6 Al 4 Silicone 21 G.P.	Good	25 Al 15 Silicone	Failed
6 Al 7 Silicone 18 G.P.	Good	20 Al 20 Silicone	Failed
6 Al 10 Silicone 15 G.P.	Good	12 Al 20 Silicone	Failed

TABLE XII - NON-METALLIC PIGMENTED SILICONES

Coating Composition	Appearance After 16 Hrs. At 750°F.	Coating Thickness Mils	Bend on Heated Sample
10 TiO ₂ 20 Silicone	Failed		
15 TiO ₂ 20 Silicone	Failed		
20 TiO ₂ 20 Silicone	Failed		
30 TiO ₂ 20 Silicone	Failed		
40 TiO ₂ 20 Silicone	Failed		
15 Iron Oxide 3 Asbestine 20 Silicone	Good	0.5	Failed
20 Iron Oxide 4 Asbestine 20 Silicone	Good	approx. 1	Failed
25 Iron Oxide 5 Asbestine 20 Silicone	Good	1.0	Failed
30 Iron Oxide 6 Asbestine 20 Silicone	Good	1.2	Failed
*37 Iron Oxide 7½ Asbestine 20 Silicone	Good	1.0	Failed

NOTE: The silicone used was Dow Corning #802. The iron oxide used was Osborn #2510 Pure Black Oxide of Iron. The titanium dioxide used was Krebs Ti-Pure R-150.

- * The very heavily pigmented iron oxide samples tended to be just slightly powdery.

be noted from the data that no satisfactory coatings were obtained when using titanium dioxide pigments in various pigment to vehicle ratios, but that satisfactory coatings were obtained with iron oxide, and the metallic pigments.

In general, the heavily pigmented silicones are brittle and will not pass a bend test. In particular, the silicones containing substantial amounts of non-metallic pigment appear to be more brittle than the metallic pigmented silicones. For instance, coatings containing a pigment composed of zinc oxide and zinc dust appeared to be much more brittle than the coatings containing only zinc dust. This is easily seen by referring to Table XIII. The coatings composed of zinc dust and silicone are the only coatings of this type which are able to pass a bend test over a $\frac{1}{2}$ " mandrel.

TABLE XIII - HEAVILY PIGMENTED SILICONES

Coating Composition	Coating Thickness mils	After Heating to 750°F. for 24 Hours	
		Scratch Adhesion Test	Bend Test
20 Zn 0.5 ZnO 7 #802	1.2 & 0.8	Good	Fair $\frac{1}{2}$ " Bend
20 Zn 1.0 ZnO 7 #802	1.5 & 1.3	Fair	Fair 1" Bend
20 Zn 2.0 ZnO 7 #802	1.3	Fail	Fair 1" Bend
20 Zn 4.0 ZnO 7 #802	2.7	Fail	Fair $1\frac{1}{2}$ " Bend
20 Zn 4.0 ZnO 7 #802	2.3	Fail	Fair 1" Bend
16 Zn 2.0 Al 4 #802	1.0	Good	Fair $\frac{3}{4}$ " Bend
16 Zn 2.0 Al 7 #802	1.0	Good	Fair 1" Bend
16 Zn 2.0 Al 10 #802	0.6	Good	Good $\frac{1}{2}$ " Bend
16 Zn 2.0 Al 10 #802	2.0	Good	Fail
16 Zn 2.0 Al 20 #802	0.6	Good	Good $\frac{1}{2}$ " Bend
16 Zn 2.0 Al 20 #802	2.7	Good	Fail
10 Zn 4.0 Al 5 #802	1.0	Good	Fair 1" Bend
10 Zn 4.0 Al 5 #802	0.5	Good	
10 Zn 4.0 Al 10 #802	0.5		Fair 1" Bend

Note: #802 is a Dow Corning Silicone (50% solids).

SUMMARY AND CONCLUSIONS

Data obtained to date indicate that the following are unsatisfactory coatings:

1. Unpigmented or lightly pigmented silicones.
2. Coatings in which the vehicle is composed of chlorinated diphenyl and silicone.
3. Coatings containing cadmium sulphide pigments.
4. Coatings composed of vehicles which volatilize at high temperatures, and which contain lead pigments.

Coatings composed of a vehicle which volatilizes at 750°F. or lower, and which contain zinc dust, cadmium powder, aluminum bronze, tin powder, or various combinations of the same, appear to deposit a residual coat on heating above the volatilization temperature of the vehicle which is satisfactory in all respects but the washing tendency of said coatings. Zinc dust appears to offer considerable cathodic protection of the metal as judged by the superior performance of zinc containing coatings over the coatings in which the other metals alone are present. Aluminum pigment aids in the suspension of the heavier pigments, and appears to cause better coverage as compared with those coatings which contain no aluminum. Preliminary indications are that cadmium-zinc pigmented coatings are very adherent and weather resisting coatings.

In general, heavily pigmented silicones appear to be satisfactory in many respects but in those combinations of properties shown by a bend test. Heavily pigmented coatings containing predominantly zinc dust pigment assist in alleviating this difficulty.

Glycerol phthalate-silicone coatings appear to possess advantages over the heavily pigmented silicones, the most important of which is their ease of drying as compared with the straight silicone. Coatings have been prepared which preliminary tests indicate will satisfactorily meet all the requirements set for a high temperature coating by the Navy, but more data should be obtained on these coatings.

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APPENDIX

TABLE XIV - PROPRIETARY COATINGS

Identification Number	Material
1	AN TT V116 with AN TT A461 Aluminum Powder
2	Navy Aluminum Paint 52P19
3	Perseal #728
4	Goodyear All Weather Kote
5	Kemick #11
6	Type I AN TT E501 Heat Resisting Glycerol Phthalate
7	Type II AN TT E501 Heat Resisting Glycerol Phthalate

Suffix D indicates two coats applied as shown in the following table.

Coating	Blistering & Flaking 16 Hrs. 750°F.	Powdering 16 Hours 750°F.	Bend Over $\frac{1}{2}$ " Mandrel 16 Hrs. 750°F.	Remarks
1	None	Slight	Powdered	Chalky
1-D	None	Slight	Powdered	Chalky
2	None	Slight	Powdered	Chalky
2-D	None	Slight	Powdered	Chalky
3	None	None	Slight Powdering Outer Bend Flaked Off Inner Bend	Very Good
4	White Powdery Residue	Completely Powdered	-----	Very Poor
5	Soft Carbonaceous Residue	Very Soft	-----	Not intended For Outdoor Use
6 & 7	No Film Left	-----		

TABLE XV - PLASTICIZED SILICONES

Vehicle Composition			Parts of Pigment Per 30 Parts of Vehicle	Appearance 12 Hours at 625° F.	Bend After Heating to 625° F. for 12 Hrs.
2	#1268	40 #801	7 CdS	Poor	
5	#1268	40 #801		Poor	
5	#1268	40 #801	7 CdS	Poor	
10	#1268	40 #801	7 CdS	Good	Fair
5	#1268	30 #804		Poor	
10	#1268	30 #804		Fair	Fair
5	#1268	30 #804		Poor	
15	#1268	30 #804		Fair	Fair
5	#5460	20 #801		Fair	Fair
10	#5460	20 #801		Poor	
10	#5460	20 #801	10 CdS	Fair	Poor
1	#5460	30 #804		Fair	
2	#5460	30 #804		Fair	
4	#5460	30 #804		Fair	
4	#5460	30 #804		Fail	Fail
6	#5460	30 #804		Fail	Fail
8	#5460	30 #804	10 Al	Good	Fail
2	#1260	30 #804		Poor	
4	#1260	30 #804		Fair	
8	#1260	30 #804		Good	
4	#1260	30 #801		Fair	

TABLE XV - PLASTICIZED SILICONES (Cont.)

Vehicle Composition			Parts of Pigment Per 30 Parts of Vehicle	Appearance 12 Hours at 625° F.	Bend After Heating to 625° F. for 12 Hrs.
8	#1260	30 #801		Fair	Poor
8	#1260	30 #801	10 Al	Poor	
8	#1260	30 #801	15 CdS	Fair	
8	#1260	30 #804	10 Al	Good	Poor
1	#1268	30 #802	7 Al	Good	Fair
1	T.C.P.	40 #801		Fail	
2	T.C.P.	40 #801	7 CdS	Fair	Fair
$\frac{1}{4}$	T.C.P.	30 #802		Good	Good
$\frac{1}{8}$	T.C.P.	40 #804		Fair	
$\frac{1}{8}$	T.C.P.	40 #804	10 CdS	Poor	
$\frac{1}{8}$	D.P.P.	30 #802		Good	Fair
$\frac{1}{8}$	D.P.P.	30 #804		Poor	
1	D.P.P.	30 #804		Poor	

Note: Numbers 1268, 5460, and 1260 are Arochlors (Chlorinated Diphenyls).

D.P.P. is an abbreviation for Diphenyl Phosphate.

T.C.P. is an abbreviation for Tri Cresol Phosphate.

TABLE XVI - COATINGS CONTAINING LEAD

Pigment	Vehicle	Appearance After Heating at 750°F. for 16 Hrs.	Bend After 16 Hours At 750°F.
20 Pb	30 Phenolic Varnish	Red Lead	
40 Pb	40 Lac.	Red Lead	
15 Pb, 2 Al	30 Phenolic Varnish	Powdery	
10 Pb, 3.5 Al	30 Phenolic Varnish	Slightly Powdery	Powdered
5 Pb, 5 Al	30 Phenolic Varnish	Slightly Powdery	Powdered
5 Pb, 1 Al, 10 Zn	30 Phenolic Varnish	Good	Slight Powdering
10 Pb, 1 Al, 5 Zn	30 Phenolic Varnish	Good	Slight Powdering
0.5 Pb, 10 Zn, 0.3 Mg	Alkyd	Powdery	
10 Pb, 1 Mg	Alkyd	Powdery	
2 Pb, 1 Sn, 4 Al	Alkyd	Slightly Powdery	Peeled
3 Pb, 1 Sn, 4 Al	Alkyd	Powdery	Slight Powdering
10 Pb, 2 Sn, 1 Mg, 1 Al	Alkyd	Powdery	Slight Powdering
5 Pb, 2 Al, 1 Mg	Alkyd	Powdery	Slight Powdering
10 Pb, 2 Al, 1 Mg	Alkyd	Powdery	Slight Powdering
2 Pb, 2 Al, 1 Mg	Alkyd	Powdery	Slight Powdering
2 Pb, 2 Sn, 1 Mg	Phenolic	Powdery	Powdered

TABLE XVI - COATINGS CONTAINING LEAD (Cont.)

Pigment	Vehicle	Appearance After Heating at 750°F. for 16 Hrs.	Bend After 16 Hours At 750°F.
5 Pb. 5 Zn. 1 Mg	Phenolic	Powdery	Powdered
10 Pb. 1 Zn. 1 Mg	Phenolic	Oxidised	
1 Pb. 1 Al. 10 Zn. 5 Sn	Phenolic	Slightly Powdery	
2 Pb. 1 Al. 10 Zn. 4 Sn	Phenolic	Slightly Powdery	
3 Pb. 1 Al. 10 Zn. 3 Sn	Phenolic	Slightly Powdery	
4 Pb. 1 Al. 10 Zn. 2 Sn	Phenolic	Powdery	
5 Pb. 1 Al. 10 Zn. 1 Sn	Phenolic	Powdery	
6 Pb. 1 Al. 10 Zn. 2 Sn	Phenolic	Powdery	
10 Pb. 5 Zn. 1 Al	Phenolic	Flaked Powdery	
7½ Pb. 5 Zn. 1 Al	Phenolic	Flaked Powdery	
5 Pb. 5 Zn. 1 Al	Phenolic	Powdery	
2½ Pb. 5 Zn. 1 Al	Phenolic	Powdery	Fair
1 Pb. 5 Zn. 1 Al	Phenolic	Very Slt. Powdery	Fair
10 Pb. 5 Zn	Phenolic	Powdery	
10 Pb. 3 Al	Phenolic	Very Powdery	

TABLE XVII - COATINGS CONTAINING TIN

Samples Also Containing Lead Are Omitted Below

Pigment	Vehicle	Appearance After 16 Hours At 750°F.	Bend After 16 Hours At 750°F.
1.7 Sn 2 Al	*Alkyd	Chalky	
1.5 Sn 0.6 Al 10 Zn	Alkyd	Chalky	
3 Sn 0.6 Al 10 Zn	**Phenolic	Good	
2 Sn 2 Al 2 Zn	Phenolic	Slightly Chalky	Powdered
1 Sn 3 Al 1 Zn	Phenolic	Slightly Chalky	Peeled
4 Sn 2 Al 2 Zn	Phenolic	Slightly Chalky	Powdered Slightly
6 Sn 2 Al 2 Zn	Phenolic	Slightly Chalky	Powdered Slightly
8 Sn 2 Al 2 Zn	Phenolic	Slightly Chalky	Powdered Slightly
10 Sn 2 Al 2 Zn	Phenolic	Slightly Chalky	Powdered Slightly
12 Sn 2 Al 2 Zn	Phenolic	Slightly Chalky	Powdered Slightly
6 Sn 1 Al 4 Zn	Phenolic	Slightly Chalky	Powdered Slightly
6 Sn 2 Al 3 Zn	Phenolic	Slightly Chalky	Powdered
6 Sn 3 Al	Phenolic	Chalky	
6 Sn 2 Al 1 Zn	Phenolic	Slightly Chalky	Powdered Slightly
6 Sn 1 Al 6 Zn	Phenolic	Slightly Chalky	Powdered Slightly
6 Sn 1 Al 10 Zn	Phenolic	Slightly Chalky	Good
10 Sn 1 Al 6 Zn	Phenolic	Slightly Chalky	Powdered Slightly
10 Sn	Phenolic	Slightly Chalky	Powdered Slightly

*Alkyd - 40% Glycerol Phthalate and 60% Linseed Oil.

**Phenolic - Heat Reactive Clear Phenolic Varnish.

TABLE XVIII - COATINGS CONTAINING CADMIUM

Composition	Appearance After 16 Hours At 750°F.	Bend After 16 Hours At 750°F.
$\frac{1}{2}$ Cd 1 Al 5 Zn	Good	Slightly Chalky
1 Cd 1 Al 5 Zn	Good	Slightly Chalky
2 Cd 1 Al 5 Zn	Good	Slightly Chalky
3 Cd 1 Al 5 Zn	Good	Slightly Chalky
5 Cd 1 Al 5 Zn	Good	Slightly Chalky
7 Cd 1 Al 5 Zn	Good	Slightly Chalky
12 Cd 1 Al 5 Zn	Good	Slightly Chalky
10 Cd	Poor	
*4 Cd 1 Zn	These coatings were in general inferior to similar coatings containing aluminum which are described above. They gave fairly good protection against corrosion when placed in the mist chamber and did not show much signs of washing. The inability to obtain as fine a metallic cadmium powder as desired hindered this investigation, and might have been responsible for some of the unsatisfactory results obtained.	
*4 Cd 2 Zn		
*4 Cd 4 Zn		
*2 Cd 4 Zn		
*2 Cd 6 Zn		
*1 Cd 5 Zn		

TABLE XIX - COATINGS CONTAINING IRON

Pigment Composition	Vehicle	Appearance After 16 Hrs. At 750°F.
$\frac{1}{2}$ Fe 6 Sn 4 Zn 1 Al	30 Phenolic	Good
1 Fe 6 Sn 4 Zn 1 Al	30 Phenolic	Good
2 Fe 6 Sn 4 Zn 1 Al	30 Phenolic	Good
4 Fe 6 Sn 4 Zn 1 Al	30 Phenolic	Good

Note: The addition of iron produced no noticeable improvement in the residual film after heating to 750°F. for 16 hours in a muffle furnace, but no harmful effect appeared to be produced by its presence. A bend test was run on all the samples.

TABLE XX - SILICONE-GLYCEROL PHTHALATE

Composition of Vehicle	Pigment	Appearance After 16 Hrs. At 750°F.	Bend On Heat Tested Panel	Washing In Spray 300 Hrs.
Glycerol Phthalate	Zinc	Good	Good	
23 G. P., 2 Silicone	Zinc	Fair		
21 G. P., 4 Silicone	Zinc	Good	Good	Good, no washing on bend
18 G. P., 7 Silicone	Zinc	Good	Good	
15 G. P., 10 Silicone	Zinc	Good	Good	Good, slight wash on bend
10 G. P., 15 Silicone	Zinc	Good	Good	
7 G. P., 18 Silicone	Zinc	Good	Good	
4 G. P., 21 Silicone	Zinc	Fair	Fair	
2 G. P., 23 Silicone	Zinc	Fair	Fair	

Note: These samples were not dispersed as well as would have been liked. Small lumps were present which were very hard to break up. Also bad settling occurred.

TABLE XXI

SILICONE VARNISH HEAVILY PIGMENTED WITH ZINC AND ZINC OXIDE

Zinc oxide is added to aid in suspension of zinc
and is twenty per cent of the zinc content.

Vehicle used is Dow Corning Silicone #802.

Coating Composition	Coating Thickness	Appearance After 16 hrs. at 750° F.	Bend on Heat Tested Sample	Scratch Adhesion Test
16 Zinc, 25 Silicone	1.4 mils	Failed in spots		
	1.0 mils	Failed in spots		
20 Zinc, 25 Silicone	Approx. 1 mil	Failed in spots		
25 Zinc, 25 Silicone	Approx. 1 mil	Failed in spots		
30 Zinc, 25 Silicone	1.3 mil	Failed in spots		
35 Zinc, 20 Silicone	1.0 mil	Failed in spots		
35 Zinc, 20 Silicone	Approx. 1 mil	Good	Failed	Fail
40 Zinc, 20 Silicone	2 mil	Good	3/4 in. bend or above fair	Fail
40 Zinc, 15 Silicone	2.7 mil	Good	Fair 1" bend	Fail
	2.5 mil	Good	Fair 1" bend	Fail
45 Zinc, 15 Silicone	4.0 mil	Good	Failed	
	2.0 mil	Good	Good 1" bend	Fail

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VITA

Irvin Henry Lutz, son of Mr. Herman Eugene Lutz, and Mrs. Emma (Pakiser) Lutz, was born the sixth day of September, 1923. He received his elementary education at Isaac Shelby School of Louisville, Kentucky, and his junior high school education at Eastern Junior High School of the same city. His secondary education was obtained at duPont Manual Training High School of Louisville from which he graduated in January, 1941. He began the study of chemical engineering at the University of Louisville in September of the same year, and obtained the degree of Bachelor of Science in Chemical Engineering in November, 1945. After a period in the service of the United States Navy he further pursued his studies of chemical engineering in the Graduate School of the University of Louisville from which institution he received the degree of Master of Science in Chemical Engineering in 1947.