WADC TECHNICAL REPORT 54-209

SURFACE TREATMENTS OF LOW ALLOY STEELS

SAM TOUR

SAM TOUR & COMPANY, INC.

NOVEMBER 1954

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-406
PROJECT No. 7351

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
500 - 15 March 1955

FOREWORD

This report was prepared by Mr. Sam Tour of Sam Tour & Co., Inc. under Contract No. AF 33(616)-406. The contract was initiated under Task No. 73512 (formerly RDO No. 619-11, "Critical Materials") and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center with Lt J. R. Miller acting as project engineer.

ABSTRACT

This report is to be used as a guide to Air Force Contractors in the selection of surface treatments of low alloy steels for corrosion and oxidation resistance at a minimum expense in critical materials. Forty metallic and nineteen paint types of heat resistant coatings applicable to plain carbon and low alloy steels are described and evaluated. Relative temperature, corrosion and abrasion resistances are given. Effects on base metal, formability of coated steel, weldability, joining characteristics and costs per square foot of surface coated are shown. A brief description is given of the processes used for applying and the nature of each of the coatings. Available information and sources of supply are given.

The scope of the protective treatments field is too broad to include all coatings; however, as many coatings were covered as possible. Further, because of the specialized applications involving combinations of elevated temperatures and corrosive environments mentioned in this report, many treatments were evaluated in applications for which they were not intended. Therefore it is not to be assumed that the results tabulated herein are equally valid for other applications or conditions of test.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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CHAPTER I

INTRODUCTION

Throughout the history of the aircraft industry, the use of carbon and low alloy steels for airframes, accessories and conventional piston engines has been both successful and extensive, at least until relatively recent times. With the introduction of gas turbine and jet powered aircraft, there have been many new material problems, particularly in connection with heat resistance, and there has been an understandable tendency to find solutions in the highly alloyed steels, the nickel and cobalt base alloys, and other rich and expensive materials.

Past experience indicates that something less than complete objectivity is sometimes shown in the selection of materials. Procurement, production, engineering efficiency and other considerations warrant material standardization to the greatest possible extent, but standardization rarely justifies the use of materials of excess cost nor can it justify the use of materials actually or potentially in short supply.

The development of the highly heat resistant and corrosion resistant alloys has been and continues to be a fine tribute to metallurgical science. As far as is known today, the high-performance turbine engines would not be in existence if the so-called super alloys had not been available for certain of the components. Alloys capable of withstanding even higher temperatures are apparently necessary for future engines. All parts are not exposed to the most severe conditions, however. Temperature and corrosion conditions vary considerably and there are many places where a "second look" should be taken to determine if a super alloy is actually needed.

Conservation of some of the strategic metals used as ingredients in the rich alloys is, of course, a prime reason for careful examination of requirements. Many manufacturers are highly cooperative in this regard. The recent development of lean alloy steels containing titanium and boron which have good strength characteristics at 1200°F is quite timely. Such steels should prove attractive alternates for the more critical ones for a number of applications.

In general, the use of carbon and low alloy steels whenever possible is good engineering, not only from an original cost standpoint, but as a matter of manufacturing satisfactoriness and serviceability as well. Carbon and low alloy steels are rarely "tricky" materials. The general knowledge that their forming, welding, machining and other characteristics are often superior to those of the highly alloyed steels merits repetition. Embrittlement at moderately high temperatures is rarely a problem.

It is a well known fact that the carbon and low alloy steels require surface protection if exposure to corrosion or oxidizing environments is expected during service. For many years a relatively brief list of finishes, such as cadmium plating, zinc chromate primers and the spar varnish base enamels were adequate for a large percentage of the applications. Today, the need and the list of available finishes is considerably larger.

Several ceramic coatings have been developed during the past few years by various independent and government agencies. These ceramic coatings are being exploited at length for possible use in aircraft engine parts. While ceramic coatings have their place, it is felt that a number of other types of coatings are more useful for certain applications than ceramic coatings. No one universal coating suitable for all base materials for all types of service should be expected. Where the coating is expected to come in contact with the products of combustion of fuels containing tetraethyl lead, there is need for a coating which will be resistant to the lead compounds and to the bromine and bromide compounds present. Where the conditions are severely oxidizing, it is necessary that the coating system be one which will resist these oxidizing conditions and at the same time be impervious so that the base metal underneath will be protected. Where high velocities of gases are encountered, it is necessary that the coating have adequate resistance to the erosive action which occurs.

Where the coating is to be used on plain carbon or low alloy steels, it is obvious that the coating need not be resistant to higher temperatures than that at which such low alloy or plain carbon steels can be used. Engine parts which reach operating temperatures of 1400 or 1500°F and above, must be made of materials which will have adequate physical properties at these elevated temperatures. The ordinary low alloy and plain carbon steels are entirely too soft at such temperatures. In the lower temperature field, that is in the range of temperatures from 400 to 1200°F, there are numerous parts of aircraft engines which are currently made of stainless or high alloy materials because of the need for resistance to oxidation, corrosion and erosion within this temperature range. In this field of temperatures, a low alloy steel or plain carbon steel might be used if a suitable surface treatment could be found and applied to it.

Any coating used in the manner indicated above for protection against oxidation and corrosion at slightly elevated temperatures must also be resistant to failures as a result of temperature changes, expansion and contraction, mechanical shock and vibration in service. In some parts, the fabrication problem requires that the coating be applied after the part is fabricated. In these cases, the coating must be capable of being applied to the surfaces which must be protected and must be applied in a practical and economical fashion.

Under a research and development contract with the Air Forces, Sam Tour & Co., Inc. gathered the material necessary for the preparation of this manual on "Surface Treatments of Low Alloy Steels" for the purpose of reducing the content of nickel and other critical metals in engine and aircraft components.

The manual is intended to be used as a guide to Air Force Contractors in the selection of surface treatments of low alloy steels for corrosion and oxidation resistance. It is, therefore, a compilation of information and data. It includes general descriptions of techniques, analysis of temperature ranges to which each technique is applicable, cost and life limitations of each treatment, possibilities of treatment of assemblies, formability and weldability of materials treated before assembly. Also, it includes lists of sources or facilities where each of the surface treatments can be accomplished.

The manual also includes an analysis and evaluation of all data and observations with particular reference to optimum applicability of the various treatments and techniques and their present and potential future use and distribution in industry.

The survey is comprehensive with respect to types of coatings. Particular emphasis is placed on aluminum coatings, nickel coatings, diffusion coatings (siliconizing, chromizing), miscellaneous metallic coatings and certain heat resistant paints. Ceramic coatings are beyond the scope of the manual.

In the gathering of the above information, many manufacturers of airplanes, engines, engine components, heat exchangers and related equipment were visited. Also, visits were made to facilities for surface treatment of steel and to laboratories conducting research on evaluation of surface treatments.

One of the principal problems encountered in connection with the gathering and tabulating of the information contained in this manual was that of obtaining corroborative information in the form of service verification of the numerous claims made for many of the coatings studied. Many over optimistic statements and much wishful thinking of proponents and of sales literature in connection with some products and some surface coating processes were not confirmed by industry service performance data. In many cases the claimants referred to specific users and when those specific users were contacted they did not confirm the claims made. Since the manual is intended as a guide for the selection of surface treatments, it must be factual, candidly critical and conservative in nature. It has been necessary to reject many unsubstantiated claims and to tone down many other claims. If errors have been made it is hoped that they are on the conservative side and that the surface treatments involved are better rather than inferior in performance.

The surface coating field is rife with processes and products involving so-called "trade secrets" and "secret formulations". Many materials are sold under trade names with little or no assurance from the manufacturer that the formulation will not be revised within the near future. An example is in the silicone paint field, where individual manufacturers refuse to state what silicone resin is used or even the approximate quantity of such resin used in their products.

This manual is not intended as a listing of approved or qualified products by trade names. An effort has been made to avoid reference to trade names of any products involving "secret formulations" or a listing of manufacturers of such products. No doubt certain useful and commendable products have been excluded due to this refusal upon the part of their manufacturers to describe them in an adequate manner and remove them from the "secret formulation" category.

In this manual no attempt is made to single out what aircraft engine parts are being made of high alloy heat and corrosion resistant metals where strength at elevated temperatures is not the reason for their use. Similarly, this manual does not attempt to tabulate what aircraft engine parts reach what operating temperatures. For ease of handling and because no one surface treatment may be expected to be the universal answer to all requirements, the operating temperature ranges of 400 to 600°F, 600 to 800°F, 800 to 1000°F, 1000 to 1200°F, and 1200°F and above have been selected on an arbitrary basis. Temperatures below 400°F are not considered as within the scope of elevated temperatures as covered by this manual. Temperatures much above 1200°F, certainly 1400°F and above, are beyond the range where plain carbon or low alloy steels may be expected to have sufficient inherent strength to hold their shape, irrespective of surface protection.

In studying service histories of various parts, specific instances have been found where low alloy or plain carbon steel parts have been tried in service with various types of surface coatings. Some parts have failed, due to oxidation, some due to corrosion and some due to inherent weakness of the base metal, while some parts have given fully satisfactory service. It has become quite clear that many tail pipes, some combustion chamber liners and many heat exchanger parts could be made of low alloy or plain carbon steels if given suitable protective treatments. However, no abstract generalizations are possible. Each part is a structure in itself and must be considered individually and in the light of as much information as possible. This consideration must be left in the province of the design engineer. This manual is intended to assist him by pointing out the conditions he should consider, the various types of surface treatments which might be adaptable and the advantages and disadvantages of each such treatment. The ultimate decision as to which combination of base metal and surface treatment system to use is and must be his responsibility.

The degree of resistance to corrosion, oxidation and/or erosion required to be provided by a surface treatment applied to a plain carbon or low alloy steel is a function of the service conditions to be encountered. The relative severity of corrosion versus oxidation and versus erosion conditions involved in a particular part must be evaluated by the design engineer in order that a satisfactory surface treatment may be selected. In discussions of these various factors of service conditions and of the resistant properties of surface treatments, the terms used must be understood clearly. A glossary and definition of terms as used in this manual are given in Appendix I. Where possible, the definitions used are those given in the Corrosion Handbook of the Electrochemical Society and the Metals Handbook of the American Society for Metals.

Aircraft engine parts may be subject to any or all of the following eight conditions, and the surface treatment must be such as to offer protection to the base steel under those conditions.

1. Elevated temperatures only in uncontaminated air. For this condition, the surface treatment required is one that offers protection from oxidation attack only, but it must have adequate adherence to withstand repeated cycles of temperature between below zero and the elevated temperature involved. This simple case is rare.

2. Elevated temperatures in uncontaminated air plus condensation of moisture (dew) during time intervals between operations. For this set of conditions the surface treatment required must provide protection from oxidation, have adequate adherence and provide corrosion protection, when moistened with condensate. This case is fairly common.

3. Elevated temperatures in air contaminated with products of combustion (exhaust gases) of fuels not containing tetraethyl lead or similar additions plus condensation products from these exhaust gases plus condensation of moisture during time intervals between operations. Although the fuel used contains no tetraethyl lead addition it may contain traces of sulphur, sodium, and vanadium. These contaminants appear in the products of combustion as sulphur dioxide (SO_2), sodium sulphate (Na_2SO_4) or vanadium pentoxide (V_2O_5). The products of combustion of all liquid fuels contain moisture and carbon dioxide as well. As the exhaust gases cool the vanadium pentoxide and the sodium sulphate condense and deposit on surfaces still at quite high temperatures. As the gases cool further, some of the water condenses and carries with it some of the sulphur dioxide. Depending upon the sulphur content of the fuel, the condensate from the exhaust gases may carry from 0.008 to 0.024 grams of sulphate per 100 ml of condensate. Below 100°F the condensate may contain sufficient sulphurous acid (SO_2 in solution) to have a pH ranging from 2.4 to 2.9.

4. Elevated temperatures in air contaminated with products of combustion (exhaust gases) of fuels containing tetraethyl lead or similar additions. These addition agents will appear in the products of combustion (exhaust gases) as lead oxide, lead sulphate, lead bromide, hydrobromic acid and free bromine. The bromine content of the condensate may vary from 0.13 to 0.49% and the lead content from 0.05 to 0.33%. The bromine and lead contents may be in any of the forms or combinations indicated above. During cooling of the exhaust gases a fractionation type condensation occurs in which the lead oxide condenses first, the lead sulphate next, then the lead bromide and finally the hydrobromic acid and free bromine together with the water. Here again, the condensate may be highly acid in nature.

In either case 3 or case 4 above, the surface treatment system used must provide protection against oxidation at the elevated temperatures reached, have adequate adherence for the temperature cycles involved, provide corrosion protection against the acid condensate and provide corrosion protection when the acid condensate is further diluted with moisture condensed from the air.

5. Any one of the conditions 1, 2, 3, or 4 plus erosion due to turbulent air or exhaust gas flow plus particulate solid matter or droplets of liquid entrained in the air or exhaust gases. For this added erosion condition of service superimposed on the temperature and corrosion protection, the surface treatment must have adequate wear resistance.

6. Any or all of the conditions 1 to 5 inclusive plus thermal shock. Ground temperatures may be as low as minus 65°F. Parts may heat rapidly to their operating temperature when the engines are started. Parts may cool rapidly from operating temperatures towards ambient temperatures when engines are stilled. The surface treatment must be such as to withstand these thermal shocks. Coatings must not crack or lose their bond due to these thermal shocks.

7. Vibration superimposed on any or all of the conditions 1 to 6 inclusive. For resistance to vibration the coating or surface treatment must have adequate adherence and must not be so brittle as to crack or peel as a result of vibration within the limits that the base metal is durable and will be required to withstand in service. As adherence and resistance to vibration are superior in thin coatings, the tendency is to use as thin a coating system as possible and that will still provide the oxidation, corrosion and erosion requirements. Where vibration is encountered, the effect of a surface coating on the fatigue properties or endurance limit of the part must be considered. Hard and brittle surface coatings integral with the surface metal may be prone to the initiation of fatigue cracks and early failure. Surface coatings in tension as deposited may reduce endurance limits appreciably. All these factors must be considered in the selection of the surface treatment to be used on any particular part.

8. Splash of hydraulic oils, lubricating oils and liquid fuels in addition to any or all of the conditions 1 to 7 inclusive. Some of the hydraulic oils are excellent paint strippers for many of the usual types of paints. For parts that may be subject to contact or splash with oils or fuels, the surface treatment or coating must be selected accordingly.

It is evident from the above, that the design engineer must know the service conditions to which each particular part is to be exposed before he may select an appropriate material of which to make a part and a suitable surface treatment to apply to that part. This manual has been prepared in an effort to assist in the selection of suitable surface treatments. It is not intended as a fear breeder to cause the design engineer to avoid surface treatments. Usually fear is based on lack of knowledge. It is hoped that this manual will supply some of the knowledge needed for the intelligent selection of proper surface treatments.

The various types of coatings (other than ceramic) that might be considered as useful in the surface treatment of plain carbon and/or low alloy steels for use in aircraft engine parts are quite numerous. In order to describe and compare them, some basic classification was thought necessary. The idea of classification by temperature ranges of applicability was considered and discarded as too confusing. The idea of classification according to metal or material of the coating has been used in part and a classification based on the general nature of the process of application has been used in part.

The inclusion in this manual of any specific coating is not to be considered as a recommendation of that coating for general consideration. Some, for example, such as electroplated aluminum and vacuum evaporated aluminum, have been included because certain requests for information about them were voiced by representatives of some of the aircraft engine builders and others. In view of this interest, it was deemed advisable to round out this manual for the benefit of the design engineers by the incorporation of such items in the various applicable chapters.

All types of aluminum coatings are described in one chapter. All types of nickel and nickel alloy coatings are described in another chapter. Separate chapters are devoted to "Diffusion Coatings", "Miscellaneous Metallic Coatings" and "Paint Coatings". The classes of coatings are evident in the Table of Contents and in the succeeding chapters of this manual.

It will be noted that chromium plating followed by heating to a temperature high enough and for a time sufficient to cause alloying and diffusion is included in the chapter on diffusion coatings rather than along with simple chromium electroplating. On the other hand, corronizing is included in the chapter on nickel coatings rather than with diffusion coatings. During the heat treatment following the electroplating, some alloying and interdiffusion does occur. However, it is primarily within the electroplated metals rather than with the base metal, even though some degree of alloy bonding may result.

Nine types of miscellaneous metallic coatings are grouped in a separate chapter. Six of them are electroplated metallic coatings and three are coatings produced by other methods.

All paint coatings are treated in one chapter. It is unfortunate that the paint descriptions cannot be given in more specific terms. The general refusal of the paint manufacturers to disclose even general formulations is the primary cause of this lack of specific data.

The final chapter is devoted to comparisons of the many coatings and coating systems as to their various physical characteristics, applicable temperature range, adaptability to fabrication, and relative costs.

Throughout the various chapters, references to pertinent sources of information are given in figures in parentheses. These figures refer to the bibliography, Appendix II. No attempt has been made to compile a complete bibliography on all of the literature on all of the coatings.

CHAPTER II

ALUMINUM COATINGS

Section 1. General Discussion

That aluminum coatings on iron or steel would provide high resistance to oxidation and scaling at elevated temperatures has been well known for at least forty years. One of the earliest commercial applications was the hot dip coating of the thin sheet metal and wire support parts for Welsback incandescent gas mantles. About the same time that this first hot dip method was developed, the dry retort method was developed. Both methods were referred to as calorizing. From 1915 to date, the literature on various methods of applying aluminum coatings to iron and steel and on the oxidation protective values of such coatings is enormous.

That small percentages, four percent or over, of aluminum in iron give an alloy with good oxidation resistance properties was shown over 20 years ago.(1) Iron with 8% aluminum was found to be superior to 80% nickel 20% chromium alloys. That aluminum diffuses into iron, forms a compound with iron and goes into solution in iron has been known also for over forty years. A logical operation to produce an oxidation resistant surface on iron or steel is to add some aluminum to that surface in such a manner as to cause it to be partially alloyed or combined with the iron at the surface.

That aluminum coatings on iron or steel offer considerable in the way of corrosion protection was proven over 30 years ago in connection with aluminum coating by metallizing or spraying. For corrosion protection, it is necessary to have some free aluminum present on the surface as distinguished from high temperature oxidation protection where only a small percent of aluminum alloyed with iron is necessary for protection. The iron aluminum compound which forms on the surface of iron or steel in the usual calorizing processes gives some corrosion protection but does not provide complete protection. An aluminum coating on iron or steel for protection against corrosion in the presence of moisture must contain some free aluminum, unalloyed and uncombined with the basis metal. In the presence of moisture, aluminum is anodic to iron (i.e. aluminum is a sacrificial metal) and protects the iron by being corroded itself. Because of its sacrificial nature, the aluminum coating need not be pinhole free. In this respect, the wet corrosion protection of iron provided by aluminum is similar to that provided by zinc coatings.

From the above, it is obvious that combined high temperature oxidation and wet corrosion protection of iron or steel should be obtained by aluminum coating in such a manner as to give both iron-aluminum alloying and free or uncombined aluminum on the surface. Many processes have been developed for accomplishing these results. If the aluminum for the coating is applied to the surface of the iron or steel at a low temperature, only corrosion protection is obtained. If such an applied aluminum coating is then heated under suitable protective conditions until it is partially alloyed or combined with the iron, the result is a coating that combines corrosion protection with high temperature oxidation protection. If the aluminum for the coating is applied originally at a temperature at which partial alloying is obtained, the result is both corrosion and oxidation protection. If the method of application or later service condition results in all of the aluminum in the coating being in the state of iron aluminum compounds or in solution in the iron, only oxidation protection is provided.

The aluminum coating may contain four different zones. Starting from the exterior surface they are: 1) aluminum oxide, 2) pure aluminum or aluminum alloy as deposited, 3) iron-aluminum compound, and 4) solid solution of aluminum and iron. The thickness and proportions of the zones formed are a function of the temperature of the process and subsequent heat treatment. Zone 3, iron-aluminum compound, is composed of brittle intermetallic compounds, largely $FeAl_3$ with about 57-59% aluminum, which have refractory characteristics affording protection against scaling by oxidation. Zone 4, oxidation resistant iron-aluminum solid solution, contains up to 35% aluminum.

Aluminum coatings may be created on the surfaces of iron or steel articles by painting them with suitable aluminum powder pigmented paints and heating under such controlled conditions that the aluminum alloys with the steel as the paint vehicle burns away. This procedure is the basis for many of the so-called heat resistant aluminum paints on the market. The quantity of aluminum which may be applied to a surface by this method is limited, the burning in an alloying process tends to be spotty, the final result tends to be a non uniform combined aluminum layer of limited thickness with little free aluminum remaining. Some reasonable oxidation resistance is obtained, but the corrosion resistance remaining after the heating operation is limited.

Aluminum coatings have been applied to iron and steel surfaces by a replacement reaction in the vapor state. When aluminum chloride vapor is brought in contact with iron at a temperature of 1400' to 2000°F, aluminum in the vapor is replaced by iron and the free aluminum is deposited on and becomes alloyed with the iron. United States patents along this line were issued in 1924 (Weber, 1,497,417) and in 1930 (Martin 1,770,177). The coatings formed are almost fully alloyed and provide excellent protection against oxidation at elevated temperatures. The nature of the replacement reaction precludes the deposition of an additional layer of free aluminum so that ample wet corrosion protection is not obtained.

A similar replacement reaction type of aluminum coating is obtainable by immersion in a molten salt bath consisting of sodium chloride and aluminum chloride. In this process, the low boiling point of aluminum chloride is a great disadvantage and causes almost insurmountable difficulty for commercial application. The coating result is similar to that obtainable from the vapor phase method and is subject to the same limitations.

Seven other methods for affixing an aluminum coating to iron or steel are described in the following sections of this chapter.

Section 2. Aluminized Sheet Steel

Sheet or wide strip steel given an aluminum coating by hot dip plus a rolling process is called aluminized sheet steel. Aluminized sheet steel, as a raw material for fabrication into articles, is in commercial production. The material is available in both flat and coil form in thickness from 0.0155" to 0.1124" in widths up to 36", in soft satin or extra smooth finish. The aluminum coating is on both surfaces and is about 0.001" in thickness.

The production process is a continuous one. Cold rolled steel is precleaned, then preheated in a controlled atmosphere and is then passed through a bath of molten aluminum kept under a controlled atmosphere. In the bath, the aluminum wets and alloys with the surfaces of the steel. As the strip emerges from the bath and while the aluminum is still molten, the strip is passed between rolls which squeezes off the excess aluminum and leaves a smooth uniform coating.

The corrosion and high temperature oxidation resistance of aluminized sheet steel are substantially the same as for steel coated by the various hot dip processes described in Section 4 of this chapter.

The general characteristics of the alloy layer formed, the depth of alloying, the quantity of iron aluminum compound present, the diffusion of the aluminum during subsequent heating, etc. for aluminized sheet steel are the same as for coatings formed by the hot dip processes and are also given in Section 4.

Aluminized sheet steel is being used in the manufacturing of parts of objects or whole objects where resistance to corrosion and high temperature oxidation are necessary.

The aluminized sheet will withstand cold bending 180° over a diameter equal to twice its own thickness without peeling or flaking of the coating.

Joining

Aluminized sheet steel can be joined by any of the following processes:

1. oxyacetylene welding,
2. electric arc welding,
3. spot welding,
4. seam welding,
5. atomic hydrogen arc welding,
6. inert gas metal arc welding,
7. brazing using special rods and fluxes and either the carbon arc or oxyacetylene torch,
8. soldering; here, however, difficulties of "wetting" the coating exist due to the presence of aluminum oxide.

The manufacturer claims that all types of welding have been used successfully.

Costs

Following are examples of costs of aluminized sheet steel coated on both sides.

For a sheet coil 36" wide, 0.0655" approximate mean thickness, minimum order 10,000 lbs., $9.475 per 100 lbs. Per unit area, the cost is approximately $0.252 per square foot of sheet.

For a sheet coil 36" wide of 0.0186" approximate mean thickness, minimum order 10,000 lbs., $14.67½ per 100 lbs. Per unit area, the cost is approximately $0.102 per square foot of sheet.

Availability

Aluminized sheet steel is produced by the Armco Steel Corp., 3050 Curtis Street, Middletown, Ohio. Further information is available from them or their sales offices throughout the country.

Section 3. Aluminum Clad Steel

Aluminum clad steel is the product of a process of placing a surface sheet or plate of aluminum on iron or steel and applying pressure, mechanical work and heat sufficient to create an alloy bond. The method is referred to, often, as the sandwich rolling method. The cladding can be applied to one or to both surfaces of a slab or flat bar. The process is not adaptable to the production of rounds or to heavy plate. Since the process does not involve molten aluminum in contact with the iron or steel, the amount of iron aluminum compound formed at the interface is less than for any of the molten aluminum methods for producing an aluminum coating. If the mating surfaces of both the iron and the aluminum have been properly cleaned of all oxides, have been adequately protected from oxidation during heating and if the pressure and mechanical work during the first passes in the rolling mill are sufficient, the result is a well bonded bi-metal. The bond is an alloy bond of a strength equal to the strength of the aluminum. If all the conditions are not correct, the two metals are only mechanically bonded. The areas with only a mechanical bond are prone to blister, buckle, lift or peel.

The thickness of the aluminum layer is varied with respect to the iron layer to produce a composite of the desired ratio. Whereas the hot dip methods of producing an aluminum coating are limited in the thickness of the coating of free aluminum that can be obtained, the cladding method is not limited.

The aluminum cladding of iron or steel was developed in Europe where the product is known under the names of Feral and Feran. A similar product is being produced by at least one company in this country.

It is obvious that the temperatures used to create a bond in the hot sandwich rolling method must not only be below the melting point but also below the hot short range of the aluminum or aluminum alloy used. The hot rolling temperatures are limited to a maximum of 900°F. Annealing after hot rolling or between subsequent cold rolling reductions, limited to about 1000°F, produces additional bonding of the aluminum to the iron.

The hot rolling operations are carried out in what is commonly considered as the blue heat range. The basis iron or steel used, therefore, must not be subject to "blue brittleness". After the initial hot rolling to obtain bonding is completed, further reductions are by means of cold rolling. Iron and steel work harden very rapidly. The aluminum layer limits the annealing temperatures that may be used. Full annealing of the steel is impossible. Dead soft or a deep drawing grade of aluminum clad steel is not possible.

To promote the alloy bonding during the process, various types of preparation of the mating surfaces of both the aluminum and the steel may be used. A thin electroplate of pure iron or a thin electroplate of silver are two such methods.

Corrosion Resistance

The corrosion resistance characteristics of the aluminum surfaces on aluminum clad steel depends upon the purity of the aluminum, assuming that the aluminum layer is not perforated. High purity aluminum (99.5% or above) is superior for severely corrosive conditions. Normally, such high purity aluminum is not used. The coatings are completely nonporous and uniform and their corrosion resistance is that of the aluminum surface.

Oxidation Resistance

No data are available on the oxidation resistance at elevated temperatures of aluminum clad steel. It is believed, however, because of the nonporous nature of the aluminum layer, that the resistance is high at temperatures up to the melting point of the aluminum layer.

With thin coatings, 0.0005" for example, the aluminum appearance of the surface becomes lost and the surface becomes darkened on exposure to temperatures of the order of 1200°F. This is believed to be the result of the formation of an iron aluminum compound.

The formation of the iron aluminum compound is retarded by the presence of silicon in both the steel and in the aluminum. For this reason, silicon containing low carbon steel and silicon-aluminum alloys may be used in combination to produce aluminum clad steel.

Erosion and Abrasion Resistance

No data are available on the erosion and abrasion resistance of the coating. It is obvious that these properties are in the aluminum layer itself and are dependent upon the aluminum alloy used to produce the coating.

Joining

Joining of aluminum clad steel might present some difficulties arising from the exposing of the base metal at joints or where holes are drilled. Some of these difficulties can be avoided by proper designing. Spot welding is being done successfully. If the thickness of the aluminum layer on the surface were reduced to that on aluminized sheet steel, as described in Section 1 of this chapter, all of the methods of joining described therein might be usable. Such thin coatings on aluminum clad steel are not unusual.

Mechanical Properties

The manufacturer of aluminum clad steel in this country states that the physical properties of the product 0.005" thick, with aluminum layers of 0.0005" on each side, are:

1.	Rockwell Hardness 15T	- 82
2.	Erichsen Cup Test (14 mm ball)	- 5.0 mm
3.	Ductility - $\frac{1}{2}$" die, $\frac{1}{4}$" punch	- 0.110"
4.	Springback after 90° bend	- 22°

Uses

Aluminum clad steel is being produced in widths up to 12". It has found considerable use in heat transfer applications. It is reported being used for heat exchanger tubes, component parts of space heaters, water heaters, cooking ranges and toaster parts. It is reported used also for firewalls in aircraft.

Costs

The current prices quoted, by the one producer in this country, of aluminum clad steel are approximately as shown below for 8" wide strip with 10% aluminum cladding on each side.

$0.18 per sq. ft. of 0.005" thick sheet
$0.24 per sq. ft. of 0.007" thick sheet
$0.36 per sq. ft. of 0.010" thick sheet

Actual prices depend upon quantities, widths and finish. The above prices were calculated from net prices per pound.

Availability

Aluminum clad steel is available in this country from Metals and Controls Corporation, General Plate Division, Attleboro, Massachusetts.

Organic Solvents Methods

Two plating bath compositions have been developed, as follows:

A. Plating bath composition: 32% (by weight) of a fusion product of 1 mole of ethyl pyridinium bromide, plus 2 moles of aluminum chloride, 67% toluene (sp. gr. 0.866), plus 1% methyl t-butyl ether. Temperature of plating bath: 86°F. The direct current density on the cathode: 10-20 amps per sq. ft. A superimposed alternating current of 1.5 to 2.5 volts improves physical characteristics of the deposit.(24)

B. Plating bath composition: 265 to 400 g. of aluminum chloride in 1 liter of ethyl ether, plus lithium hydride or lithium-aluminum hydride in concentrations of 4 to 8 g. per liter. The bath is operated at room temperature. Current densities up to about 50 amps per sq. ft. Anode and cathode efficiencies are about 100%.(25) The bath is in a closed container to prevent the entrance of moisture. A glass vessel with a polyethylene lid is best. Anodes of aluminum rod pass through the lid. The objects to be plated are introduced and removed through a central hole in the lid which is kept closed during plating. Agitation is undesirable as it raises particles which get entrapped in the plating. The bath is reported to deteriorate quickly due to ingress of air and moisture and must be replenished.

Molten Salt Method

Plating bath composition: 80% aluminum chloride (anhydrous), 20% sodium chloride, 350°F operating temperature, 15 amps per sq. ft. current density. Small objects can be plated in pyrex container. Large objects can be plated in 2S aluminum tanks, with 2S Al anodes. Throwing power of the bath is poor. Auxiliary anodes have to be placed inside or near the recesses in the objects to be plated. Aluminum chloride must be added frequently to replace losses from fuming and hydrolyses. Rate of deposition is about 0.3 g. per amp hour or 0.0004" in thickness in 30 minutes at 18 amps per sq. ft. Current efficiency is about 80%. With agitation, the deposition is faster but current efficiency is reduced.(26)

Characteristics of the Deposits

Electrodeposited coatings of aluminum vary considerably in appearance and physical properties, depending upon slight variations in the composition of the plating bath and operating conditions. These processes are still in the experimental stage. Many compounds were added to the bath in attempts to improve the properties of the coatings and some successful results obtained. For example, chromium compounds are reported to give semi-bright, strong, springy deposits; lead and tin compounds, formates and cyanides yielded good matte deposits. The deposits were smooth up to a thickness of 0.003". When they become thicker, they increase in roughness and, beyond a thickness of about 0.005", they grow into a mass of nodules.(25) The throwing power of fused baths is poor.

2. The vacuum deposits are porous. As such, they must be "seal-treated" to close the pores before being used for protection against corrosion or high temperature oxidation.

3. The process is not adaptable to objects of all shapes. The vaporized aluminum travels in straight lines and any area which is shadowed from the source of evaporation of aluminum may remain uncoated.

4. The abrasion or erosion resistance and durability of vacuum deposited aluminum may be inferior.

Facilities and Sources of Additional Information

Additional information on vacuum coatings and vacuum coating equipment can be obtained from:

1. F. J. Stokes Machine Co.
   Philadelphia 20, Pa.

2. Distillation Products Industries
   Rochester 3, N.Y.

3. National Research Corporation
   Cambridge, Mass.

4. Consolidated Vacuum Corporation
   285 Madison Avenue
   New York, N.Y.

The above manufacturers, upon request, will supply lists of facilities in specific areas of the country.

Section 8. Electroplated Aluminum

Aluminum, an alkaline earth metal, is one of the "hard-to-plate" metals. It cannot be deposited from aqueous solutions because it is so much less noble than hydrogen.

The two general methods by which aluminum can be electrodeposited are:

1. Deposition from organic solvent solutions.
2. Deposition from fused salt baths.

Surface Preparation Required

The steel parts to be plated should be cleaned using an hydrochloric acid solution, rinsed and wiped dry.(26)

The adhesion of vacuum deposited coatings is purely mechanical; no alloying of any kind takes place during the deposition. Many factors influence the adhesion of the deposits.(18) The most important among them are: the surface preparation, the vacuum obtained, trapping media and the intensity of deposition. Heavy films have a tendency to peel.(20) Some authors(19,22) state that vacuum deposits have poor abrasion resistance as compared to electrodeposited coatings. However, it should be pointed out that they were comparing thin vacuum coatings with electrodeposited coatings of much greater thickness.

When thick coatings of aluminum are created by vacuum deposition methods, the process becomes more expensive. A considerable amount of the aluminum that is vaporized does not deposit on the surfaces desired to be coated and so is wasted.(19)

Since no alloying takes place during the deposition, vacuum deposited aluminum coatings consist exclusively of one layer of the aluminum or aluminum alloy which was evaporated. Some amount of aluminum oxide is believed to be present in the coating.(20)

If an alloy bond is desired between a vacuum evaporated aluminum deposit and a steel surface, it might be obtained by a fusion of the aluminum in situ and under proper conditions. To accomplish such bonding or alloying, the aluminum must be of sufficient thickness that it will completely wet the surface when molten and the aluminum must be protected from oxidation during the fusion process. Information with respect to fused aluminum coatings is contained in Sections 1, 2, 4 and 5 of this chapter.

No information or data were found on the application of vacuum deposited coatings for corrosion or high temperature oxidation resistance. There is no reason to believe, however, that, with the present development of high vacuum techniques, the process cannot be used to produce coatings for limited corrosion and high temperature oxidation resistance.

Costs

Initial costs for vacuum evaporation equipment for commercial scale production are quite high. Operation costs can be quite competitive with other means of coating if very thin coats are permitted. For example, thin evaporated aluminum coatings on thin acetate sheet have been stated to cost only $0.06 per square foot.(21)

Where coats of sufficient thickness for corrosion or oxidation protection are desired, the costs would be at least ten times as high. However, no direct cost figures are available on evaporated aluminum coatings on steel.

Limitations

1. The process is limited to comparatively thin coatings up to 0.001" thick. Thicker coatings have poor adherence.

After this order of vacuum has been reached and maintained, to assure the degasification of the surfaces, the aluminum is evaporated and it deposits on the objects located near the point or place of evaporation. Commercially pure, 99+%, aluminum is used. The aluminum is evaporated from direct resistance heated coiled tungsten filaments, from a high voltage arc or from a crucible where the aluminum is heated by high frequency induction.(16)

As is evident by the fact that aluminum is vacuum evaporated on cellophane, cloth and plastics, the process does not involve any appreciable raising of the temperature of the object being coated. Since the deposit is a cold deposit, no alloying action occurs.(17,20)

Most commercial vacuum evaporation systems employ both mechanical and diffusion pumps to create the vacuum.

The parts to be coated are located on holding fixtures which then slide into the vacuum chamber to position the parts around the source from which the aluminum will be evaporated.

Aluminum vapor travels in straight lines from the source to the objects and condenses on the surfaces located in the vacuum chamber and facing at least one source.(15) Multiple points or sources of evaporation may be used in a single chamber.

Vacuum chambers have been built where objects as large as 16 feet in diameter can be coated.(19) Units built for continuous coating of rolls of plastic sheet include reeling and unreeling equipment to traverse sheets up to 48" wide at speeds up to 100 feet per minute. Other types of equipment have been developed for mass production of vacuum deposits on small articles.(17)

Characteristics of the Coating

Vacuum deposited coatings are seldom built to an appreciable thickness; the thickness range is usually between 0.000003 to 0.001". (19,20,21,22) The thickness of the coating is controlled by the rate of evaporation of aluminum and by the length of time of evaporation towards a surface.

The thickness of the coating also depends upon the distance of the object from the source, as well as upon the angle of inclination of the surface to the source.

The disadvantage of vacuum deposited coatings lies in their porousness. The thinner the coating, the greater is the porosity. For corrosion and high temperature oxidation protection, the microscopic pores must be filled and sealed.(15)

The high brilliance and smoothness of aluminum vacuum deposits are well known. For that reason, they have been used in reflectors and for decorative purposes for many years.

Aluminum vacuum deposits reflect well over 80% of the incident light. The high reflectivity does not decrease by aging.(20,21, 23)

Air preheaters
Heat exchangers
Calcining tubes and retorts
Carbon and bone black retorts
Muffles
Diesel engine spoons and combustion plates
Stove linings
Turbine blades

Costs of Applying

The cost of calorizing depends upon the thickness of the coating applied, the volume of objects, their shape, quantity, weight, etc. The cost of application is estimated to be ½ to 3 times the cost of fabricated mild steel.

Facilities Available for Applying and Sources for Additional Information

The Calorizing Co., Wilkinsburg Station, Pittsburgh, Pa., is the only company that calorizes steel on a large scale job shop basis.

Section 7. Vacuum Evaporated Aluminum Coatings

Aluminum coatings may be applied by vacuum deposition methods. Vacuum deposited aluminum coatings are used where high brilliancy of the surfaces is desired as in the manufacturing of reflectors or for decorative purposes. This type of coating is used little for protection against corrosion, high temperature oxidation or erosion. The reason lies in the comparative high cost of the process when thicker coatings are concerned. For decorative purposes, the usual thickness of the deposited film is in the order of a few millionths of an inch.

For vacuum deposition, of all metals, aluminum is used the most. The preference lies in its low cost, high reflectivity, and high resistance to tarnishing.(15,21)

Surface Preparation

Obtaining a clean surface, free of grease, is a necessity for vacuum deposition. The importance of degreasing is demonstrated by the fact that grease can be used to mask an area to be left uncoated. Following degreasing, the surfaces must be degassed before metal may be evaporated onto them.

Coating Process

Vacuum chambers are loaded with the parts to be coated, sealed and evacuated to a pressure of one micron or below.(15,16,18,22)

The oxide layer will provide protection only if it is continuous. If removed or broken, it will form only if the object is again exposed to high temperatures and provided that the exposed alloy is sufficiently high in aluminum content to form the Al_2O_3.

When the object is exposed to high temperature, the diffusion of aluminum takes place slowly up to 1650°F, but it becomes quite rapid at 1850°F and higher.

Calorized iron objects have a very long life when exposed to temperatures below 1650°F. The calorized steel objects have about 20 times the life of untreated steel objects. At 1800°F to 2000°F, however, the life of calorized steel is five times as long as untreated steel.

Resistance to Corrosion

Besides resistance to high temperature oxidation, the calorized coating has a number of anti-corrosion features. It is resistant to corrosion by sulphur dioxide (from room temperature up to the temperatures where the base metal still has useful strength) to sulphur trioxide up to 1700°F, to sulphur vapor and liquid (provided there is no glowing coke present at the same time), to hydrogen sulphide up to 1300°F above which temperature the corrosion occurs rapidly, to carbolic acid (phenol), to hot tar and pitches, and to carbon monoxide. In this last case, the coating prevents the formation of iron-penta-carbonyl which occurs at 350 F to 430°F when carbon monoxide is in the presence of iron.

The general remarks contained in this chapter, Section 3 (Hot Dip Aluminum Coatings) in regard to "Ability to be Joined", "Mechanical Properties of Coatings" and "Effect of Mechanical Properties of Base Metal" apply to calorized coatings.

Since a calorized coating consists of the brittle iron-aluminum compound and iron-aluminum solid solution alloy in thickness greater than that obtained in hot dip coatings, objects can not be deformed after the calorizing process.

Uses and Applications of Calorized Products

Calorized parts are used for tubes in air heaters, in exhaust pipes, for furnace parts and in many other applications where there are requirements for high temperature oxidation resistance.

Good results have been reported as obtained by the General Electric(14) Company with the following calorized articles at service temperatures up to 1650°F:

Annealing containers and equipment
Parts of continuous furnaces
Pyrometer protection tubes
Thermostat fire ends
Burner nozzles for oil or gas furnaces

Objects to be coated are charged into retorts which can be hermetically sealed and rotated. The charging is done in a manner such that during rotation, the surfaces of the parts are brought into direct contact repeatedly with the calorizing mixture during the time they are heated. The hydrogen atmosphere is maintained during all stages of the process, including the cooling period.

After the calorized parts are cooled, the objects are removed from the retorts and are wire brushed to remove excess calorizing compound. The parts may then be given a diffusion treatment for 12 to 48 hours at 1500-1800°F to cause penetration of the aluminum by diffusion. This treatment results in a decrease in the aluminum content to approximately 25% or less at the surface of the part which increases the toughness and ductility of the coating while maintaining resistance to heat and oxidation.

For articles of light gauge or irregular shape that may be damaged in a rotating retort, the following modification of the process is used. This is accomplished by packing the articles with the calorizing compound in stationary boxes that are sealed tight during heating. The parts are then soaked for 6 to 24 hours at 1500-1800°F, combining the coating and diffusion treatment.

Characteristics of the Coating

Calorized coatings can be applied to iron and steel, alloy steels containing nickel, chromium and tungsten, and non-ferrous metals such as copper, brass, bronze, nickel and monel metal. The outstanding property of calorized articles, especially those made of iron, steel and certain ferrous alloys, is to withstand oxidizing up to approximately 1650°F.

It must be remembered, however, that the iron-aluminum compound and alloy layer formed in calorized surfaces does not contain free aluminum on the surface. For maximum corrosion resistance, some free aluminum is required.

Calorizing is preferably applied on objects of rather thick steel, since thin steel sheets are embrittled by the process.

Resistance to High Temperature Oxidation

The calorized coatings give protection against temperatures up to 1650°F. At higher temperatures, the aluminum from the coating diffuses deeper and deeper causing a decrease in aluminum content on the surface. It is considered that the coating gives adequate protection where the outer layer has 12 to 14% aluminum.

When the objects are exposed to air at elevated temperatures, a skin of a thin aluminum oxide developes on the surface. Because of its very high melting point (4,200°F) and its imperviousness, it gives good protection against high temperature and to deterioration by scaling.

Section 6. Calorizing

One of the earliest methods of applying a coating of aluminum to steel is known as the calorizing process developed by General Electric Company. This process is sometimes referred to as the "dry" or powder calorizing method. Another process, known as dip calorizing or the immersion process, consists of treating the cleaned article with a flux and submerging it in a bath of aluminum. Since the latter method is covered in section 4 (Hot Dip Aluminum Coatings), this section will be devoted to a discussion of the "dry" or powder calorizing method and will hereinafter be referred to as calorizing.

Calorizing is essentially a cementation process in which steel is packed or tumbled in a mixture of aluminum powder, alumina and aluminum chloride in a container in the presence of a neutral atmosphere at a high temperature.

The coating obtained by the calorizing method consists of iron-aluminum compound and iron-aluminum solid solution. The range of thickness of coatings is generally from 0.005" to 0.040".

Surface Preparation

The steel surface to be calorized must be perfectly clean. Usually, it is sand blasted, pickled in hot, diluted sulphuric acid and inspected for possible leftover surface scales or other surface impurities. Any remaining unclean spots are removed by fine sand, sand blasting or with a stiff wire brush.

Description of Process

The calorizing process consists of tumbling the steel objects in a calorizing compound mixture for 4 to 6 hours at temperatures of 1600-1750°F.

The following substances make up the calorizing compound:

a. Powdered aluminum (10 mesh per sq. in. or finer) to provide aluminum metal for coating.

b. Powdered alumina (40-100 mesh per sq. in.) to prevent coalescence of the aluminum powder.

c. Aluminum chloride, to provide a fluxing agent.

During the process, a hydrogen atmosphere is maintained in order to provide a reducing atmosphere.

The use of different ratios of aluminum to alumina is governed by the operating temperature of the process. In order to prevent coalescence of the aluminum powder at the higher temperatures, a higher proportion of alumina must be used.

Costs

The approximate price range for materials to be metallized are given below. It must be borne in mind that some variations exist due to the fact that the shape, weight and handling of the article must be taken into consideration.

Processes	Price (Per Sq. Ft.)
120	$0.50 to $1.00
11, 33, 45	$1.00 to $3.00

Facilities Available

Many firms have installed their own equipment for metallizing. A list of the licensed Metcolizing Contract shops is shown in Table 4.

Table 4

Metcolizing Contract Shops

1. Akron Sand Blast Co.
   50 E. Springfield Road
   Barbarton, Ohio

2. Alloy Welding & Engineering, Inc.
   831 S. Xanthus Place
   Tulsa, Oklahoma

3. Dix Engineering Co.
   1415 Dix Road
   Lincoln Park 25 (Detroit), Mich.

4. Forney's Inc.
   209 Elm Street
   New Castle, Pa.

5. Metal Cladding Co.
   128 Lakeview Avenue
   Buffalo, New York

6. Metallizing, Inc.
   3844 S. Wallace
   Chicago, Illinois

7. St. Louis Metallizing Co.
   625 S. Sarah Street
   St. Louis, Missouri

8. Tranter Mfg. Co.
   105 Water Street
   Pittsburgh 22, Pa.

9. Clark Metallizing Co.
   506 30th Street
   Newport Beach, Calif.

10. Metallizing Engineering Co., Inc.
    38-14 30th Street
    Long Island City 1, New York

Additional Information

Additional information on metallizing is available from any of the firms selling metallizing equipment and supplies, from the many metallizing contractors throughout the country and from references (11), (12) and (13).

Table 3

Corrosion and Oxidation Resistance of Sprayed Aluminum Coatings

Process	Corrosion Resistance	Oxidation Resistance
120	Resistant to marine and industrial atmospheric corrosion, sulphur compounds, salt spray test satisfactory up to 4000 hrs.	Max. 900°F
11	Sulphur gases on type 304 stainless steel, protection against V_2O_5.	Max. 1600°F
33	Corrosive gases containing only small percentages of sulphur. Also decomposition of tetraethyl lead and presence of V_2O_5 where stainless steel is coated.	Max. 1800°F
45	Corrosive gases including those containing sulphur.	1800°F

Effect on Mechanical Properties of Base Metal

High temperature tests were conducted on low carbon steel panels coated with sprayed aluminum and nickel chromium alloys as described in processes 11, 33 and 45. As a result of subjecting the coated panels in the temperature range of 1000 to 2000°F for periods of time up to 60 minutes, it was found that iron oxide scale formed only on the uncoated side of the panels. Tensile strength values after exposure were retained to an acceptable degree except at 2000°F for 60 minutes. These results are reported by W. Mutchler in "The Effect of Temperature on Sheet Metals for Aircraft Firewalls", National Bureau of Standards, N.A.C.A. Technical Note No. 965, Dec. 1944.

Reported Uses and Results

The method is applied mostly to large objects such as bridges, towers, hulls of ships and as a patch up of spots of coatings made by other processes. However, it has been used also with great success on smaller parts exposed to high temperatures and corrosive gases. Satisfactory results have been obtained with sprayed air cooled cylinders for aircraft, exhaust manifolds of aircraft engines, flanges of aircraft cylinders, jet combustion chambers, cylinder barrels, jet engine mounting brackets, supports on jet engine exhaust couplings, outer burner shells, arrester hooks, fire bars in stationary boilers, annealing box covers, lead pots and salt pots in heat treating furnaces.

33. Pure aluminum is then applied by metallizing on top of the chromium-nickel coating. Next, a bitumastic sealer containing aluminum pigment is applied on the outside of the aluminum. No heat treatment is required since the first heat of the part will cause alloying.

As in the case of Process 33, the aluminum rapidly penetrates into the porous structure of the chromium-nickel coating, forming an alloy bond with the base metal. The larger amount of aluminum used in this process also causes a more complete alloying throughout the mass of the coat. As this alloying takes place, the coating, while still somewhat porous, becomes impervious to the penetration of gases.

The essentials of the four processes described above are shown in Table 2 and the resistance to corrosion and oxidation of these various types of sprayed aluminum coatings are shown in Table 3.

Table 2

Metallizing Processes

Process	120	11	33	45
Surface Preparation	Grit Blast	Grit Blast	Grit Blast	Grit Blast
Thickness of Aluminum Sprayed Coat (inches)	0.006	0.006	None	0.004 Sprayed on top of Ni-Cr alloy layer
Ni-Cr Alloy Spray Coating Thickness (inches)	None	None	0.010	0.015
Type of Sealing Agent used	Silicone base plus Aluminum Two coats	Bitumastic base plus Aluminum	Bitumastic base plus Aluminum	Bitumastic base plus Aluminum
Heat Treatment	None	1450°F for 40 min.	None	None

cause penetration of the aluminum into the iron or steel surface. The sealing coat protects the aluminum from oxidizing, and gives it time to absorb into the iron or steel. Eventually the sealer burns through, permitting the external surface of the aluminum to oxidize. The final coating, therefore, consists of an external surface of aluminum oxide, and under this a coating of aluminum in solid solution in iron. Near the surface, the concentration of aluminum is relatively high.

After heat treating, the article is wire brushed, and has a dull silvery appearance. The process protects steels satisfactorily up to temperatures of 1600°F, and will withstand the action of sulphur gases. In some applications is used at even higher temperatures.

Representative uses:

Aircraft Exhaust Stacks
Damper Plates
Crown Sheets, etc.

PROCESS 33: For Temperatures up to 1600 to 1800°F

Process 33 is used for the protection of iron and steel against the action of corrosive gases where temperatures range from 1600 to 1800°F and where the gases do not contain large amounts of sulphur. This process is applied by first grit blasting the surface and then spraying on a thickness of approximately .010" of a special chromium-nickel alloy. The sprayed surface is then painted with a special bitumastic sealer containing metallic aluminum. No heat treatment is required; any alloying of the metals takes place in the first heat when the part is put in use.

Separate heat treatment is avoided with this process because the porous, sponge like structure of the sprayed chromium-nickel layer presents an absorbent base into which the aluminum paint penetrates. Although very little aluminum is present, it is thought that it alloys with chromium, nickel, and iron, and may penetrate through the sprayed coating and alloy to the base metal to form an actual alloy bond consisting of the alloy of chromium, nickel, aluminum and iron. This helps seal the pores against the penetration of gases. However, as no appreciable amount of aluminum remains on the outside, the chromium nickel alloy is exposed to hot gases. Therefore, the coating will not withstand the corrosive action of strong sulphur gases.

Representative uses:

Steel engine parts subject to high temperatures.

PROCESS 45: For Temperatures of 1800°F and higher

Process 45 provides maximum protection against heat oxidation, withstanding even strong sulphur gases. It is applied on iron or steel by first grit blasting the surface, and then spraying on a coating of a special chromium-nickel alloy to a thickness of approximately 0.15". This is 50% thicker than the coating used in Process

In ordinary metallizing the bond between the coating applied and the base metal is due to interlocking on a roughened surface rather than due to alloying of the particles of sprayed metal with the surface being sprayed.

The sprayed metal layer as deposited by a metallizing gun is inherently porous. The wide application of metallized coatings for corrosion protection has brought with it the development of numerous methods of sealing or impregnating the porous metallized coating. Top coats applied upon impregnated metallized layers make them even more resistant and impervious in corroding environments.

Improvements in the types of metal coatings applied by the metallizing process have been along the lines of heat resisting, corrosion resisting and wear resisting coatings.

There are four systems or metallizing processes in use for the protection of steel at elevated temperatures. System 120 is used for temperatures up to 900°F. The remaining three coatings are often referred to as "Metcolized", a trade name of the Metallizing Engineering Co. Process 11 is used for temperatures up to 1600°F. Processes 33 and 45 are used for even higher temperatures and are covered by Patent No. 2,300,400 issued to Metallizing Engineering Co. Each may be used for a particular range of temperature and service conditions as outlined below.

SYSTEM 120: For temperatures up to 900°F

System 120 is a satisfactory means of protecting iron and steel from atmospheric corrosion at relatively elevated temperatures up to approximately 900°F. The surface to be protected is first grit blasted and then metallized with a coating of aluminum .006" thick. Two coats of a special sealer are then applied to the sprayed metal. The sealer is a silicone type and contains aluminum pigment. The sealer fills the pores of the sprayed metal with a moisture repellent material. The resulting combination of coatings will resist severe atmospheric corrosion and is suitable for exposed parts operating at temperatures up to 900°F.

Representative uses:

Diesel Engine Exhaust Stacks
Damper Plates
Crown Sheets
Engine Supports, etc.

PROCESS 11: For Temperatures up to 1600°F

Process 11 is an inexpensive yet satisfactory method of protecting iron or steel surfaces from the corrosive action of hot gases. The surface to be protected is first grit blasted and then metallized with a coating of aluminum. A special sealer is then applied to the sprayed metal coat. This sealer has a bitumastic base and contains aluminum pigment. The article is then heat treated to

Section 5. Metallizing With Aluminum

The term "metallizing" is a general term applicable to the various processes used for applying a metallic surface by means of a spray or blast of molten or semimolten metallic particles. The blast or spray of molten or semimolten particles of metal may be obtained by the atomizing of previously molten metal, which in the molten condition is introduced into a blast nozzle to atomize it and project it as a spray. This is known as the molten metal spray system. In general this system is limited to metals with reasonably low melting temperatures. The spray or blast of molten or semimolten particles may be obtained by introducing the metal in powder form into the heart of a blast burner to convert the powder particles to molten or semimolten condition and project them in the form of a stream. This is known as powder metal spraying. The third method is to introduce the metal in wire form into the hot zone of a blast torch and as rapidly as the end of the wire melts to convert the molten material into a spray of finely divided molten metal particles. This method is known as the wire gun method. Methods using an electric arc as the source of heat for melting wire and compressed air for atomizing the material so melted have been invented but have not reached success in commercial adaptation. The bulk of metallizing today is being done with the wire type of gun. This discussion on metallizing will be limited to metallizing with the wire type of gun.

1. Metallizing is the only aluminum coating method where the process can be carried to the work.

2. Coatings can be built up to any desired thickness.

3. Spraying is used to salvage defective coatings sometimes made by other aluminum coating processes.

4. Sprayed coatings can be applied to any size or shape of article.

5. Coatings can be applied at a greater rate than with other methods.

6. The thickness range of sprayed coatings varies from 0.002" to 0.020".

The complete process of metallizing requires more than just a metallizing gun. Proper gun auxiliary equipment is required. Improvements in auxiliary equipment during the past ten years have been instrumental in making the metallizing process the controllable process that it is today.

Surfaces must be prepared to take the coating of sprayed metal. Methods of preparing surfaces and auxiliary equipment for use in such preparation of surfaces have been the subject of numerous improvements during the past decade.

6. If required, it is possible to anodize or apply a chromate coating to the aluminum finish for oxidation resistance.

7. The coating produced by this process consists of two layers, a bonding layer of iron-aluminum compound and a layer of pure aluminum or aluminum alloy on top.

The approximate cost per 100 square feet of surface treated is $0.75 if applied to 24 gauge steel. Depending upon the price of the metal, cost of power, quantity of material treated, the cost may fluctuate.

Application Facilities and Sources of Additional Information

American Mollerizing Corporation, 9489 Dayton Way, Corner Rodeo Drive, Beverly Hills, California, H. E. Linden - President.

Section 4(C) Alfin Coatings

The Alfin patented process(7) was originally developed for steel-aluminum bi-metallic castings such as brake drums and pistons. This method differs from the two discussed in that there is no fluxing step introduced for the surface preparation of the steel.

The first step in this process, as in others, consists of cleaning the steel parts to be coated. Next, the part is given a hot dip treatment by immersing the part in a molten aluminum bath, creating an iron-aluminum compound layer and aluminum layer approximately 0.001" thick on the surface of the steel. While the bond is still molten, the coated article is removed from the bonding furnace, placed in a mold and aluminum or aluminum alloy is cast around the part.

Cost

The only available data on the cost of application is that it does not exceed 10% of the cost of casting of similar size and complexity.

Application Facilities and Sources of Additional Information

Two licencees are specializing in aluminum bonded coatings.

1. Arthur Tickle Engineering Works, Inc., 21 Delevan Street, Brooklyn 31, N.Y., and 2. National Steel & Shipbuilding Corporation, Harbor Drive at 28th, San Diego 12, California.

Cost of Applying

The cost of application of hot dip aluminum coating is similar to that of galvanizing. It is governed largely by the size and shape of the parts involved, also by the volume of parts, particularly if the design is such as to permit mechanical handling.

The price of a simply shaped piece is approximately $0.80 per square foot.

Application Facilities and Sources of Additional Information

Research Laboratories Division, General Motors Corporation, Detroit, Michigan, D. K. Hanink and A. L. Boegehold.

Licencee of the Aldip process, Arthur Tickle Engineering Works, 21 Delevan Street, Brooklyn 31, N.Y.

Section 4(B) Mollerizing

The following steps are used to produce hot dipped aluminum coated products by the Mollerizing Process:

1. Parts to be coated are degreased, descaled, cleaned and dried.

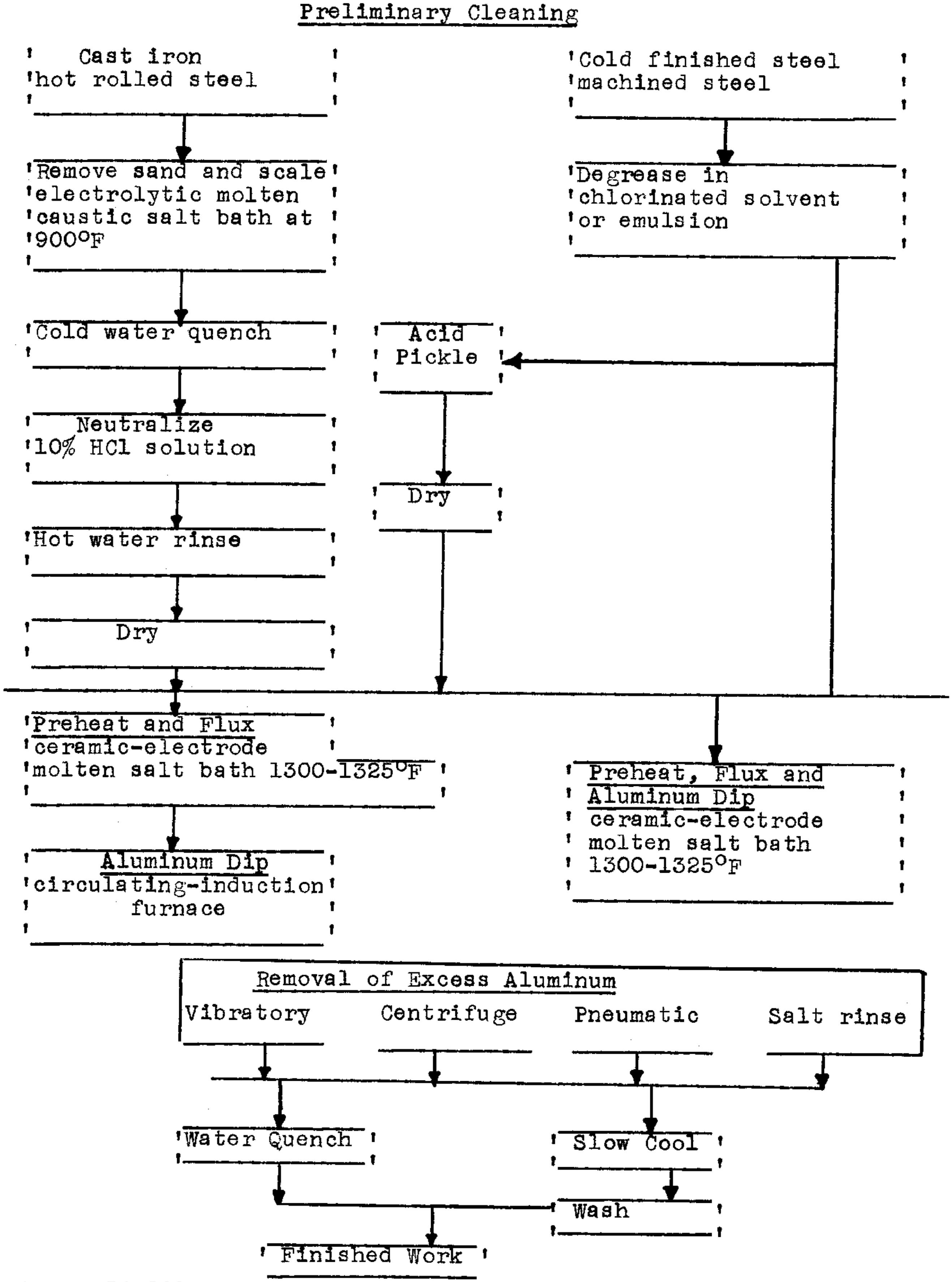
2. Objects are then immersed into a bath containing molten aluminum (2"-4" thick) floating on molten flux which consists of a mixture of sodium chloride, barium chloride and cryolite. Vapors from the cryolite escape around the edges of the aluminum layer and form a protective layer of gas, preventing the formation of aluminum oxide on the surface of the molten aluminum. This molten salt and aluminum mixture are held in a ceramic lined, submerged electrode salt bath furnace.

3. The immersion step consists of lowering parts through the aluminum layer into the molten salt for fluxing. After the parts have been maintained at a temperature of 1500°F for a short period of time for fluxing, they are withdrawn through the aluminum layer on the top of the bath upon which is superimposed a direct electrical current to create an affinity between otherwise electrically incompatible metals.

4. The thickness of the coating can be varied by controlling the speed of withdrawal and the temperature of the bath. An average thickness of 0.005" is usually obtained.

5. Removal of excess aluminum is accomplished by either centrifuging, vibrating, or with air jets. A hot water wash is used to remove any adhering salt.

Figure I - The Aldip Process



The information in the foregoing portion of this section dealt with the hot dip process in general.

The remainder of this section will be devoted to specific information in reference to each of the three hot dip processes: Aldip, Alfin and Mollerizing.

Section 4(A) Aldip Coatings

A description of how the coating is applied by the Aldip process is outlined below. Reference should be made to the accompanying flow sheet in Figure 1.(4)

1. Cleaning

The surfaces of the articles to be coated are prepared by caustic bath dipping, pickling or degreasing, depending on the condition of the surface and type of metal as shown in the flow chart.

2. Preheat and Flux

The second step in the process consists of immersing the base metal part in a molten salt bath at 1300-1325°F which preheats and fluxes the steel.

3. Aluminum Dip

After preheating and fluxing, the parts are then either dipped in molten aluminum beneath the salt or are transferred to a furnace containing molten aluminum for a predetermined period of time, usually 2 to 6 minutes.

4. Removal of Excess Aluminum

The last step in the process consists of removing excess aluminum from the surface of the part by use of vibratory, centrifuging, pneumatic or salt rinse methods. Preferably, the parts should be given a salt rinse in the preheat flux, followed by air blasting.

5. Diffusion Treatment

In order to produce more iron-aluminum compound of the required thickness to increase heat resistance and resistance to thermal shock, the part can be further treated by subjecting it to a diffusion treatment at temperatures in the vicinity of 1775°F.(4) The time at temperature varies directly with thickness of compound required.

Coated sheet steel exposed to temperatures in the range of 1000 to 2000°F for periods of time up to 60 minutes have been found to offer protection to the steel base metal. It was found that the tensile strength of the coated material was not reduced more than 25% after exposure under the above mentioned conditions while the tensile strength of the base metal was reduced considerably, especially at the higher temperatures.(9)

Reported Uses

Table I summarizes several successfully reported applications of hot dipped aluminum coatings:

Table I

Applications of Hot Dip Aluminum Coatings

Application	Process	Reference
1. Military Tank Heat Exchangers	Aldip	4
2. Exhaust Pipe Adapters	"	"
3. Furnace Trays	"	"
4. Hooks for Salt Bath Heat Treating	"	"
5. Spacer Supports for Carburizing Side Gears	"	"
6. Heat Exchanger Tail Pipe Tubes	"	"
7. Diesel Engine Manifolds	"	"
8. Coating of Titanium with Al	Mollerizing	6
9. Landing Gear Struts	"	"
10. Bi-metallic Bearings, Pistons, Brake Drums and Heat Exchangers for Aircraft Engines and Radiators	Alfin	7

Limitation

The most objectionable feature of the hot dipped coating is that it results in a non-uniform and lumpy coating. Another objection is that the fatigue strength of materials coated has been found to be lowered by the coating process.(9)

Mechanical Properties of Coating

The hardness of an aluminum coating depends upon the nature of the coating, that is, whether it is combined aluminum in the form of iron-aluminum compound or uncombined aluminum. The hardness of the former is in the order of 875 Diamond Pyramid Hardness, while the hardness of the latter is similar to pure aluminum or aluminum alloy, depending on which is being used in the dipping process.

The hardness of the aluminum iron solid solution is approximately 300 Diamond Pyramid Hardness.

Since the iron-aluminum compound is hard and brittle, the ductility of the coating depends on the amount of this constituent. When this constituent is kept to a minimum, the ductility of the coating is increased. The compound can be controlled by varying the dip time, diffusion temperature and silicon content of the base metal in the aluminum bath. The tensile strength of the compound bond has been found to be 11,000 to 17,500 psi, varying with bond thickness and aluminum analysis. Temperatures up to 500°F do not reduce the bond strength.(5)

Forming

Data on the formability of hot dipped coatings are limited. Due to the brittleness of the iron-aluminum compound, the aluminum coating to be cold formed must contain a minimum of this constituent. It has been reported that aluminum coated titanium sheet can be pressed with greater ease since the coating acted as a lubricant during forming.(6)

Effect on Mechanical Properties of Base Metal

The mechanical properties of steel processed by the hot dip method is dependent upon the temperatures to which it is exposed during the processing. For example, cold rolled steel would show a decrease in hardness and tensile strength after dipping, while an annealed steel would not exhibit a change. However, there would be a size effect. A thin annealed sheet with a hot dipped coating which had been diffusion treated would have its properties altered since the iron-aluminum compound layer would constitute a considerable portion of the cross sectional area of the material. Some of its hard and brittle characteristics would then be imparted to the entire material. However, if the material is of a large enough section, the coating effect would be negligible provided that the effect of hot dipping temperature and/or diffusing temperatures would not normally alter the properties of the base material.

An example of this is shown(5) where the tensile properties of SAE 4140 were not reduced by hot dipping. Since endurance limit values of coated samples were compared with polished steel specimens, results were lower for coated than uncoated steel. Available information from aircraft manufacturers indicate that hot dipped coatings cause a decrease in endurance limit.(9)

Corrosion Resistance

On the basis of a limited amount of corrosion test data,(2,3) it has been shown that hot dipped aluminum coatings have corrosion resistant properties similar to that of aluminum metal. The results have been based on coatings which contain free aluminum on the surface. Specifically, hot dipped aluminum coatings were found to be superior to galvanized or tinned steels in salt fog, water fog and fatty acids.(3)

Oxidation Resistance

The application of hot dipped coatings of aluminum to steel has resulted in increasing the oxidation resistance of steel. The coating can be expected to withstand temperatures up to 900°F without discoloration. Between temperatures of 180°F to 900°F, aluminum coating can reflect 80% of radiant heat. When temperatures exceed 900°F, aluminum begins to alloy with the base metal forming an adherent, refractory aluminum iron compound. Resistance to oxidation and scaling is satisfactory up to a temperature of 1600°F.(4)

Specific examples of oxidation resistance of aluminized steel are as follows:

1. Aluminized 1020 steel when compared with uncoated steel at 1300°F for 240 hours, 1500°F for 272 hours and 1700°F for 128 hours showed considerable superiority of the aluminum coated steel.(3)

2. In the presence of sulphur bearing gases, aluminized steel showed exceptionally good oxidation resistance at temperatures of 1350 and 1700°F.(2)

3. Hot dipped aluminum coatings were found to prevent formation of iron oxides on low carbon steel sheet when exposed to temperatures in the range of 1000 to 2000°F for periods of time up to 60 minutes when heated in an electric furnace. Partial melting occurred when the coated steel was subjected to flame impingement tests where flame impinged at 1800°F for 5 minutes or at 1600°F for larger periods of time.(8)

4. Hot dipped vapor cone assemblies (low carbon steel) have withstood temperatures of 1600°F for 94 hours without signs of oxidation.(10)

Ability to be Joined

Hot dipped aluminum coated steels have been satisfactorily brazed. Definite information on welding processes on hot dipped coatings is lacking. However, since aluminized sheet steel has been successfully joined (see section on aluminized sheet steel) when suitable precautions are taken, it may be inferred that hot dipped coatings of the same thickness as aluminized sheet steel coatings can also be joined.

Section 4. Hot Dip Aluminum Coatings

Of all the methods used for applying a coating of aluminum to steel, the "hot dip" process should be the most obvious. However, due to the difficulty in the past in preparing the steel surface for coating, preventing the steel surface from oxidizing during dipping and maintaining an oxide free surface on the coating bath, progress in this field of application has been slow. At the present time, the proponents of several methods of "hot dipping" claim to overcome all of the previous difficulties. These processes are: Aldip, Alfin and Mollerizing.

In general, these methods are similar in that they all require satisfactory preparation of base metal which is then dipped in molten aluminum or an aluminum alloy. The results of the coating processes are essentially the same; aluminum is bonded to steel by the formation of an aluminum-iron compound, the thickness of which may be controlled by the process.

The variation in the processes used to obtain an aluminum coating by hot dipping will be discussed in greater detail towards the end of this section. The first portion of this section will be devoted to a general discussion of the characteristics of the coatings which are alike in all processes.

Surface Preparation

Articles to be coated with aluminum by the hot dip process must have all oxides, grease, dirt and any other foreign matter removed by some adequate cleaning operation prior to hot dipping. The cleaning process may involve any one or a combination of the following operations: sand blasting, electrolytic caustic bath, degreasing, acid pickling, or fluxing. The choice of method depends on the nature of the matter to be removed and type of material cleaned.

Characteristics of the Coating

The coating obtained by the hot dip method is composed of different zones in the as dipped condition. Starting from the outer surface, these zones are: aluminum oxide film, aluminum (or aluminum alloy), brittle iron-aluminum compounds, mainly $FeAl_3$, and iron-aluminum solid solution. The proportions of these zones can be varied by subjecting the material to a diffusion treatment in the range of 1300-1900°F with the higher temperatures accelerating diffusion. This treatment results in a decrease of the aluminum surface layer, with an increase in the iron-aluminum compound and solid solution layers. The total thickness of the aluminum containing coating increases with diffusion temperature and time. A variation in thickness of 0.001" to 0.015" is possible with hot dip methods. The average thickness of most processes is 0.005".

As previously mentioned, Aluminum Coatings - General Discussion, free uncombined aluminum provides corrosion protection and the iron-aluminum compound provides high temperature oxidation resistance.

The organic solvent baths are very sensitive to atmospheric moisture and after a short time yield poor deposits. In the case of the hydride bath, fresh hydride is added to replenish the bath.

The coatings obtained by the molten salt method have no interfacial layer of iron aluminum alloy such as occurs in hot dipping. The coating is smooth matte-type. A test run is made first to remove moisture and impurities from the bath which are plated out in preference to aluminum.

Reported Uses and Results

The electrodeposition of aluminum was used as per method Organic Solvents Method A in electroforming of lightweight waveguides that could be tested for radar wave transmission characteristics. The aluminum deposits were dense, strong and ductile.(24) The thickness of those deposits was 0.025" or more. The bath required agitation to avoid porous deposits.

CHAPTER III

NICKEL AND NICKEL ALLOY COATINGS

Section 1. General Discussion

One of the primary purposes of the surface treatments of low alloy steels, as described in this manual, is the conservation of the critical metals used in the high alloy steels. Nickel is one of the important alloying metals that it is desired to conserve. In the operating temperature range up to about 1200°F the high alloy steels to be replaced, for conservation purposes, contain 8 to 10% of nickel. If nickel or nickel alloy coatings are to be used to protect plain carbon or low alloy steel parts, for conservation of nickel it is obvious that the amount of nickel used in such protective coatings should represent much less than 10% of the weight of the finished article.

If the equivalent of 0.001" of coating is necessary on each of two surfaces involved, it is evident that conservation of nickel will not result on parts whose finish thickness is 0.020" or less. If the steel thickness is 0.040" or more, an appreciable saving in nickel will result.

From an economical or cost standpoint, it is clear that savings will not be accomplished if the cost of surface treatment is equal to the cost of high alloy steel per square foot of the same thickness. Assuming that high alloy steel costs about $0.40 per pound above the costs of plain carbon or low alloy steel of the same thickness, the cost figures in Table 5 would apply.

Table 5

Limiting Costs of Surface Protection

Thickness	Weight per sq. foot - Pounds	Added Cost of Alloy Steel per sq. ft. Dollars	Limiting Cost of Surface Protection - two sides - per sq. ft. of surface. Dollars
0.010"	0.50	0.20	0.10
0.020"	1.00	0.40	0.20
0.040"	2.00	0.80	0.40
0.080"	4.00	1.60	0.80

From the above, it is evident that from a cost standpoint the nickel coating process used must not cost more than $0.40 per square foot of surface protection on steel 0.040" thick and that the thinner the steel is the cheaper must be the surface treatment.

It is clear that the above comments with respect to the cost of surface treatments are equally applicable to all surface treatments to be considered and are not peculiar to nickel or nickel containing coatings. In the case of nickel, the actual material involved in one square foot of coating 0.001" thick is approximately 0.05 pounds. For electroplated nickel and for electroplated nickel-tin coatings the actual cost of the materials in a coating 0.001" thick is, therefore, under $0.05 per square foot of surface.

If a nickel or nickel alloy coating of only one half mil thickness, or 0.0005" is suitable, a material saving of $0.025 per square foot becomes possible and a nickel conservation becomes possible on parts made of 0.020" thick steel.

From the corrosion protection standpoint, it should be remembered that in an electrolyte nickel and most nickel alloys are noble or cathodic with respect to plain carbon or low alloy steels. This means that if there is a pin hole or holiday in the coating, the so-called protective coating will form a local galvanic cell with the base steel and accelerate corrosion at that area. Since nickel and nickel alloy coatings are not sacrificial to steel, it is evident that such coatings must be free from pin holes and holidays to give adequate protection. In practically all nickel coating processes the minimum thickness for satisfactory performance is the minimum thickness necessary to obtain freedom from pin holes. Sealing treatments, such as burnishing, diffusion heat treatments or top coatings that close or bridge pin holes, permit the use of thinner coatings.

Nickel and nickel alloys at temperatures from 500 to 1000°F in air and in atmospheres reasonably free from halogen and sulphur compounds form tight oxide films that are self sealing and protective against further oxidation. While they do not maintain their bright metallic surfaces, they do not continue to deteriorate with time; the oxide tarnish films formed in this temperature range are adherent, reasonably nonporous and protective against further similar attack. Neither pure nickel nor the oxide film formed on nickel is thoroughly resistant to halogen or sulphur compounds. The products resulting from the attack of these compounds are not adherent or protective. A simple nickel coating will not withstand the attack of bromine, lead bromide and hydrobromic acid from the combustion of fuels containing tetraethyl lead additives. Some alloy nickel coatings such as nickel-zinc, nickel-tin and possibly nickel-cadmium (see Section 5, Corronizing) offer much better resistance to these compounds than relatively pure nickel.

Six different types of nickel and nickel alloy coatings are discussed in the following six sections of this chapter.

Section 2. Electroplated Nickel

Electrodeposition of nickel is accomplished by passing direct current through a suitable water solution of nickel salts. The nickel is deposited at the cathode. The composition, structure, physical characteristics and adherence of the deposit vary and are dependent upon the nature and concentration of the nickel salts and other chemicals in the solution, the temperature, the acidity or alkalinity of the solution and the quantity of current employed per unit area (current density). The deposit may be pure or almost pure nickel, an alloy of nickel with a small amount of cobalt or an alloy of nickel with other metallic or non-metallic elements. Since many elements can be deposited by the passage of electricity through their solutions, it follows that two or more elements may be co-deposited by the passage of electricity through a solution containing them, if the conditions for deposition are simultaneously suitable for them. Certain nickel alloy electroplates such as nickel-phosphorus, nickel-tin, nickel-zinc and nickel-cadmium are treated in other sections of this chapter. In this section, "Electroplated Nickel", there are included in the type called bright-nickel the nickel-cobalt alloy plates in which the cobalt addition is primarily as a brightener rather than for its alloy effect.

In practically all commercial nickel electroplating processes, the nickel in the solution is continuously replenished by nickel dissolved from the anodes used in the plating process. Either cast or rolled nickel anodes are used. The solution must be kept adjusted to maintain the desired rate of solution at the anode. The ratio of nickel anode area to cathode area must be maintained so that the quantity of nickel dissolved at the anodes is about the same as the quantity deposited on the work being plated.

Nickel electroplates properly applied are recognized as satisfactory for the protection of steel against atmospheric corrosion and against corrosion by certain solutions of chemicals.

There are four major types of nickel electroplates, as follows: 1. Dull matte or white; 2. bright; 3. hard; 4. compression.

According to the type of nickel plating desired and the composition of the nickel plating bath, nickel plating is done at temperatures from room temperatures (called cold nickel baths) to as high as 160°F (called hot nickel baths). Usually, increasing the temperature results in faster deposition, a softer, more ductile deposit, and better throwing power.

Nickel electroplating solutions operate within a total pH range of 1.5 to 6, but any one particular solution must be maintained to a much closer pH range such as ±0.5 pH, i.e., 4.5 - 5.5 or 5.0 - 6.0, etc. In general, a lower pH permits higher current density and higher rates of deposition without cracking and peeling of the coating, although the cathode efficiency is reduced to some extent.

Higher concentrations of metal in the solution make for higher current densities, higher rates of deposition, better throwing power, and better cathode efficiency. Chloride concentration in the solution controls the rate of anode corrosion to replace the nickel in the solution as metal is deposited at the cathode. Increases in chloride content tend to give harder deposits. Boric acid tends to control the pH of the bath and, in controlled amounts, tends to make the deposits smoother, whiter and more ductile. Relative motion between the plating solution and the surface being plated is essential. This is obtained by agitation (motion) of the part being plated or by forced circulation of the plating bath.

Surface Preparation

In order to obtain a good adherent nickel electroplate, it is necessary that the surface to be plated be very clean. Freedom from scale, loosely adherent particles of dirt, oil, grease, corrosion products, etc., is essential. On unpolished steel surfaces, acid pickles plus alkaline or alkaline electrocleaners are usually used.

For decorative purposes and for corrosion protection only, it is common to use an underplate of copper, since electrodeposited nickel on copper is more adherent and has less pin holes than electrodeposited nickel direct on steel. A reasonably pin hole free layer of copper can be buffed to be even more pin hole free and become a good base for a subsequent deposit of nickel. In some cases only a copper strike is used as an underplate. For use at elevated temperatures, no such copper undercoat or strike is permissible and the steel surface must be suitably prepared and treated for direct plating of the nickel on the steel. The surface preparation necessary for good electrodeposits of nickel is practically independent of the type of nickel plating to be applied.

Dull Matte or White Nickel Electroplating

The most common solutions for this type of nickel electroplating are called the Watts type and may be subdivided into two classes according to pH. Typical solutions are shown in Table 6.

An all-chloride bath may be used. It has some advantages in producing smoother, finer grained, stronger deposits, but the disadvantage is that the deposits are less ductile and more highly stressed than from the Watts baths. A typical all-chloride bath is shown in Table 6.

A composite of the Watts bath and the all-chloride bath is used sometimes and is called the chloride-sulphate bath. It produces a deposit that is finer grained than those from a Watts bath and more ductile than those from an all-chloride bath. A typical bath is shown in Table 6.

Table 6

White Nickel Plating Solutions

	Watts High pH	Watts Low pH	All Chloride	Chloride Sulphate
Nickel sulphate oz/gal.	32	44	-	26
Nickel chloride oz/gal.	6	6	40	23
Boric acid oz/gal.	4	5	4	5.5
pH	4.5-6.0	1.5-4.5	2	1.5
Temperature °F	115-160	115-140	120-160	115
Current density a.s.f.	20-100	25-100	25-100	25-100

Bright or Lustrous Nickel Electroplating

Bright or lustrous nickel electrodeposits are obtainable from a number of different types of plating solutions plus various addition agents as so-called "brighteners". Maximum brightness is obtained when the basis metal has been polished before plating.

Over twenty five United States patents have been granted on brightening agents for use with the Watts type of plating solution previously described. In most cases, the low pH class of Watts bath is used. These brighteners are mainly organic in nature. Some organic brighteners seriously embrittle the deposit, so other organic materials which counteract this tendency must be added. In using these proprietary brighteners or proprietary bright plating solutions, it is essential that the operating instructions of the vendor be followed. A complex inter-relationship exists between solution formulation, temperature, pH and current density.

Bright nickel deposits are obtained also from cobalt-nickel solutions. Three different formulations of this type solution are used, depending upon the brightness and hardness of deposit desired. These three baths differ in cobalt concentration ranging from 0.35 to 2.0 ozs. per gallon of cobalt sulphate. Additional control over deposit ductility is had by adjusting the pH. The solutions, in addition to the cobalt sulphate, contain nickel sulphate, nickel chloride, boric acid, nickel formate, ammonium sulphate and formaldehyde.

Hard Nickel Electroplating

In most cases, the addition of sodium, potassium and ammonium salts to nickel plating solutions causes increases in the hardness and brittleness of the deposit. When a hard nickel deposit is desired, it is common to use ammonium chloride in a nickel sulphate solution. A typical hard nickel bath is as follows:

Table 7

Hard Nickel Plating Solution

Nickel sulphate	24 ozs/gal.
Ammonium chloride	3.3 ozs/gal.
Boric acid	4.0 " "
pH	5.6 - 5.9
Temperature °F	110 - 140
Current density amps/sq. ft.	25 - 50

This is a special purpose solution where a comparative high hardness is required. For the uniformity of the physical properties of the plate produced from this bath, close control of the pH and temperature is necessary. Slight changes in these two variables cause decided changes in the physical properties.

The deposits from this type of bath do not possess a hardness comparable to chromium. This nickel bath has definitely better throwing power and rate of deposition than any chromium bath. Where thick deposits of high hardness are required, the major thickness can be made up of hard nickel which acts as a supporting base for a hard chromium plate. This solution does not produce a coating as hard as that obtainable by electrodeposition of a nickel-phosphorus alloy as described in Section 3 of this chapter, nor as obtained by the electroless nickel procedure described in Section 4.

Compression Nickel Electrodeposits

Types of baths which will produce a nickel plate in compression have been recent developments and include a modified Watts bath plus an organic addition and the sulphamate type of bath. This latter plating solution is reported to contain nickel sulphamate, nickel chloride, boric acid, anti-pit agent and possibly a buffer. The nickel content of the bath is 10 ozs. per gallon. The major interest in the sulphamate bath is its high rate of deposition and the freedom of the nickel deposits from stress. This solution has aroused interest in the electroforming and electrotyping industries, but little experience has been gained to date.

Corrosion Resistance

Nickel plate has long been recognized as a satisfactory material for the protection of steel against atmospheric attack. There are no data available at present on the corrosion resistance properties of nickel in contact with the condensate produced from combustion products from aircraft engines as a result of cooling to room temperature after high temperature service. Dry gases are not actively corrosive to nickel at or near room temperature. However, nitrogen oxides, chlorine, other halogens, sulphur dioxide and ammonia are appreciably corrosive to nickel in moist atmospheres.

As stated previously, the corrosion protection provided to steel by a nickel deposit is a function of its freedom from pin holes. Thicker deposits have less through pores and, therefore, less pin holes. The corrosion resistance of a nickel plated article is recognized as being proportional to the thickness of the nickel deposit; this is shown by the specifications of the American Society for Testing Materials.

Effect of Elevated Temperatures

The first effects of heating electrodeposited nickel coatings may be release of stresses, release of occluded gases and the development of changes in the bond between the deposit and the base metal. Poor coatings will blister and peel while good adherent coatings will develop even better adherence. In general, minor changes occur in the structure and properties when heating dull nickel deposits up to 750°F. After being heated at temperatures of 1100 F to 1800°F, most such deposits consist of large equiaxed grains with pronounced grain boundaries at which oxides and other impurities have segregated. The hardness and tensile strength are decreased. The elongation is increased up to 750°F and then decreased. Most bright nickel deposits show a much larger decrease in hardness and tensile strength when heated, but show little increase in ductility. Many voids may be produced on heating the bright nickel deposits.

Deposits from most nickel baths show a high contractive internal stress. If it is desired to remove this stress, a 2 hour anneal at 570°F can be used for the chloride and Watts deposits. Deposits from the hard nickel baths should not be heated over 450°F if the "as plated" hardness is to be retained.

In England it is considered that a 2 hour anneal at 400°F is an important step in nickel plating. It is felt that it should not be omitted as it expels some of the hydrogen, removes some hydrogen embrittlement and improves adhesion.

Oxidation Resistance

The only data available on the use of nickel electrodeposits for protection of steel at high temperatures (over 400°F) are statements by representatives of various aircraft manufacturers as to their practice. Limits adopted to date as to the maximum temperature of exposure for nickel electroplate vary from a low of 700°F to a high of 1000°F.

Very little work has been done on the high temperature oxidation protection and corrosion protection of nickel plate. In the absence of sulphur in the atmosphere, nickel electroplate should protect steel against oxidation up to 800°F and possibly as high as 1000°F. In a sulphur containing atmosphere, nickel will be readily attacked at temperatures over 600°F. Sulphur attacks the nickel intergranularly. This attack is greater under reducing conditions than under oxidizing conditions. These characteristics are applicable to pure nickel, nickel clad on steel, nickel plate, and electroless nickel.

On exposure to temperatures above 1200 or 1400°F the nickel plate diffuses gradually into the steel and iron diffuses into the nickel layer. The resultant nickel iron alloy layer will have lower corrosion resistance than pure nickel. This nickel iron alloy layer may eliminate the pitting type corrosion, but steel panels covered with such a nickel iron alloy layer will show an overall rust layer. This nickel iron alloy layer offers no improvement over nickel against high temperature attack.

As sulphur is the biggest enemy (lead also is reported to embrittle nickel on exposure to temperatures above 600°F) to nickel plate for high temperature service, the bright nickel plating baths which contain sulphonates or other sulphur bearing organic derivatives should be avoided. Straight Watts or high chloride baths are preferable for nickel plating for high temperature service.

Proper surface preparation of material to be plated and proper control of plating bath and plating conditions are a prime necessity if nickel electroplate is used for protection of steel against high temperature oxidation and corrosion attack.

A binary alloy based on electroplating nickel followed by chromium is not satisfactory unless it is given a long time heat treatment at high temperatures.

The expansivity of nickel plate (especially thick coats) and its relation to steel is important in the use of nickel plate on steel for high temperature service. The literature reports that in the range of 68 to 1110°F, the average coefficient of expansion of nickel is 15.6, very close to that of steel. Some bright nickel deposits show erratic coefficients.

One of the aircraft manufacturers is doing experimental work with a sulphamate nickel plating bath and another with the modified Watts bath which produces nickel plate in compression. No test results have been reported.

Erosion and Abrasion Resistance

No specific data has been found in the literature as to the erosion and abrasion resistance properties of electroplated nickel coatings. One of the aircraft manufacturers, based on study of various coatings, reports that electrodeposited nickel has good abrasion resistance. The hard nickel deposits should have good abrasion resistance as this plate is primarily used for a wear resistance surface. Wrought nickel is reported to be resistant to erosion by steam at high velocities.

Joining

Nickel plated steel can be soft or hard soldered and welded. There is no knowledge, though, that nickel plated steel has ever been brazed. Welding must be done with submerged or inert arc methods as the usual fluxes used for welding cause cracks in the nickel plate. The lower melting silver solder should be used for "hard" soldering operations.

Mechanical Properties

The mechanical properties of the dull, bright and hard nickel electroplates are shown in Table 8.(27) The term "stress, 1000 lbs. per sq. in." in Table 8 is the tensile stress in thousands of pounds per square inch in the nickel plate in the "as plated" condition.

Table 8

Properties of Nickel Electrodeposits

	Dull Watts		Dull All Chloride		Bright Organic Add.		Bright Co-Ni		Hard	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range*	Av.	Range
Hardness Vickers	192	140-400	270	200-390	467	350-820	-	300-600	425	350-525
Tensile Strength, 1000 lbs. per sq.in.	78	50-115	108	90-150	183	140-220	-	-	152	144-160
Elongation per cent	19	2-31	9	4-17	3	1-5	-	-	6	4-9
Stress, 1000 lbs. per sq.in.	31	15-54	40	25-55	-	-	-	-	?	?

*Dependent on the type of bath used.

As can be seen from the above data, there is a wide variance in physical characteristics of a nickel electroplate within each group. For a particular type of bath containing a minimum amount of impurities, the factors which affect the nature and mechanical properties of the plate are: 1. pH of the plating solution; 2. temperature of the bath; 3. current density used. The effect of each factor is not independent, but is related to all others.

The necessary work to determine the mechanical properties of the nickel deposit from the sulphamate bath for compression nickel plates is in progress. The very limited hardness data available are shown in Table 9.

Table 9

Hardness of Compression
Nickel Electroplates

Temperature of Bath	Current Density Used (ASF*)		
	24	48	96
85°F	493 VHN**	505 VHN**	532 VHN**
105°F	497 "	509 "	545 "
120°F	418 "	502 "	566 "
140°F	325 "	389 "	477 "

*ASF = amperes per square foot

**VHN = Vickers Hardness Number 50 gm load.

It appears that the nickel sulphamate baths will produce comparatively hard nickel deposits. No data are available on the effect on the physical properties of exposure to elevated temperatures. The stresses produced by the nickel plate from the sulphamate bath will be discussed later in "Effect on Base Metal."

Thin nickel plates tend to be porous. A coating thickness of over 0.001" is usually required to produce a porous free layer of nickel electroplate.

The uniformity of the plate thickness is dependent on the shape of the part to be plated and its relationship to the anode. The nickel plate tends to build up on sharp corners and to fail to plate in deep recesses. Unless special techniques are used, it is not possible to plate on the inside diameters of tubing or pipe. By special techniques nickel coats are plated on the inner surfaces of 20' lengths of pipe and tubing from 2" to 18" in inside diameter. This latter process claims to produce a ductile nickel deposit with depressions in the steel more heavily coated than high spots, and claims complete adherence to base metal in thicknesses from 0.005" to 0.100".

Effects on Base Metal

It is known that during the electrodeposition of metals, especially hard metals such as nickel, large internal stresses may be set up in the plate. Various theories have been offered as to the causes of these internal stresses. The usual stresses in nickel electroplates are "tensile". Thin articles may become warped or distorted by depositing metal on them. If the stress is greater than the tensile strength of the deposit and the base metal is rigid so that there is no opportunity for the stress to relieve itself, a network of cracks may form or peeling may occur. These effects are important for electroplates that are required for corrosion and oxidation protection.

The magnitude of the stresses can be very high. Tests at the National Bureau of Standards showed that deposits produced from an impure Watts plating bath may be stressed to 50,000 psi. With adequate purification and with plating control, the stress in the plate produced was reduced to 15,000 psi. Certain organic additions have been reported which will further reduce the stress. The addition of nickel benzene disulfonate to a modified Watts bath has been reported to have completely reversed the stress.

Tensile stresses in the nickel electroplate lower the fatigue strength of the part. This has caused some aircraft manufacturers to avoid the use of these nickel electroplates on some aircraft components. Because of this, some interest has developed in the use of the baths which produce nickel plates in compression. Although one aircraft manufacturer is experimenting with the Modified Watts, no data have been received to date. Another aircraft manufacturer is experimenting with a nickel sulphamate plating bath but, again, no data have been made available. One company, working with the sulphamate bath, reports that plating between 120°F and 160°F from 20 to 140 amperes per square foot produces nickel electroplates which are compressive and which should not affect the mechanical properties of the base metal.

Uses and End Results

Some aircraft manufacturers are using nickel electroplating for protection of steel at temperatures up to 1000°F. The data received from them are not too complete as to whether this protection is complete against corrosion attack of condensates formed on cooling of exhaust gases.

All data indicate that nickel electroplates give protection to steel against corrosion, erosion and/or oxidation attack on exposure to temperatures up to 700°F and possibly to 1000°F.

Costs

It is impossible to give even approximate figures as to the costs of nickel plate or any other plate per square foot of surface. Many factors play important parts in the final costs and must be taken into consideration in each case, such as:

1. Thickness of the plate.
2. Size, shape and complexity of the part to be plated.
3. Cleaning operations necessary to prepare the surface.
4. Rack design, rack maintenance, loading and unloading of racks.

5. Drag out losses.

6. Manual or automatic operation.

7. Anode design required.

Costs for automatic plating of nickel on such items as auto bumpers stock (a highly competitive item) are estimated at from $1.00 to $1.25 per lb of nickel deposited plus the cost of the nickel. On a comparative basis, nickel electroplating is cheaper than chromium electroplating, but more costly than zinc electroplating. For simple shapes with no internal surfaces to be plated, in reasonable quantities at one time the costs may vary from $0.40 to $1.00 per square foot of surface plated 0.001" thick.

Facilities Available and Sources of Information

Nickel electroplating of the dull, bright and hard varieties is adequately handled by many commercial electroplaters all over the U.S.A. Most of them have the necessary knowledge to produce a plate of the desired properties. Many industrial firms operate their own electroplating departments. General information on the subject of nickel electroplating is available from the International Nickel Company, 67 Wall Street, New York, N. Y., the American Electroplaters Society, the American Electrochemical Society and the technical magazines in the electroplating field. The many equipment and supply dealers offer technical advice and assistance. The sellers of proprietary processes, solutions and addition agents supply detailed instructions with their products.

Section 3.

Electroplated Nickel-Phosphorus Alloys

Nickel-phosphorus alloys containing as high as 15% of phosphorus can be electrodeposited from a solution containing nickel chloride or nickel sulphate plus phosphoric acid. The original development work was done at the National Bureau of Standards.(28,29) The process is in use by at least one commercial firm. The coatings produced are somewhat similar to those from the "Electroless Nickel" process described in Section 4 of this chapter. The process for electrodeposition of these hard nickel-phosphorus alloys is somewhat less expensive than the Electroless Nickel process and does not require as high a temperature or as long a time for an equivalent thickness of coating.

Surface Preparation

The requirements for surface preparation prior to the deposition of the nickel-phosphorus alloy are the same as for electrodeposition of pure nickel.

Plating Solutions and Procedures

The National Bureau of Standards reports that the plating baths for the deposition of the nickel-phosphorus alloys are rather simple. They consist of nickel chloride and sulphate together with phosphoric and phosphorous acids. The acids act as the source for the phosphorus in the deposit.

The compositions of some of the baths are shown in Table 10.

Table 10

Nickel-Phosphorus Alloy Plating Solutions

	Low Phosphorus-Nickel	High Phosphorus-Nickel
$NiSO_4 \cdot 6H_2O$ (gms/liter)	175	150
$NiCl_2 \cdot 6H_2O$ (gms/liter)	50	45
H_3PO_4 (100%) (gms/liter)	50	50
H_3PO_3 (100%) (gms/liter)	1.3	40

The pH of this bath must be less than 1.0. The pH should be raised to a value between 0.5 and 1.0 by adding nickel carbonate. The low phosphorus baths are operated at a pH of between 0.5 and 1.5 depending on composition. Phosphoric acid also acts as a buffer to maintain the desired acidity in the cathode film. The plating takes place at 165°F and above. At room temperature the cathode current efficiency is very low and the deposits are very weak. Current densities should be between 5 and 40 amperes per square decimeter (about 45 to 370 amperes per square foot). At about 10 amperes per square decimeter (92 amperes per square foot) the rate of deposition is fairly high, amounting to a few thousandths of an inch per hour.

The nickel phosphorus bath is reported to have excellent throwing power. In operation, the baths require less critical control than for proprietary bright nickel plating baths.

Characteristics of the Plate

The characteristics of the nickel-phosphorus electroplate, as reported by the National Bureau of Standards and one commercial firm, are shown in Table 11.

Table 11

Characteristics of Nickel-Phosphorus Alloy Electroplate

	N.B.S.	Commercial Firm
Corrosion Resistance	Alloys with high % of P are resistant to corrosion and chemical attack exceeding, in this respect, the pure metal.	Corrosion resistance equal to that of pure nickel
Oxidation Resistance	No data.	No data.
Abrasion Resistance	A hard wear resistant coating. It is recommended where resistance to wear is important.	Good wear resistance.
Joining	No data.	No data.
Hardness as plated	350 to 720 Vickers with increasing P content.	About 600 Vickers.
Hardness as heat treated	At 400°C - 10% P alloy - 1100 Vickers.	At 600°F - 900 to 950 Vickers.
Ductility	Over 1% P is generally brittle. Heat treat 800°C still brittle.	No data.
Hot Hardness	Alloys have poor "hot hardness" and above 600°C are softer than unalloyed nickel.	No data.
Effect on Base Metal	No data.	No data.
Brightness	Alloys less than 2% P - smooth matte finish. As P increases they become brighter, reaching peak at 10% P. Lower reflectivity than buffed nickel plate.	No data.

Although no data are available on the effect of this plate on the base metal, there is reason to believe that endurance limits will be reduced materially.

Uses

This nickel-phosphorus electroplate has been recommended as a coating on parts where anti-scuffing properties and resistance to wear are important factors. In such cases, the more rapid rate of deposition and the greater throwing power, as compared with chromium plate, should be advantages.

It is reported that nickel-phosphorus plate is being used on General Motors and Cummins diesel engines. Details as to the parts being plated and actual service life results are not available.

Costs

No data are available on the costs of applying this hard nickel-phosphorus electroplate, except a statement that it is cheaper than "electroless nickel" deposition.

Facilities Available

One commercial source for hard nickel-phosphorus electroplate is:

Surface Alloys, Inc.
Los Angeles, California.

Section 4. Electroless Nickel Coatings

"Electroless nickel plating" and "electroless cobalt plating" are the terms which were suggested in 1947(32) to be used to designate the processes of deposition of nickel and of cobalt by chemical reduction. The first reports(30,31) on the process were in 1946 and concerned the deposition of nickel from an ammoniacal solution containing hypophosphite. The processes were then extended to include the deposition of nickel from acid solutions and of cobalt and cobalt nickel alloys from ammoniacal solutions. On December 5, 1950, United States Patent #2,532,283 on "Nickel Plating by Chemical Reduction" was issued.(33) Under the terms of issuance, the process may be used by or for the Government of the United States without the payment of any royalty.

In this electroless nickel process an alloy of nickel and phosphorus is deposited as a result of chemical reactions rather than by the passage of an electrical current. Initially, because of the high costs of the chemicals, it did not seem that the method would find wide commercial application. More recent information indicates that improvements in production methods and increased quantities of production have reduced the costs of the chemicals materially

The process involves the reducing action of hypophosphites in a solution of nickel or cobalt at 195°F or above in the presence of certain catalytic metals such as iron, nickel, gold, cobalt, aluminum, palladium and possibly silver. Zinc surfaces reduce some nickel, but the deposits have very poor physical properties. Glass, plastics, lead and cadmium are non-catalytic and deposition does not take place on their surfaces.

The deposits produced are hard and are claimed to be substantially nonporous. Hydrogen is liberated as the deposition takes place.

As deposited, the electroless nickel deposit is an alloy of nickel and phosphorus containing up to 5% of phosphorus. The deposit is hard and non-magnetic. Heat treatment is claimed to relieve stresses in the deposit, promote adherence, seal imperfections and cause some precipitation hardening. One firm reports that when heat treated, the electroless nickel may become magnetic. Electroless nickel is reported to have poor adherence on high chromium steels, and on titanium some batches will plate well and others poorly.

The electroless nickel alloy, as deposited, has a hardness of 35 to 40 Rockwell C. By suitable heat treating the hardness can be increased to about 60 Rockwell C.

Surface Preparation

To obtain an adherent nickel deposit by these processes, the surface cleaning methods must yield a meticulously clean surface. Cleaning cycles equal to or superior to those required for good electroplating are necessary. A predip in a surface activating solution is considered desirable by some. The nature of the predip solutions used are not divulged.

Alkaline Process

The typical composition of a satisfactory alkaline bath is shown in Table 12.(32)

Table 12

Compositions of Alkaline

Electroless Nickel Solution

Nickel chloride	30 grams/liter
Sodium hypophosphite	10 " "
Ammonium chloride	50 " "
Sodium citrate	100 " "

Ammonium hydroxide to a pH of 8 to 10

Such solutions deposit nickel at the rate of 0.0002" to 0.0003" per hour. The effect of concentration of hypophosphite, and temperature, are shown in Tables 13 and 14.(32)

Table 13

Deposition Rates of Alkaline

Electroless Nickel Solution

Concentration of Hypophosphite grams/liter	Rate of Deposition inches/hour
2	0.00003
4	0.00006
10	0.00024
50	0.00075

Table 14

Deposition Rates of Alkaline

Electroless Nickel Solution

Temperature °F	Thickness per Hour inches
129	0.000031
154	0.000076
172	0.000128
189	0.000188
207	0.00022

Varying the concentration of nickel salts from 15 to 60 grams per liter has no appreciable effect on the rate of deposition. The alkaline baths are reported to yield good sound deposits. The objections to their use are: 1. high temperature of operation; 2. rapid loss of ammonia; 3. disagreeable fumes.

Acid Process

Typical compositions of acid baths are shown in Table 15.(32)

Table 15

Composition of Acid Electroless Nickel Solutions

	Bath			
	I	II	III	IV
	g/liter	g/liter	g/liter	g/liter
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30	30	30	-----
Nickel sulphate, $NiSO_4 \cdot 7H_2O$	-----	-----	-----	30
Sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$	10	10	10	10
Sodium hydroxyacetate, $NaC_2H_3O_3$	50	10	-----	-----
Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$	-----	-----	-----	10
Sodium citrate, $Na_3C_6H_5O_7 \cdot 5\frac{1}{2}H_2O$	-----	-----	10	-----
Rate of deposition, inches/hour	.0006	.0005	.0002	.001
Appearance of deposit	Semi-bright	Semi-bright	Semi-bright	Rough, dull
pH	4 to 6	4 to 6	4 to 6	4 to 6

At a pH of 5, nickel deposition will occur in a solution containing only soluble nickel salts and sodium hypophosphite. The reaction is vigorous, and the reduction of nickel is very rapid. Without any regulation of the pH, the latter drops rapidly, and at a pH of 1 to 2, the rate of deposition is low. Salts of organic acids are added as buffers, the most satisfactory being sodium acetate and salts of certain hydroxycarboxylic acids. The hydroxycarboxylic salts prevent precipitation of basic nickel salts.

Sodium acetate concentration must be carefully regulated. Large variations in the rate of nickel deposition results from changes in the acetate concentration. The rate of deposition reaches a maximum in the nickel-chloride bath with an acetate content of 2.5 grams per liter, and in the nickel-sulphate bath, of 4.3 grams per liter.

The nickel content may vary from 3 to 50 grams per liter without appreciably altering the rate of deposition, but with a nickel content of 100 grams per liter the rate of deposition is somewhat decreased. Sodium hypophosphite can be used in concentrations from 10 to 100 grams per liter without appreciably affecting the rate of the process. This is in contrast to the behavior of the alkaline solution, in which the rate of deposition is nearly proportional to the concentration of hypophosphite. Both the acid and alkaline baths have the same weight efficiencies (weight of nickel produced per unit weight of hypophosphite present). The rate of nickel deposition is larger in the acid baths.

When the acid solution is used at elevated temperatures, no fumes or loss of constituents by vaporization occurs. The solution is more easily controlled and the deposits are produced at a faster rate than from alkaline solutions.

Other Processes

In addition to the original processes as described in the patent and publications from the National Bureau of Standards, there are two commercial processes available. One firm supplies proprietary plating solutions and offers engineering service in setting up plating operations. It is reported by this company that they have installed plating operations in at least three plants. The other process is trade named and is controlled by its developer in whose plant the actual plating operation is carried out. This firm reports that it plans to license other plants and interested industries.

Based upon the information in the literature, a number of firms have installed equipment and have developed various modifications of the processes for their own use.

Thickness and Uniformity

One firm reports that at least 0.0002" thickness of coating is required to avoid porosity, another firm reports the plate is "fairly pin hole free" at thicknesses of less than 0.0003".

To obtain uniformity and freedom from pin holes, the work must be agitated or the solution moved with respect to the work. Some non-uniformity of deposit may be caused by poor cleaning and the position of the surface in the plating bath. Small particles of material that settle out of the solution onto the surface may cause roughness.

In one case, electroless nickel was applied on hardened steel spline shafts of about .180" diameter by 6" long. The coat was non-uniform from top to bottom. In another case, electroless nickel was applied to Ni Resist castings. The coat sealed some castings and was non-uniform in thickness. On one casting where the leakage was 100 cc per minute at 100 psi the electroless nickel cut this leakage down to 12 cc per minute.

One firm reports that for corrosion protection a plate thickness usually of 0.0005" is sufficient, but for wear resistance 0.0015" is recommended.

One firm reports that parts which have been formed before electroless nickel plating have given trouble with gas pockets in sharp corners.

An average of 0.0001" per hour is plated, usually, although a maximum rate of deposition of 0.002" per hour has been reported as achieved. Higher rates are achieved at higher temperatures. If the temperature is too high, the deposit becomes black in color.

Corrosion Resistance

Data on the corrosion protection provided by electroless nickel is very desultory. Tests reported thus far (based on ½ mil plating thickness) indicate that the heat treated electroless nickel plate on steel offers similar, or possibly superior corrosion protection in comparison to nickel electroplate. These findings are based on salt spray and humidity tests only.

Many claims are made that the deposits are free of pores, that they can be used to seal porosity in castings and that deposition takes place in small crevices and recesses. If such claims were correct, the corrosion protection by the application of such deposits would be superior to that possible by electrodeposition methods. Since hydrogen is evolved in the deposition, some gas pocketing and some resulting porosity or lack of penetration into sharp corners and recesses is to be expected. Such failures are being found in service trials.

Electroless nickel was applied by one firm to a 356 alloy aluminum casting. In salt spray testing the coating showed pin holes and severe blisters and peeling. Apparently the deposit was not pore free and, therefore, promoted corrosion.

One firm has made salt spray tests on plates as deposited on steel from freshly prepared acid baths versus baths that had been in operation for some time, with the following results:

New Bath

pH 4.5	.0001 -	72 hour salt spray
	.0005 -	4 day " "
pH 5	.0001 -	24 hour " "
	.0005 -	4 day " "

Old Bath - 200 hours operation

pH 4.5	.0001 -	48 hour salt spray
	.0005 -	4 day " "

Temperature Characteristics

Data on temperature, especially high temperature, characteristics of "electroless nickel" are very limited. One source has stated that electroless nickel plate is unaffected as low as minus 100°F, and that tests performed at one of the aircraft engine manufacturers indicated that the hardness remained fairly constant at 59 Rockwell C before and after a 2000 hour exposure at 900°F.

Another source reports that "Resistance of the coatings at elevated temperatures (over 500°F) is poor, due to a low hot hardness". One of the subcontractors plating aircraft engine parts with electroless nickel reports that he is fairly sure that electroless nickel plated parts are being successfully used for temperature exposures in excess of 400°F.

One of the proponents of electroless nickel puts forth the claim that the coating is satisfactory up to its melting point of about 1800°F. Tests at one aircraft plant at 900°F have shown some alloying with the steel to have occurred after 2000 hours of heating. A program of 200 to 500 hours exposure in air at 1000oF to be followed by salt spray tests is under way in one plant. Another aircraft company reports that 800°F is about the temperature limit for the use of electroless nickel.

Erosion and Abrasion Resistance

One of the advantages of electroless nickel processes is that the deposits are of high hardness. A plate thickness of 0.0015" is reported to offer good wear resistance. Electroless nickel plate has been recommended as a hard wear resistant plate to build up worn surfaces. One subcontractor reports making aircraft parts with plating thickness of 0.0003" to 0.0005" for corrosion-erosion protection against air blasts at 500-600°F. Another aircraft manufacturer reported that unlubricated bearings operating warm lasted ten times longer when given an electroless nickel plate than before.

The high hardness of the electroless nickel deposit, as deposited, and the increased hardness that can be obtained by a heat treatment, both indicate that this type of plate offers great promise where abrasion or erosion resistance is desired.

Forming

Because of high hardness the electroless nickel coatings should not be expected to withstand severe forming operations. However, one firm reports applying the process to 9/16" O.D. by 0.010" wall steel tubes and then forming them successfully into rectangular shapes without breaking the plating with an average thickness of 0.0003". No heat treating after plating was applied in this case.

Joining

Electroless nickel coated steel can be arc, spot and seam welded. Control of welding conditions is very important.

Both soft soldering and silver soldering by torch methods have been found satisfactory.

Mechanical Properties

After proper surface preparation, the coating of electroless nickel is reported to be almost as adherent as nickel electroplate. Heat treating at 750 to 900°F is claimed to decrease the porosity of the electroless nickel plate. It is stated that the heat treatment causes a "flow" of nickel, closing up pores in the plate and providing a 100% inspection of plate bond. Poor adherence is indicated by appearance of blisters and peeling.

The hardness of electroless nickel, as plated, is equivalent to 45 to 48 Rockwell C. On heating for one hour at 750° to 900°F, the hardness is increased to 60 or above 60 Rockwell C without significant changes in ductility.

Actual tensile strengths of electroless nickel deposits have not been determined, but one firm has estimated approximately 125,000 pounds per square inch.

No data are available as to stresses that may be present in the plate as deposited.

Effects on Base Metal

Hydrogen embrittlement from prepickling treatments prior to electroless nickel plating must be guarded against.

With so hard a coating, it might be expected that the coating would crack and that these cracks would initiate fatigue failure, yet two aircraft companies have reported that, based on limited studies, electroless nickel plate does not affect the fatigue strength of the base material. One manufacturer has used this plate satisfactorily on some coil springs.

One aircraft company has a program under way to determine the effects of electroless nickel plate on the endurance limits of several low alloy S.A.E. steels.

Uses

While much experimental work is progressing, the actual uses of electroless nickel plating to date on regular production items are very limited. It has been used and found satisfactory on injector heads, to reduce the size of oversize holes, on thin walled steel heat exchanger tubes, on steel castings, on dense grey iron castings, on unlubricated bearings and on coil springs.

The process seems to be superior to electroplating of nickel for such purposes as (a) to plate evenly over complex shapes and internal surfaces, without edge or corner build-up. Complex assemblies, threaded parts, pumps, and the interiors of radiators and heat exchangers are examples. (b) For precision plating over machined parts to avoid the remachining often required to remove edge build-up from electroplating. (c) For extra hardness, obtained by heat treating at 750°F, comparable to industrial hard chrome at temperatures below 400°F and harder than chrome in the range 500 - 750°F. (d) For brightness without mechanical buffing. Electroless nickel has a slight leveling effect; therefore, brightness of a rough surface will increase as the plating thickness increases. For small, intricate objects which are difficult to polish, this property may provide important cost reductions.

With quality of finish being independent of shape, electroless nickel is especially adaptable for plating after assembly, provided the assembly does not include (1) cadmium, lead, or zinc, which may inhibit the plating unless masked, or (2) materials which may be harmed by the cleaning solutions or the high temperatures (190-212°F) used in the process.

Costs

The following comments as to costs have been received from different sources who do electroless nickel plating. (1) "Men working closely with the process agreed that it could be economically compared to silver plating." (2) "In plating complex parts, where the process is best used, we have found our costs to run in the vicinity of 75¢ per sq. ft. This is not an absolute value." (3) "Cost depends on the nature of the base metal and on the shape of the item. It ranges between 50¢ to $1.00 per mil plated per square foot of area. The higher cost is for aluminum alloys, magnesium alloys, glass and plastic, where special pretreatments are required. It should be noted a much thinner coating of plate is necessary for full protection than would be the case with electroplating." (4) "The experimental and developmental nature of our work provides little information on comparative production costs. The chemicals required for electroless nickel are roughly ten times as costly as the equivalent nickel anodes alone. This difference is partly offset by the cost of electroplating solutions, electrical equipment, and maintenance, and by the reduction in total nickel required for a given minimum plate thickness. The differences in labor and capital requirements vary with the item, quantity, and regularity of production. The process does not appear currently feasible for automobile bumpers, for example, but wherever the purposes are important, the additional chemical cost should be negligible compared to the savings derived."

Facilities Available

The following companies report having facilities for electroless nickel plating. No data have been received as to what extent their facilities are available to do commercial electroless nickel plating:

1. General American Transportation Co., Chicago, Ill. A pilot plant and a production plant operating in East Chicago, Indiana. Another production plant being erected in Los Angeles, California. Planning to license interested industries.

2. Metal Processing Company, Cedar Grove, New Jersey. Supplies electroplating solutions and offers engineering advice in setting up plating operations in plants. Have installed a number.

3. Thompson Products Corporation, Cleveland, Ohio. The plating equipment is basically a laboratory setup.

4. North American Aviation, Inc., Downey, California. A series of plating beakers, baths and tanks ranging to a maximum of 350 gallon capacity and eight feet in length primarily for experimental rather than routine production.

5. Philadelphia Rust Proof Co., Philadelphia, Pa. Three 130 gallon tanks in operation. Have been using the process for over 2 years.

6. The following companies are said to be doing electroless nickel plating, but no information is available as to the extent of their facilities:

General Electric Company, West Lynn, Massachusetts.

Eastman Kodak Company, Rochester, New York.

Curtiss-Wright Corporation, Wright Aeronautical Division, Woodridge, New Jersey.

Bridgeport-Lycoming Division, Stratford, Connecticut.

American Metal Products, Detroit, Michigan.

Gilbert Tramer Company, Cleveland, Ohio.

Chem-Nickel Company, Southgate, California.

Section 5. Corronizing

Corronizing is a trade name originally applied to coatings resulting from heat treating a composite nickel plus zinc or nickel plus tin electroplate. For the purposes of this manual, the term is extended to include nickel plus cadmium electroplates and heat treated alloy plates of nickel-zinc, nickel-tin or nickel-cadmium. The heat treatment operation is claimed to result in a rather complete interdiffusion and alloying of the nickel with the other metal in the plated deposit. The coatings are reported to provide good protection against corrosion and oxidation up to temperatures of 700 to 1000°F.

"Corronizing" is a development and patented process of the "Standard Steel Spring Company". The metals are electroplated in succession and then given a controlled heat treatment which converts the layers into a "Corronized Coating".(34)

It is clear that the same or similar results would be and are obtained if the electroplating solutions are such as to deposit both the nickel and the desired alloying element, such as tin, simultaneously. Also, it appears that somewhat similar results can be obtained by applying either or both of the metal layers by metallizing (spraying) with a wire gun.

A primary advantage of the process using electroplated nickel is that only 0.0002" to 0.0004" of nickel is required.

A limited amount of information is available on a nickel cadmium type of heat alloyed coating which may be considered as a type of corronizing. The method is the same as outlined above except for the use of cadmium instead of zinc and the introduction of a chromate dip treatment before heat treatment. The heat treatment is at a slightly lower temperature.

Surface Preparation

In all the corronizing process, the surface of the steel is given the normal cleaning required for electroplating. Degreasing, pickling as needed, electrocleaning, are the usual operations.

Nickel Plating (First Plating)

For all of the processes of corronizing, the ordinary standard types of Watts nickel plating baths may be used. These are described in Section 2 of this chapter. For all three types of corronizing, the amount of nickel used is 0.0002" to 0.0004" over all significant areas.

Second Plating

The nickel-zinc combination seems to be more useful than the nickel-tin combination. The nickel-zinc seems to offer superior protection from moisture, fumes, brine and heat.(35) Any of the standard alkaline or acid zinc plating baths may be used as described in Chapter V, Section 7 on Zinc Coatings. The zinc electroplate applied is from 0.0001" to 0.0003" in thickness.

When the second metal coat is tin, it is applied from any of the well known acid sulphate, acid fluoborate or alkaline stannate baths normally used for tin plating. The tin electroplate applied is from 0.0001" to 0.0003" in thickness.

For the newly developed nickel-cadmium type of heat treated coating, the cadmium deposit on the nickel is applied from an acid fluoborate or from a cyanide plating solution. Cadmium plating is described in Chapter V, Section 2 on Cadmium Coatings. After the cadmium top coat has been applied and before the heat treating operation, the article is given a treatment.

Heat Treatments

After the composite plate has been applied, the alloying or interdiffusion of the two metals is accomplished by heating. For the nickel-zinc combination, the heating is at 700 to 800°F for 20 minutes to one hour. For the nickel-tin combination, somewhat lower temperatures are used, 600 to 700°F for the same period of time. For the nickel-cadmium combination, the treatment is at 625 to 650°F for 30 minutes to one hour. In all cases, a controlled low oxygen atmosphere is used in the heat treating furnace. Both induction heating and oven heating have been used.

In all types, if the proper ratio of second metal to nickel first metal has been used, after the heat treatment, no free second metal remains on the surface. The two plated metals have become alloyed together. The alloys formed have rather high melting points. It is reported that in the nickel-zinc combination, the melting point of the coating is in the neighborhood of 1500°F.

General Characteristics

Corronized coatings are smooth, will not peel, crack, or flake when bent around a diameter equal to the thickness of the steel. Corronized steel can be formed and drawn within limits. Also, it can be soldered, brazed, spot and arc welded. In seam or butt welding, some loss of corronized material occurs at the welded edge. In spot welding the loss is at a minimum. It is claimed that paint adheres well to corronized surfaces. It is reported that the corronizing process has no effect upon the properties of the base steel other than the drawing of cold work temper that might result from the heating operation.

Corrosion and Oxidation Resistance

Nickel-zinc corronizing was given extensive tests by one of the large automotive companies. In these tests it is reported that after 1536 hours of the standard salt spray test, a 0.0003" thick corronized layer allowed 2% rust and showed excellent resistance to attack after 16 months exposure to weather. Corronized steel has been reported to have shown marked superiority to electroplated zinc, hot dipped zinc and terne plate steel when exposed for 1100 hours to the Exhaust Muffler Condensate Corrosion Test (Condensate spray: Sulphuric-Hydrobromic acid - Lead compound; pH 3.2, temperature 97°F).

A stove company reports that a corronizing coating of 0.0003" nickel plus 0.0001" zinc alloyed at 750°F for twenty minutes provided protection against corrosion of gas burners made of steel and reaching temperatures of 1300°F. Also, they report this coating as very satisfactory for blue flame oil burner combustion tubes such as are used in cooking stoves and small portable room heaters. They report that in some cases the corronized coating lost its bond when submerged or wetted in kerosene.

Corronizing was tested in connection with cylinders in aircraft engines.(36) The test consisted of an 8 hour run on a test stand followed by 10 days of exposure to outdoor marine atmosphere in Florida with engines up and spark plug holes open. The results reported are shown in Table 16.

Table 16

Corronizing of Aircraft Engine Cylinder

	Treatment	Results
(1)	Untreated cylinders	Walls (total area) covered with heavy rust.
(2)	0.00015" Ni + 0.00005" Zn heat treated 15 minutes at 700°F air cooled.	44% and 53% of area covered with rust, respectively, on two samples tested.
(3)	0.0001" Ni + 0.0001" Zn heat treated 15 minutes at 700°F air cooled.	66% and 53% of the area covered with rust, respectively, on the two samples tested.
(4)	As (2) above followed by 0.0001" Sn.	75% of the area unaffected. Duplicate samples showed 7 to 2.5% rust on remaining 25% of the area.
(5)	As (3) above followed by 0.0001" Sn.	Upper 5" covered with layer of rust - About 44% of total area covered by a heavy film of rust. Both duplicate samples were very similar.

The nickel-cadmium coatings have been tested by one of the Aircraft companies. Plates consisting of 0.0002" to 0.0004" of nickel plus 0.0001" to 0.0002" of cadmium were heated at 630°F for 30 minutes in the preparation treatment. The plates were then heated in air to 700°F for 23 hours followed by one hour at 1000°F and air cooled. Following this treatment, the plates withstood a 100 hour standard salt spray test.

Uses

Nickel-zinc corronizing has been used by a stove manufacturer as a gas burner coating and on the combustion tubes of kerosene burners. It has been seriously considered by an automobile manufacturer as a coating for exhaust mufflers.

A question has been raised as to the possibility that zinc from a corronized coating may embrittle steel. Stainless steel has been found to be embrittled by zinc when the steel is heated to a red heat or higher. There is no evidence that the alloyed zincs in a corronized coating will be liberated at any temperature at which such coatings might be used in aircraft or aircraft engine parts.

The aircraft engine manufacturer using the nickel-cadmium type of corronized coating reports that this plate is more durable than aluminum pigmented silicone paint coatings, that it is thinner and can be used on parts with close tolerances and it appears to have excellent resistance to products of combustion and to gas erosion. It is being used on discs and spacers in gas turbines.

Costs

The costs of corronizing are similar to the costs of electroplated nickel coatings, as discussed in Section 1 of this chapter. The dollar savings in amounts of nickel used are lost in the necessity for a second plating and a heating operation. From the conservation of nickel standpoint, the corronizing process is superior to other nickel plating processes.

Additional Information Source

Information as to patents, licenses and additional information on the process itself may be obtained from the Standard Steel Spring Company, Corronizing Division, Hammond Building, Coraopolis, Pennsylvania.

Section 6. Nickel From Carbonyl

In 1890, Dr. Ludwig Mond of England applied for U. S. Patent #445,230, issued June 30, 1891, on a process of depositing nickel from nickel carbonyl and described its use in producing nickel coatings on both metallic and non-metallic surfaces. The process has been used to produce thousands of tons of high purity "Mond" nickel. It has been used to make nickel deposits on glass, ceramics, plastics and diamonds, as well as on steel.

Nickel deposition from nickel carbonyl can be used to build up worn surfaces, to decrease the size of drilled holes or to form a continuous coating over any surface that can be maintained at a temperature between 350° and 400°F for the necessary length of time. In this temperature range, nickel carbonyl decomposes into carbon monoxide and metallic nickel. The metallic nickel forms a coating on the hot surface with which the carbonyl comes in contact.

Nickel carbonyl at ordinary temperatures is a volatile liquid which boils at about 110°F. It is a compound of nickel and carbon monoxide which is POISONOUS when breathed and should be used only with very thorough ventilation. The vapor is heavier than air, is inflammable, and has a peculiar odor of its own described by some as sootlike and by others as similar to chloroform. The gas is decomposed in the lungs, spreading very finely divided nickel over the pulmonary surfaces, by which it is absorbed in soluble form and spreads throughout the system. It is gradually eliminated by normal body processes in non-fatal cases.

Surface Preparation

Surfaces to be plated with nickel by decomposition of nickel carbonyl must be thoroughly cleaned. Adsorbed oxygen must be avoided. Vacuum pretreatments after the usual chemical treatments are most effective for the removal of adsorbed oxygen.

Plating Process

The plating chamber must be such that the work to be plated may be placed in it and heated to the decomposition temperature without the chamber walls being heated at the same time. The work must be so arranged within the chamber and the plating atmosphere so introduced and moved within the chamber as to obtain a uniform contact of the atmosphere with all portions of the surface to be plated. The chamber and the work must be thoroughly purged of all traces of oxygen before the work is brought up to temperature.

Heating of the work must be uniform. This is a problem which must be solved for each shape and size of article to be plated. Since heating should be limited to the items to be plated, it is desirable to keep the walls of the plating chamber cool by means of a water jacket.

The nickel carbonyl vapor is introduced together with a carrier gas of hydrogen, purified nitrogen or carbon dioxide. Carbon dioxide is the usual carrier gas. The plating atmosphere consists of 20% nickel carbonyl and 80% carrier gas by volume. Total pressures equal to atmospheric pressure are maintained in the plating charge during the decomposition. After plating has been completed, the plating chamber is purged with dry carrier gas to rid it of nickel carbonyl, vapor and the carbon monoxide products of the decomposition. The exhaust gases must be analyzed to determine when it is safe to open the plating chamber.

For the deposition of "thick" nickel plate, the base material is cleaned by abrasion or blasting, a thin coat of nickel is deposited, using the precautions as above, the work is annealed at about 800°F and then the deposit of the desired film thickness is applied. This latter procedure is reported as necessary to obtain proper adhesion of the nickel plate.

It is also very important that the object to be plated is not heated over 400°F during plating. At temperatures over 400°F, nickel acts as a catalyst to accelerate the dissociation of carbon monoxide into carbon and carbon dioxide. This reaction results in the deposition of a heterogeneous mixture of nickel and carbon which has no commercial value at present. Below 350°F, the decomposition of nickel carbonyl is nil.

One American company that has done considerable development work reports a pilot set up for continuous gas plating.

Applicability of the Method

The process plates irregular surfaces as well as inner surfaces. It produces films at a much higher rate than it is possible to obtain by electroplating. (It is claimed that it can deposit 0.001" films in 3 to 5 seconds.)

Characteristics of the Coating

The purity of nickel deposited from the carbonyl is very high; it is of the order of 99.95+% pure. This high purity assures the deposit of having good resistance against high temperature oxidation and corrosion. While it is believed that some porosity may exist in the deposits, they are less porous than nickel deposits made by other methods. The deposit is adherent, ductile and tough. The "throwing power" of the method is much superior to that of electrodeposition.

The nickel deposit is darker than silver, but its reflectivity for long waves is high: 96 to 98% for heat waves, whereas silver is about 97 to 99% for the same range.

The coating is softer than that produced by electroplating of nickel and, therefore, may be somewhat less resistant to abrasion and erosion than other types of nickel coatings.

No specific data are available as to joining methods that might be used. It is understood that although adhesion is good, it is not adequate to withstand severe forming operations. Undoubtedly, carbonyl plated articles may be welded in the same manner as similar articles nickel coated by other means.

Costs

The initial installation costs for suitable and safe equipment for gas plating from nickel carbonyl are high as compared to other methods of nickel plating. With suitable equipment installed, and after the heating problem is solved for a particular article to be plated, the costs of plating by this method should be as low as, or somewhat lower than, the costs for electroplating of nickel.

Facilities Available

The Commonwealth Engineering Company of Dayton, Ohio, has developed and patented equipment for gas plating from carbonyl vapors.

Section 7. Nickel and Nickel Alloy Clad Steels

A clad steel plate is a composite plate made up of a commercial grade of steel plate, to one or both sides of which there is uniformly and permanently joined a veneer or cladding of a corrosion or heat resistant metal. The clad metal is bonded to the base metal by one of several methods, such as: 1. Heat and pressure, 2. casting, 3. intermelting, 4. arc welding, 5. fusion welding, 6. resistance welding. The details and applicability of each method are available in the literature.(37)

In the place of a commercial grade of steel plate, other backing plate material can be used. Advantage can be taken of materials which have high tensile strength such as the low alloy steels, or the elevated and subzero temperature properties of special steels.

The corrosion resistant metals used as cladding are homogeneous and dense in structure. They are unchanged in any way by having been bonded to steel.

This section discusses the nickel and nickel alloy clad steels. A later section (Chapter V, Section 10) discusses the stainless steel clad steels.

Types of Nickel and Nickel Alloy Clad Steels

The following grades of nickel and nickel alloy clad steels are available: 1. Nickel; commercially pure nickel with an average nickel content of 99.4%. 2. "L" Nickel; a special low carbon (0.02 Max.) grade of nickel used for high temperature service. 3. Inconel; a 78% nickel, 14% chromium, 6% iron alloy. This alloy combines the quality of nickel with the extra resistance to heat and oxidation of chromium. 4. Monel; a 67% nickel and 30% copper alloy. This is a general purpose corrosion resistant alloy with the strength and toughness of structural steel. Although this alloy is not heat-treatable, a wide range of strength is obtained by mechanical working.

Corrosion Resistance

A. Nickel and "L" Nickel Clad

The discussion of corrosion resistance properties of Electroplated Nickel in Chapter III, Section 3 is applicable to the nickel clad steels.

B. Inconel Clad

Inconel shows the same high corrosion resistance to alkaline solutions and reducing conditions as nickel. Inconel is superior to nickel and monel in its resistance to alkaline sulphur compounds and hydrogen sulphide at atmospheric and high temperatures. Because of its chromium content, it is also superior in resisting strongly oxidizing acid solutions and dilute organic acids. Inconel is not affected by dry gases, steam, air and CO_2 at atmospheric temperatures nor by steam at elevated temperatures.

C. Monel Clad

Monel Metal Clad Steel is used in industry where the corrosive conditions involve contact with common salt, dilute sulphuric acid, cold dilute hydrochloric, hydrofluoric and phosphoric acids, and strong caustic soda. It is not resistant to certain oxidizing corrosives such as nitric acid, sulphurous acid and ferric chloride.

Effect of Elevated Temperatures

A. Nickel Clad Steels

The high temperature properties of the nickel on nickel clad steel are similar to those of the Electroplated Nickel Steels as discussed in Chapter III, Section 3. Nickel generally retains its strength at elevated temperatures and its strength, ductility and toughness in the subzero ranges.

B. "L" Nickel Clad Steel

The "L" Nickel is a grade of nickel used for high temperature service. It is recommended in general for fused salts at 300 -1100°F, and specifically for fused caustic and fused nitrates. This type of nickel is preferred for continuous service in the range of 600--1100°F, or for vessels which require a stress relief treatment.

C. Inconel Clad Steel

Inconel combines the qualities of nickel with the extra resistance to heat and oxidation of chromium. Inconel is reported free from intergranular deterioration at high temperatures. It may be heated and cooled repeatedly from 0° to 1600°F without embrittlement.

D. Monel Clad Steel

Monel metal is somewhat similar to nickel in that it cannot be used at temperatures over 600°F in a sulphurous atmosphere. Monel metal is less resistant to oxidation attack than pure nickel. The limiting temperatures for nickel and monel in an oxidizing sulphur free atmosphere are 1900° and 1000°F respectively. Monel, like inconel and nickel, has excellent properties at subzero temperatures. It retains its strength and hardness with decreasing temperature without an appreciable decrease in ductility and impact value.

Erosion and Abrasion Resistance

Specific data on abrasion and erosion resistance of nickel and nickel alloys are limited. It can be expected that these materials, depending upon their hardness, will show comparatively high abrasion and erosion resistance.

Monel, nickel and inconel metals are reported to have high resistance to cavitation-erosion attack.

Mechanical Properties

The mechanical properties of the clad metal are dependent upon the backing or base metal and the cladding metal used. Actual test data on the mechanical properties of the various nickel or nickel alloy clad steels are not readily available. Some data on the mechanical properties of hot rolled nickel clad on low carbon steel are shown in Table 17.

Table 17

Mechanical Properties Hot Rolled Nickel Clad Steel

Yield Strength	35-45,000 psi
Tensile Strength	60-70,000 psi
Elongation 8"	35-25%
Reduction in Area	65-50%
Hardness Brinell	
3,000 kg	125-150
Rockwell B	70-80

The ASME Boiler Code and the ASTM Specifications require a minimum bond shear strength for clad steels of 20,000 psi. One manufacturer reports the following typical shear strength values of the bond obtained by tests on production plates in the annealed condition: Nickel 46,300 psi, Monel 48,000 psi, Inconel 48,700 psi.

Fabrication

These clad steels are amenable to practically all of the normal manufacturing or fabricating procedures. Data are available in the literature(38,39) on: 1. Various conditions for welding clad metals; 2. Shearing and punching; 3. Bending and rolling; 4. Machining; 5. Flame cutting; 6. Grinding; 7. Buffing and polishing; 8. Sandblasting; 9. Pickling; 10. Cleaning and passivating; 11. Heat treating.

It is beyond the scope of this manual to discuss these operations in detail. The nature of the backing material and of the clad metal are important factors.

The clad steels must be handled carefully during shipment, storage and fabrication. Scratches, gouges and embedded material reduce the cladding thickness at those points and often act as focal points for corrosion. Tools used in fabrication of clad material should be wiped clean of any loose scale particles or foreign matter which can become embedded in the clad surfaces.

Cost and Availability

Generally, the widest possible sheet or plate that can be used should be specified. It is more economical to use a single wide plate than two plates of half width. The wider plates require considerably less finishing, grinding and other preparation than are required for two plates of lesser width.

It is not economical or feasible to produce clad metals much thinner than 3/16". For thinner materials, the cost of clad metals approaches the cost of the solid corrosion resistant material of the same thickness. It may be possible to lower the cost if the tonnage requirements are high. Where conservation of critical alloys is a necessity, the cost factor may not be the criterion.

Plate sizes of clad steel generally available range from 3/16" (width 48" to 132") to 2" (width 48" to 178"). Not all sizes and thicknesses are available in all grades. For more details, it is best to inquire of the various producers of the clad metals.

Uses

The chemical, petroleum, paper and pulp industries and others have adopted the use of clad materials to replace the solid corrosion and/or temperature resistant alloys. This has resulted in a tremendous saving of critical alloys and of costs. Clad metals can be used in those instances where the high temperatures do not drastically affect the strength of the backing material.

In aircraft and aircraft engine parts, from the economical and critical alloys conservation standpoint, clad steel might be used in place of solid nickel, monel or inconel metal where the strength at elevated temperatures of the backing material is adequate. Of the three nickel alloys, nickel, monel, and inconel, the latter is now used in aircraft parts exposed to temperatures in excess of 1200°F. In this instance, it may not be possible to replace inconel metal by inconel clad steel as the steel backing material may not have sufficient strength at the temperatures involved.

Facilities Available and Sources of Information

Firms reported as producers of clad steels are shown in Table 18.

Table 18

Producers of Clad Steels

1. Alan Wood Steel Company	Conshohochen, Pa.
2. Allegheny-Ludlum Steel Corporation	Brackenridge, Pa.
3. Copperweld Steel Company	Glassport, Pa.
4. Granite City Steel Company	Granite City, Ill.

Table 18 (cont'd)

5. Ingersoll Steel Division - Borg Warner Corporation	Chicago, Ill.
6. Jessop Steel Company	Washington, Pa.
7. Lukens Steel Company	Coatesville, Pa.
8. Superior Steel Company	Carnegie, Pa.

CHAPTER IV

DIFFUSION COATINGS

Section 1. General Discussion

Diffusion coatings on steel are created by the addition of an alloying element to the surface of the steel and simultaneously heating to a temperature below the melting point of the steel, but of a sufficiently high temperature to cause diffusion and for a sufficient time to allow for the desired migration. Diffusion, in this case, is the movement of atoms of the added element in solid solution in the steel. Since the alloying element is at a high concentration, as added to the surface, the direction of migration is inward away from the surface.

The rate at which an added element will diffuse into steel is controlled by the size of the atom of the added element, its solubility in the steel to which it is added, the tendency of the element to combine with iron or with other elements in the steel to form stable compounds of larger size and lower solubility in the steel, temperature and time. Depth or thickness of the diffusion coating that can be formed is greatest under the following conditions: 1) the smaller the size of the atom being added, 2) the higher its solid solubility in the steel, 3) the less it tends to form compounds, 4) the higher the temperature and 5) the longer the time.

Strictly, the iron and the coating element interdiffuse, iron atoms diffusing outwards into the alloy layer at the same time that the alloying element diffuses inward. This is in accord with the basic rule that the movement of atoms is usually in the direction from regions of high concentration toward regions of low concentration in order to achieve homogenity.

The mechanism of the reaction that brings the alloying element to and deposits it on the surface of the steel may vary considerably. The carrier of the alloying element to the surface may be a gas containing a gaseous compound of the addition element, a liquid containing a high concentration of the addition element or compound of the element, a pulverized mixture of the addition element in a ceramic type of material or the addition alloying element may be brought in direct physical contact with the steel surface. Packing in a powder of the addition element and electrodeposition of a layer of the addition element are among the methods used to create the intimate physical contact needed for diffusion to take place. The required intimate contact may be the result of a metal replacement reaction taking place at the surface of the steel in such a manner that iron is removed from the surface as the addition element is added.

Carburizing, cyaniding, nitriding and carbonitriding are examples of the oldest and most widely used processes for the creation of diffusion coatings. Actually, diffusion coatings are formed in the hot dip coating processes used on steel such as in aluminizing and galvanizing which are discussed in Chapter II and Chapter V, Section 7, respectively, in this manual. Carburizing and nitriding, or combinations thereof, do not offer much of value as diffusion coatings for protection against corrosion and oxidation at temperatures above 500°F.

Among the elements which may be used to produce diffusion coatings of possible value for the desired protection are chromium and silicon. Methods of chromizing and siliconizing are, therefore, the subjects of the following sections of this chapter. One outstanding advantage of diffusion methods of coating is the tendency of such coatings to approach freedom of pin hole porosity. The diffusion process extends both inwardly from the surface being treated and parallel to the surface so as to tend to fill in any spots or voids in the layer of alloying element brought to the surface. In other words, inherently the processes yield almost pin hole free coatings as opposed to most other coating processes.

Section 2. Chromizing - General Discussion

Chromizing processes are those which create diffusion coatings with chromium as the addition element. Chromium and high chromium steels and irons are noted for their corrosion and oxidation resistance. Eight chromizing processes are available.

1. Kelley process.(44,53,57,58) In 1919, Kelley and his co-workers carried out the first systematic investigation of chromium diffusion and developed a process of chromizing by solid contact with chromium powder. The process employs temperatures of 2350-2500°F and produces rather hard surfaces. A treatment of approximately 4 hours at a temperature of 2350°F gives a penetration of 0.005". Because of the high temperatures involved and the rapid rate of deterioration of the chromizing compound, this process, today, has more historical than practical value.

2. Bergman process.(44,47,53,54) This is a salt bath chromizing process. There is some controversy as to the cost and simplicity of this process, although there are a number of attractive features in this method. Some technical difficulties, such as the serious corrosive action of the salt bath chlorides on the pots, the size of the ceramic coated pots required when electrode furnaces are used, and how to cool the chromized articles have not been overcome so as to make the process commercially feasible.

3. B.D.S. process.(44,48,53) (Becker, Daves and Steinberg) This is a gaseous chromizing process. It consists of packing the articles in a mixture containing chromium chloride and a porous porcelainic material and heating to high temperatures. The porcelain material is previously saturated with chromous chloride. This is done by passing hydrogen and gaseous hydrochloric acid into a mixture of chromium metal and porous porcelain maintained at a high temperature. In the chromizing operation, temperatures of 1650 to 2100°F are used.

4. Marshall process.(44,53) The B.D.S. and the Marshall processes are very similar to each other, as both are gaseous chromizing processes utilizing chromium chloride. The difference lies in the fact that the latter method produces chromium chloride during the chromizing process by using a mixture of powdered chromium, alumina and ammonium chloride. Temperatures of 1650° to 2100°F are used. The resulting surfaces, however, are rather rough.

5. Process of Diffusion Alloys Ltd. - Diffusion Alloys Corporation.(40,41,42,43,44,46,51,53) This process also is a gaseous process, although carried out in closed retorts or boxes heated in conventional furnace equipment. The mixtures used in the boxes consist of ferro-chromium powder, ammonium iodide and unvitrified kaolin. Temperatures of 1650° to 2100°F are used.

6. Onera process.(44,48,53) In this process, the objects are packed in a mixture of pieces of chromium metal and broken porcelain. Underneath this pack mixture is a layer consisting of powdered chromium, alumina and ammonium fluoride which generates chromium fluoride. Hydrogen is introduced into the box or retort to eliminate oxygen and to act as a carrier gas for the vapors of chromium fluoride. Temperatures of 1900 to 2050°F are used.

7. Johnson process - Paint Chromizing. This process is a very recent invention that has not yet been adequately developed, but for which a United States Patent has just been issued to Mr. Wallace Johnson. The steel to be chromized is painted by brush or dip methods. The coated article is introduced into an ordinary furnace with no atmosphere control. As the article heats, the vehicle used in the slurry burns out, the ceramic frit melts to form an impervious and protective molten blanket which holds the chromium bearing material in close contact with the surface of the article. The chromizing reaction takes place at temperatures between 1800° to 2000°F. A chromized surface is obtainable in 15 to 30 minutes at the maximum temperature. The article is removed from the furnace and allowed to cool in air. The enamel coating is readily cracked off leaving the chromized surface.

8. Chromium Electroplating plus heating. Chromium of the desired amount is electroplated direct on the surface to be chromized and the article is then heated to a temperature of 1850°F or higher for a sufficient time to cause the desired diffusion into the steel. (50)

In all chromizing operations the degree of diffusion penetration of chromium which is obtained is influenced by the composition of the steel, particularly the carbon content, that is being used. Chromium combines readily to form chromium carbides. Chromium carbides are much less soluble in iron than chromium metal, especially below temperatures of 1800 to 1850°F. Indications are that the chromium carbides are much less soluble in iron at 1850°F than they are in chromium metal. Carbon tends to act as a barrier to chromium diffusion because of this low solubility of the carbides in the iron and because of the lesser mobility of the chromium carbide complex as compared to the chromium metal atom itself. This tendency of carbon to interfere with chromium diffusion becomes of importance with 0.10% of carbon in the steel.(44,52)

Chromium carbides by themselves are hard and brittle. Chromium carbides dissolved in iron or steel are strong hardeners for the iron or steel. However, it cannot be said that chromized layers on high carbon steels are brittle or have a tendency to peel. Although the layers are shallower and harder, they are firmly and thoroughly alloyed with the steel and do not have peeling tendencies. Chromizing has been applied successfully to plain carbon steels with carbon contents as high as 1.30%, to various types of tungsten and tungsten molybdenum high speed steels, to both medium and low carbon low alloy steels and to low carbon steels.

Most of the alloying elements normally used in steel, other than carbon, have no effect or a somewhat beneficial effect on the rate of diffusion of chromium in the steel and, therefore, on the ease with which the steel may be chromized. Particularly beneficial in steels containing about 0.20% carbon are carbide forming elements such as columbium, tantalum, titanium, molybdenum, tungsten and manganese. To the extent to which these other carbide forming elements combine with the carbon present in the steel, there is less carbon available to form chromium carbides and act as a barrier to diffusion of chromium. A number of low alloy low carbon steels are available and suitable for chromizing. It is obvious that a deep decarburizing treatment could be applied to a medium or high carbon steel before chromizing in order to obtain a surface layer into which chromium would diffuse most readily. In any such attempts, it must be remembered that the rate of carbon diffusion is much greater than the rate of chromium diffusion. While the chromium is diffusing inwardly from the surface, into the decarburized skin, carbon diffuses outwardly from the undecarburized core into the skin to meet the chromium coming from the other direction. To be effective, any prior decarburizing must be to a depth of several times as great as the chromized layer desired.

Certain investigators(49,60) report that increased depths of diffusion of chromium are obtainable if the treatment is modified so as to include silicon alone or some silicon and some aluminum in the reaction mix for chromizing. The claims are that the depth of diffusion of chromium is greater when the chromizing operation takes place simultaneously with some siliconizing or some siliconizing and aluminizing. Just how silicon atoms can act as carriers, drivers or leaders for chromium atoms in the diffusion process is quite obscure.

Section 3. Pack Chromizing

Pack chromizing is being done commercially by methods 3, 4, 5 and 6 as outlined in Section 2. The results are surface layers of high chromium content, of appreciable controlled depth, of good resistance to corrosion, oxidation and erosion at elevated temperatures. The surface characteristics in these respects are superior to those of the straight chromium stainless steels. The straight chromium stainless steels owe their surface stability to a chromium content of 13 to 22%, whereas the chromized layers on steel have much higher chromium content than that found in chromium stainless steel.

The parts or articles to be chromized are packed in the dry chromizing compounds in sealed boxes or retorts and heated to temperatures of 1650 to 2100°F for 2 or more hours.(43,44,45,46,47, 49,51,53) The temperature and time depend on the steel being treated, the size and shape of the part and the depth of layer desired. A neutral or reducing atmosphere in the boxes or retorts is desirable. The chromizing mixture may contain some aluminum or silicon or both, depending on the desired composition of the layer to be formed. During the period at the elevated temperature, the work is supported somewhat by the mixture in which it is packed so that distortion is reduced.

The actual chromizing reaction takes place in the gaseous phase. Vapors of chromium compounds are formed in the mix and travel to the surfaces of the articles in the pack and deposit the chromium on these surfaces. After deposition on the surface, the diffusion process proceeds. Since the gaseous vapors carry to all points within the box or retort, the throwing power of the process is very high. A case is produced in cavities and crevices, wherever the reactive gases may enter.

To a large extent, the actual chromium deposition on the surface of the steel is the result of an exchange or metal replacement reaction. Atoms of iron are removed from the surface as atoms of chromium take their places. Since atoms of chromium and of iron have similar atomic weights, structures and diameters, there is no appreciable build up and resulting dimensional changes from the formation of the coating. The rate of diffusion is much slower than the rate of supply of fresh atoms of chromium to the surface and, therefore, the diffusion process controls the thickness of layer produced. A concentration gradient is necessary for diffusion to take place. The chromium concentration at the extreme surface is highest and it decreases towards the core of the article being chromized.

Surface Preparation

Surfaces to be chromized must be free of scale and rust. These are removed by the usual processes of pickling, mud blasting or by mechanical means. Small tarnish areas remaining or formed after cleaning do not interfere.

Chromium Content

The typical structure and composition of chromized surface layers are shown in Fig. 2, a photomicrograph at 200X, and Fig. 3, a graph of chromium concentration versus depth of layer on a low carbon steel.(40) In Fig. 2: A - represents the thickness of the case as usually reported; it is the distance from the surface to the dividing line which appears after etching, B - represents the actual penetration of chromium.

The chromium content of the case, as shown on the above graph, is approximate and depends upon the conditions of the chromizing treatment and the composition of the steel. Usually, it is between 40-50% at the surface and decreases towards the center of the object.(40,42,43,44,48,49,51,53) Twenty four percent chromium content of the case is considered the average. The dividing line, as it appears after etching, separates the different transformation phases of the steel which develop at approximately 13% chromium.(40, 43,44,47,49,53,58)

The chromized case on low carbon steels resembles in its behavior the type 400 series stainless steels. The outermost surface resembles type 446 stainless for a small depth only. At the dividing line, which under the microscope appears to be the end of the case, type 410 composition prevails.

Hardness and Ductility

Chromized cases may be hard or relatively soft depending upon the composition of the base steel and the treatment used.

Hard cases have high chromium carbide content. They have high erosion and abrasion resistance and are used in some aircraft components. For the purpose of this report, however, the softer highly corrosion and heat resistant types of coating are considered.

The surface hardness of chromized low carbon steel is about 120 Brinell. As the carbon content of the steel increases, a very considerable increase occurs in the hardness of the chromized surface. For 0.3% C, it is in the region of 250 Brinell, and for 0.5% C it is about 500 Brinell.(44,49) For still higher carbon, it may be as high as 1500 Vickers.(43)

To determine the hardness of these coatings, microhardness test methods must be used with loads not exceeding 100 gr. Conventional Rockwell and Brinell tests cause penetration of the indenter through the coating and give misleading results.

The ductility of the case, developed on low or medium carbon steels, is good.(40,42,43,44,48,53) The gradual decrease of chromium content favors absorption of mechanical deformation and minimizing of internal stresses caused by thermal changes.

Thickness

The thickness of the chromized case may vary from a thin (0.0007")(42) and extremely hard one (VHN 1500) on high carbon steels to a thick (0.035")(51) and ductile one on low carbon steels. The thickness is a function of the composition of the steel, composition of the chromizing compound, temperature and time of the process and surface conditions. For all gaseous chromizing processes, a layer of 0.002 to 0.004" is obtained after 3-4 hours on a low-medium carbon steel.(44,53)

The carbon content of the core impedes the penetration of chromium and may prevent the obtaining of a thick case. For thick cases low carbon steels should be used. When it is desired to have medium or high carbon properties of the core, heavy decarburization of the surface before chromizing is necessary.

Some alloying additions have great effects on the diffusion rate of chromium. They can bind carbon and may influence the lattice structure so as to speed penetration by chromium.

The higher the temperature of the chromizing process, the faster are the reactions and the faster the formation of the case. Longer time favors thicker case formation. High temperature and time, however, may produce excessive grain growth and distortion. The conditions of temperature and time must be such as will give the optimum results.

Uniformity

In this process the reaction gases penetrate into pores, holes and slots as well as inside of long tubes. In general, there is no build up of the case at the corners of the objects.

As an example of this characteristic, rectangular tubes 37½" long, 1½" wide and ½" deep (strip heater casings) are being chromized to a uniform case depth over the entire inside as well as outside surface.(43)

Adherence

Due to the gradual decrease of chromium content, formed by the substitution and diffusion reactions of the process, the case forms an integral part with the body of the object to which it is adherent and cannot be stripped off by merely mechanical means. The chromized case is an iron chromium solid solution, it is ductile and adherent at room and elevated temperatures. Under certain conditions, when high or medium carbon steels are treated, a soft, decarburized layer may form underneath the hard carbide containing skin. This effect is undesirable and decreases both the adherence and the mechanical properties of the carbide containing layer.

Appearance

Most chromized surfaces are silvery gray with a satin smooth finish. The smoothness depends to some extent on the finish of the base prior to treatment as well as on the composition of the chromizing mix. High luster can be obtained by subsequent polishing.

Corrosion Resistance

In some applications chromized steels have replaced both ferritic (straight chromium) and austenitic (chromium nickel) stainless steels. Chromized surfaces are resistant to atmospheric corrosion including industrial atmospheres containing sulphur compounds. They are unaffected by petroleum oils, hot or cold water, steam, sea water and nitric acid. They are not fully resistant to phosphoric acid and bleaching solutions. They are not resistant to dilute hydrochloric or dilute sulphuric acid. They are not resistant to free halogens such as bromine or to free halogen acids such as hydrobromic acid.

By combining siliconizing with chromizing to produce a silicon bearing high chromium layer, some added resistance to the dilute acids and the halogen compounds may be obtainable.

Some estimation of the corrosion resistance of chromized surfaces may be obtained by comparing them with the iron chromium alloys.

Full protection to atmospheric corrosion requires 12 to 18% Cr. The low carbon plain chromium steels with as much as 30% Cr are resistant to oxidizing acids, such as boiling nitric and dilute aerated sulphuric acids.(55)

A chromized surface corresponds in corrosion resistance to a steel with more than 30% chromium. It is, therefore, better in many respects than other more weakly alloyed stainless steels and even better than 18-8 steel.(59)

Oxidation Resistance

One of the great advantages of chromized surfaces is their ability to resist oxidation at elevated temperatures. A survey of the claims in the literature indicates that the life of chromized low carbon steels with the 0.004 to 0.006" coating is practically unlimited up to 1200°F;(40,43,48) at 1470° to 1560°F they can be used for several hundred hours;(48,53) at temperatures up to 1560°F chromized steels show excellent oxidation resistance and might be usable for engine and furnace parts;(44,49,52,56) at 1650°F the chromized steels can be used for prolonged periods and even at 1800°F for short time when mechanical stresses are low;(40,43) at temperatures of 1830 to 2010°F the layers disappear after a few hours.(48) Other investigators, however, claim even longer life for chromized steels at temperatures of 1800°F and above. For example, R. L. Samuel and N. A. Lockington(44) state that "---up to 1830°F, if parts are not likely to be knocked, chromized steel has a reasonable life, since the scale first formed adheres well".

Among chromized coatings, the most resistant to high temperature are those containing, besides chromium, aluminum, silicon or both.(40,43,44,48,49) It is claimed that by the formation of a complex oxide film a full protection is then obtained up to at least 1920°F.(49,60)

An investigation of oxidation resistance of iron chromium alloys shows that at 22 or higher percent chromium, the alloys have a negligible weight loss after oxidation tests at 1832°F for 48 hours.(55) A 37% Cr 7½% Al alloy is resistant to oxidation at temperatures approaching 2400°F.(55) In comparing these alloys with chromized steels, it must be borne in mind that the latter has a high chromium content limited to a thin layer only.

Joining

Welded or riveted assemblies can be pack chromized. Although the process has high throwing or penetrating power, it will not penetrate to the faying surfaces of a lap joint nor will it bridge a gap or opening at the edge of a lap joint. Brazed assemblies cannot be chromized because the chromizing temperature is too high. For uniform coverage over weld beads it is obvious that the weld rod material must be of a suitable composition for chromizing.

Most of the known joining methods can be used on chromized parts. However, when joining is done after the treatment, care should be taken that the application does not remove the skin at any spot and does not expose the base metal underneath. Joining of chromized parts is best done by spot, seam or stud welding. Riveting or staking is also satisfactory. Fusion welding as well as brazing is possible.(40,42,43) When riveting has to be used it is preferred to punch the rivet holes before chromizing. Stainless or chromized rivets should be used. Fusion welding can be hand or automatic, inert gas shielded or conventional. Care must be taken that the bare base metal is not exposed by fusion welding. Stainless welding rods should be used.

Brazing can be done with fluxes and rods designed for stainless steel. Brazing is limited to the metals which are corrosion and heat resistant, and which when molten, will "wet" the chromized layer and which can be applied with ordinary fluxes and by ordinary methods.

Formability and Additional Treatments

The process when applied to low carbon steels produces ductile cases which can endure rather severe forming operations such as bending, drawing, crimping, stamping and bumping. Therefore, sheets can be treated first and then formed to desired shapes.

Surface finishing operations such as grinding, lapping or honing of treated parts are not recommended as they will remove the layer with the highest chromium content. Chromized parts can be subjected to any forming operation which does not remove the outermost layer. Where chromizing is used for corrosion or heat resistance, parts are frequently used in the "soft" condition. In some instances, this presents an advantage in subsequent forming operations.

Chromized steels can be heat treated to get different properties of the core than those remaining after chromizing. Special or standard heat treatment, normalizing, or hardening suitable for the steel involved can be used without affecting the chromized case. Where relatively high ductility and low strength are objectionable, heat treatments may be used. This technique has been used on bolts of SAE 1020 steel. After chromizing the steel is coarse grained and fully annealed and not sufficiently strong to resist the torques involved, also due to the softness, the threads are easily damaged. These shortcomings are overcome by a heat treatment at 1525°F. The thin, tightly adhering oxide film formed during heating and cooling makes the surface well resistant to seizing.

The surface produced by the chromizing process presents a good base for other finishes such as paints, lacquers, plating, etc.

Effect on the Steel Base and Dimensional Stability

The temperatures for chromizing are above the critical range of the base steels used. Invariably the base steel becomes fully annealed and any hardening through cold working or prior heat treatment is removed. Also, grain growth can and often does occur at the high temperatures and for the long times involved. However, the steel can be heat treated to restore or improve the former characteristics of the base metal as described under Formability and Additional Treatments.

Thick cases should not be obtained on the expense of excessive grain growth of the base metal by long treatments at high temperatures. During treatment some distortion and size change of the objects may take place. Actual dimensional changes are small and often negligible. This is especially true, when parts are small, free from high internal stresses, symmetrical and well supported during the treatment by the chromizing mixture. The weight change during the treatment is insignificant.

Little specific data have been made available as to the effect of chromizing on endurance or fatigue limits. On low carbon steels, where the chromized layer is ductile, little adverse affect is to be expected. On medium or higher carbon steels where the chromized layer is high in chromium carbides and is hard there may be an adverse affect. Some of the aircraft engine companies are attempting to evaluate this problem.

Limitations

All coatings lose usefulness suddenly when pierced by corrosive or mechanical action. With chromized articles the graded composition must be considered. Each fraction of a thousandth of an inch removed or penetrated exposes a lower grade alloy which has less resistance to the attack and a gradual reduction in effectiveness results.

During the chromizing process any internal stresses are relieved, and the parts undergo some thermal expansion. Under these conditions it is too much to expect that long shafts, slender pieces of tubing or complicated bulky castings will retain tool tolerances. The chromized case is thin, therefore, subsequent grinding cannot be used to compensate for dimensional changes. However, these slight dimensional changes can be offset successfully by straightening parts which have warped and by restoring close tolerances by cold coining.

It is obvious that pack chromizing is limited to such sizes and shapes as may be packed in available treating boxes or retorts. The boxes or retorts themselves are a major, important and costly part of the process. Large boxes are slow in heating and slow in cooling. Treating capacity is lowered by these long time periods.

While little information is available as to life of or regeneration additions to the packing mixes used it is clear that the control and **replacement** or regeneration of such mixes must be a portion of the overall process.

If parts to be chromized are bulky and made of thin sheet metal the operation of packing so as to be adequately supported by the mix while at a temperature in the neighborhood of 1900°F becomes a difficult one.

If thin sheet metal of the order of 0.010" thick is to be chromized on both surfaces it is obvious that 0.005" depths of chromizing are out of the question. The total depth of the two chromized layers may become a major portion of the thickness.

Uses

Electric strip heater casings of chromized steel are being used quite successfully. Acceptance testing is based on 1000 hours at 1200°F. In this case, 410 stainless steel is being replaced by chromized SAE 1010 steel. The ductility of the chromized part is sufficient to permit flattening and crimping at room temperature.

It is claimed that chromizing has proven satisfactory in such applications as carburizing boxes, furnace skids, high temperature steam and soot blower nozzles, cyaniding retorts, annealing baskets, racks and grids and other items of heat treating furnaces. Some are reported to have been used at 1650 to 1850°F. It is claimed that at temperatures over 2000°F service for upwards of 600 hours have been obtained.(49)

Another reported heat resistant application is dousers for carbon arc searchlights where the assembly consists of pairs of telescopic rings made from chromized iron. It is reported that chromizing of steam turbine rings is in production. The rings are machined to size, processed and assembled. Dimensional changes are insignificant. Corrosion and steam erosion resistance are reported as good.

It is reported that chromizing is being tested in the following parts:(41) a) heat shields for rocket motors, b) sheaths for electric space heaters, c) nuts and bolts which are subject to heat, d) burner shields and tips, e) combustion and exhaust parts for engines, rockets, guided missiles, etc., f) steam turbine parts, g) auxiliary components for jet engines.

The British Intelligence Objectives Sub-Committee, sent into Germany to make a thorough study of chromizing development during World War II, found many examples of successful chromizing on a broad commercial scale.(58) Typical examples were:

1. Chromized valves for controlling fluid flow. This application helped to conserve the scarce copper base alloys previously used, in addition to supplying superior corrosion protection.

2. Chromized bolts. By chromizing the bolts before the threads were rolled, increased corrosion protection was obtained on the threads and the chromized layer was work hardened by the rolling operation.

3. Chromized manifolds for internal combustion engines. Reports indicate that these tubes operated satisfactorily at 850°C (1560°F) even where the service at this temperature was continuous.

4. Chromized pre-heater tubes. These tubes were used for preheating air for combustion in the engine of a destroyer. They operated at 750°C (1380°F) with the air passing through while the fire passed around the outside. Tubes were examined at the end of 19 months service and found to be in very good condition.

5. Chromized thin walled tubing. This development permitted the use of low carbon steel tubing with its excellent drawing and fabricating characteristics in a number of installations which previously required the high corrosion resistance of stainless steel.

6. Chromized turbine blades. Chromized turbine blades replaced chromium plating on exhaust gas turbine blades because of its non-scaling properties.

To investigate the values of chromizing, one aircraft company had some parts processed. The parts were 1" diameter spline shafts 12" long of 4130 and 4340 steel. Under salt spray tests and under humidity cabinet tests there was an initial corrosion attack on the edges but this stopped quickly. The coat was .0001" thick. The surface, although too thin to test, was reported as being not hard. Superficial Rockwell hardness readings were lower after the chromizing treatment. It was reported that the specimens were treated at 1650°F for 8 hours. They were packed in powder and allowed to cool in the furnace. They were reheated and hardened after the chromizing treatment. The reheating for hardening was done in air in a gas muffle furnace. There was no scaling but some discoloration. The case did not spall off in the heat treatment. Under the salt spray test rusting was encountered in holes and slots. The treatment may not have penetrated these areas.

In another case and for another company, some 1095 spring steel parts were chromized. The coating was about .005" thick. The material was heat treated after the chromizing process. The surfaces were harder than the core after heat treating. These parts are in use satisfactorily on a commercial plane.

In another case chromizing is being considered for a part to be made of SAE 8740 steel. A coating thickness of 0.0005 to 0.002" is being considered. Such a case will contain an appreciable amount of carbides and will have a relatively high hardness and the possibility of brittleness and surface crack initiation must be evaluated.

Costs

Generally, chromium-stainless steel costs several times as much per pound as carbon steel in tubing, sheet, or bar form. Therefore, chromized steel used in place of stainless steel may present considerable saving.

In pack chromizing processes the treatment cost of the parts depends primarily upon the space the parts occupy in the retorts and the duration of the process. For large production runs, a more accurate cost calculation can be made on the basis of the amount of regenerated compound used per part treated, the labor required for powder preparation, stacking the parts, sealing the retort, charging and unloading the furnace, cleaning the parts, inspection, shipping, and handling. Fuel cost, retort depreciation, as well as general maintenance, supervision and overhead charges must be included. As seen from the large number of variables, processing of each part must be calculated individually.

The cost savings of chromized steel when compared with stainless steel come from (a) eliminating the need for highly alloyed steels, (b) replacing two or more heat treatments by one chromizing operation, and (c) decreasing of fabrication difficulties. Although chromizing is claimed to be less expensive than hard chromium plating, this is doubted. It is much more expensive than conventional surface hardening methods (e.g., cyaniding). The process is flexible and lends itself both to small lots and mass production. The cost per unit varies widely with quantities.

Available Facilities

The chromizing process was introduced in this country in 1948-9 by a branch of Diffusion Alloys Ltd. called Diffusion Alloys Corporation, sometimes called Fusion Alloys Corporation. Chromizing is being done on a contract basis by Chromalloy Corporation of New York (109 West 64th Street, New York 23, N.Y.) and Chromizing Company of California, in North Hollywood, California. Further expansion by establishment of other plants or through license agreements for large users is expected.

Section 4. Paint Chromizing

Among the various processes for chromizing as listed earlier in this chapter is process number seven called the Johnson

Process of Paint Chromizing. The chromized surface obtained is similar to that obtained in the pack chromizing methods described in Section 3 of this chapter.

As for pack chromizing the surfaces to be treated must be free of oil, rust and scale so that the paint used may be applied direct to the surfaces.

The paint mixture used consists of a slurry of a low melting ceramic frit, powdered chromium metal or ferrochromium, a suitable catalyst and a vehicle. Some silicon or ferrosilicon powder may be incorporated in the slurry if combined chromizing and siliconizing is desired. The paint slurry is applied by brush or dip methods. One, two or more coats may be applied. After the paint coating has air dried it is further dried by preheating in air to a few hundred degrees for a few minutes and it is ready to be placed into a furnace.

Any ordinary furnace is suitable. No atmosphere control is necessary. During heating in the furnace the articles must be supported so as not to touch the furnace hearth or brick work.

As the temperature rises in the furnace some of the vehicle used is vaporized and protects the surface from oxidation in the furnace atmosphere. At higher temperatures the balance of the vehicle carbonizes and the residual carbon in the paint coating continues the protection. At a red heat the low melting point ceramic frit melts and forms an impervious and protective molten glaze coating in close contact with the surface being treated. This molten glaze contains the necessary chromizing materials and as chromizing temperatures of 1800°F or higher are reached the chromizing reaction takes place.

Probably due to the intimate contact the chromizing reaction takes place with considerable speed. Considerable chromizing can be obtained in 15 to 30 minutes at temperatures of 1900 to 2000°F and in 30 to 60 minutes at 1850°F.

After furnace heating the article can be removed and allowed to cool in air. As cooling continues the enamel like coating freezes, shrinks and cracks off in part. The balance is loosely adherent and is easily removed mechanically to expose the chromized surface.

The chromium content of the surface layer produced is similar to that from pack chromizing except that less diffusion has taken place and a sharper concentration gradient of the chromium content is present. This is the natural result of the much shorter time that the work is held at the temperature of chromizing.

The chromized layers obtained by paint chromizing are somewhat harder than those obtained by the pack chromizing methods and are of the order of 0.001 to 0.005" thick. Some slight roughening of the surface takes place during the paint chromizing process.

The corrosion and oxidation resistance of the paint chromizing process coatings have not been adequately investigated to date. Further evaluation of the process and the product is necessary.

To date the principal work done on this process has been in the laboratories of Sam Tour & Co., Inc., 44 Trinity Place, New York 6, N.Y. It is obvious that if this method can be developed to the point of commercial application that it will be much simpler and cheaper than any of the pack chromizing methods.

Section 5. Chromium Electroplating Plus Heating

Chromium electroplating followed by heating was listed earlier in this chapter as process number eight. The amount of chromium in the chromized layer, the degree and the depth of diffusion of this layer into the base steel are readily controlled. Electrodeposited chromium is pure chromium. As diffusion occurs during heating the electrodeposited layer on the surface of steel the apparent thickness increases and iron diffuses into the chromium as chromium diffuses into the iron. With sufficient time and temperature for the diffusion process the resulting chromium alloy layer is similar to that obtained by other chromizing processes.

The process is not new. It was practiced over 25 years ago, was not patented and was disclosed in 1929.(50) Chromium is deposited direct on the steel surface by electrodeposition from a chromic acid-sulphate 100:1 bath of the usual strength. The higher temperatures necessary for bright chromium plating together with the lower efficiency of plating at those higher temperatures are not necessary.

Surface preparation necessary is pickling and cleaning with a brief anodic treatment in the plating bath or prior to immersion in the plating bath for plating of the chromium direct on the steel. No copper or nickel strike is used. The amount of chromium deposited on the surface is a function of the time and current used during plating, 0.0005 to 0.001" of chromium can be deposited in less than one hour. For further information on electrodeposition of chromium see Chapter V, Section 3.

Since all chromium electrodeposits are somewhat porous or cracked it is preferable to do the heating, subsequent to plating, in an atmosphere that is non-scaling to steel. Combusted gas atmospheres are fully satisfactory. Some alloy bonding of the chromium plated layer begins at temperatures of 1500°F, although active diffusion does not take place until temperatures of 1650°F or higher are reached. At temperatures of 1800 to 1900°F the diffusion process goes quite rapidly and at higher temperatures even more rapidly. The diffusion process seals all the pores and cracks in the original electrodeposited coating and a continuous uniform high chromium alloy layer results.

The well diffused layer is similar in all ways to those obtained by pack or paint chromizing. The effects of carbon and of other alloying elements in the base steel are the same as in pack chromizing. The chromized layer becomes an integral part of the steel and is thoroughly adherent.

This process has been applied to 0.70% C tungsten high speed steels, to 0.30% C hot working die steels, to 0.40% C chrome-vanadium die steels, to 0.90% carbon oil hardening tool steels and to plain carbon steels for use in the die casting industry. There should be little question but that the high chromium alloy surface produced by the process would be satisfactory for resistance to many forms of corrosion and oxidation attack.

Section 6. Siliconizing - General Discussion

Siliconizing processes are those which create diffusion coatings with silicon as the addition element. High silicon iron alloys, containing over 10% of silicon, have been proven to have remarkably good corrosion and oxidation resistance in actual service experience and in numerous laboratory tests. The use of such irons has been limited by their brittleness and limited fabricating qualities. High silicon content cases on plain carbon or low alloy steel tend towards a combination of the high corrosion and oxidation resistance of the solid silicon alloys with the desirable properties of the steel core.

Siliconizing has attracted considerable attention and has been the subject of much research and development effort for many years. Various investigators have shown that the siliconizing is possible by the use of pack methods, by the use of vapor phase metal replacement reactions and by the use of paint methods.

Low sulphur forged, cast or rolled steels are the most readily siliconized. Sulphur is believed to cause formation of a silicon sulphide which is not corrosion resistant and which may cause local penetration of the case allowing the core to be attacked with subsequent cracking and spalling of the case.

High carbon, low sulphur steels and irons can be siliconized although the time element for a given thickness of case is increased. For example SAE 1045 steel takes twice as long as SAE 1015 steel. White cast iron and malleable iron can be siliconized but, because of their higher sulphur content, the resulting cases are not as resistant. Cast iron, because of its high sulphur content and because of its growth on heating cannot be siliconized successfully.

Insufficient information is available on the effect on siliconizing of various other alloying elements in irons and steels. Indications are that chromium and nickel in the iron or steel act somewhat like carbon in reducing the rate of the siliconizing reaction. No information is available, as yet, on the effects of using some chromium in the siliconizing mixtures. On the converse situation, it has been found that the use of some silicon in chromizing mixtures increases the rate and depth of chromizing.

Siliconized cases, however produced, can be thought of as thin 14.5% silicon iron alloy on the surface of the object. The composition of the alloy seems to remain consistent for about 50% of the case depth. The difference is in some porosity of the coating. 14.5% silicon iron alloy is known for its satisfactory resistance against sulfuric, nitric, acetic, formic, lactic and many other commercial acids. It is known from experience that a composition of 14 to 15% silicon results in maximum corrosion resistance, and little improvement is obtained with an increase of silicon beyond this amount.(68)

Section 7. Pack Siliconizing

By pack siliconizing, a case or coating 0.004" thick can be obtained in about two hours. The silicon content of the case at the surface is approximately 14%. The coating gives high protection against many corrosive media and to high temperature oxidation.

The process consists of packing the descaled samples in a rotary type furnace in a mixture containing silicon and heating the furnace for several hours at 1680-1860°F. The mixture usually consists of a source of silicon such as ferrosilicon or silicon carbide and firebrick of a grain size of 20-30 mesh. Heating is under a controlled atmosphere containing some HCl or Cl_2 to increase the speed of formation of the case. In two hours at around 1775°F, a siliconized case of up to 0.030" is obtained.

The only pack siliconizing process being operated on an industrial scale in this country is Ihrigizing. The process meets the above description.

Surface Preparation

Usually no special preparation of the surface to be treated is necessary. Light mill scale need not be removed, but heavy annealing scale should be. Other imbedded impurities should be removed by pickling or sand blasting.(61)

Corrosion Resistance

Siliconized coatings are resistant to HNO_3, H_2SO_4, HCl, with a decreasing resistance in the order named, water and steam corrosion.

Dolin and Benninger(69) have run air and corrosion fatigue tests with silicon impregnated steel and other impregnated and coated steels. The results are shown in Table 19.

Table 19

Corrosion Fatigue Strengths of Coated Steels

Material	Endurance Limit in Air, psi	Endurance Limit in Water, psi	Ratio of Endurance Limit in Water to Endurance Limit Uncoated or in Air, %
Uncoated SAE 3140	67,000	15,000	22.4
Cd Plated SAE 3140	No data	17,000	25.4
Zn Plated SAE 3140	No data	28,000	41.8
Cyanided SAE 3140	No data	16,000	23.8
Nitrided SAE 6120	105,000	85,000	80.9
Si Impregnated SAE 1020	22,500	22,500	100.0

The most corrosion resistant cases are formed on low carbon, low sulphur steels. The carbon should be below 0.25% and the sulphur below 0.04%.(63)

Tests were made(61) to determine the corrosion resistance of siliconized steel against different corrosive media. In 10% boiling sulphuric acid siliconized steel lost 7% in weight during 240 hours with only 0.3% loss during the 10th 24-hour period. Objects of the same size made of common steel were entirely dissolved in 18 hours and those made of 18-8 stainless steel were dissolved in 24-30 hours. In a hydrochloric acid pickle tub a galvanized elbow installed in a steam line failed in less than two weeks; the silicon impregnated one was still without serious attack after five months of service. Siliconized surfaces tend to become passivated so that very little galvanic action results when siliconized articles are in contact with other metals.

The only large industrial user of siliconized (Ihrigized) steel(65) states that the case is porous and certain corrosive liquids might penetrate the case and attack the core. In certain media, however, the case gives corrosion protection. Its best performance is in connection with nitric acid. It also has some application in the handling of sulphuric acid. It is reported that the case offers better protection against sulphuric acid after first being passivated by exposure to nitric acid.

It is reported that corrosion protection against the non-oxidizing acids is increased when the steel base contains about 3% molybdenum.(64)

Oxidation Resistance

Siliconized parts have given long service at temperatures of 1200 F to 1600°F.(61) Silicon impregnated steel is resistant to scaling in air up to 1400°F.(63) The upper limit of temperature of heat resistance is claimed(62) to be 1680°F.

The industrial user, however, does not claim such high resistance of the coating against corrosion and oxidation and is of the opinion that for heat and corrosion resistance the coating is not promising. He reports that Ihrigized steel held about 50 hours at 1100°F showed marked expansion of the case on the core with the case protruding beyond the ends of the piece and/or bulging outward. That effect vitiates, in their opinion, any claim that might be made for oxidation resistance of the case at high temperatures.

Erosion and Abrasion Resistance

As claimed by the industrial user of siliconized (Ihrigized) steel, the case is rather porous and furnishes a very good bearing surface for oil and grease. It was found that such a surface has considerable merit for scoring and galling resistance.

Joining

No information is available on the joining of siliconized steel by any of the methods such as welding.

Mechanical Properties

Siliconized coatings can be made of any desired thickness from 0.005" to 0.100". The silicon content of the coating is approximately 14% and is constant for the first 50% of the case depth and then falls off gradually. The coating is brittle.

The coating can be ground, but not machined or cut by ordinary means. The coating will not spall off under vigorous hammering but will chip on sharp corners.

During the siliconizing process, a small volume increase takes place. Parts swell about 0.001 to 0.005", although they lose weight. Distortion due to heating in the siliconizing process is minimized by a prior annealing operation.

Uses

Siliconizing has been used in applications to resist corrosion, heat, and wear in automotive water pump shafts, rocker arms, cylinder liners, valve guides, valve fittings, bolts and nuts, exhaust manifolds for large marine engines.

Over 200,000 water pump shafts have been treated and some have been in use for ten years in heavy duty internal combustion engines. The service operation has often taken place under heavy loads and with corrosive waters.(63)

Costs

The cost of pack siliconizing depends upon the size of the parts and quantity to be siliconized.

A 1946 cost estimate on a typical run of 250 water pump shafts 7/8 x 11 in. showed $0.1078 per lb. or $41.282 per run of about 450 lbs. of solid parts.(63)

The industrial user reports(65) the cost for Ihrigizing a retort load at about $100.00. The retort has inside dimensions of about 5' x 9" I.D.

Facilities Available

The Crane Co. of Chicago, Ill. is the only reported industrial user of the pack siliconizing process. They are a large producer and user of siliconized steel, have been operating the process for many years and do "Ihrigizing" on a job shop or commercial basis.

Section 8. Paint Siliconizing

Siliconizing can be done by a paint method (Johnson Siliconizing Process). The coating obtained resembles, in many respects, that of pack siliconizing.

The method of application is similar to paint chromizing (Johnson Chromizing Process) described in Section 4 of this chapter.

Surface Preparation

The surface of steel objects may be prepared for the treatment by surface grinding, steel grit, sand blasting or pickling. It is believed that a good case can also be obtained on rusted surfaces.

The Process Temperatures and Time Involved

The process itself consists of a preparation of the mixture, application of a paint slurry, drying, heating and cooling.

The paint mixture consists of a slurry of a low melting ceramic frit, powdered silicon or ferrosilicon, catalysts and a binder. The mixture may be applied by brushing or dipping. Usually several coatings are applied with time allowed for each coating to dry. Before firing, the coated objects are preheated in air to a few hundred degrees.

Firing is done in any ordinary furnace and in an atmosphere of plain air. During firing, the steel is protected against oxidation by vaporizing and burning of the binder and at higher temperatures by the melting of the ceramic frit, which then forms a molten glass envelope coat. At approximately 1700°F, silicon from the coating begins to alloy with the steel surface and to diffuse inward. At 1850°F the rate of diffusion is so high as to produce a heavy case in 15 to 30 minutes.

After the heating, the samples are removed from the furnace and allowed to cool in air. During the cooling period, the glass layer cracks and is easily removed by mechanical means.

Characteristics of the Case

The average total depth of the case produced at 1850°F for 15 minutes, is approximately 0.012". The case has some voids in the upper zone; the lower zone, however, is homogeneous. Compared with cementation processes, the paint method gives cases with a sharper gradient of silicon concentration. The case is slightly rough. It is golden brown in color.

The case is resistant to many corrosive agents, such as a 35% HNO_3, as well as to high temperature oxidation. Samples of paint siliconized low carbon steel heated in air at 1350°F for 128 hours were not affected.

The case is brittle and cannot be bent or deformed without cracking.

To date, work on this process has been in the laboratories of Sam Tour & Co., Inc., 44 Trinity Place, New York 6, N.Y.; further development of the process, evaluation and testing of the resultant siliconized panels is in progress. The process gives high promise that it will be cheaper and simpler in producing the silicon case than any of the pack methods.

CHAPTER V

MISCELLANEOUS METALLIC COATINGS

Section 1. General Discussion

Of the nine miscellaneous metallic coatings discussed in the following nine sections of this chapter, six are electroplated coatings and three are coatings applied by other means. Among the many metals which are electroplated, only six have been selected for detailed discussion. Cadmium has been included because it is being used extensively for temperatures up to 400°F and, in some cases, up to 500°F. Chromium has been included for obvious reasons. Copper electroplate has been included although it is seldom used bare for temperatures of over 400°F. Copper is used often as a base plate for other metals. Silver has been included because of its extensive use. Tungsten alloy electroplate has been included because of its promising properties. Electroplating of aluminum and of nickel have already been discussed in Chapters II and III respectively. Gold and platinum metal electroplates have not been included because of the high cost of these materials although they may be of interest in connection with special applications where their peculiar properties are of value and cost is no object. Tin plating has not been included in this chapter as it is seldom used alone at elevated temperatures. Tin in combination with nickel has been discussed in Chapter III in connection Corronizing. Lead plating and indium plating have not been included because of the low melting points of these two metals.

Section 2. Cadmium Electroplate

The primary use of cadmium electroplate is for the protection of other metals against corrosion. Cadmium, like zinc, is anodic or sacrificial to iron and protects it by preferential corrosion. It is less effective than zinc in this respect and does not protect as wide an exposed area.

Electroplated cadmium has a pleasing silvery white color of good lustre. Under certain conditions of exposure, it will retain this color and sheen for long periods of time.

Cadmium electroplated coatings are peculiarly resistant to attack in the standard salt spray test and, in this test, appear superior to zinc coatings. In normal atmospheric exposures or in industrial atmospheres containing some sulphur compounds, the cadmium coatings do not appear to be superior to zinc coatings.

Electroplated cadmium tends to have less pin holes than other electroplates and full coverage is attained with thinner deposits. Plate thicknesses of 0.0001 to 0.0003" are quite usual.

The high throwing power of cadmium plating baths and the low thickness of plate required have made the use of cadmium electroplating quite common on threaded parts and close tolerance parts.

Surface Preparation

A typical sequence for cleaning or surface preparation prior to cadmium plating is as follows:

1. Solvent degrease (trichlorethylene)
2. Cathodic alkaline cleaner
3. Rinse
4. Muriatic acid dip (1:1)
5. Rinse
6. Cyanide dip
7. Rinse
8. Then to the plating solution.

Processes

Both cyanide and fluroborate cadmium plating baths are in use. The cyanide baths are made up with cadmium oxide and sodium cyanide or cadmium cyanide. Caustic soda is an optional addition, usual for barrel plating, only to give maximum conductivity and production. Various types of patented organic addition agents are used for the purpose of obtaining brighter deposits from the cyanide baths. The fluoborate baths are made up with both cadmium and ammonium fluoborates plus an organic addition agent. Anodes of pure cadmium metal are used in both types of bath. It is claimed that the fluoborate baths have almost 100% cathode efficiency, therefore, little or no hydrogen liberation and little or no danger of hydrogen embrittlement of the steel being plated.

Corrosion Resistance

The cadmium electroplate is used mainly for the protection of other metals against corrosion. Cadmium protects steel by its galvanic action and corrodes itself in preference to steel. Cadmium offers good protection against normal atmospheric conditions. It operates to best advantage in indoor service in air of moderate or low humidity. It becomes less effective at high humidities. In industrial atmospheres where sulphates are among the corrosion products, cadmium shows low resistance to corrosion because of the high solubility of cadmium sulphate.

The corrosion products of cadmium are not bulky and do not accumulate like those of zinc; it is desirable to use cadmium plate on close tolerance or small clearance moving parts.

An important application of cadmium plate is where dissimilar metals are in contact with each other where, in the presence of moisture, a galvanic cycle will result. Plating both metals with cadmium eliminates or drastically reduces the galvanic corrosion effect.

Oxidation Resistance

Cadmium metal melts at 608°F. At 570°F it slowly forms a thin brown oxide layer which becomes quite impervious and brings oxidation to a halt. Tests up to 400 hours indicated no further oxidation took place. This data is based on cadmium metal, but cadmium electroplate should exhibit similar properties if sufficient is present to form the oxide layer.

One aircraft company has found cadmium coatings satisfactory for service at temperatures up to 500°F.

Erosion and Abrasion Resistance

Cadmium is a soft material (even softer than zinc), and should not be expected to have good erosion and abrasion resistance. Its low hardness at elevated temperatures combined with the thinness of the usual coating makes cadmium electroplates susceptible to perforation by the abrasive action of dust, etc. in high velocity gases.

Joining

Cadmium plate can be soft soldered easily, but such joints are not suitable for temperatures of operation of 400 to 600°F. Where welding or hard soldering is required, the cadmium plate should be stripped in the region of the joint. Cadmium vaporizes readily at red heats and the cadmium fumes are quite poisonous.

Mechanical Properties and Adherence

Cadmium electroplates are relatively soft and ductile. The ductility and adherence of cadmium are so good that flat blanks may be plated and then formed to the desired shape.

Effect on Base Metal

Hydrogen embrittlement of the base metal can occur as a result of the cathodic electrocleaning, acid dipping and/or plating operation. This embrittlement can be eliminated by heating the plated part at 350 to 400°F for 1 hour.

One aircraft manufacturer reports that cadmium electroplate plus the heat treatment did not affect the fatigue strength of the base metal.

Uses

Cadmium plate is used on structural steel parts which are imbedded in concrete, automotive bolts, nuts, screws and washers, builders' hardware, aircraft parts, marine hardware, malleable fittings, wire screens, springs, etc. Cadmium has been used on root serations of compressor blades.

Cadmium is not used as a chemical resistant coating. It is fairly resistant in weak alkali solutions and is used whenever parts come in contact with washing soaps.

Costs

At the present market price of $2.00 per pound of cadmium, the cost of cadmium metal per mil per square foot of surface is about 9¢. Since the average cadmium coat is much less than one mil in thickness it is evident that the base cost of the cadmium used is not a major factor. Actual total costs involve the many factors of labor, cleaning, racking, etc. The final total cost of cadmium plating is only slightly higher per square foot than for zinc electroplating.

Facilities Available

Cadmium electroplaters are located in almost every manufacturing area of the country. Many manufacturing firms have installed their own units to do cadmium electroplating.

E. I. duPont de Nemours of Wilmington, Delaware, Hanson Van Winkle-Munning Company of Matewan, New Jersey, and Udylite Corporation of Detroit, Michigan, are some of the companies which prepare proprietary material for cadmium electrodeposition. Their manuals and technical service departments provide information and assistance.

Section 3. Chromium Electroplate

Chromium electroplating plus heating to form a chromium diffusion layer on the surface of steel has been described in Chapter IV, Section 5.

The general high hardness, corrosion and oxidation resistance of chromium deposits make them ideal for applications for which these characteristics are desired. Chromium deposits are generally classified as decorative or industrial.

Chromium plate for decorative purposes is usually applied as a very thin (0.00001 to 0.00003") bright plate on underplates of other metals such as copper plus nickel. For corrosion protection of the base metal in the decorative field, the main reliance is on the underplates rather than on the superficial top coat of bright chromium. The primary function of the top chromium coat is tarnish resistance, although it also provides some abrasion resistance as well. Typical requirements for underplating for decorative chromium plate on steel for rather severe outdoor service are 0.0006 to 0.001" of nickel on an equal amount of copper.

Chromium plating for industrial use involves much thicker layers of chromium with no underplates of either copper or nickel. Industrial chromium deposits are referred to often as hard chromium deposits, although they are not harder and probably not as hard as the bright chromium deposits used for decorative purposes. The industrial chromium deposits are sometimes considered as in a different category than porous chromium deposits as used on piston rings and in cylinder bores of aircraft and Diesel engines. Porous chromium deposits are regular industrial chromium deposits made rough or porous by suitable means. One method is to roughen the surface to be plated upon before plating. Other methods are to produce the porosity by etching, either chemical or electrolytic, of chromium deposits from plating baths operated at a lower temperature than normal or with a higher sulphate content than normal.

Surface Preparation

To secure good adhesion and good quality of electrodeposits it is essential that the base metal surface be free from pits, cracks and other flaws and be chemically clean. The cleaning operation usually consists of degreasing and pickling. For industrial chromium direct on steel, electrolytic cleaning in alkaline solutions and anodic etching in chromic or sulphuric acid are used to achieve better adherence.

Solutions

Chromium plating solutions contain, usually, chromic acid and certain acid radicals such as sulphate which facilitate the plating of the chromium without themselves entering into the reaction.(74) An essential factor is that the ratio of the chromic acid (CrO_3) to the acid radical ($SO_4^=$) be about 100:1.

The commonly used operating conditions are shown in Table 20.

Table 20

Chromium Plating

Type of Coat	Composition of Bath ounces per gallon	Temperature °F	Amperes per sq. ft.	Volts
Decorative	35-55 chromic acid 0.35-0.55 sulphuric acid	110-120	150-300	8-12
Industrial	35-55 chromic acid 0.2-0.7 sulphuric acid	140-150	200-300	8-12

Insoluble anodes of lead-tin alloy are used. Since the throwing power of the solutions is very low, the anodes' shape and position will have appreciable influence on the deposit. Articles to be chromium plated also have to be racked properly if good deposits are to be secured. Efficient racking is an art which can be learned only through experience.

Heat Treatment

A major disadvantage of industrial chromium deposits is the quantity of hydrogen liberated simultaneously with the chromium causing hydrogen embrittlement of the steel. This effect may be reduced by heat treatment at 300°F to 750°F for ½ to 1 hour after plating. The higher the temperature and the longer the time, the more efficient is the removal of hydrogen. If fatigue resistance (high endurance limit) is desired the baking temperature should be as high as possible.

Thickness

The thickness of an industrial chromium deposit is determined by the end use intended. For simple wear resistance, thicknesses of 0.0002 to 0.001" are used. For surfaces to be ground, thicknesses up to 0.050 may be used. For chromium deposits to be made porous by etching methods, an allowance of about 0.001" to be removed by the etching is common. For nondecorative protection of steel against oxidation and corrosion with no underplate, thicknesses of 0.0005 to 0.005" are suggested. Certain aircraft specifications suggest 0.002" minimum.

Hardness

In both types of coatings, the chromium usually has a hardness of 500 to 1250 BHN.

The term "hard" plate is really not exact and the name "thick" plate would be more appropriate. The hardness of electrolytic chromium has a relation to its grain size and the amount of inclusions which, in turn, depend upon the conditions of deposition, such as bath, rate, temperature and current density.

At temperatures of 750°F or higher, there is some softening of the chromium deposit. This may be associated with the driving off of some or all of the hydrogen remaining from plating. At temperatures high enough to cause diffusion of some of the chromium into the steel, 1850 to 2250°F the softening may be counteracted by a carbon migration from the steel into the chromium layer. This depends upon the carbon content of the steel.

Adherence and other Physical Characteristics

There is no great difficulty in securing good adhesion of chromium if the techniques of electrocleaning (usually cathodic followed by anodic) are followed. However, chromium itself is apt to fail within itself. The main cause of its weakness is its susceptibility to cracking. Chromium electrodeposits are highly stressed. Cracking of a deposit is not in itself an indication of the magnitude of stress, but rather it is an indication of the lack of ductility of the deposit and that the maximum stress at certain points exceeds the tensile strength of the material. Cracking can be induced either by conditions which increase the stress or lower the tensile strength. For example, inclusions, such as oxides, may not actually raise the stress, but they may lower the tensile strength of the deposit. Chromium electrodeposits with only a few cracks per inch have much higher residual stresses than deposits with hundreds or thousands of cracks per inch. In highly cracked industrial deposits most of the cracks are not entirely through the deposit. Cracks which form during the process of plating are plated over and are partially healed cracks.

The crack pattern in industrial chromium deposits is particularly important on parts such as shafts or spindles, exposed to cyclic stresses. For such parts, the chromium deposits with many (thousands) cracks per inch are preferable. Baking treatments of 750°F are recommended for improved fatigue resistance.

Crack-free chromium deposits, obtained by special methods, are described in recent literature.(70)

Chromium electrodeposits, as all electrodeposits, are porous to some extent. Pores are caused usually by particles of basic salts or extraneous matter which settle upon the work in the plating bath and interfere locally with the deposition. Pits may be produced also by bubbles of hydrogen adhering to the work. Other causes of discontinuity of the plating are inclusions or pits in the base metal.

With a sound, well prepared base metal, proper baths and particular co-ordination of plating conditions, an impervious chrome plate can be obtained.

Other important characteristics of the chrome plate are low coefficient of friction and non-galling properties.

Corrosion Resistance

Chromium is cathodic to steel. Under reducing conditions and in the presence of an electrolyte, it may tend to cause accelerated local corrosion of any exposed base metal. For this reason, it is essential that the coating be as free as possible from pinholes, cracks or other discontinuities. Under oxidizing conditions the chromium becomes passivated and such galvanic corrosion does not take place.

Thicker chromium coats increase the resistance to corrosion by becoming less porous, but they become more liable to cracking. The minimum thickness for industrial chromium deposits to avoid porosity is believed to be somewhere around 0.0005".

Chromium plate is not subject to oxidation at atmospheric temperatures (tarnish) under usual conditions.

The resistance of chrome to corrosion is due to its passivity which depends on the presence of oxidizing agents in the medium to which the chrome is exposed. In that respect, it resembles in its general corrosion behavior the more highly alloyed stainless steels.

In contact with reducing solutions or with the halogen acids or sulphuric acid, its corrosion resistance is less, but in comparison with most other metals chromium is well resistant. It is quite resistant to attack by sulphur and reduced sulphur compounds. It is strongly resistant to nitric acid.

Heat treatment of the electrodeposited chromium plate considerably improves its resistance to corrosion.(71)

Resistance to Oxidation

Chromium electrodeposits are excellent for service at high temperatures. The resistance of chromium to oxidizing and other chemical agents at high temperatures is such that the plate remains bright up to 500°F. On prolonged heating of chromium plate to temperatures of the order of 1000°F in air, the oxide film grows in thickness and darkens. At higher temperatures, a black or green-black oxide layer is formed. At temperatures of the order of 1850°F an oxide layer forms on the surface and an extremely hard chromium nitride layer forms between the oxide and the chemically unaffected portion of the plate.(72)

At temperatures in the range of 1380 -1740°F, chromium begins to diffuse slowly into the steel base, but the life of the part is not affected because the high chromium alloy first formed is itself resistant to corrosion.(73)

Resistance to Erosion

Resistance to erosion requires that the coating shall be hard and tough in addition to being resistant to the corrosive attack by the surrounding medium. Chromium meets these requirements closer than any other single plated metal and is used extensively on many parts and tools exposed to wear.

No detailed data on the resistance of the chromium plate to erosion are available in the literature. It is logical to assume that a dense and high tensile material is required to resist erosion. A strong bond with the base metal is essential also.

Uses

Industrial chromium plating is being used extensively for improving the life of

1. Lathe tools
2. Cutting tools (milling cutters and reamers)
3. Metal drawing and forming dies
4. Rolls and drums
5. Gages
6. Flood light reflectors
7. Oil refining and cracking equipment
8. Liners for slush pumps
9. Pump plungers
10. Glass molds

11. Plastics molds
12. Evaporator tubes in the paper industry
13. Ironing shoes
14. Steam turbine blades
15. Aluminum pistons
16. Piston rings
17. Internal combustion engine cylinders
18. Rotary files
19. Movie camera scraper plates and shutters
20. Water meter parts
21. Marine crank shafts
22. Motor boat shafts and bearings.

There should be little question as to the ability of industrial chromium plate to protect plain carbon or low alloy steels from corrosion, oxidation and abrasion in aircraft engine parts operating within the limitations of the physical properties of such steels at elevated temperatures. The primary limitations of such applications are the poor throwing power of chromium plating baths and the cost of such plating.

Costs

As in any other type of electroplating, it is impossible to give even approximate figures as to the costs of industrial chromium plating per square foot of surface plated or per any other basic unit. For each design of part to be plated, it is necessary to develop suitable formed and placed anodes, racks and agitation or rotation jigs.

As compared to other types of plating, industrial chromium plating may cost about twice as much as nickel electroplating, slightly more than electroless nickel plating but less than tungsten alloy plating.

Facilities and Sources of Information

Industrial chromium electroplating is adequately handled by many commercial electroplaters in all regions of the country. Many industrial firms operate their own chromium plating facilities.

Specific information is available from equipment, supply and proprietary process firms with sales offices and service men in many cities.

The literature on the subject is enormous. Only a few references have been given in this section.

Section 4. Copper Electroplate

Copper was one of the first metals to be electrodeposited from solution. The acid sulphate bath has been used for well over 100 years. The various types of commercial copper plating are as follows: A. Acid Baths - (1) Acid Sulphate, (2) Fluoborate, B. Alkaline Baths - (1) Standard Cyanide, (2) Rochelle Cyanide, (3) High Speed, (4) Pyrophosphate.

Numerous other baths are described in the literature.

Copper is cathodic to iron. The coating, therefore, must be continuous and free from pores. A thin porous coating of copper may accelerate corrosion of steel.

Copper electrodeposits (flash and very thin) are often used as base coats prior to nickel or nickel and chromium electroplating.

Surface Preparation

Prior to copper plating, surfaces should be (1) degreased in a solvent, or alkaline soak solutions, (2) alkaline cleaned, electrolytically, (3) dipped in 4-15% hydrochloric or sulphuric acid or treated electrolytically in 2-6 ozs. per gallon sodium cyanide solution.

Processes

The various copper plating processes(79) are summarized in Tables 21, 22, and 23.

Table 21

Acid Copper Plating

	Acid Copper	Fluoborate(76)
Bath Compositions	Copper Sulphate 27 oz/gal. Sulphuric Acid 6.5 oz/gal.	Copper Fluoborate 30 oz/gal.
Operating Conditions	Temp.--75-120°F C.D.--15-40 A/ft^2 (higher with agitation) Anodes--Rolled Copper Voltage--.5-2.0	Temp.--80-170°F C.D.--75-125 A/ft^2 Voltage--3-5 v. pH--0.8-1.4 (color) Anodes--Rolled electrolytic

Table 21 (con't)

Acid Copper Plating

	Acid Copper	Fluoborate(76)
Advantages	Simple to operate and control. Suitable for heavy deposits, electroforming. High current densities and efficiencies. Rapid deposition of heavy deposits.	Suitable for heavy deposits, electroforming. Fine grained deposits, easily buffed. High speed plating. High efficiencies, approaching 100%. Bath available as a concentrated solution, requiring only dilution.
Dis-advantages	Cannot be used directly over steel, iron or zinc. For these metals, a preliminary coating from a cyanide bath is required. Coatings are dull in appearance and rough if over .001 inches thick. Baths have poor throwing power. No cleansing action on the plated parts.	Cannot be used directly over steel. A preliminary strike in a cyanide bath is required. Bath has no cleansing action on plated parts.
Special Notes	Lead lined or rubber lined tanks suitable. Glue often used as an additive.	Rubber lined tanks required. Lead not suitable.

Table 22

Alkaline Copper Plating

	Standard Cyanide	Rochelle Cyanide
Bath Compositions	Copper Cyanide 3 oz/gal. Sodium Cyanide 4.5 oz/gal. Sodium Carbonate 2 oz/gal.	Copper Cyanide 3.5 oz/gal. Sodium Cyanide 4.6 oz/gal. Rochelle Salt 4 oz/gal. Sodium Carbonate 4 oz/gal.
Operating Conditions	Temp.--75-100°F C.D.--3-15 A/ft^2 Voltage--1.5-2.0 v. Anodes--Rolled annealed Copper	pH--12.6 Temp.--140-160°F C.D.--20-60 A/ft^2 Voltage--2.3 v. Anodes--Rolled annealed Copper
Advantages	Same bath useful for tank or barrel plating. Soft deposits produced, easily buffed. Low concentration lessens dragout. Can be used directly over steel and iron.	Fine grained, bright deposits. May be used directly over steel, iron and zinc. Cleansing action on the plated parts. Dense deposits produced, useful as carburizing stop-offs.
Dis-advantages	Rate of deposition is slow. Deposits are dull. Useful for light deposits only, due to low plating rate.	Control within close limits very important for consistent results. Rate of deposition is low.
Special Notes	Unlined steel tanks satisfactory. Some brightening of deposit possible with addition agents but they are difficult to control. Bath has a cleansing action on the plated parts.	Unlined steel tanks satisfactory.

Table 23

Alkaline Copper Plating (con't)

	High Speed*	Pyrophosphate
Bath Compositions	Copper Cyanide 16 oz/gal. Sodium Cyanide 18 oz/gal. Sodium Hydroxide 4 oz/gal. or Potassium Hydroxide 5.6 oz/gal. Brightener and Anti-pit agent*	Copper Pyrophosphate 14.7 oz/gal. Potassium Pyrophosphate 54 oz/gal. Ammonia 0.4 oz/gal. Citric Acid 1.3 oz/gal.
Operating Conditions	pH--12.8-13.3 Temp.--170°F C.D.--10-100 A/ft^2 Voltage--1-2.5 v. Anodes--Electrolytic cathode copper	pH--8.5 Temp.--120°F C.D.--5-50 A/ft^2 Anodes--Rolled electrolytic copper
Advantages	Bright, fine grained deposits. May be applied directly over steel, iron and zinc. High speed plating (nearly twice that of standard bath).	Bright, fine grained deposits. May be directly applied to steel, iron or zinc. No addition agents required. Control and operation relatively simple.
Disadvantages	*Requires use of proprietary addition agents. Solution control must be close. Requires constant agitation of bath or work. Flash deposit from regular cyanide bath usually required for best adhesion.	Low current densities used require longer plating times. No cleansing action on plated parts. Requires air agitation. Rubber lined tank required.
Special Notes	Unlined steel tank suitable.	This is a patented bath.

Corrosion Resistance

In order that a copper plate protect steel against corrosion attack, the copper deposit must be free from pores. On exposure to the atmosphere, copper slowly develops a thin, protective coating or patina. Sulphur compounds derived from products of combustion (especially sulphur dioxide) are agents in the formation of the patina. The patina, green in color, consists essentially of basic copper sulphate. If chlorides are present in the atmosphere the patina contains some copper oxychloride. While normal and industrial atmospheres are not too corrosive to copper, other factors may lead to active corrosion of copper.

"Line" corrosion can occur where water is retained by a heavy solder bead or seam permitting a concentration cell and active attack. Corrosion-erosion attack of a copper surface may result from dripping water contaminated with products of combustion in industrial areas.

In the absence of oxygen or oxidizing agents, copper is resistant to the attack of nonoxidizing acids. It is rapidly corroded by such oxidizing acids as chromic and nitric. Acids containing metallic salts, such as iron, will dissolve copper rapidly. Copper is also resistant to alkaline solutions that do not contain ammonium hydroxide, substituted ammonium compounds, or cyanides. Copper has excellent resistance to most nonoxidizing salts provided that ferric, stannic, mercuric, cupric, ammonia ions, etc. are absent.

Copper withstands corrosion in sea water as satisfactorily as any of the commercially available metals, provided that the relative velocity with respect to water is low.

Natural waters and steam condensates containing carbon dioxide and oxygen are corrosive to copper. Moist hydrogen sulphide, ammonia, phosphorous, chlorine, sulphur dioxide and sulphur trioxide are very corrosive to copper.(75)

Oxidation Resistance

At about 210°F, an initial thin oxide film forms on copper. The thickness increases irregularly with time and temperature. These low temperature oxide films are classified as temper films and have varied colors depending on the temperature of exposure. Beyond this temper film thickness (at temperatures over 750°F) the rate of oxide film growth increases rapidly with temperature and time.

Hot oxygen, sulphur vapor, sulphur dioxide, hydrogen sulphide, phosphorous, halides and some acid vapors (such as HCl), definitely attack copper at elevated temperatures. Copper generally is inert to reducing gases such as hydrogen, carbon monoxide, hydrocarbon gases, etc. Alternate exposure to oxygen and to one of the reducing gases greatly accelerates the oxidation rate by destroying the protective continuity of the scale. Cyclic variations in temperature have a similar effect. Oxygen bearing copper is embrittled by hydrogen, dissociated water vapor and dissociated ammonia.

Erosion and Abrasion Resistance

The limited data available indicate that copper has poor resistance to erosion and possible abrasion.

Joining and Forming

Copper coated surfaces may be soft soldered, but soft solder joints are not suitable for operations involving temperatures of 400 to 600°F. Hard soldering or brazing involves temperatures that may be detrimental to the copper plate and cause perforations. Copper plated parts may be spot, arc or resistance welded. After welding, it may be necessary to repair the copper plate in the regions of the weld.

No difficulty is encountered in forming copper plated parts.

Mechanical Properties and Adherence

Heavy adherent copper electrodeposits are obtainable from the acid copper plating baths provided the surface is properly prepared and given a strike or flash coat of copper from a cyanide bath. All the other baths produce adherent copper deposits. The physical characteristics and properties of copper electroplates depend on the solution composition, current density, temperature, agitation and addition agents used.

Copper electrodeposits are comparatively soft. The cyanide copper deposits are somewhat harder than the acid copper deposits.

Effect on Base Metal

The acid pickling process and the actual plating process (especially the acid baths) may cause hydrogen embrittlement of the base metal, steel. None of the data available indicates that copper electrodeposits affect the fatigue life of the base metal. Some limited data indicate that the copper deposits are in compression and, therefore, should have no adverse effect on the properties of the base metal.(77)

Uses

The major applications of copper electroplate are as a base for subsequent nickel and/or nickel-chromium deposits.(78) Many production parts are copper plated. Bare copper electroplate offers little value as protection of steel against attack in service at elevated temperatures.

Costs

Copper plating is comparatively a low cost plating. Metal costs per mil per square foot, on the basis of 50¢ per lb. for cast copper anodes, are about 25¢. Other costs are dependent on cleaning costs, complexity of part to be plated, racking problems, quantity to be plated at one time, and whether plating is manual or automatic.

Facilities Available

Copper plating plants are located in almost every manufacturing area of the country. Detailed information on copper electroplating can be found in the "Metal Finishing Guidebook".(74) High speed copper plating baths are available from:

Mac Dermid Inc.	Waterbury, Connecticut
Lea Mfg. Co.	Waterbury, Connecticut
Hanson-Van Winkle-Munning Co.	Matewan, New Jersey
E. I. du Pont de Nemours Co.	Wilmington, Delaware.

Equipment and procedures to be followed are available in manufacturers' handbooks and instruction manuals.

Section 5. Silver Electroplate

An important factor in electroplating is the distribution of the deposit over the part to be plated. On odd shaped parts it is sometimes necessary to over-plate some sections in order to get a minimum thickness on other sections. Because of the high cost of silver this factor is very important in silver electroplating. An excess of silver must be avoided if costs are to be kept to a minimum. For odd shaped parts, the throwing power of a silver plating solution is important.

Silver can be plated from a variety of baths such as thiocyanate, thiourea-nitrate, and iodide. Except in special cases, the cyanide type bath is used. The latter contains silver, sodium or potassium cyanide in excess of that needed to keep the silver in solution (called "free cyanide"), and either potassium or sodium carbonate, or possibly potassium nitrate. A solution containing these substances in proper proportions and operated properly produces a smooth adherent matte white deposit. Semi-bright deposits are obtained by the addition of carbon disulphide or ammonium thiosulphate to the plating solution.

It is customary to use two or more baths for silver plating. The first baths are called "strike solution" baths. These baths have low silver and high cyanide concentrations. They are used to get the first covering of silver, after which the silver is built up in the regular cyanide plating bath. The "strike solution" serves to prevent the deposit of silver by "immersion" with resultant poor adhesion of the ultimate deposit, improve the covering power and, indirectly, the throwing power, and assist in cleaning. It is not advisable to omit the striking operation or to attempt to use the strike solution to build up appreciable deposits.

The following factors are important in obtaining deposits of uniform hardness and free of porosity: 1. components of the solution - silver cyanide, free cyanide, potassium carbonate and brightener content, 2. absence or presence of impurities in the bath, 3. temperature of the solution and degree of agitation.

High purity silver anodes act as the source for silver. The free cyanide is necessary to form the soluble complex silver cyanide and to dissolve the silver from the anodes at a sufficient rate to replenish the solution.

Traces of such impurities as bismuth, manganese, lead, iron, antimony, selenium, tellurium, etc. in the order of hundredths of a percent or less may cause the anodes to be covered with a dark scum which will interfere in normal anode corrosion and cause rough spots on the work due to migration of the sediment.

Temperature and agitation of the plating bath have a more pronounced effect than the solution composition. An increase of a few degrees in temperature greatly increases the permissible current density without burning of the silver plate. Agitation is necessary to replenish the silver at the work and remove it at the anode. Agitation can be obtained by moving the silver solution with a pump and filter unit, and/or by movement of the work. Agitation is essential to obtain smooth bright deposits at higher current densities and to improve the throwing power of the solution.

Surface Preparation

The surface preparation for nickel electrodeposition (see Chapter III, Section 2), is applicable for the surface preparation of steel prior to silver plating. Two strike solutions and two strike operations are used for silver plating on iron or steel.

Processes

Typical strike solutions(74) used for iron and steel are shown in Table 24. Typical plating solutions and conditions are shown in Table 25.

Table 23

Silver Strike Solutions

	1st Strike Solution	2nd Strike Solution
Bath Makeup		
Silver Cyanide	0.25 oz/gal.	0.5-0.7 oz/gal.
Copper Cyanide	1.50 oz/gal.	---
Sodium Cyanide	10.00 oz/gal.	8.0-10.0 oz/gal.
Operating Conditions		
Free Cyanide	8.0 oz/gal.	8.0-10.0 oz/gal.
Metallic Copper	1.0 oz/gal.	---
Metallic Silver	0.2 troy oz/gal.	0.4-0.5 troy oz/gal.
Temperature	Room	Room
Current Density	15-25 asf*	15-25 asf*

*amperes/sq. ft.

Table 24

Silver Plating Solutions

	1 oz/gal.	2 oz/gal.	3 oz/gal.	High Speed oz/gal.
Bath Makeup				
Silver Cyanide	4.0	4.0	3.2	14-19
Potassium Cyanide	7.5	-	-	15-18
Sodium Cyanide	-	6.4	4.5	-
Potassium Carbonate	6.0	6.0	as low as possible	2-10
Potassium Hydroxide	-	-	-	0-4
Potassium Nitrate	-	-	15	-
Brightener (carbon disulphide)	1/8*	1/8*	1/8*	-
Operating Conditions				
Metallic Silver	3.0**	3.0**	3.0**	-
Free Cyanide	5.0	4.0	2.5	-
Temperature °F	72-78 latter preferred	72-78 latter preferred	72-78 latter preferred	100-120
Current Density (asf)	5-15	5-15	5-15	75-100

*fluid ounces per gallon to a new solution.
**troy ounces per gallon.

Agitation is obtained usually by rotation of the work at 100 to 200 rpm and by rapid circulation of the electrolyte (plating solution).

Corrosion Resistance

Silver is one of the noble metals and is cathodic to almost all other metals. Galvanic corrosion must be considered when silver is brought into contact with another metal in any structural design.

The corrosion resistance characteristics of silver are outlined(73) in Table 25,

Table 25

Corrosion Resistance of Silver Plate

Medium & Conc.	General	Effect of Moisture	Effect of Oxygen	Effect of Elevated Temperature	Effect of High** Temperature
HCl	Immersed in HCl a film of silver chloride forms which inhibits further corrosion*	--	Accelerates corrosion attack	--	In presence of oxidizing agent corrosion is accelerated
Organic Acids	Resistant	--	--	No effect	--
Dilute Mineral Acids	Resistant	--	--	No effect	--
Nitric Acid	Rapidly attacked	--	Accelerates attack	Accelerates attack	--
Sulphuric Acid-over 85%	Rapidly attacked	--	Accelerates attack	Accelerates attack	--
Hydrofluoric Acid	Not appreciably attacked	--	Accelerates the attack	--	--
Chlorine	Similar to HCl				
Alkalies except ammonia & cyanides	Highly resistant	--	Accelerates, but still somewhat resistant	--	--
Cyanides, moist ammonia & substituted ammonium hydroxide	Corrodes silver	--	Accelerates	--	--

Table 25 (con't)

Corrosion Resistance of Silver Plate

Medium & Conc.	General	Effect of Moisture	Effect of Oxygen	Effect of Elevated Temperature	Effect of High** Temperature
Sulphides	Attacks silver, "tarnishes" forming black silver sulphide	Moisture must be present. Dry H_2S does not attack silver	--	--	--
Moist Atmospheres	Resistant to attack	--	--	--	--
Oxygen	Resistant to attack	Resistant to attack	--	--	Resistant to attack
Bromine	Similar to Chlorine - but slightly more active				
Dry NH_3, CO, H_2, F, N	No effect at ordinary temperature	--	--	--	--
Sulphur Dioxide	Slight attack at ordinary temperature	--	--	--	--

*The resistance to hydrochloric acid and halides depends on the formation of the silver halide salt which inhibits further corrosion. The degree of resistance to corrosion will, therefore, depend on the degree to which this halide salt film adheres to the silver surface.

**Additional data see section "High Temperature Resistance".

Oxidation and High Temperature Resistance

For high temperature service, care must be taken to provide a sufficient thickness of silver to prevent oxygen from diffusing through the silver and attacking the base metal. There is a general agreement that oxygen will diffuse through commercially pure silver at elevated temperatures. The rate of diffusion increases rapidly above 750°F.

A study in "Blistering of Silver Plating at High Temperatures" was reported in the literature(80) as follows:

> "In the operation of turbines and jet engines it is desirable to maintain a bright metallic surface on some of the parts to decrease heat absorption. Silver plating has been proposed but has given considerable trouble due to blistering when heated under oxidizing conditions.
>
> It was established that the formation of blisters required the presence of oxygen or of water vapor. The most probable reaction was the oxidation of hydrogen absorbed by the silver during plating.
>
> Sixteen test coupons representing different conditions of plating were cut in half. One set was heated in air for control purposes. All specimens thus treated formed blisters. The other set was heated in nitrogen at 1400°F for 5½ hr. With a minor exception, all specimens were bright and smooth after this treatment. These samples were then heated in air at 1200°F for 5½ hr. followed by another exposure to air at 1400°F for 3½ hr. None of them developed any blisters.
>
> These observations can be explained in the following way: If the specimens are first heated in nitrogen for a sufficient length of time and at a high enough temperature, hydrogen present is removed by outward diffusion. On the other hand, if the specimens are heated in air, oxygen diffuses into the silver before hydrogen has been reduced to a low concentration; insoluble water vapor then forms as the solubility product of oxygen and hydrogen in silver is exceeded."

Silver is not attacked when annealed in an atmosphere of superheated steam at 1100 to 1300°F. Silver is attacked by gases containing sulphur. This attack is accelerated by increasing temperature.

Hydrogen does not react with silver, but diffuses slowly through the metal at elevated temperatures to react with any oxygen which may be present and may cause embrittlement and surface blisters. Silver is resistant to hydrogen chloride and chlorine gas at temperatures below 800°F.

Erosion and Abrasion Resistance

Specific data are not available on this subject for silver electroplate. Silver is softer than nickel, therefore silver can be expected to have a lower abrasion resistance than nickel. Silver, as a bearing material, has been found to have higher fatigue strength than other bearing materials.(81,82)

Mechanical and Physical Properties

One source(83) reports that an 100 D.P.H. (Diamond Pyramid Hardness) was obtained on electrodeposited silver that had a higher electrical resistivity than wrought silver.

Electroplated silver is very ductile and can operate successfully under repeated stresses. Because of its high thermal conductivity, the heat created at hot spots is completely dissipated. Its hardness of about 25 BHN (very soft) is retained at elevated temperatures.

Uses and Results

Silver electroplate is used for surfacing ultra-high frequency conductors for radar. Heavy electrodeposits can be used for surfacing chemical equipment and for bearings. One aircraft manufacturer reports using silver plate up to 750°F. Some discoloration was noted after the exposure. Another fabricator of aircraft parts reports using silver electroplate (up to 1400°F) on high temperature joints to stop galling. Silver electroplate is used for cushioning and anti-galling on compressor blades.

Costs

The factors which determine the final cost of any electroplating operation are discussed under "Costs" in "Nickel Electroplating", Chapter III, Section 2. These factors are also applicable to silver electroplating. The major costs for silver and nickel electroplating are basically the same. The only additional cost for silver electroplating is the metal cost, which would be about 14 fold greater than nickel. (This is based on $1.00 per troy of silver to $1.00 per avoirdupois lb. of nickel.) The electrical cost for plating a mil thickness of silver is less (a small factor in final costs) than for plating 1 mil of nickel.

Facilities Available

Silver electroplating facilities are available in most manufacturing areas of the country. Many manufacturing concerns have installed their own departments for doing this type of work. Equipment and supplies for the silver plating baths are available from various manufacturers and distributors. Many of them also can supply instruction manuals.

Section 6. Tungsten Alloy Electroplate

The electroplating of tungsten alloys is a development of the National Bureau of Standards.(84) It has not been possible to electroplate pure tungsten. Alloys of tungsten with metals in the iron group can be electroplated. Alloys of tungsten with nickel or with cobalt seem to offer promise as methods of coating for protection against oxidation, corrosion and erosion.

The deposits are smooth and strong, but have a tendency to brittleness. However, the alloys become ductile on heating. As plated, the nickel and cobalt alloys have a hardness of 350 to 700 Vickers, and iron alloys 700 to 900 Vickers. The alloys undergo precipitation hardening and the cobalt-tungsten alloys retain their hardness when "hot".

Only the cobalt-tungsten alloys have had commercial applications, therefore all discussions in this section will be centered on those alloys.

Surface Preparation

It is reported that any accepted cleaning method can be used. However, when high carbon steel is plated after a conventional treatment the adhesion is poor.

In the latter instance, a special procedure is necessary, as follows: 1. anodic etch, 2. cobalt strike in a special cobalt-HCl solution, 3. treatment in 1:1 HCL with an alternating current, 4. preplate in plating solution with alternating current, 5. direct current plating.

The plating solutions consist essentially of the appropriate metal salts together with salts of certain hydroxy-organic acids in ammoniacal solutions at pH about 8.5. The National Bureau of Standards reports that the following bath and conditions are satisfactory: cobalt as chloride or sulphate - 25 gms/liter, tungsten as sodium tungstate - 25 gms/liter, Rochelle salt - 400 gms/liter, ammonium chloride or sulphate - 50 gms/liter, NH_4OH added to pH of 8.5, temperature 90°C and above, current density 2 to 5 amps/dm^2.

By varying the composition of the solutions and conditions of plating, the tungsten content of the tungsten-cobalt alloy can be varied from 15 to 50%.

Recommended anodes are tungsten, cobalt, or tungsten-cobalt alloys. The tungsten is most satisfactory as it corrodes cleanly and smoothly with 100% efficiency. If the anode area is less than 1/3 of the cathode area it becomes passive.

The major objections to this process are reported to be the elevated temperatures required (90°C and over) and the continued addition of ammonia required to maintain the pH. However, one commercial user of the process reports that: 1. the alkaline plating solution is stable and relatively harmless to plating tanks, 2. the process is easy to control, 3. any metal that is normally electroplated can be plated; (attempts to plate titanium have been unsuccessful), 4. the throwing power of the solution is better than nickel and lies approximately between nickel and copper, 5. the rate of plating is slow, about 0.0008" per hour; a desirable plate thickness lies between 0.001" and 0.0015".

Corrosion Resistance

A cobalt-tungsten alloy plate over 0.0005" thick showed good resistance in the salt spray test. The National Bureau of Standards states:

> "Cobalt-tungsten alloy plates on steel gave outstanding protection in atmosphere exposure tests when compared to nickel coatings of equal thickness."

Oxidation Resistance

The commercial user of the process claims that this cobalt-tungsten plate on molybdenum gives good surface protection up to 1600°F and that exposure to 1300 and 1400°F for a "long time" caused no blistering or peeling. The National Bureau of Standards reports that the protection against oxidation at elevated temperatures obtained from this class of alloys is no better than that provided by pure nickel. The commercial user reports that when the cobalt-tungsten alloy is applied on 4130 steel it gives better protection than that provided by pure nickel.

Erosion or Abrasion Resistance

Specific use data are not available on this subject. The cobalt-tungsten alloys have high hardness at room and at elevated temperatures. On this basis, they should have good abrasion and erosion resistance at elevated temperatures up to 1200°F.

Ability to be Joined

No data are available as to welding, brazing or soldering characteristics.

Mechanical Properties

The tungsten-cobalt plate containing about 25% tungsten has a plating hardness of 400 to 500 Vickers. Heating to 1100°F for one hour hardens the plate to 800 Vickers. The hot hardnesses of the various cobalt-tungsten alloy plates as determined by the National Bureau of Standards are shown in Table 26.

Table 26

Hardness of Tungsten-Cobalt Electroplates

Type Coating	Hardness - Vickers		
	At 20°C or 64°F	At 700°C or 1292°F	At 800°C or 1472°F
12% W Balance Co	500	198	42
15% W " "	500	95	34
20% W " "	540	210	82
25% W " "	520	370	220
23% W " " (a)	510	150	53
23% W " " (b)	560	160	64
23% W " " (c)	610	300	180
Stellite	470	300	-
Cobalt Electroplate	300	65	55

a = as deposited,
b = heated at 1000°C (1832°F) 1 hour and 850°C (1562°F) 1 hour,
c = heated at 1200°C (2192°F) and precipitation hardened for 100 hours at 600°C (1112°F).

Effect on Mechanical Properties of Base Metal

No data on this subject are available.

Reported Uses and Results

A potential value of the cobalt-tungsten alloy deposits lies in their good hot hardness properties.

It has been reported that the cobalt-tungsten plate stood up well on 4130 steels in a combustion chamber.

Costs of Applying

Detailed cost figures on the electrodeposition of cobalt-tungsten alloy are not available. It would appear that the process at present is about twice as expensive as chromium plating, but costs might be reduced to about those of hard chromium plating.

Facilities Available

The original work by the National Bureau of Standards is reported in reference 84.

The Surface Alloys, Inc., of Los Angeles, California, electroplate cobalt-tungsten alloys on a commercial basis.

Section 7. Zinc Coatings

Zinc coatings of many types are used widely for protection against corrosion. Zinc is anodic (electronegative) towards iron and steel and provides protection by its sacrificial action. Where an electrolyte is present, a zinc coating need not be free of pin holes, porosity or small imperfections, as the zinc extends its protection over small adjacent areas. It has been recognized for a long time that the service life of a zinc protective coating on steel under corrosive conditions is a function of the weight of zinc per unit area of surface.

The various types of zinc coatings are characterized by the process used in the application of the coating, as follows:

1. Hot dip zinc galvanized coatings are formed on steel by dipping a suitably cleaned surface of the steel in molten zinc. Some alloying and formation of a brittle zinc-iron compound occur at the interface. Dependent upon time and temperature in the molten bath and the amount of wiping off after removal from the bath, the amount of zinc-iron compound and the amount of free zinc on the surface may be varied within limits. The zinc used may contain small amounts of cadmium, lead, aluminum, and other metals. The finished surface may be a matte or a reflecting spangled surface.

2. Electrodeposited zinc coatings, sometimes called electrogalvanized coatings, are formed on steel by electrodeposition from zinc containing solutions of various types as will be described below. Unless a heat treatment is applied after electroplating of the zinc (galvannealing) no alloying or formation of zinc-iron compounds occur. The heat treating process can be applied to any of the zinc electrodeposited coats. Dependent upon the electroplating process used, the zinc coating may have a dull matte finish or may have considerable reflectance. The amount of zinc per unit area of surface may be varied at will in the process.

3. Sherardizing is another method of applying zinc coatings. In this process the article to be coated is tumbled in zinc powder at a temperature of about 700°F (below the melting point of zinc). The temperature, however, is sufficient for the formation of an alloy bond and some zinc-iron compounds. The weight of zinc per unit area of surface that can be applied by this procedure is less than is applied in the hot dip process. The coating is smooth and uniform and dull gray in appearance.

4. Metallizing is another method of applying zinc coatings. In this process molten zinc droplets are sprayed onto a suitably roughened surface. The zinc droplets may be obtained by atomizing from a bath of molten zinc, by the passing of zinc powder through a high temperature flame or by continuously melting and atomizing of zinc wire. The coatings produced are not alloyed with the surface of the steel unless an after treatment is applied. The coatings adhere to the surface by mechanical interlocing with roughened (grit blasted) surface of the steel. The coatings are

somewhat porous. The process permits applying the coatings to desired areas in desired thickness up to 0.010", which is much thicker than can be obtained commercially by any of the other processes. The coatings are fairly rough and are dull gray in appearance.

5. For information regarding zinc coatings applied by the peen plating process, see Section 9 on "Peen Plated Coatings".

6. For information regarding metallic zinc pigmented paints, see Chapter VI, Section 6, on "Zinc Metal Paints".

Surface Preparation

Acid pickling is used as the surface preparation for hot dip galvanizing. Alkaline cleaning with or without an acid dip is used as the surface preparation for electroplating of zinc. Acid pickling is used usually as the pretreatment for sherardizing. Grit (abrasive grain) blasting to produce a good anchor pattern is the required surface preparation for metallizing.

Processes

The hot dip galvanizing, the sherardizing and the metallizing processes have been described above. For more information on the metallizing process, see Chapter II, Section 5, "Metallizing with Aluminum", also the "Recommended Procedures for Metallizing for Corrosion Protection" as issued by the American Welding Society.(85)

For electrodeposition of zinc, there are four commercial processes as follows: 1. acid zinc, 2. zinc chloride plus acetate (rapid zinc process), 3. cyanide zinc, 4. fluoborate zinc.

The acid zinc plating solutions are based upon the use of zinc sulphate in a solution with a pH of 3.5-4.6 and at a temperature of 75-120°F. The process is characterized by a high rate of deposition and low operating costs in quantity production. The main disadvantage is the relatively poor throwing power of the solution which limits the use of this process to simple shapes.

The zinc chloride plus acetate process is relatively new and is sometimes called the rapid zinc process. The plating solutions are made with zinc chloride and zinc acetate with substantially no addition agents and operates at a temperature of 75-85°F. This process is similar to the acid zinc plating process with respect to throwing power and also is limited to simple shapes.

The cyanide zinc plating process uses zinc cyanide solutions which are more expensive and more difficult to maintain than the other types of zinc plating solutions. While the rate of deposition is lower from the cyanide solutions, the throwing power is very high and plating can be applied in deep angles and recesses. Using 100 amperes per square foot of surface, a plate thickness of 0.005" to 0.006" can be obtained in one hour. Various types of cyanide baths are in use. The straight cyanide baths yield a matte deposit. Zinc-mercury baths give a more uniform and whiter plate. Other modifications produce semi-bright to mirror bright plates which give little tendency to staining during rinsing and handling. Equipment costs for cyanide zinc plating are low as plain steel anodes and tanks can be used.

The fluoborate zinc plating process offers the advantages of simplicity of preparation and control, operation at near room temperature, almost 100% anode and cathode efficiencies and high rates of plating. The deposits are fine grained and of good color. Cast iron and malleable iron can be plated direct in this process.

Corrosion Resistance

Zinc coatings are used primarily for protection against corrosion under wet or humid conditions. As stated above, zinc is sacrificial to steel. Zinc protects steel by its galvanic action and in doing so the zinc itself is corroded rather than the steel. Since the zinc itself corrodes, zinc coatings cannot be considered satisfactory under severe corrosive conditions, as in the presence of acids. Zinc offers good protection against normal atmospheric corrosion.

For additional corrosion protection on zinc coated surfaces, paint coatings can be applied. In the case of smooth zinc coatings, some roughening or etching of the surface of the zinc is necessary to provide adhesion of the paint. Metallized and sherardized zinc surfaces are sufficiently rough and porous to give great adherence for paint coats that are compatible with zinc.

Oxidation Resistance

Zinc coatings begin to oxidize if heated to temperatures above 500 or 600°F. The zinc oxide film formed is somewhat protective against further oxidation, providing higher temperatures are not reached. One aircraft company has found zinc coatings satisfactory in service at 500°F. In one case, it is being used on a part operating at 500 to 600°F.

Erosion and Abrasion Resistance

As zinc is a soft material, it cannot be expected to offer good resistance to erosion and abrasion attack. Because of low hardness, at elevated temperatures zinc coatings are susceptible to removal by the abrasive action of dust, etc., during operation.

Joining

Zinc coated surfaces may be soft soldered but soft soldered joints are not suitable for operations involving temperatures of 400 to 600°F. Zinc coated surfaces may be brazed or silver soldered but the temperatures involved are much higher than the melting point of zinc and the temperatures required for the zinc to alloy with the iron to form brittle zinc-iron compounds or to penetrate into the steel to cause zinc embrittlement. When welding is desired, it is preferable that the zinc coating be removed along the line of the weld before the welding operation, although some arc resistance and spot welding is practical without removal of thin zinc coats.

Mechanical Properties and Adherence

Hot dip galvanized and thin electrogalvanized zinc coatings are relatively soft and ductile. Considerable forming is possible after coating and without damage to the coatings. Adherence is good. Sherardized coatings have high adherence but the brittle zinc-iron compound predominates and little forming may be done. The weakest point of metallized coatings is the adherence or bond. Some deformation is permissible where the coatings are only 0.002" to 0.003" thick but none for thicker metallized coatings.

Effect on Base Metal

All acid pickling processes used in pretreatments for plating involve dangers of hydrogen embrittlement. Where subsequent heating operations are involved, as in hot dip galvanizing, galvannealing or sherardizing, the hydrogen is driven out by the heating operation. In electrogalvanizing not followed by heating, some slight danger of hydrogen embrittlement is involved but the primary source of such embrittlement, if it is present, is in the pretreatments such as pickling or cathodic electrocleaning. No hydrogen embrittlement is involved in zinc coating by any of the metallizing processes.

One aircraft company reports that their tests show that zinc electroplate does not adversely affect the fatigue strength of the base metal. Little information is available as to the effect of hot dip galvanizing or sherardizing on the fatigue strength of the base metal. Indications are that the angular grit blasting used as a surface preparation for metallizing may have a tendency to reduce the fatigue strength a few percent.

Zinc embrittlement must be considered in connection with the use of zinc coatings at elevated temperatures. For temperatures below 600°F there is no danger. At temperatures of 800 to 1100°F the zinc may act in two ways, one, direct alloying and combining with the iron to form brittle zinc-iron compounds, or two, intergranular penetration into the base metal. At temperatures above 1100°F the zinc may volatilize and be carried over to parts that are at still higher temperature and attack such parts. It is reported that zinc vapors attack the austenitic stainless steels quite rapidly, causing severe intergranular embrittlement.

Uses

Hot dip galvanizing is commonly used for zinc coating of sheet steel, structural shapes, wire, tanks, pipe, containers and hardware. Electrogalvanizing is commonly used for zinc coating of wire, strip, wire cloth, hardware and ridged roofing stock. Metallizing with zinc is commonly used for outdoor metal trim, water tanks, containers and conduits. Although the main use of zinc coatings is for protection against atmospheric and water corrosion, they can be used for parts that reach operating temperatures of 500°F.

Costs

Among all of the many types of metallic coatings that are applicable to steel, the zinc coatings are the lowest in cost. In part only is this due to the lower cost of the metal itself. The major reason for the lower cost is the relative ease with which the metal can be applied. As in all manufacturing operations, the final cost per unit is dependent upon the complicity of the unit itself, the extent to which the operation has been tooled up and the quantity produced as well as the cost of raw materials. On the basis of manual operations rather than continuous line automatic production facilities, and on the assumption that the parts to be coated are not excessively complicated in shape or size, the relative costs per square foot for applying the various types of zinc coatings are approximately as shown in Table 27.

Table 27

Costs of Zinc Coatings, Cents per Square Foot

Process	1/2 mil Coating	1 mil Coating	5 mil Coating	10 mil Coating
Hot dip	25	30	--	--
Electro Acid	25	35	60	--
Chloride	25	30	50	--
Cyanide	30	45	90	--
Fluoborate	30	40	60	--
Sherardizing	25	--	--	--
Metallizing	--	--	70	100

Facilities Available

Galvanizing, electroplating and metallizing firms are located in every manufacturing area of the country. Hundreds of manufacturing concerns have installed their own departments for doing these types of work. Equipment for each of the processes is available from the manufacturers of each type along with handbooks and instruction manuals.

Section 8. Molybdenum Plate from Carbonyl Vapor

The deposition of molybdenum by pyrolytic decomposition of molybdenum hexacarbonyl is a new method that has not yet been operated on a commercial process. Successful research work on this method has been done at Bell Telephone Laboratories, Murray Hill, N. J. and at Sam Tour & Co., Inc., New York, N. Y.

Molybdenum hexacarbonyl is a white volatile solid. The vapors decompose at a temperature of approximately 300°F to deposit metallic molybdenum.

The partial pressure of the carbonyl vapor over the carbonyl crystals is around 0.1 mm Hg at room temperature. When the vapors come in contact with a surface at 300°F or above, they decompose and molybdenum deposits on the surface together with small amounts of carbon while the gases are being removed from the system. Under certain conditions, the molybdenum deposit is adherent and forms a continuous layer on the surface of the object.

Titanium alloys have been plated with molybdenum from carbonyl vapor. Wear tests have shown(86) that the molybdenum plate has remarkable nongalling and wear resistant properties. These properties of molybdenum metal have been found, also, for metallized (sprayed) molybdenum surfaces on iron and steel.

Surface Preparation Required

Similar to most plating methods, surface preparation is an important step in securing good adhesion of the deposit. Mechanical cleaning, sand blasting or pickling followed by degreasing is a satisfactory cleaning procedure.

Description of the Process

The vapor plating procedure consists of the following steps: 1. setting the object, closing and tightening the system; 2. evacuating the system; 3. vapor plating; 4. finishing operations.

The object is placed inside of a pyrex or quartz chamber surrounded by an high frequency induction heating coil. Temperature control is obtained by the use of a thermocouple located preferably inside the object. The system is closed, tightened and evacuated to a pressure of about 1×10^{-3} mm Hg for such time as is required to remove most of the moisture. The system is then flushed with the carrier gas.

The heating is started and when the object reaches a temperature between 750 and 1300°F, the plating vapors are allowed to enter the chamber. The plating atmosphere consists of the carrier gas, plus the carbonyl vapor.

The carrier gas may be hydrogen, hydrogen sulphide or any gas which does not enter into reaction with any of the constituents present in the plating chamber. The system must be exhausted continuously in order to remove the waste gases, to avoid unnecessary oxidation and to keep the total pressure below 1.0 mm Hg.

When the desired amount of plate has been deposited the valves in the lines to the plating chamber are closed, the high frequency induction heating stopped and the temperature allowed to drop.

The rate of deposition is proportional to the partial pressure of the carbonyl in the plating atmosphere, to the rate at which the gases are carried over the work and to the temperature of the object.

At a carbonyl pressure of about 0.2 mm Hg and with the work at a temperature of 1100°F, the plating rate can reach 0.002"/hour.(87)

The equipment consists of four major units:

1. plating atmosphere generator,
2. plating chamber with high frequency induction heating coil,
3. vacuum pumps and gages,
4. temperature controlling and recording instruments.

High frequency induction heating is preferred, as radiant or indirect heating from the outside causes most of the molybdenum to deposit on the inner walls of the plating chamber instead of on the work. The high frequency converter can be connected with the temperature controlling and recording system. The converter must be large enough to be able to raise the temperature of the objects to at least 1200°F and the coils must be designed to give uniform heating of the work.

In order for the molybdenum to form an adherent layer, the plating must be done under controlled conditions as to total pressure and partial pressure of carbonyl.

Characteristics of the Coating

The molybdenum coating deposited from molybdenum carbonyl by pyrolytic decomposition consists of molybdenum and molybdenum carbide. Their relative amounts are controlled by and to a great extent are dependent upon the conditions of plating.

The amounts of carbide control the hardness and ductility of the coating. It may be very low resulting in a very soft coating, as low as 200 DPH, it may be intermediate, or it may consist almost entirely of molybdenum carbide which results in a very hard coating of approximately 1500 DPH.(87) It has been found(86) that 0.001" thick coatings as hard as 800 DPH are ductile, uniform and adherent.

The process is subject to a "flow effect" which consists of the building up of the heaviest deposits at the surface facing the gas inlet and a gradual decrease in amount of deposit with the distance from the inlet. To overcome the "flow effect" the plating atmosphere can be introduced at different points, or the flow of the atmosphere can be reversed periodically. An improvement results from increasing the amount of hydrogen in the atmosphere.(86)

Not much is known about the corrosion and high temperature oxidation resistance of the coating. It is believed that some porosity of the coating may exist.

Pure molybdenum is resistant to hydrochloric and hydrofluoric acids, hot or cold, to air and oxidizing atmospheres at temperatures up to 930°F, (its resistance to reducing atmosphere is higher).

The properties which restrict the use of molybdenum are embrittlement when overheated and difficulties in joining.

Section 9. Peen Plated Coatings

The coating resulting from the peen plating process consists of metal powder particles bonded upon the surface of the object to produce a relatively dense and continuous metallic coating. Zinc, aluminum, tin, lead, copper, brass, stainless steel and titanium coatings can be produced.

No special surface preparation, other than cleaning, is required. There are wet and dry methods of applying the coating. In the wet method the work to be plated is tumbled or milled with steel balls and a slurry or suspension of the metal powder. The vehicle liquid contains secret activator reagents to promote bonding. Operation is at room or only slightly elevated temperatures.

In the dry process some protective atmosphere and slightly elevated temperatures are used in the tumbling or ball milling operation.

The size and quantity of steel shot used with the powder is controlled by the nature of the metal being applied and by the shape and intricacy of the object being coated.

In either method the time of processing is a matter of 2 to 24 hours dependent upon the nature of the powdered metal being used and the thickness of coating desired. Either granular, spherical atomised or flake powders may be used.

Thin coatings have a fair degree of adherence to the surfaces. The compacted layer of added metal on the surface contains some impurities and some porosity and has less density than the coating metal in wrought form. In some cases, especially in the dry process at elevated temperatures for some metals, a slight alloy bonding may be reached at the interface. Thick coatings do not seem to have the mechanical strength and wear resistance of thinner coats similarly applied.

Since the coating is not pin hole free it offers protection against corrosion only if the coating metal applied is anodic to the base metal of the object that has been coated. Zinc peen plate coatings on nuts, bolts, screws and such parts provide corrosion protection in proportion to the quantity of zinc applied. Aluminum peen plate coats do not offer corrosion protection to steel at high humidities. There are indications that an aluminum-zinc alloy peen plated coating would offer superior corrosion protection to steel than that offered by aluminum alone. Such metals as copper and titanium tend to promote the corrosion of the steel at every pin hole in the plate. It should be acknowledged that this difficulty due to pin hole porosity applies in all types of coatings on steel irrespective of the coating process used.

No data are available as to the oxidation resistance of peen plate coatings themselves or as to the protection against oxidation that they might offer to steel used at elevated temperatures.

The "peening" is applied to the metal powder and is not such as to cause peening of the steel surface and probably does not affect the endurance limits of the base metal.

The process is quite new and little information is available as to its commercial use and as to service results. The costs of applying peen plate coatings on small objects done on a quantity or bulk basis are comparable to the costs of electroplating. No work has been done on large (over 12") intricate shapes or thin sheet metal parts.

The peen plating process is a development of and is patented by The Tainton Company of Baltimore, Maryland.

Section 10. Stainless Clad Steels

The remarks and data on fabrication, availability, costs, facilities available and sources of information given in Chapter III, Section 7 on "Nickel and Nickel Alloy Clad Steels" are applicable to "Stainless Clad Steels". This section is devoted to data that are applicable specifically to the stainless clad steels.

The following grades of stainless clad steel are reported as available:

1. Chromium Steels

This group is made up of alloys of the straight chromium type.

Type 405 (Low Hardenability) (Ferritic Martensitic) (Magnetic). This is a modification of Type 410 and has low hardenability when air cooled from high temperatures. It is used extensively for oxidation and corrosion resistance at elevated temperature.

Type 410 (Hardenable) (Martensitic) (Magnetic). This type is air hardening when cooled from high temperatures and also has excellent resistance to oxidation and corrosion at high temperatures. It is available with 0.06 maximum carbon content.

Type 430 (Non-hardenable) (Ferritic) (Magnetic). This type is non-hardenable when air cooled from high temperatures. The heat affected zones of the welded material are brittle and have little ductility unless annealed. It has excellent resistance to oxidation and corrosion.

Fourteen to sixteen Cr (Hardenable) (Ferritic Martensitic) (Magnetic). This type is intermediate between the martensitic (lower chromium) and the ferritic (high chromium) types. It is less hardenable than the lower chromium and is more ductile than the high chromium types. For this reason it is more easily welded. It has good resistance to oxidation and corrosion.

2. Chromium-Nickel Steels

This group is made up of alloys containing chromium (16.0 to 26.0%) and nickel (6.0 to 22.0%) as the chief alloying elements. Elements such as titanium, columbium and molybdenum may also be present. These alloys cannot be hardened by heat treatment and are non-magnetic, but some types may become magnetic and may be hardened when severely cold worked. When annealed, the microstructures are composed primarily of austenite and these steels are referred to as "austenitic" stainless steels.

Type 301. This is a 17-7 chromium-nickel analysis used under comparatively mild corrosive conditions and extensively for sanitary and decorative applications.

Type 302. This is an 18-8 type having excellent corrosion resistance for chemical, sanitary and decorative purposes.

Type 304. This is the 18-8 type with 0.08% carbon maximum. Due to the limitation of the carbon content, this steel is less susceptible to carbide precipitation during welding than Types 301 and 302 and may be used over a wider range of corrosive conditions without subsequent heat treatment. This material is available with 0.03% maximum carbon.

Type 309. This type has a higher chromium and nickel (25/12) content than the basic 18-8 and has superior resistance in a large variety of applications combining heat and corrosion.

Type 310. This type has the highest chromium and nickel (25/20) content of the austenitic stainless steels regularly produced. It has excellent resistance both to corrosion and to oxidation at high temperatures.

Type 316. This is the 18-8 type of higher nickel (10% min.) content with the addition of 2.0 to 3.0% molybdenum. It is more resistant to corrosion than the regular 18-8 steels, with the exception of certain oxidizing acids. The molybdenum bearing stainless types are less susceptible to pitting or pin hole corrosion than the regular 18-8 types when exposed to such corrosive media as sulphuric and sulphurous acids, sulphite and cellulose solutions. Type 316 is of special service to the paper, pulp, rayon and dye industries. It is available in two special grades--with 0.03% max. carbon and a columbium bearing grade.

Type 347. This type is the basic 18-8 analysis modified by the addition of columbium to prevent the precipitation of harmful carbides. Columbium forms extremely stable carbides preferentially to chromium and prevents the sensitization phenomenon. This material (or Type 321) should be used for welded vessels under certain corrosive conditions, or if the service temperature range is 800 to 1600°F, or if a weldment is to be stress relieved. It may be employed over a wide range of corrosive conditions without subsequent heat treatment and will also withstand heat treatment without the damaging effect of sensitization.

Type 321. This type is the 18-8 analysis modified by the addition of titanium to prevent the precipitation of harmful carbides. Titanium forms extremely stable carbides preferentially to chromium and prevents the sensitization phenomenon. This material (or Type 347) should be used for welded vessels under certain corrosive conditions, or if the service temperature range is 800 to 1600°F, or if the vessel is to be stress relieved. As titanium cannot normally be transferred through the arc, columbium bearing (Type 347) electrodes are used for welding Type 321 material.

The oxidation and corrosion resistance of the different grades of stainless clad steel have been indicated above. The various grades of austenitic stainless steel show different degrees of carbide precipitation when exposed to elevated temperatures.

When austenitic stainless clad steels of all types, except 321, 347 and special types of 316, are in a temperature range of 800 to 1600°F, chromium carbides are precipitated in the grain boundaries. In this temperature range, the carbon separates from the solid solution and joins with chromium at the grain boundaries to produce chromium carbide. This rejection of the carbides rich in chromium, from the body of the grain into the grain boundaries, reduces the chromium content of the grain to a point where the corrosion resistant properties of the material may be lost. Two types of attack can take place if the material is then exposed to highly corrosive environments; the chromium carbides around the grain may dissolve, or the chromium depleted austenitic grain may be attacked. In both cases the grains lose cohesion and the material, as a whole, loses ductility and strength.

The rate and amount of chromium carbide precipitation depend upon a number of factors.

1. As each part of carbon will combine with 17 parts of chromium, by weight, undissolved or precipitated carbon will combine with and remove 17 times the amount of chromium. The lower the carbon, the less there is available to be precipitated.

2. The longer the time in the critical temperature range, 800-1600°F, the more carbides precipitated.

3. The closer the temperature is to 1200°F, the more rapid will be precipitation.

4. The greater the amount of chromium and nickel, richer than 18-8, compared to the carbon, the less rapid will be the precipitation.

When chromium carbides have been formed, they can only be removed by heating the material to a proper temperature to redissolve the carbides and quickly cooling to below 800°F. The precipitation of chromium carbides can be prevented by the addition of a carbide stabilizing element, such as titanium or columbium. As titanium is oxidized in the arc stream during welding, columbium stabilized material is used in welding electrodes. The stabilizing element combines preferentially with the carbon and, as a result, there are little or no chromium depleted areas and the corrosion resistant properties of the material are maintained.

For weldments which will be stress relieved and vessels which will operate in the carbide precipitation range, either Type 321 (titanium stabilized) or Type 347 (columbium stabilized) should be used. When Type 316, the molybdenum bearing stainless, is required to meet the above conditions, an 0.03% maximum carbon grade should be used. Type 316, stabilized with columbium, is also available.

Erosion and Abrasion Resistance

Specific data on the abrasion and erosion resistance of the various grades of stainless clad steels are not available. These clad materials, depending on their hardness, can be expected to have comparatively high abrasion and erosion resistance.

Mechanical Properties

The mechanical properties of the stainless clad steels are dependent upon the type and metallurgical conditions of the cladding and of the backing material. Actual figures on the strength of the stainless clad steels are not readily available.

Adhesion

The ASME Boiler Code and the ASTM specifications require a minimum bond shear strength for clad steels of 20,000 psi. One manufacturer reports the typical shear strength values of the bond obtained by tests on production plates in the annealed condition as shown in Table

Table 28

Bond Shear Strengths of Stainless Clad Steels

Type	Gage	% Clad	Shear Strength psi (Aver.)
304	½"	20	49,900
316	½"	20	44,500
316	3/4"	10	48,300
347	½"	10	46,200
410	1"	10	44,800

The quenching in water of stainless clad steel plates, with high coefficients of linear expansion, from a temperature of 1800°F has shown no evidence of bond failure after 20 cycles of heating and quenching. To approximate conditions encountered in fractionating towers, coking drums and similar equipment which is subjected to extreme thermal shock, samples of 20% Types 347 and 410 clad, were heated to 1000°F, and water quenched to below 400°F. This cycle was repeated 350 times with standard ASME shear tests made at intermediate points. The results indicated that the shear strength is not affected and remains approximately double that of the minimum requirement of the ASME Boiler Code specification.

Costs and Availability

The comments in Chapter III, Nickel and Nickel Alloy Coatings, Section 1, General Discussion, regarding the limiting costs for surface protection of low alloy steel are applicable to the stainless clad steels. When the cost of producing stainless clad steel becomes equal to or higher than the cost of solid stainless steel of the same thickness it is obvious that nickel conservation alone must be the only justification for the use of the clad steel.

The comments in Chapter III, Section 7, Nickel and Nickel Alloy Clad Steel, regarding costs and availability, facilities available and sources of information are equally applicable to the stainless clad steels.

CHAPTER VI

PAINT COATINGS

Section 1. General Discussion

Within certain limits, high temperature paint coatings offer possibilities for the protection of steel against oxidation and/or corrosion attack during and after exposure to temperatures above 400 or 500°F. Many manufacturers claim to produce paint products which protect steel against oxidation and/or corrosion attack during high temperature exposure.

To collect as much data as possible, individual letters were sent to over 50 paint manufacturers or formulators. Over 30 companies replied that they had one or more products which could be used for the protection of steel against oxidation and/or corrosion attack at temperatures over 400°F. With these replies came the usual promotional type of literature and varied but "marvelous" claims. Where "users" were mentioned, these users were asked to report on their experiences. An effort was made to tabulate all data under the following headings: 1. manufacturer, 2. products of each manufacturer, 3. composition, 4. recommended or maximum temperatures for use, 5. surface preparation required, 6. method of application, 7. number of coats required, 8. curing temperature required - or air drying, 9. coverage per gallon, 10. cost per gallon or cost per square foot of surface, 11. manufacturers' test results, 12. users and users' comments.

Although data were received from over 30 different companies, with their reported characteristics of one or more recommended paint products, the tabulation did not include all manufacturers. Additional data in the literature and visits to aircraft plants indicated that there are numerous other paint formulators claiming to have products which protect steel on exposure to temperatures in excess of 400°F. The compilation of additional data can be an endless job. It is doubted that such additional compilation would yield any more interesting or informative data than that which has already been received.

Unfortunately, the paint coating field is rife with products involving so-called "trade secrets" and "secret formulations". The following are typical illustrations of the type of information supplied by the makers as to the formulation of their paint products: 1. modified phenolic type resin plus an inert pigment, 2. silicone resin vehicle plus a ceramic type heat resistant paint, 3. aluminum plus silicone to which a quartz like silica is added, 4. modified silicone enamel, 5. modified silicone and aluminum, 6. 100% silicone resin, 7. straight silicone liquid plus aluminum pigment, 8. silicone aluminum (formula confidential), 9. varied colored pigmented silicone paint, 10. epon and epoxyl resin base, 11. mixture of sodium silicate, chromates plus fine particles of zinc dust, 12. conventional paint plus zinc metal pigment.

In some cases, the manufacturers refuse to give any information as to the general composition of their products. It is impossible to evaluate different types or classes of paints based solely on such vague information as indicated above. There is little or no assurance from any manufacturer that the formulation or raw materials used today will not be revised tomorrow. For example, many manufacturers classify their products under the general name "silicone liquid plus aluminum pigment", but do not state what silicone liquid resin is used or how much silicone resin is used. Apparently some so-called silicone paints contain only a few percent (less than 10%) of silicone liquids while others may contain 30 to 40%. It is obvious that names on this general type of information as to "make up" cannot be used as a basis of classifying or grouping for the purpose of evaluation.

There are hundreds of so-called high temperature secret formulation paints on the market of which the makers refuse to disclose the general "make up". Each is ready to supply testimonials as to where his product is or was used, etc., etc. In numerous cases, efforts to check such references met with no response or "We bought some for trial", "We do not use it", "We have not tried it", "We use it to a limited extent but not at high temperatures", or "It is not as good as claimed". In a few cases, the replies indicate that the makers' claims are authentic. In many cases the experiences of different users, under somewhat different conditions of use, are quite contradictory. It is unfortunate, but true, that the situation is quite confusing.

In one instance, the claims made by a manufacturer and the results reported by two users varied so much that it appeared that each was discussing a different paint. In another instance, a paint manufacturer reported that his product offered satisfactory protection to steel up to 1000°F based on thermal shock tests at 500, 800 and 1000°F. This same material was reported as unsatisfactory in salt spray tests conducted by the Army Air Forces. Another manufacturer recommended two products (formula a secret) claiming that these would offer protection to base metals up to temperatures of 2800°F and higher. Two aircraft companies tested these products. One reported that both failed after 16 hours exposure at 1400°F, the second stated that one flaked very easily and that the other was not satisfactory for high temperature service. In several instances, when comments were received, the product described by the user had a different code or type number than that reported by the manufacturer.

Until formulations are less secret so that specifications can be written and paints tested for conformance to such specifications, each individual paint product must be evaluated by actual test. No fully satisfactory method for testing high temperature paints for use on aircraft or aircraft engine parts has been developed, although work is proceeding along such lines. Using such test methods as are available, plus pilot service trials, several aircraft manufacturers have chosen specific grades of high temperature paints for certain applications where the temperatures involved are well over 400°F.

In spite of the confusing nature of the situation, it is possible to classify or group the high temperature paints into 5 general classes or groups as follows: 1. refractory pigmented paints, 2. aluminum pigmented paints with other than silicone vehicles, 3. silicone paints, 4. miscellaneous paints, 5. zinc metal paints.

Each of the above classes will be discussed separately in sections of this chapter. Requirements as to surface preparation, methods of application, effects on base metal, fabricating characteristics, are substantially the same for all types of high temperature paints and are discussed in general in this section.

Surface Preparation

It is stressed at this point that the successful use and to obtain expected service of any protective coating depend on the adherence of the coating to the surface it is to protect. Any loose, non-adhering material such as oil, dirt, mill or heat treating scale, corrosion products, etc., any old paint or coating, even those lightly adherent, which do not have the desired high temperature properties, and any material which may be softened by the solvents of the paint, must all be completely removed. This can be done by an abrasive medium such as sand blast, shot blast, or wire brush and/or by treatment in acid pickling and alkali cleaning solutions. After removal of all of the foreign matter, the abrading media, or cleaning solution, and/or pickle solution must be thoroughly washed off and the surface dried. The paint coating must be applied immediately before the active surface of the steel begins to corrode.

Proper surface protection and proper application (following of the manufacturers' instructions) are two musts for the successful use of paints for protection of steel against effects of high temperature exposure and/or to corrosive media.

One aircraft company that has done a great deal of test work on high temperature aluminum pigmented silicone paints states, "Up to 750°F, a phosphate undercoating has a definite advantage as a paint base, but above this temperature it behaves erratically. Above 750°F, it is recommended that the surface to be painted be blasted with aluminum oxide grit prior to painting of a two coat silicone aluminum system".

In most cases the manufacturer offers suggestions for surface preparation dependent on the type and condition of the base metal. In all instances, it is desirable that the manufacturer's recommendations be followed.

Methods of Application

Most high temperature paints can be applied by either brush or spray. Some manufacturers also advise application by dipping. Some recommend only spray application as acceptable. A user of silicone aluminum pigmented paints suggests that for best adhesion qualities, thin wet coats of paint, about 0.001" thick, should be applied each time. Excessive spray gun pressures and excessive distances from the part will give thick, dry coats that are not as impervious as the thin wet coats. The platelets of aluminum in the pigments must be allowed to flow together, giving an overlapping barrier to penetration.

In most instances, at least 2 coats are required to obtain maximum protection against oxidation on exposure to elevated temperatures. In a few instances, one coat was reported as adequate, while on the other extreme, one manufacturer suggests at least 5 coats. Air drying between coats is usually adequate although some paints require a low temperature cure or bake between coats.

In general, one gallon of high temperature paint covers 350 to 600 square feet of surface with a one mil thick coat. The nature and condition of the base metal surface are important factors in the coverage obtained in a first coat.

Corrosion Protection and Chemical Resistance

The data on the corrosion protection offered by the various high temperature paints and their chemical resistance are fragmentary and inconclusive.

These characteristics of any paint coating will, of course, depend upon: 1. the chemical nature of the dried and/or cured film, 2. the imperviousness of the dried film, 3. the adhesion of the coating.

It appears that the silicone aluminum pigmented paints in their cured condition will resist jet fuels (kerosene), oils, and materials generally used in solvent washes. For curing to resist such liquids, a minimum cure of 2 hours at 425°F is recommended.

The effect of hydraulic fluids such as Skydrol and Hydrolube must be taken into consideration. One aircraft manufacturer has tested over 300 different coatings, including silicone epoxyls, etc., and found none that will resist Skydrol and Hydrolube. It appears that these tests were based on air dried films. It is reported that baking enamels will withstand Skydrol.

Lead bromide, lead oxide and other lead compounds in exhaust gases are reported as active in attack on aluminum, and are reported to cause failure of ceramic coatings.

Most of the "high temperature" paints are reported to have good resistance in the salt spray test. Very limited data are available on the corrosion protection offered by the coatings after varied periods of exposure at elevated temperatures. On visual examination, some coatings appear satisfactory after exposure to high temperatures, yet fall apart or show marked porosity on exposure to the salt spray test. One company reports that the addition of zinc metal increases the salt spray resistance of a refractory pigmented paint coating.

Abrasion and Erosion Resistance

It has been reported that the abrasion resistance of most silicone aluminum paints is low. They should not be used in streams of rapidly moving gases, especially when such gases contain abrasive particles.

It can be expected that those paints which produce a hard ceramic appearing surface after curing have higher resistance. On the other hand, these may have poor impact resistance.

Because of the variety of high temperature coatings on the market, each must be evaluated as to abrasion and/or erosion resistance.

Fabricating Characteristics

In almost all instances, paint coatings must be applied after the complete fabrication of a part and, possibly, after the complete assembly of a unit. Most paints, especially those which have been cured, are comparatively brittle and will chip, crack and/or fail during even the simplest fabrication operation.

One firm using high temperature paint reported that they have arc welded painted surfaces followed by touch up in the area of the arc.

Effect on Base Metal

The base metal may be affected by surface treatments prior to application of paint. Hydrogen embrittlement, as a result of pickling for surface preparation, must be guarded against.

Several of the high temperature paints must be cured at temperatures as high as 750°F to obtain maximum properties. This heat treatment, especially in the higher ranges, can reduce the strength of heat treated parts or cold rolled steel and can cause distortion of some parts with thin sections.

Uses

Many of the high temperature paints are of comparatively recent developments. Insufficient accumulated or reported data are available for a complete evaluation. This has been further complicated by the exaggerated claims made by some manufacturers and by the variance in their products within the same general classification. The absence of any indication as to formulations makes it almost impossible to subdivide the different paints in the same classification.

In spite of all this conflicting data, it appears that some paints are available which will offer protection to steel against oxidation and/or corrosion on exposure to temperatures above 400°F. In some cases, the maximum temperature for some paints may be limited by the elevated temperature properties of the base metal.

Paint coatings may be used to protect steel parts on exposure to elevated temperatures when: 1. tolerances of the parts are not critical, 2. the temperature required for the curing will not reduce the strength nor cause distortion of the part, 3. the critical areas of the fabricated part or complete assembly can be completely coated, 4. the required surface preparation will not in any way affect the components of the assembly.

Comments from various users indicate that high temperature paints are being used for: 1. gas burner and oven parts, 2. stacks subjected to elevated temperatures, 3. automobile exhaust mufflers, 4. some aircraft parts on a limited scale.

The general comments received to date indicate some users are satisfied for temperatures of exposure below 750°F, while others state they are making the best use of what is available, but are still looking for a better product.

Costs

The data received, (based on manufacturers' claims), indicate costs as shown in Table 29.

Table 29

Costs of Paints

Type Paint	Coverage per Gal.-Sq. Ft.	Approx. Costs per Gallon
Aluminum Pigmented Silicone plus addition of some refractory like material.	One brand 250 to 450. Others 600 to as high as 1000.	$16.00 to $24.00
Aluminum Pigmented Silicone two different ranges.	400 to 750 (some as low as 250 feet).	$5.50 to $10.00 and $15.00 to $20.00
Epon Resin Base Paint	-	$4.00 to $5.00
Zinc Pigmented	400 to 550	$10.00

Facilities and Sources of Information

It is not intended to list names of manufacturers or the trade names of their products. The following aircraft companies are reported as doing some evaluation work on high temperature paints: 1. General Electric Company, Aircraft Gas Turbine Division, Cincinnati 15, Ohio; 2. Douglas Aircraft Company, Los Angeles, California; 3. Westinghouse Electric Corporation, Philadelphia, Pennsylvania; 4. North American Aviation Company of Los Angeles and Downey, California; 5. Ryan Aeronautical Company, San Diego, California; 6. Boeing Airplane Company, Seattle, Washington; 7. Airesearch Company, Los Angeles, California; 8. Pratt and Whitney Aircraft Division, United Aircraft Corporation, East Hartford, Connecticut.

Section 2. Refractory Pigmented Paints

Included in this general class are all paints, of whatever vehicle, pigmented with refractory materials such as silica, quartz, mica, ceramic frits. The ordinary titanium dioxide pigmented white paints and enamels are not included in this class but such special formulations as the butyl titanate paint, described below, are included.

An article in the literature(90) outlined a formula for a high temperature coating as shown in Table 30.

Table 30

Formulation of a Refractory Pigmented Paint

Ingredient	Parts by Weight
Aluminum Flake XX Fine	30
Butyl Titanate	50
High Bake Alkyd Resin	5
Butyl Alcohol	15

The following comments were made as to its characteristics: The package stability is good. The air dried film will slowly hydrolyze to form a non-adherent white powder. Baking at 572°F produces a sort of titanium dioxide - aluminum frit which possesses excellent adhesion, durability, heat resistance, and moderate corrosion resistance. The product is a sort of vitreous enamel surface with superior resistance to mechanical and thermal shock. Applied to steel panels and exposed to 1112°F for prolonged periods (actual period of time not indicated) improved rather than deteriorated the film properties. Adhesion is so great that removal is not possible without injuring the underlying steel. In one series of tests, coated panels were heated 3 times to 1100°F, then immediately quenched in water, without showing any effect. The main objection to its use is that there is only a limited supply of butyl titanate. This product is now being produced in pilot plant production.

The Vita-Var Corporation of Newark, New Jersey, did some extensive work on the development of heat resistant paints as part of a Department of Army Contract DA-44-009 ENG 963. Six detailed reports were issued. In the final report, it is stated that the formulation shown in Table 31 exhibited the best overall results over the entire temperature range (400 to 1400°F), and resistance to high humidity and to salt spray test after varied and repeated times of exposure in these temperature ranges.

Table 31

Heat Resistant Paint Formulation

Frit #1 (Special mixture - see Progress Report #2)	150 lbs.
Frit #4 O. Hommel Co. Frit #3E 46R	113 "
Frit #6 O. Hommel Co. Frit 263	113 "
Chrome Oxide Green	56 "
Clay	62.5"
Red Iron Oxide	4 "
Manganese Dioxide	1 "
Aluminum Stearate	3 "
Mica	75 "
Silicone Resin Solution 60% NV (G.E. Silicone Resin Solution SR82)	270 "
Butyl Alcohol	15 "
Toluol	25 "
Xylol	25 "

Wt. per gallon 12-15 lbs.

One paint manufacturer reports two refractory pigmented paints and claims maximum temperature resistances of 2800 and 4000°F. Two aircraft manufacturers tested these products and found them unsatisfactory.

One paint manufacturer reports a series of silicone base paints mixed with a ceramic type heat resistant paint. They claim temperature resistances of 500°F for the white paint to 1500°F for the silicone aluminum paint. One aircraft manufacturer reports the satisfactory use of the silicone aluminum paint. They do not report the maximum temperature of exposure. They report also that two other paint manufacturers produce equivalent products, although they may vary in composition.

Another aircraft manufacturer reports the use of two different refractory pigment type paints. These coatings, when fired hot, form a glazed surface with the appearance of a ceramic coated surface. Adherence of these coatings is a problem. Their heat resistance is about 2000°F, but they offer poor protection against corrosion.

Another paint manufacturer reports a silicone paint pigmented with aluminum plus the addition of a quartz like silica. The manufacturer claims satisfactory properties up to 1000°F. One user reported satisfactory service in hot oil pump up to 550°F, while another has found it satisfactory on a surface up to 800°F after 7 months. Tests performed at Wright Field(91) indicated satisfactory properties as to 100 hours in motor fuel, as to hydrocarbon resistance, as to flexibility ($\frac{1}{2}$" dia.) and as to 1000 hours at 1000°F, with maximum temperature until failure of 1220°F. The effect of salt spray or other corrosive media after the 1000 hours at 1000°F was not determined.

It is possible that refractory type paints which, after drying or a high temperature cure, form a "ceramic type" film may be one satisfactory method of protecting steel at temperatures as high as 1200°F or higher. The maximum temperature, of course, will be limited by the high temperature properties of the binder and of the base material. Refractory pigmented films should offer higher abrasion resistance and be more brittle than other types of paint coatings. Although only two formulations for refractory pigmented coatings are given above, there may be many more.

One major problem with these hard films may be adherence. It is possible that variance in manufacturers' claims and users' reported results can be attributed to poor adherence or failure of bond at higher temperature rather than to failures of the film.

While refractory pigmented films may have good heat and abrasion resistance they may not be resistant to lead oxide and the bromide residues from the combustion of fuel containing tetraethyl lead additions. More experimental work and service trials of refractory type coatings are necessary before recommendations or conclusions can be arrived at.

Section 3. Aluminum Pigmented Paints with other than Silicone Vehicles

So-called "heat resistant aluminum paints" have been on the market and have had extensive use for many years. Many types of vehicles are used. Some claim resistance to temperatures of 350 to 400°F, others claim 400 to 500°F, still others claim higher temperatures. All such claims raise the questions of "how tested" and "what criteria are used to determine failure or resistance".

Several accelerated test methods have been used in both indoor and outdoor exposures. One indoor exposure test method consists of heating the inside of a painted test pipe with a gas flame and observing the effect on the test surface. Another indoor method heats one end of a painted bar to produce a temperature gradient in the bar and observes the effect on the paint. Such visual observation cannot disclose the corrosion protection quality of the paint either before or after heating. One outdoor method uses a painted test pipe heated internally by a nichrome electrical resistance element wound on a ceramic cylinder. Repeated heating and cooling is combined with atmospheric exposure in the evaluation of the paint. This outdoor test procedure is superior to the indoor methods, but is dependent upon the particular atmospheric conditions at the test site during the specific period of the test.

The aluminum pigmented heat resisting paints with other than silicone resin containing vehicles may be classified according to the vehicles used. The vehicles may be of the drying oil, the phenolic resin, the alkyd resin, the epoxy resin or the bitumastic type. The drying oil types are not suitable for temperatures above 250 to 300°F. Some of the phenolic resin, the alkyd resin and the epoxy resin types may be satisfactory for temperatures of 350 to 400°F, although some claim even higher temperature resistance. The bitumastic types have been used for years on furnaces, stacks, etc., in temperature ranges up to 400 or 500°F.

The bitumastic type of vehicle has been the standard base for aluminum paints used for paint "calorizing" of steel surfaces. In this procedure, the vehicle acts as a protection to the steel surface and to the aluminum flake powder during the initial heating to above the melting point of the aluminum. The aluminum then alloys with the steel surface while the residual of the vehicle is burned away. Such paint "calorized" steel surfaces have fair resistance to oxidation but the coating contains insufficient aluminum and is too discontinuous to provide adequate corrosion protection.

A new coating of the paint "calorizing" type has been reported. The reported mechanics of the coating are as follows: "As the temperature rises to 500°F certain portions of the binders are released by evaporation and part of its former pigmentation becomes the binder, at 800° a portion of the binder again evaporates and another portion of the former pigmentation becomes the vehicle at the end point about 1500°F the metallic portion of the pigment fuses to the metal. In this manner it is possible to obtain metal protection at all operating temperatures and retard corrosion and oxidation from heat attacking low alloy steels." To date, the above coating has been given preliminary tests only.

Section 4. Silicone Paints

The silicones have become prominent in the high temperature paint field. The several producers of silicone resins have carried out extensive development work on the uses of the silicones and certain modified silicones in many types of paints. The silicone resins are fairly expensive, in the neighborhood of $35.00 per gallon. Silicone paints carrying considerable percentages of silicone resins in their formulations are somewhat expensive. It is obvious that a paint selling at $8.00 per gallon cannot contain a large percentage of a $35.00 ingredient. The use of the term "silicone" is questionable when the amount of silicone resins present is only 3 to 5%. Needling or doctoring a paint with a dash of silicone resin should not justify calling the product a silicone paint.

In the so-called silicone paint field, there seem to be four classes of paints, as follows: 1. high silicone paints with over 35% of silicone resins; 2. intermediate silicone paints with 16 to 35% of silicone resins; 3. low silicone paints with 6 to 15% of silicone resins; 4. silicone treated paints with 5% or less silicone resins.

It is unfortunate that the makers of these paints refuse to give even approximate statements as to the quantities of the silicones used per gallon or as to the type of silicone resin used.

Beside being classified on the basis of quantity of silicone resin, the silicone paints of today may be classified further according to the nature of the pigments used, as follows: (a) unpigmented; (b) pigmented - not aluminum; (c) aluminum pigmented; (d) aluminum plus refractory pigmented; (e) silicone-alkyd copolymers plus aluminum and refractory pigments.

Since the percentage of silicone present is not disclosed by the manufacturers of the paints, it is necessary to discuss the silicone paints on the basis of the above classification alone.

(a) Unpigmented Silicone Paints.

One aircraft manufacturer has made some preliminary tests on some unpigmented silicone paints understood to be of the class 1 or high silicone variety and reports them satisfactory for use up to a maximum temperature of $700^{\circ}F$. The particular types of silicone or modified silicone resins included in the formulations tested are unknown. Depending upon the type and quantity of resin used, these paints may fail at a lower temperature.

The unpigmented silicone resins begin to darken in color at temperatures of around 550 to $600^{\circ}F$. When temperatures of the order of $700^{\circ}F$ are reached, the discoloration is great. There is considerable question as to whether such greatly discolored films will continue to provide protection against corrosive conditions.

(b) Pigmented (Not Aluminum) Silicone Paints.

There are a number of paints on the market in the class of pigmented (not aluminum) silicone paints. These are produced in various colors. There is a wide discrepancy between the claims of the manufacturers and the results reported by users.

Since no data are available as to the composition of these paints, it would not be of value to attempt to compare any particular color among the different manufacturers. The claims as to maximum temperature for color pigmented (except aluminum) silicone paints range from 500 to 1000°F. Some of the claims for temperatures up to 750°F are partially confirmed by some users.

The temperature limitations of these types of silicone paints depend upon both the type of silicone resin used and the type of pigment used in the formulations. Refractory type pigments will produce paints with the higher temperature resistance qualities. The addition of such items as zinc, titanium dioxide, silica, and clay may further improve the high temperature properties.

In a recent publication(92) the Dow Corning Corporation outlined a typical formula of a grey high temperature silicone resin base paint, using a recently developed, rapid drying silicone resin, and reported preliminary tests indicating satisfactory service from 300 to 1000°F. The formulation given is shown in Table 32.

Table 32

Formulation of Rapid Drying Silicone Resin Paint

Silicone Resin Dow Corning 805	42.3
Zinc Oxide - lead free	13.7
Celite Superfloss	4.0
Graphite	4.7
Zinc Dust	28.3
Solvesso No. 3	7.0

This coating requires a high temperature cure to develop its maximum properties.

(c) Aluminum Pigmented Silicone Paints.

The bulk of the high temperature silicone paints on the market are aluminum pigmented. Manufacturers' claims vary from 700 to 1700°F for their products. Prices on these paints vary from $5.00 to almost $20.00 per gallon. A large number of these aluminum pigmented silicone paints have been tried by various aircraft manufacturers. Some data received from users indicate that some of these paints will withstand operating temperature as high as 1000°F, and limited operation as high as 1100°F.

However, there are grades of silicone aluminum paint on the market which will be satisfactory only up to 500 or 700°F. Care must be taken in choosing a paint in this classification. Extensive tests must be run to evaluate the product, and assurances received from the paint manufacturer that they will not change the formulation.

The Dow Corning Corporation of Midland, Michigan, suggests two formulations for high temperature resistant aluminum pigmented silicone paints, as shown in Table 33.

Table 33

Temperature Resistant Aluminum Pigmented Silicone Paints

Composition Ingredient	% by Wt.	Temp. of Exposure	Comments by Dow Corning
Silicone Resin DC805 Aluminum Paste 205 Xylene	57.8 28.9 13.3	400°F to 1000°F	Exposed at 1000°F (time?) followed by salt spray test (time?). Gave excellent protection.
Silicone Resin XR398 Aluminum Paste 205 Methyl Isobutyl Ketone Xylene	50.0 25.0 12.5 12.5	1000°F to 1200°F	Poorer corrosion resistance than above, but superior adherence to steel in the temperature range of 1000°F to 1200°F.

Another new formulation based on a faster drying silicone resin was reported(92) containing: silicone resin 50.00%, aluminum paste 25.00%, solvesso No.3 25.00%, by weight. After a high temperature bake, it is claimed that this paint may be used in service up to 1000°F.

A review of the available data on aluminum pigmented silicone paints indicates the following: (1.) Dependent upon the type and percentage of silicone resin used, an aluminum pigmented silicone paint may be resistant to temperatures of only 500 to 600°F or may withstand temperatures of 900 to 1000°F. (2.) The higher the content of silicone resin the better is the temperature resistance. (3.) Paints formulated so as to be used as air dried coatings usually have a maximum temperature resistance of 500 to 600°F. (4.) Paints formulated so as to require a high temperature cure or bake have maximum temperature resistance. (5.) Maximum properties are obtained with those formulations requiring and given a high temperature cure or bake at 425°F for two hours. (6.) Two coat systems greatly increase the life of the paint and will withstand longer periods of exposure to salt spray tests after aging at high temperatures. (7.) For temperatures below 750°F, a phosphate pretreatment gives the better adhesion and corrosion resistance of the two coat system. (8.) For temperatures over 750°F, an alumina grit blasting is suggested as the best method for surface preparation. (9.) The abrasion resistance of most silicone paints is low and they are not recommended for exposure to streams of rapidly moving gases or gases carrying abrasive particles. (10.) The silicone paints in their cured condition are resistant to jet fuels (kerosene) and to materials generally used in solvent washes.

(d) Aluminum plus Refractory Pigmented Silicone Paints.

One manufacturer reports a silicone base paint plus aluminum mixed with a ceramic type heat resistant paint and claims temperature resistance to 1500°F. One aircraft manufacturer reports the satisfactory use of this paint at much lower temperatures. They do not report the maximum temperature of exposure. They report also that two other paint manufacturers produce equivalent products, although they may vary in composition.

Another paint manufacturer reports a silicone paint pigmented with aluminum plus the addition of a quartz like silica. This manufacturer claims satisfactory properties up to 1000°F. One user reports satisfactory service in hot oil pumps up to 550°F, while another has found it satisfactory, after 7 months, on a surface up to 800°F. Tests performed at Wright Field(91) indicated satisfactory properties as to 100 hours in motor fuel, as to hydrocarbon resistance, as to flexibility ½" dia., as to 1000 hours at 1000°F, with maximum temperature until failure of 1220°F. The effect of salt spray or other corrosive media after 1000 hours at 1000°F was not determined.

(e) Pigmented Silicone-Alkyd Copolymer Resin Paints.

The Dow Corning Corporation(92) discusses some more recent developments in silicone and silicone-alkyd copolymer vehicles for high temperature service. The formulations for silicone base paints were discussed previously. The recent developments are of the high temperature bake type and of the modified air drying type of silicone-alkyd copolymer resin. The silicone-alkyd resin paints are reported to give greater adhesion and to be easier of application than those based on 100% silicone vehicles. Originally, they did not have the same order of heat stability. The newly developed copolymer containing 25% silicon and 75% alkyd solids used as a vehicle is claimed to produce a film with better durability, hardness and higher temperature resistance. Preliminary tests, as reported, indicate improved color retention over the 100% alkyd resins and excellent film properties up to 1200°F for aluminum pigmented and to 1000°F if pigmented with heat stable green or black pigments. The dried films have very low gloss, but have good adherence. Two of the suggested formulations of the high temperature bake type are shown in Table 34.

Table 34

Silicone Copolymer Heat Resistant Finishes - Bake Type

Ingredients	Black % by Wt.	Aluminum % by Wt.
Silicone Resin Copolymer	69.0	55.5
Black Oxide - ceramic type	20.6	-
Aluminum Paste	-	27.7
Methyl Isobutyl Ketone	5.2	8.4
Xylene	5.2	8.4

Both of the above require high temperature curing to obtain maximum properties. Therefore, they cannot be used for surfaces which cannot be heated.

Formulations of the air drying silicone-alkyd modified resin types are reported to withstand temperatures up to 750°F and to show good film integrity, adhesion, and weather resistance. A typical formulation for a grey enamel is shown in Table 35.

Table 35

Silicone Copolymer Heat Resistant Finish - Air Dry

Ingredient	% by Wt.
Silicone-Alkyd Modified Resin	52.0
Titanium Dioxide	20.3
Mica	2.6
China Clay	2.3
Lampblack	0.4
Yellow Iron Oxide	0.4
Solvesso No. 3	10.7
Mineral Spirits	10.7
Driers	0.6

The degree of color retention in the silicone organic blends is reported to be in direct ratio to the percentage of silicone present. Slight darkening must be expected if even a small percentage of organic resins is present.

A review of the available data on the silicone-alkyd resin paints indicates the following: (1.) The silicone-alkyd copolymer resin base paints offer possibilities for protection of steel on exposures from 500 to 1000°F with a possibility of some giving protection to as high as 1100 to 1200°F. (2.) Surface preparation is important to obtain best adherence. For exposures below 750°F, a phosphate pretreatment may be in order. For exposures over 750°F, a grit blast may be preferred. (3.) An high temperature bake (425°F for 2 hours) is required to obtain maximum properties. (4.) Aluminum pigmented films, as cured, have low abrasion resistance.

Section 5. Miscellaneous Paints

Under the general classification of "Miscellaneous Paints" are the many miscellaneous types of so-called "heat resistant" paints exclusive of the refractory pigmented, aluminum pigmented and the silicone base paints.

The conventional types of oil base paints have no high temperature resistant properties. All that remains is the organic or resin type base coating. For simplification, these can be divided into 4 groups as follows: (1.) Elastomers such as natural rubber, butadiene-styrene rubber, and neoprene. (2.) Thermoplastic coatings such as vinyls, vinylidine chloride copolymers, polyethylene, cellulose acetate, etc. (3.) Thermosetting resin coatings such as epoxyls, phenolics, furanes, special type oleoresinous oils. (4.) Fluorine complex organic resins such as Polychlorotrifluoroethylene (Kel-F and CF-3) and Polytetrafluoroethylene (Teflon).

Paints in groups 1 and 2, the Elastomers and the thermoplastic coatings, are not applicable for really high temperature service (above 400°F) as each will fail, soften and/or disintegrate at temperatures over 150 or 200°F. Consideration of the use of organic coatings in group 3 or 4 should be on the basis of physical and chemical data available on the films formed by the base material or resin. Various proprietary formulations based upon these data can be tried in a logical approach to the solution of a coating for a specific application.

Before testing any of these paints the manufacturer should be required to state the type of the basic film forming material used in his formulation.

Thermosetting Resin Paints

These paints are exemplified by the phenolics, furanes and epoxyl resins. Usually, these paints are applied as thin coatings followed by an air dry and a high temperature cure to promote polymerization. Polymerization is necessary to develop optimum physical and chemical characteristics. After polymerization they form rigid, smooth, tough films which may be resistant to higher temperatures and to general solvent action.

Oleoresinous oils are unsaturated oils which, on exposure to air, combine with oxygen to convert to a saturated film forming solid. This oxidation process, after application, improves the physical and chemical resistance. This characteristic places the oleoresinous oils in the class of thermosetting resins. However, they are not recommended for high temperature service. The general characteristics of these 3 other thermosetting resins are as follows:

(a) Phenolics: These resins are basically condensation products of phenol and formaldehyde. Owing to the necessity of eliminating the water formed by the polymerization, thin coats ($\frac{1}{2}$ to 3/4 mil) must be applied. Usually, each coat is force dried or partially polymerized before the application of the succeeding coats. To obtain maximum properties, a bake at 300 to 350°F is required. These coatings are used quite often as linings for process vessels and equipment where solvent resistance and temperatures up to 350°F are required.

These phenolic films, after polymerization, have excellent resistance to all common inorganic acids and to common solvents. They are infusible and inert up to 350°F. They produce smooth, tough films of moderate abrasion resistance. They have poor resistance to caustics (except very dilute) and to oxidizing agents.

Several proprietary phenolic base paint coatings are available. Some list maximum temperature as 425 to 450°F.

(b) Furanes: These are condensation products of furfuryl-alcohol and formaldehyde. The polymerized coatings are very similar to the phenolics. Like the phenolic, polymerization can be accomplished by baking at 300 to 350°F. Unlike the phenolic, polymerization may be accomplished at atmospheric temperatures by the addition of a catalyst. The catalyst method of polymerization is most common for the furanes.

The furanes are resistant to continuous exposure to temperature as high as 350°F. After polymerization they are resistant to common inorganic acids and organic solvents. They have considerable resistance to caustic and alkalis and have somewhat better resistance to oxidizing conditions than the phenolics. The furane coatings are more costly than the phenolics.

(c) Epoxyl Resins: These are a comparatively recent development but have attained considerable use. Data as to their characteristics are very limited. Two aircraft companies that have done some preliminary test work report that these paints give satisfactory service at temperatures up to 400 or 500°F.

Fluorine Complex Organic Compound Paints

Compared to paint coatings in class 3, the coatings in this class 4 are quite expensive.

(a) Teflon: Coatings and impregnation with Teflon can be accomplished through the use of suspensoids. Formulations have been developed which give good adherence to metal. The material is reported to have zero water absorption and exceptional resistance to chemicals. It is only attacked by alkali metals (sodium, potassium, etc.). Teflon retains its strength and dielectric properties from minus 100 to 550°F. Minute amounts of fluroine containing gases escape above 400°F. At 620°F Teflon undergoes a transition in its solid phase and suffers a sharp drop in strength. It decomposes at 750°F yielding gaseous derivatives of fluorine. Since the toxicology of these gases is not fully understood, good ventilation must be provided when Teflon is subjected to temperatures over 400°F.

(b) Polychlorotrifluoroethylene (Kel-F and CF-3): Fluid dispersions of this high polymer are available. They can be applied by spraying or dip methods followed by heat curing. This coating material is a recent development with very limited data available. Fabricators report that it can be used from minus 320°F to as high as 390°F, and is chemically inert to all acids, alkalis and solvents

Section 6. Zinc Metal Paints

There are a number of zinc metal paints on the market. The formulations vary over a considerable range as to vehicle and as to quantity of zinc metal. Powdered zinc metal is used. The claims as to corrosion protection are based on the sacrificial action of the zinc metal particles in the films. For zinc to act in a sacrificial manner to protect steel it is obvious that the zinc must be exposed. This requirement leads to the further requirements that the vehicle or binder holding the zinc metal on the surface of the steel must not be protective in itself, must not thoroughly coat the zinc metal particles, and must be permeable to moisture.

The makers of some zinc metal paints claim that the dried film on the painted surfaces consists of 90 to 95% zinc metal and is equivalent to zinc galvanizing. The application of metallic zinc coatings has been discussed in Section 7 of Chapter V of this manual.

In connection with high temperature exposures it must be remembered that the melting point of zinc metal is 788°F. It seems out of place to expect a zinc metal paint to offer much protection at temperatures above 800°F.

One of the paints with zinc metal as a pigment is reported to contain sodium silicate blended with chromates, plus fine particles of zinc dust. The manufacturer claims 1000°F as the maximum temperature in service, reportedly based on use in Air Force Jet tests (450 to 1000°F). Additional claims have to do with resistance to thermal shock tests at 500, 800 and 1000°F. No comments were received from users, except one aircraft company, which found this paint unsatisfactory. Salt spray tests conducted at Wright Field(93) classified this product as unsatisfactory for aircraft use.

Another zinc pigmented paint, reported to be a conventional paint plus zinc metal pigment, is claimed satisfactory at 800°F for continuous service and 1200°F for intermittant service. These claims are based on the following test: After application and recommended cure, the temperature was raised to 750°F and held for 3 hours and the panels were exposed then to outdoor weathering. One user reported satisfactory service on exposures as high as 750°F.

The costs of these paints are $9.00 to $10.00 per gallon.

Some of the claims as to corrosion protection offered by zinc metal paints are truly fantastic in nature and are not substantiated by user reports.

No data are available as to formability of the zinc metal paints except that the ones containing sodium silicate are brittle. Indications are that all the zinc metal paints interfere with welding operations.

One paint formulation including zinc metal powder as part of the pigment is described in Section 4 on "Silicone Paints".

CHAPTER VII

COMPARISONS OF COATINGS

Section 1. General Discussion

The lack of actual service data and the speculative nature of much of the available test data make it difficult to compare the many coatings that are discussed in this manual. The absence of any suitable test procedure for the evaluation of the protection offered by coatings on steel to the effects of hot products of combustion of aircraft engine fuels followed by condensation of moisture has prevented the obtaining of much desirable data.

For use in or around aircraft engines a proposed protective coating on a plain carbon or low alloy steel should be considered from at least nine view points as follows: (1.) temperature resistance; (2.) corrosion protection; (3.) resistance to oils, fuels and lubricants; (4.) resistance to products of combustion of engine fuels; (5.) abrasion and erosion resistance; (6.) effect on base metal; (7.) formability of the coated steel; (8.) welding or joining properties of the coated steel; (9.) costs. An effort has been made to collect such information and record it in connection with each coating that is covered by this manual. Some of the information is specific but much is in the form of generalizations. For comparison of one coating with another it is desirable to have each described in similar terms.

This chapter of the manual is devoted to such comparisons as are possible among the fifty-nine different coatings that have been described. For temperature resistance and for costs per square foot of surface coated the comparisons have been prepared in the form of bar charts. For the other properties the comparisons are in tabular form.

Each of the fifty-nine different coatings covered by this manual is shown in each of the following sections of this chapter.

Section 2. Temperature Resistance

The comparative temperature resistances of the various coatings discussed in Chapter II through Chapter VI are shown on the bar graph of Table 36. The code system used is as follows:

The clear area extends to the maximum safe service temperature at which the coating is known to be satisfactory. The hatched area indicates that limited data claim a still higher safe service temperature. Where the entire area is hatched, the data on maximum temperature for protection are very limited but indicate a possibility that the coating may be usable in the temperature range indicated. The letters N.D. indicate that no data are available on the high temperature properties of the coating.

The maximum temperatures shown are those at which the coating can be expected to protect steel against oxidation attack after hundreds of hours of exposure at that temperature in the absence of abrasives, high velocity gases, and high temperature corrosive fuel combustion products. The presence of any one or combinations of these may cause a coating to fail at a much lower temperature.

In interpreting the data on the temperature graph, the following reservations should be kept in mind: 1. The range of temperatures reported for a particular coating is based on the data available. Unfortunately, a great deal is limited and often clouded by claims made by developers, promoters and/or manufacturers. Unless conclusive and confirming data are available coatings should be tested and evaluated for a specific use. 2. For proprietary paint coatings it is not possible to give a known safe maximum temperature. Paints in the same classification have been reported to have resistance to temperatures varying from each other by 100 to 1000°. In the case of paints, the known maximum safe temperature (unhatched area of the bars) is the lowest reported maximum temperature expectations of paints of the classification shown, and the possible maximum temperature of exposure (hatched areas of the bars) is the highest maximum temperature considered applicable for a paint of that classification.

Table 36

Temperature Resistance of Coatings

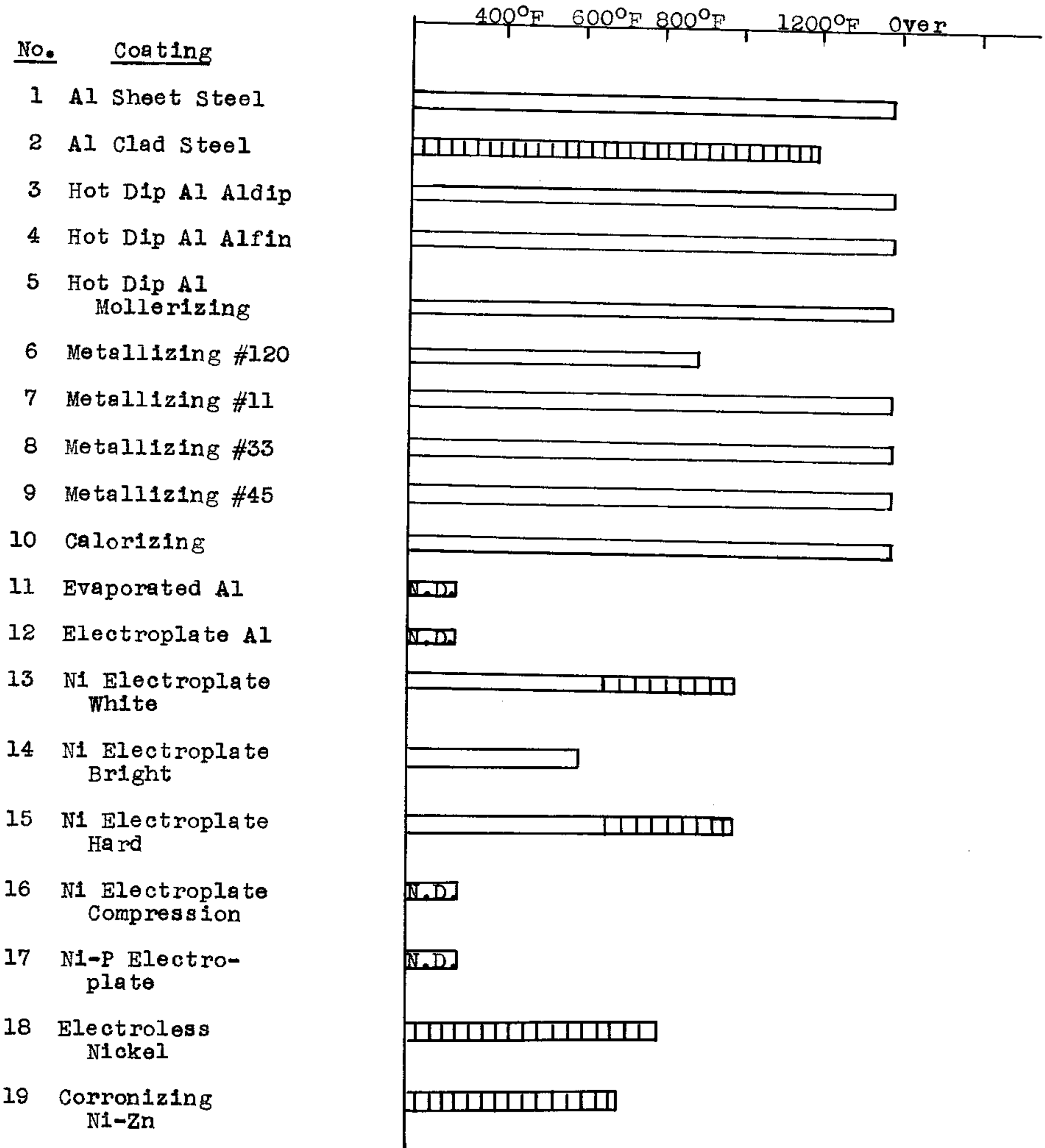


Table 36 (cont'd)

No.	Coating
20	Corronizing Ni-Sn
21	Corronizing Ni-Cd
22	Carbonyl Nickel
23	Nickel Clad
	L Nickel Clad
	Inconel Clad
	Monel Clad
24	Pack Chromizing
25	Paint Chromizing
26	Cr Plate ≠ Heat Treat
27	Pack Siliconizing
28	Paint Siliconizing
29	Cd Electroplate
30	Cr Electroplate
31	Cu Electroplate
32	Ag Electroplate
33	W Alloy Electroplate
34	Zn Hot Dip
35	Zn Electrogalv.
36	Zn Sherardizing
37	Zn Metallizing
38	Carbonyl Moly

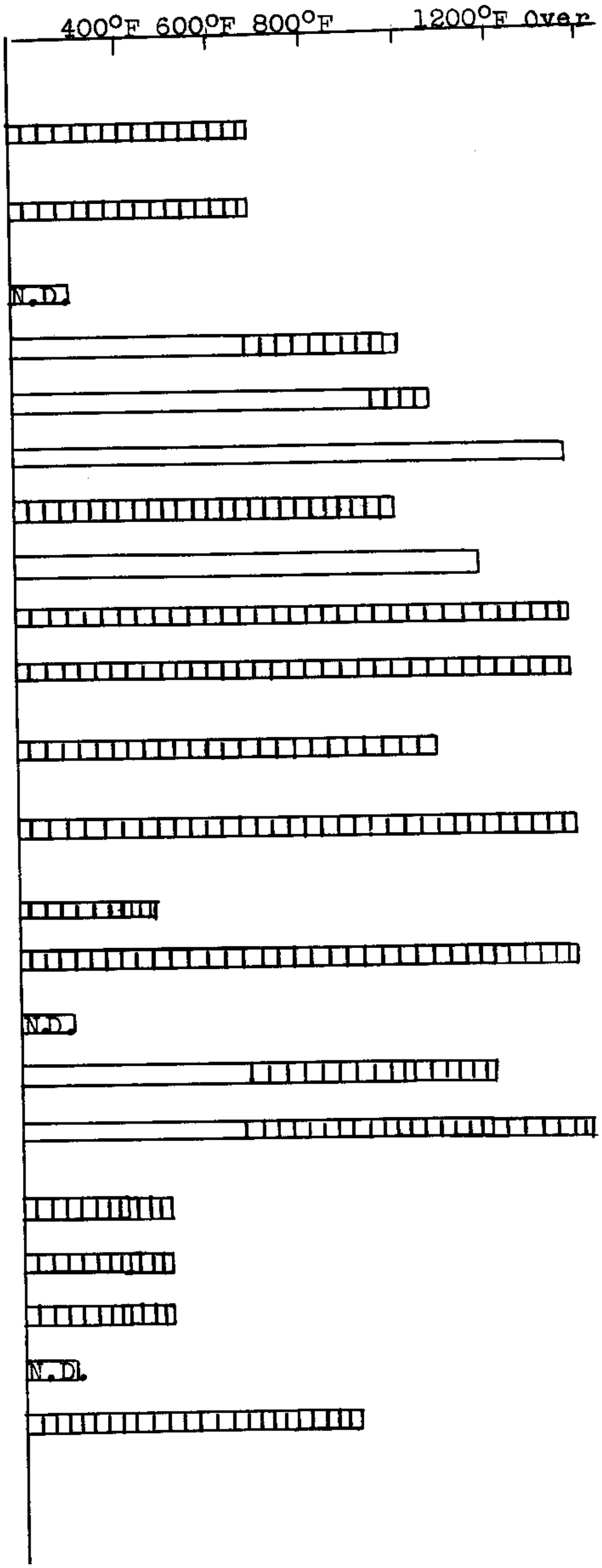
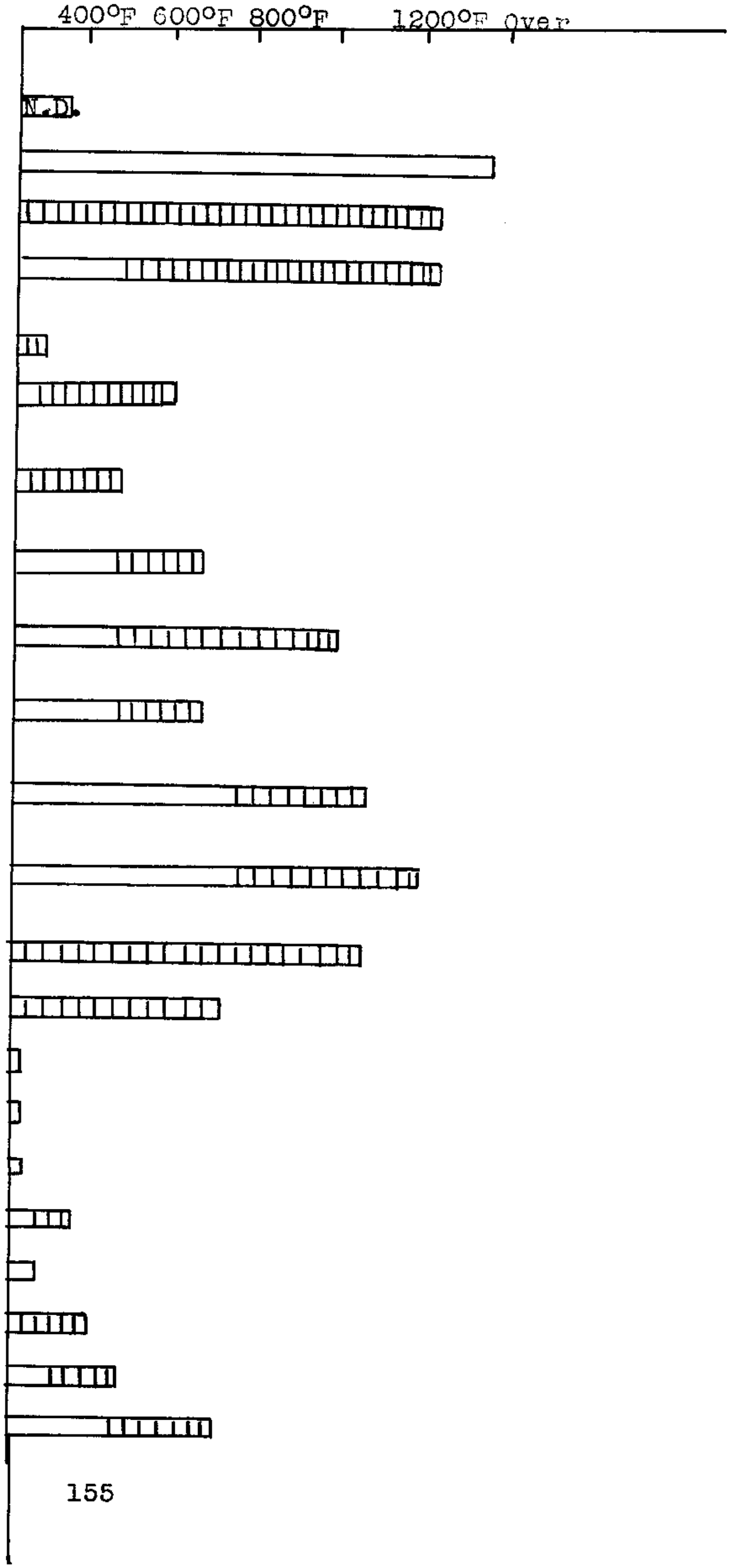


Table 36 (cont'd)

No.	Coating
39	Peen Plate
40	Stainless Clad
41	Refractory Paint
42	Refractory / Silicone
43	Al Pigm. Varnish
44	Al Pigm. Resin (not Si)
45	Al Pigm. Bitumastic
46	Unpigmented Silicones
47	Pigmented Silicone (not Al)
48	Al Pigm. in low % Silicones
	Al Pigm. in high % Silicones
49	Al / Refractory Silicone
50	Copolymer Baking
51	Copolymer Air Dry
52	Elastomers
53	Thermoplastics
54	Oleoresinous
55	Phenolics
56	Furanes
57	Epoxyl
58	Complex Fluorine
59	Zn Metal Paints



Section 3. Corrosion, Erosion and Abrasion Resistance

The corrosion protection offered by each of the 59 coatings is shown in Tables 37 and 38. Resistance to fuel oils, hydraulic lubricants, lead and bromine compounds, as well as resistance to abrasion and erosion is shown in Table 39. The code system used to indicate resistance is as follows: E - excellent, S - satisfactory, P - poor, blank space - no data or insufficient data available. In each case the resistance properties shown are based on the assumptions that the coating is adherent and is free of porosity.

Table 37

Corrosion Resistance of Coatings

No.	Coating	Anodic Cathodic or Inert to Steel	Salt Spray Salt Solution Salt Atmosphere	High Humidity	Dilute Mineral Acids Cold	High % to Conc. HNO_3	High % to Conc. H_2SO_4	High % to Conc. HCl	Steam
1	Al Sheet Steel	Anodic	S	S	S to P	S	P	P	S up to 500°F
2	Al Clad Steel	"	S	S	S to P	S	P	P	S up to 500°F
3	Hot Dip Al Aldip	"	S	S	S to P	S	P	P	S
4	Hot Dip Al Alfin	"	S	S	S to P	S	P	P	S
5	Hot Dip Al Mollerizing	"	S	S	S to P	S	P	P	S
6	Metallizing #120	"	S	S					
7	Metallizing #11	"	S	S			P	P	S
8	Metallizing #33	"	S	S			P	P	S
9	Metallizing #45		S	S			P	P	S
10	Calorizing		P	P			P	P	S
11	Evaporated Al								
12	Electroplate Al								
13	Ni Electroplate White	Cathodic	S	S	S Except Nitric	P	S to P	S to P	S
14	Ni Electroplate Bright	"	S	S	S Except Nitric	P	S to P	S to P	S
15	Ni Electroplate Hard	"	S	S	S Except Nitric	P	S to P	S to P	S
16	Ni Electroplate Compression	"	S	S	S Except Nitric	P	S to P	S to P	S
17	Ni-P Electroplate		S	S					S

Table 37 (cont'd)

No.	Coating	Anodic Cathodic or Inert to Steel	Salt Spray Salt Solution Salt Atmosphere	High Humidity	Dilute Mineral Acids Cold	High % to Conc. HNO3	High % to Conc. H2SO4	High % to Conc. HCl	Steam
18	Electroless Nickel	Cathodic	S	S	S Except Nitric	P	S to P	S to P	S
19	Corronizing Ni-Zn		S	S					
20	Corronizing Ni-Sn								
21	Corronizing Ni-Cd		S	S					
22	Carbonyl Nickel								
23	Nickel Clad	Cathodic	S	S		P	P	S	S
	L Nickel Clad	"	S	S		P	P	S	S
	Inconel Clad		S	S	S	S	S to P		S
	Monel Clad		S	S	S	P	S	S	S
24	Pack Chromizing		S	S	P	S			S
25	Paint Chromizing		S	S	P	S			
26	Cr Plate ≠ Heat Treat		S	S	P	S			
27	Pack Siliconizing	Inert			S	S	S (low %)	S	
28	Paint Siliconizing	"			S	S		S	
29	Cd Electroplate	Anodic	S	S to P					
30	Cr Electroplate	Cathodic	S	S	P	P	S to P	P	
31	Cu Electroplate	"	S	S		P	S (absence of O2)	P	P
32	Ag Electroplate	"	S	S	S	P	P	S to P	S
33	W Alloy Electroplate		S	S					
34	Zn Hot Dip	Anodic	S	S	P	P	P	P	
35	Zn Electrogalv.	"	S	S	P	P	P	P	

Table 37 (cont'd)

No.	Coating	Anodic Cathodic or Inert to Steel	Salt Spray Salt Solution Salt Atmosphere	High Humidity	Dilute Mineral Acids Cold	High % to Conc. HNO_3	High % to Conc. H_2SO_4	High % to Conc. HCl	Steam
36	Zn Sherardizing	Anodic	S	S	P	P	P	P	
37	Zn Metallizing	"	S	S	P	P	P	P	
38	Carbonyl Moly								
39	Peen Plate								
40	Stainless Clad		S	S	Corrosion resistance to other media depends on grade stainless steel used. Details available in the literature.				
41	Refractory Paint		S	S					
42	Refractory + Silicone		S	S					
43	Al Pigm. Varnish		S	S					
44	Al Pigm. Resin (not Si)		S	S					
45	Al Pigm. Bitumastic		S	S					
46	Unpigmented Silicones		S	S					
47	Pigmented Silicone (not Al)		S	S					
48	Al Pigm. Silicones		S	S					
49	Al + Refractory Silicone		S	S					
50	Copolymer Baking		S	S					
51	Copolymer Air Dry		S	S					
52	Elastomers		S	S					
53	Thermoplastics		S	S					
54	Oleoresinous		S	S					
55	Phenolics		S	S	S				
56	Furanes		S	S					
57	Epoxyl		S	S	S				
58	Complex Fluorine		S	S	S	S	S	S	S
59	Zn Metal Paints		S to P	S					

Table 38

Corrosion Resistance of Coatings

No.	Coating	Moist SO_2 or H_2S	Moist Nitrogen Oxides	Moist Halogens	Moist Ammonia	Alkaline Solution (not Ammonia)	Oxidizing Agents (Solutions)	Hot S Bearing Gases
1	Al Sheet Steel	SO_2-P H_2S-S	S	P	S	P	S	S
2	Al Clad Steel	SO_2-P H_2S-S	S	P	S	P	S	S
3	Hot Dip Al Aldip		S	P	S	P	S	S
4	Hot Dip Al Alfin		S	P	S	P	S	S
5	Hot Dip Al Mollerizing		S	P	S	P	S	S
6	Metallizing #120	S				P	S	
7	Metallizing #11	S	S		S	P	S	S
8	Metallizing #33	S				P	S	P
9	Metallizing #45	S			S	P	S	S
10	Calorizing	S	S			P	S	S
11	Evaporated Al							
12	Electroplate Al							
13	Ni Electroplate White	P	P	P	P	S	P	P
14	Ni Electroplate Bright	P	P	P	P	S	P	P
15	Ni Electroplate Hard	P	P	P	P	S	P	P
16	Ni Electroplate Compression	P	P	P	P	S	P	P
17	Ni-P Electroplate	P	P	P	P	S		P
18	Electroless Nickel	P	P	P	P	S	P	P
19	Corronizing Ni-Zn	S		S				
20	Corronizing Ni-Sn	S		S				
21	Corronizing Ni-Cd	S		S				
22	Carbonyl Nickel							

Table 38 (cont'd)

No.	Coating	Moist SO_2 or H_2S	Moist Nitrogen Oxides	Moist Halogens	Moist Ammonia	Alkaline Solution (not Ammonia)	Oxidizing Agents (solutions)	Hot S Bearing Gases
23	Nickel Clad	S to P	P	S to P	P	S	P	P
	L Nickel Clad	S to P	P	S to P	P	S	P	P
	Inconel Clad	S	S			S	S	S
	Monel Clad	S to P	P			S	P	P
24	Pack Chromizing			P				P
25	Paint Chromizing							
26	Cr Plate ≠ Heat Treat							
27	Pack Siliconizing							
28	Paint Siliconizing	P						P
29	Cd Electroplate							
30	Cr Electroplate	S		S to P			S	
31	Cu Electroplate	P		P	P	S	P	P
32	Ag Electroplate	P		S to P	P	S	P	P
33	W Alloy Electroplate							
34	Zn Hot Dip	P	P	P		P	P	P
35	Zn Electrogalv.	P	P	P		P	P	P
36	Zn Sherardizing	P	P	P		P	P	P
37	Zn Metallizing	P						
38	Carbonyl Moly							
39	Peen Plate							
40	Stainless Clad	Corrosion resistance to these media depends on grade stainless steel used. Details available in the literature.						
41	Refractory Paint							
42	Refractory ≠ Silicone							
43	Al Pigm. Varnish							
44	Al Pigm. Resin (not Si)							
45	Al Pigm. Bitumastic							

Table 38 (cont'd)

No.	Coating	Moist SO_2 or H_2S	Moist Nitrogen Oxides	Moist Halogens	Moist Ammonia	Alkaline Solution (not Ammonia)	Oxidizing Agents (solutions)	Hot S Bearing Gases
46	Unpigmented Silicones							
47	Pigmented Silicone (not Al)							
48	Al Pigm. Silicones							
49	Al + Refractory Silicone							
50	Copolymer Baking							
51	Copolymer Air Dry							
52	Elastomers							
53	Thermoplastics							
54	Oleoresinous							
55	Phenolics					P	P	
56	Furanes							
57	Epoxyl					S	S	
58	Complex Fluorine	S	S	S	S	S	S	
59	Zn Metal Paints							

Table 39

Oil, Lead, Bromine and Abrasion Resistance

No.	Coating	Fuel Oils	Hydraulic Lubricants	Lead and Bromine Compounds	V_2O_5	Abrasion and Erosion	Hot Corr. Gases
1	Al Sheet Steel	S	S	P			
2	Al Clad Steel	S	S	P			
3	Hot Dip Al Aldip	S	S	P			
4	Hot Dip Al Alfin	S	S	P			
5	Hot Dip Al Mollerizing	S	S	P			
6	Metallizing #120			P			
7	Metallizing #11	S	S		S (on stainless only)		S
8	Metallizing #33	S	S	S	S (on stainless only)		S
9	Metallizing #45	S	S				S
10	Calorizing	S	S				
11	Evaporated Al					P	
12	Electroplate Al						
13	Ni Electroplate White	S	S	P		S	P
14	Ni Electroplate Bright	S	S	P		S	P
15	Ni Electroplate Hard	S	S	P		E	P
16	Ni Electroplate Compression	S	S	P		S	P
17	Ni-P Electroplate	S	S	P		E	P
18	Electroless Nickel	S	S	P		E	
19	Corronizing Ni-Zn	P (kerosene)		S		S	
20	Corronizing Ni-Sn			S		S	
21	Corronizing Ni-Cd			S		E	
22	Carbonyl Nickel					P	
23	Nickel Clad	S	S	P		S	P
	L Nickel Clad	S	S	P		S	P
	Inconel Clad	S	S			S	S
	Monel Clad	S	S			S	
24	Pack Chromizing	S	S			S	
25	Paint Chromizing	S	S			S	
26	Cr Plate + Heat Treat	S	S			S	

Table 39 (cont'd)

No.	Coating	Fuel Oils	Hydraulic Lubricants	Lead and Bromine Compounds	V205	Abrasion and Erosion	Hot Corr. Gases
27	Pack Siliconizing	S	S			S	
28	Paint Siliconizing	S	S			S	
29	Cd Electroplate	S				P	
30	Cr Electroplate	S	S			E	
31	Cu Electroplate					P	P
32	Ag Electroplate			P		S to P	
33	W Alloy Electroplate	S	S			E	
34	Zn Hot Dip	S				P	
35	Zn Electrogalv.	S				P	
36	Zn Sherardizing	S				P	
37	Zn Metallizing	S					
38	Carbonyl Moly						
39	Peen Plate						
40	Stainless Clad	S	S			S	
41	Refractory Paint		S	P		S	
42	Refractory + Silicone	S	S	P		S	
43	Al Pigm. Varnish	P	P			P	
44	Al Pigm. Resin (not Si)					P	
45	Al Pigm. Bitumastic	P	P			P	
46	Unpigmented Silicones	S				P	
47	Pigmented Silicone (not Al)	S	S			P	
48	Al Pigm. Silicones	S	S			P	
49	Al + Refractory Silicone	S	S			P	
50	Copolymer Baking					P	
51	Copolymer Air Dry		P			P	
52	Elastomers					S	
53	Thermoplastics					P	
54	Oleoresinous					P	
55	Phenolics	S	S			P	
56	Furanes					P	
57	Epoxyl					P	
58	Complex Fluorine	S	S	S	S		
59	Zn Metal Paints					P	

Section 4. Effect on Base Metal

The comparative effects on steel as a result of the application of each of the various coatings discussed in Chapter II through Chapter VI are shown in Table 40.

The designation system used is as follows: A - altered; D - decreased; E - embrittled; I - increased; R - retained; p - possible; b - believed; r - reported; * - may be restored by a heat treatment; blank spaces - no data available.

Table 40

Effects on Base Metal

No.	Coating	Mechanical Properties (general)	Hardness	Tensile Str.	Fatigue Str.	Ductility	Shape (warping)	Volume (expansion)	Grain Size
1	Al Sheet Steel	R							
2	Al Clad Steel	R							
3	Hot Dip Al Aldip	A	Dp	Dp	D		Ap		Ap
4	Hot Dip Al Alfin	A	Dp	Dp	D		Ap		Ap
5	Hot Dip Al Mollerizing	A	Dp	Dp	D		Ap		Ap
6	Metallizing #120	R							
7	Metallizing #11	A	Dp	Dp	Dp		Ap		Ap
8	Metallizing #33	A	Dp	Dp	Dp		Ap		Ap
9	Metallizing #45	A	Dp	Dp	Dp		Ap		Ap
10	Calorizing	A	Dp	Dp	Dp	Dp	Ap		Ar
11	Evaporated Al	R							
12	Electroplate Al	R							
13	Ni Electro-plate White	Ap	E*p		D*	E*p	Ap		
14	Ni Electro-plate Bright	Ap	E*p		D	E*p	Ap		
15	Ni Electro-plate Hard	Ap	E*p		D	E*p	Ap		
16	Ni Electro-plate Com-pression	Ap	E*p			E*p			
17	Ni-P Electro-plate	Ap	E*p		D	E*p	Ap		

Table 40 (cont'd)

No.	Coating	Mechanical Properties (general)	Hardness	Tensile Str.	Fatigue Str.	Ductility	Shape (warping)	Volume (expansion)	Grain Size
18	Electroless Nickel	A			Dp	E*p			
19	Corronizing Ni-Zn	R							
20	Corronizing Ni-Sn	R							
21	Corronizing Ni-Cd	R							
22	Carbonyl Nickel	R							
23	Ni & Ni Clad Alloys	R							
24	Pack Chromizing	A	D*	D*	Dp		Ap	I*	I
25	Paint Chromizing	A	D*	D*	Dp		Ap	I*	I
26	Cr Plate + Heat Treat	A			Dp		Ap		
27	Pack Siliconizing	A	D	D	D	D	Ap	I	I
28	Paint Siliconizing	A	D	D	D	D	Ap	I	I
29	Cd Electroplate	R			D*r	E*			
30	Cr Electroplate	R			Dp	E*			
31	Cu Electroplate	R				E*p			
32	Ag Electroplate	R				E*p			
33	W Alloy Electroplate	R			Dp	E*			
34	Zn Hot Dip	R			Db				

Table 40 (cont'd)

No.	Coating	Mechanical Properties (general)	Hardness	Tensile Str.	Fatigue Str.	Ductility	Shape (warping)	Volume (expansion)	Grain Size
35	Zn Electrogalv.	R			Rr	E*p			
36	Zn Sherardizing	Ap	Dp		Dp	Dp			
37	Zn Metallizing	R							
38	Carbonyl Moly	A	Dp			Ip	Ap		Ip
39	Peen Plate	R							
40	Stainless Clad	R							
41	Refractory Paint	R							
42	Refractory + Silicone	R							
43	Al Pigm. Varnish	R							
44	Al Pigm. Resin (not Si)	R							
45	Al Pigm. Bitumastic	R							
46	Unpigmented Silicones	R							
47	Pigmented Silicone (not Al)	R							
48	Al Pigmented Silicones	R							
49	Al + Refractory Silicone	R							
50	Copolymer Baking	R							
51	Copolymer Air Dry	R							
52	Elastomers	R							

Table 40 (cont'd)

No.	Coating	Mechanical Properties (general)	Hardness	Tensile Str.	Fatigue Str.	Ductility	Shape (warping)	Volume (expansion)	Grain Size
53	Thermoplastics	R							
54	Oleoresinous	R							
55	Phenolics	R							
56	Furanes	R							
57	Epoxyl	R							
58	Complex Fluorine	R							
59	Zn Metal Paints	R							

Section 5. Formability

The comparative formability of steel after being given each of the various coatings discussed in Chapter II through Chapter VI are shown in Table 41.

The designation system used is as follows: G - good, L - limited, P - poor, NG - bad, blank spaces - no data available.

Table 41

Formability

No.	Coating	Formability
1	Al Sheet Steel	G
2	Al Clad Steel	G
3	Hot Dip Al Aldip	L
4	Hot Dip Al Alfin	L
5	Hot Dip Al Mollerizing	L
6	Metallizing #120	NG
7	Metallizing #11	L
8	Metallizing #33	NG
9	Metallizing #45	NG
10	Calorizing	NG
11	Evaporated Al	
12	Electroplate Al	
13	Ni Electroplate White	L
14	Ni Electroplate Bright	L
15	Ni Electroplate Hard	NG
16	Ni Electroplate Compression	
17	Ni-P Electroplate	P
18	Electroless Nickel	P
19	Corronizing Ni-Zn	L
20	Corronizing Ni-Sn	L
21	Corronizing Ni-Cd	L
22	Carbonyl Nickel	P
23	Ni & Ni Clad Alloys	G
24	Pack Chromizing	L
25	Paint Chromizing	L
26	Cr Plate + Heat Treat	L
27	Pack Siliconizing	NG
28	Paint Siliconizing	NG
29	Cd Electroplate	G
30	Cr Electroplate	P
31	Cu Electroplate	G
32	Ag Electroplate	G
33	W Alloy Electroplate	P
34	Zn Hot Dip	G
35	Zn Electrogalv.	G
36	Zn Sherardizing	L
37	Zn Metallizing	P
38	Carbonyl Moly	L
39	Peen Plate	NG
40	Stainless Clad	G
41	Refractory Paint	NG
42	Refractory + Silicone	NG
43	Al Pigm. Varnish	NG
44	Al Pigm. Resin (not Si)	NG
45	Al Pigm. Bitumastic	NG
46	Unpigmented Silicones	NG
47	Pigmented Silicone (not Al)	NG
48	Al Pigm. Silicones	NG
49	Al + Refractory Silicone	NG
50	Copolymer Baking	NG
51	Copolymer Air Dry	NG
52	Elastomers	NG
53	Thermoplastics	NG
54	Oleoresinous	NG
55	Phenolics	NG
56	Furanes	NG
57	Epoxyl	NG
58	Complex Fluorine	NG
59	Zn Metal Paints	NG

Section 6. Welding and Joining After Coating

The comparative weldability and ease of joining of steel as coated with each of the various coatings discussed in Chapter II through Chapter VI are shown in Table 42 and Table 43.

The designation system used is as follows: X - can be applied, L - limited to certain conditions, P - precautions are necessary, R - repairs required after welding, N - not feasible, blank spaces - no data available.

Table 42

Welding Characteristics

No.	Coating	Oxy-Acetylene Welding	Electric Arc Welding	Atomic Hydrogen Arc Welding	Inert Gas Metal Arc Welding	Submerged Arc Welding	Spot Welding	Resistance Welding
1	Al Sheet Steel	XR	XR	XR	XR	XR	X	XR
2	Al Clad Steel	LR	PLR	PLR	PLR	PLR	X	LR
3	Hot Dip Al Aldip	LR	PLR	PLR	PLR	PLR	X	LR
4	Hot Dip Al Alfin	LR	PLR	PLR	PLR	PLR	X	LR
5	Hot Dip Al Mollerizing	LR	PLR	PLR	PLR	PLR	X	LR
6	Metallizing #120	N	N	N	N	N	N	N
7	Metallizing #11	PLR	PLR	PLR	PLR	PLR	N	LR
8	Metallizing #33	N	N	PLR	PLR	PLR	N	LR
9	Metallizing #45	N	N	N	N	N	N	N
10	Calorizing	LR	PLR	PLR	N	N	N	N
11	Evaporated Al							
12	Electroplate Al							
13	Ni Electroplate White	XR	XR	XR	XR	XR	X	XR
14	Ni Electroplate Bright	XR	XR	XR	XR	XR	X	XR
15	Ni Electroplate Hard	XR	XR	XR	XR	XR	X	XR
16	Ni Electroplate Compression							

Table 42 (cont'd)

No.	Coating	Oxy-Acetylene Welding	Electric Arc Welding	Atomic Hydrogen Arc Welding	Inert Gas Metal Arc Welding	Submerged Arc Welding	Spot Welding	Resis-tance Welding
17	Ni-P Electroplate	XR	XR	XR	XR	XR	X	XR
18	Electroless Nickel	XR	XR	XR	XR	XR	X	XR
19	Corronizing Ni-Zn	PXR	PXR	PXR	PXR	PXR	X	PXR
20	Corronizing Ni-Sn	XR	XR	XR	XR	XR	X	PXR
21	Corronizing Ni-Cd	PXR	PXR	PXR	PXR	PXR	X	PXR
22	Carbonyl Nickel							
23	Ni & Ni Clad Alloys	X	X	X	X	X	X	X
24	Pack Chromizing	N	XR	XR	XR	LR	X	XR
25	Paint Chromizing	N	XR	XR	XR	LR	X	XR
26	Cr Plate + Heat Treat	N	XR	XR	XR	LR	X	XR
27	Pack Siliconizing							
28	Paint Siliconizing							
29	Cd Electroplate	PX	PX	PX	PX	PX	X	PX
30	Cr Electroplate							
31	Cu Electroplate	N	XR	XR	XR	LR	X	XR
32	Ag Electroplate	X	X	X	X	X	X	X
33	W Alloy Electroplate							

Table 42 (cont'd)

No.	Coating	Oxy-Acetylene Welding	Electric Arc Welding	Atomic Hydrogen Arc Welding	Inert Gas Metal Arc Welding	Submerged Arc Welding	Spot Welding	Resistance Welding
34	Zn Hot Dip	PX	PX	PX	PX	PX	PX	PX
35	Zn Electro-galv.	PX	PX	PX	PX	PX	PX	PX
36	Zn Sherardizing	PX	PX	PX	PX	PX	PX	PX
37	Zn Metallizing	PX	PX	PX	PX	PX	PX	PX
38	Carbonyl Moly							
39	Peen Plate							
40	Stainless Clad	X	X	X	X	X	X	X
41	Refractory Paint	N	N	N	N	N	N	N
42	Refractory + Silicone	N	N	N	N	N	N	N
43	Al Pigm. Varnish	N	N	N	N	N	N	N
44	Al Pigm. Resin (not Si)	N	N	N	N	N	N	N
45	Al Pigm. Bitumastic	N	N	N	N	N	N	N
46	Unpigmented Silicones	N	N	N	N	N	N	N
47	Pigm. Silicone (not Al)	N	N	N	N	N	N	N
48	Al Pigm. Silicones	N	N	N	N	N	N	N
49	Al + Refractory Silicone	N	N	N	N	N	N	N
50	Copolymer Baking	N	N	N	N	N	N	N
51	Copolymer Air Dry	N	N	N	N	N	N	N

Table 42 (cont'd)

No.	Coating	Oxy-Acetylene Welding	Electric Arc Welding	Atomic Hydrogen Arc Welding	Inert Gas Metal Arc Welding	Submerged Arc Welding	Spot Welding	Resistance Welding
52	Elastomers	N	N	N	N	N	N	N
53	Thermoplastics	N	N	N	N	N	N	N
54	Oleoresinous	N	N	N	N	N	N	N
55	Phenolics	N	N	N	N	N	N	N
56	Furanes	N	N	N	N	N	N	N
57	Epoxyl	N	N	N	N	N	N	N
58	Complex Fluorine	N	N	N	N	N	N	N
59	Zn Metal Paints	N	N	N	N	N	N	N

Table 43

Joining Characteristics

No.	Coating	Brazing	Soft Soldering	Silver Soldering	Riveting	Staking
1	Al Sheet Steel	L	N	L	X	N
2	Al Clad Steel	L	N	L	X	D
3	Hot Dip Al Aldip	L	N	L	X	N
4	Hot Dip Al Alfin	L	N	L	X	N
5	Hot Dip Al Mollerizing	L	N	L	X	N
6	Metallizing #120	N	N	N	X	N
7	Metallizing #11	N	N	N	X	N
8	Metallizing #33	N	N	N	X	N
9	Metallizing #45	N	N	N	X	N
10	Calorizing	N	N	N	X	N
11	Evaporated Al					
12	Electroplate Al					
13	Ni Electroplate White	L	X	X	X	L
14	Ni Electroplate Bright	L	X	X	X	L
15	Ni Electroplate Hard	L	X	X	X	L
16	Ni Electroplate Compression					
17	Ni-P Electroplate		X	X	X	L
18	Electroless Nickel		X	X	X	L
19	Corronizing Ni-Zn	X	X	L	X	L
20	Corronizing Ni-Sn	X	X	L	X	L
21	Corronizing Ni-Cd	X	X	L	X	L
22	Carbonyl Nickel					
23	Ni & Ni Clad Alloys	L	L	X	X	X
24	Pack Chromizing	N	N	L	X	X
25	Paint Chromizing	N	N	L	X	X
26	Cr Plate + Heat Treat	N	N	L	X	X
27	Pack Siliconizing					
28	Paint Siliconizing					
29	Cd Electroplate	X	X	X	X	X
30	Cr Electroplate					
31	Cu Electroplate	N	N	L	X	X
32	Ag Electroplate	X	X	X	X	X
33	W Alloy Electroplate					
34	Zn Hot Dip	PX	X	PX	X	X
35	Zn Electrogalv.	PX	X	PX	X	X
36	Zn Sherardizing	PX	X	PX	X	X
37	Zn Metallizing	PX	X	PX	X	X
38	Carbonyl Moly					

Table 43 (cont'd)

No.	Coating	Brazing	Soft Soldering	Silver Soldering	Riveting	Staking
39	Peen Plate					
40	Stainless Clad	L	N	X	X	X
41	Refractory Paint	N	N	N	X	N
42	Refractory + Silicone	N	N	N	X	N
43	Al Pigm. Varnish	N	N	N	X	N
44	Al Pigm. Resin (not Si)	N	N	N	X	N
45	Al Pigm. Bitumastic	N	N	N	X	N
46	Unpigmented Silicones	N	N	N	X	N
47	Pigmented Silicone (not Al)	N	N	N	X	N
48	Al Pigm. Silicones	N	N	N	X	N
49	Al + Refractory Silicone	N	N	N	X	N
50	Copolymer Baking	N	N	N	X	N
51	Copolymer Air Dry	N	N	N	X	N
52	Elastomers	N	N	N	X	N
53	Thermoplastics	N	N	N	X	N
54	Oleoresinous	N	N	N	X	N
55	Phenolics	N	N	N	X	N
56	Furanes	N	N	N	X	N
57	Epoxyl	N	N	N	X	N
58	Complex Fluorine	N	N	N	X	N
59	Zn Metal Paints	N	N	N	X	N

Section 7. Costs

Comparisons of the estimated costs per square foot of surface coated by the various coatings discussed in Chapter II through Chapter VI are shown in bar chart form in Table 44.

In order to arrive at a comparable basis for comparison, the coatings are compared on the basis of per square foot. Obviously, a single square foot of surface or even 100 square feet of surface could not be prepared and coated within the cost figures shown. The estimated costs are on the basis of quantity production of fairly simple shapes.

Table 44

Costs

No.	Coating	Remarks
1	Al Sheet Steel	0.0186"
2	Al Clad Steel	0.010"
3	Hot Dip Al Aldip	Simple shapes
4	Hot Dip Al Alfin	No data
5	Hot Dip Al Mollerizing	Simple shapes
6	Metallizing #120	
7	Metallizing #11	
8	Metallizing #33	
9	Metallizing #45	
10	Calorizing	No data
11	Evaporated Al	No data
12	Electroplated Al	No data
13	Ni Electroplate White	Simple shapes per mil thick
14	Ni Electroplate Bright	Simple shapes per mil thick
15	Ni Electroplate Hard	Simple shapes per mil thick
16	Ni Electroplate Compression	Simple shapes per mil thick
17	Ni-P Electroplate	No data
18	Electroless Nickel	Per mil thick
19	Corronizing Ni-Zn	

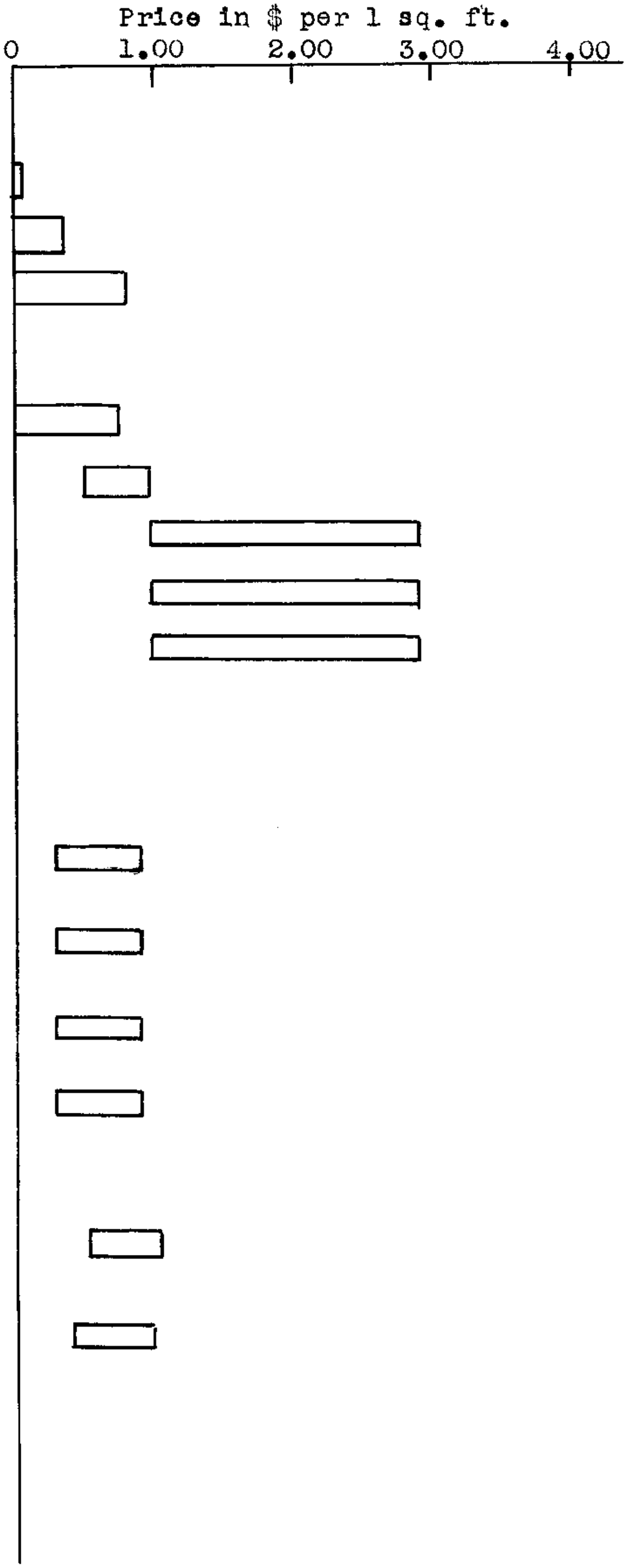


Table 44 (cont'd)

No.	Coating	Remarks
20	Corronizing Ni-Sn	
21	Corronizing Ni-Cd	
22	Carbonyl Nickel	No data
23	Ni & Ni Clad Alloys	Heavy sheet and plate only
24	Pack Chromizing	No data
25	Paint Chromizing	
26	Cr Plate + Heat Treat	
27	Pack Siliconizing	No data
28	Paint Siliconizing	
29	Cd Electroplate	Per mil
30	Cr Electroplate	
31	Cu Electroplate	
32	Ag Electroplate	
33	W Alloy Electroplate	
34	Zn Hot Dip	
35	Zn Electrogalv.	
36	Zn Sherardizing	
37	Zn Metallizing	
38	Carbonyl Moly	No data
39	Peen Plate	No data

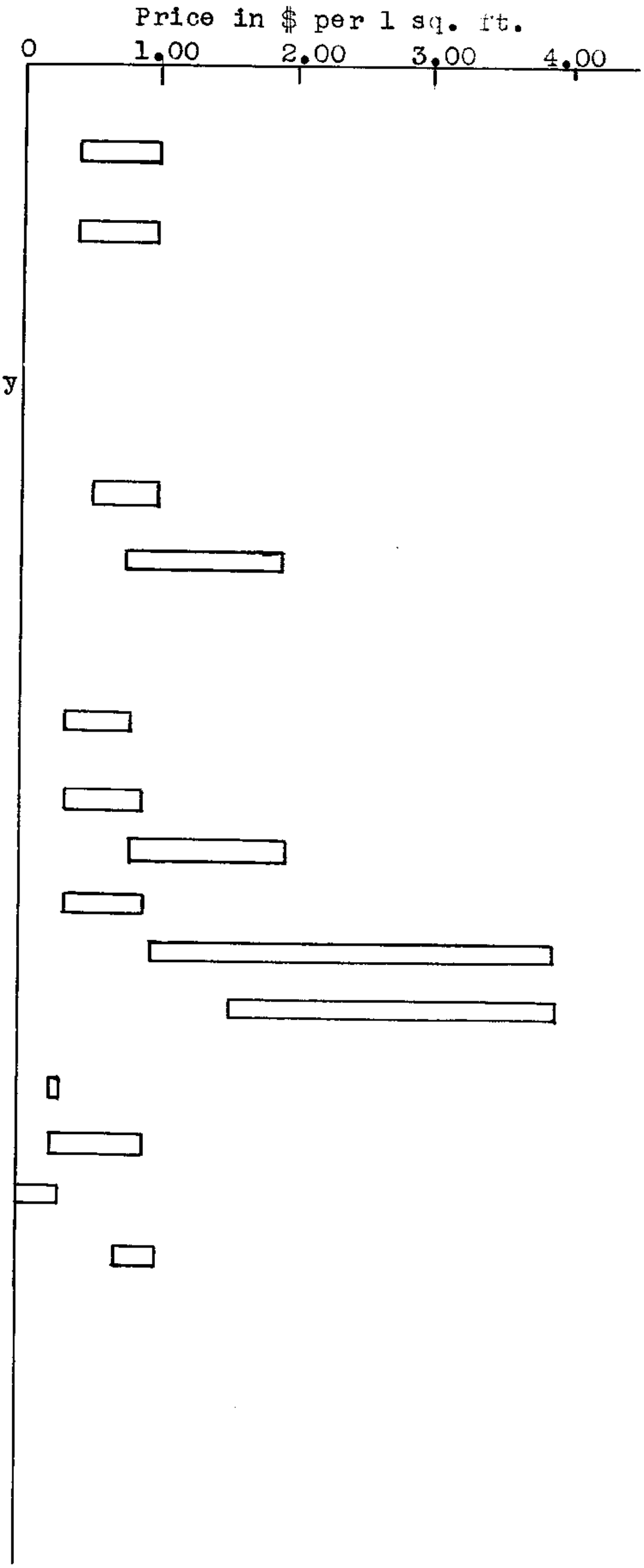
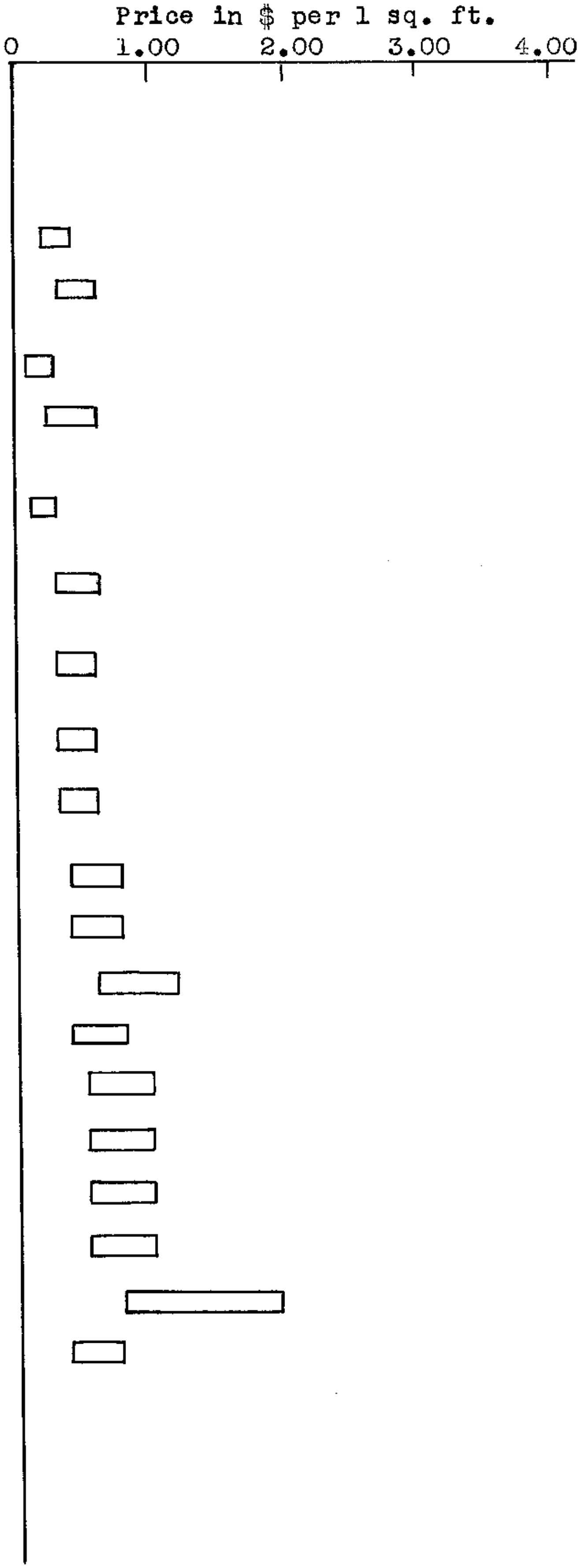


Table 44 (cont'd)

No.	Coating	Remarks
40	Stainless Clad	Heavy sheet and plate only
41	Refractory Paint	
42	Refractory ⌿ Silicone	
43	Al Pigm. Varnish	
44	Al Pigm. Resin (not Si)	
45	Al Pigm. Bitumastics	
46	Unpigmented Silicones	
47	Pigmented Silicone (not Al)	
48	Al Pigm. Silicones	
49	Al ⌿ Refractory Silicone	
50	Copolymer Baking	
51	Copolymer Air Dry	
52	Elastomers	
53	Thermoplastics	
54	Oleoresinous	
55	Phenolics	
56	Furanes	
57	Epoxyls	
58	Complex Fluorines	
59	Zn Metal Paints	



Appendix I

GLOSSARY AND DEFINITIONS OF TERMS

acid bath - A solution of an acid or acid salts in water. In electroplating, a plating bath that is acid in nature.

acid brittleness - The brittleness induced in steel when pickled in acid - commonly attributed to the absorption of hydrogen.

adherence - The degree of attachment of a coating to the base metal.

alkaline bath - A cleaning solution that is alkaline in nature, i.e. has a pH above 7.

alloy bond - Adherence resulting from an interdiffusion between a coating and a core or base metal.

alloy elements - Elements added for the purpose of improving properties.

alloy steel - Steel which owes its properties chiefly to various percentages of alloying elements other than carbon.

aluminizing - Adding aluminum to a base alloy by heating the metal below the melting point of the base alloy in contact with aluminum bearing solids, liquids or gases.

anchor pattern - The mechanical configuration of the surface to which a protective coating is to be applied. Polished, matte, pickled, sand blasted, rough grit blasted, knurled, etc.

anode - The electrode of an electrolytic cell at which oxidation occurs. In corrosion processes, usually the electrode that has the greater tendency to go into solution.

anodic - The state of being the anode with respect to a cathode in an electrolytic cell.

anodizing (nonferrous met.) - Subjecting metal to anodic oxidation by making it the anode in a suitable electrolyte.

austenitic stainless steels - Stainless steel of which the structure remains austenitic after commercial annealing and cooling.

bark - The decarburized skin or layer just beneath the scale on steel.

barrel plating - A mechanical method of plating small parts in which the parts are placed in a container, usually a perforated cylinder, that rotates submerged or partially submerged in a plating bath.

base metal - The metal on which a coating has been or is to be applied.

basic salts - A compound of bases and acids in which not all of the hydroxide of the base has been replaced by an acid radical, i.e. shows an alkaline reaction.

binary alloy - An alloy containing two principal elements.

binder - As used in this manual a binder is a material added to a mixture to keep the various heterogeneous materials together on a surface when the mixture is applied as a coating.

Bitumastic base - Tars from bituminous coal. A trade name, generally applied to materials containing a major proportion of coal tars.

Bitumastic resin - See Bitumastic base.

blue brittleness - Brittleness occurring in steel when in the temperature range of 400-700°F or when cold after being worked within this temperature range.

blue heat range - The temperature range in which plain or low alloy steels develop a thin blue film of oxide when heated in air (650 to 850°F).

bond - The nature of the adherence between basis metal and a protective coating. Mechanical, chemical, molecular, alloyed, etc.

brazing - Joining metals by fusion of nonferrous alloys that have melting points above 800°F but lower than those of the metals being joined. This may be accomplished by means of a torch (torch brazing) in a furnace (furnace brazing) or by dipping in a molten flux bath (dip or flux brazing). The filler metal is ordinarily in rod form in torch brazing; whereas in furnace and dip brazing the work material is first assembled and the filler metal may then be applied as wire, washers, clips, bands, or may be integrally bonded, as in brazing sheet.

Brinell hardness - The hardness of a substance as measured by the force which must be exerted upon it by a rigid sphere of given radius to produce an indentation of given area.

burnishing - Plastic smearing such as may occur on metallic surfaces during buffing or tumbling.

Calorizing - An aluminum plus aluminum oxide coating process in which the iron base alloy is tumbled in a mixture of aluminum plus aluminum oxide under a non-oxidizing atmosphere and at a temperature above the melting point of aluminum but below the melting point of the iron base alloy.

carbide precipitation - In stainless steels, the precipitation of chromium carbides from the matrix. Such precipitation, at the grain boundaries, results in susceptibility to intergranular corrosion.

carbon arc welding - An arc welding process in which one or more carbon or graphite electrodes are used, with or without the addition of filler metal.

carbonitriding - A process in which a ferrous alloy is case hardened by first being heated in a gaseous atmosphere of such composition that the alloy absorbs carbon and nitrogen simultaneously, and then being cooled at a rate that will produce desired properties.

carbonization - Coking or charring of organic or carbonaceous matter as a result of heating.

carbon steel - Steel which owes its properties chiefly to various percentages of carbon without substantial amounts of other alloying elements. Also known as ordinary steel or straight carbon steel or plain carbon steel.

Carburizing - Adding carbon to a base alloy by heating the metal below the melting point of the alloy in contact with carbonaceous solids, liquids or gases.

carburizing stop-off - A coating used to cover a portion of the surface of a piece to be carburized so as to prevent Carburizing of that portion. Electroplated copper is used quite often.

carrier gas - A gas used to carry or transport another gas or vapor.

case - In a ferrous alloy the surface layer that has been made substantially harder than the interior or core by a process of case hardening.

catalyst - A substance which changes the speed of a chemical reaction, probably by taking part in its chemical reaction, but which is formed again as a reaction product; hence is again present in its original concentration at the end of the reaction.

cathode - The electrode of an electrolytic cell at which reduction occurs. In corrosion processes, usually the area that is not attached.

cathodic protection - The use of a particular metal as a cathode in the corrosion cell as a means of protecting that metal against electro-chemical corrosion. This may be accomplished by the attachment of a more anodic metal or by the use of an applied potential.

caustic embrittlement - Embrittlement of a metal resulting from contact with an alkaline solution.

cavitation-erosion - Damage to a material in contact with a moving liquid, associated with the formation and collapse of cavities in the liquid at the solid-liquid interface.

cementation - A process for obtaining a metal from a solution of one of its compounds through displacement by a more electropositive element.

ceramic frit - See frit.

chalking - The development of a loose removable powder in or just beneath a surface coating.

checking - The development of slight breaks in a coating which do not penetrate to the underlying surface.

chemical conversion coating - A coating produced in situ by chemical reaction with the metal at its surface.

chemical reduction - A reaction in which one or more valence electrons are added to an atom. This process is the exact reverse of oxidation and both occur concurrently.

chromium carbide - A binary compound of chromium and carbon.

chromizing - Adding chromium to iron base alloys by heating the metal below its melting point in contact with chromium bearing solids, liquids or gases.

cladding - The process of applying surface layers of one metal to another metal which involves heat, pressure and mechanical work sufficient to create an alloy bond.

cold coining - A cold forming operation in which the blank is made to conform to the die impression while the metal is at normal atmospheric temperature.

cold working - Permanent deformation of a metal below its recrystallization temperature.

columnar structure - A structure in which the individual grains are in somewhat parallel arrangement and are of great length with respect to cross-section (column like).

composite nickel - A coating consisting of two or more metallic layers, one of which is nickel. The nickel can be in the form of a deposit or as wrought material.

concentration cell - An electrolytic cell, the e.m.f. of which is due to a difference in concentration of ions in an electrolyte.

concentration gradient - Change in concentration per unit distance.

cored structure - A structure having its interior or core of different structure or material from the exterior.

Corronizing - The process of electroplating steel with nickel and subsequently with zinc, tin or cadmium and then applying a low temperature anneal to cause interdiffusion.

corrosion - Destruction of a metal by chemical or electrochemical reaction with its environment.

corrosion fatigue - Reduction of fatigue durability by a corrosive environment.

corrosion fatigue limit - The maximum repeated stress endured by a metal without failure in a stated number of stress applications under defined conditions of corrosion and stressing.

covering power - In paint, the ability to cover a surface, commonly expressed in terms of square feet of a single coating per gallon of paint.

cracking (of coating) - Breaks in a coating which extend through to the underlying surface.

crazing - A network of checks or cracks appearing on a surface.

crevice corrosion - Corrosion in a sharp corner or confined space between two faces of a metal in contact with a corrosive environment.

current density - The magnitude of a current per unit cross-sectional area; in the case of the electric current, it is commonly expressed in amperes per unit area.

current efficiency - The proportion of the current that is effective in depositing metal at the cathode in accordance with Faraday's Law.

Cyaniding - A process of case hardening a ferrous alloy by heating in a molten cyanide, thus causing the alloy to absorb carbon and nitrogen simultaneously. Cyaniding is usually followed by quenching to produce a hard case.

cyclic stress - A stress that is repeated in successive periods of time. The stress may alternate from tension to compression and back again or may vary entirely in one direction.

decarburization - The removal of carbon (usually refers to the surface of steel).

deposit attack - Corrosion occurring under or around a discontinuous deposit on a metallic surface.

deposited coating - A coating deposited on a surface by any means.

Diamond Pyramid hardness - A hardness number on a special scale corresponding to the area of indentation produced by a pyramid shaped diamond under a given load.

diffusion - A movement of atoms within a solution. The net movement is usually in the direction from regions of high concentration toward regions of low concentration in order to achieve homogeneity of the solution, which may be a liquid, solid or gas.

diffusion coating - A coating created by the addition of an alloying element to the surface and heating below the melting point to cause migration.

diffusion heat treatment - Heat treatment for the purpose of causing diffusion to take place.

dissociated ammonia - A mixture of 75% hydrogen and 25% nitrogen gases produced by dissociating ammonia (NH_3) by heating.

dissociated water vapor - Hydrogen and oxygen from the breaking up of molecules of water at elevated temperatures.

dissolved carbon - Carbon in solution in iron in the solid state.

drying oil - In paints, an oil which slowly absorbs oxygen from the air and becomes hard and resinous, such as linseed or tung oil.

ductility - The property that permits permanent deformation before fracture by stress.

efficiency (of plating) - The ratio of weight of metal deposited to the maximum theoretical weight that could be deposited by the same amount of electricity.

18-8 stainless steel - Austenitic stainless steel containing approximately 18% chromium and 8% nickel.

electrocleaning - Alkaline cleaning during which a current is passed through the cleaning solution and the metal to be cleaned. Rapid evolution of gas on the work surfaces loosens dirt and other foreign materials so as to effect rapid cleaning.

electrodeposit-electroplate - A coating of metal deposited on a surface by the use of an electric current through a solution containing the metal to be deposited.

electroforming - The production or reproduction of articles, printers' type, etc. by electrodeposition.

electrogalvanizing - Coating of a metal with zinc by electrodeposition.

elongation - The amount of permanent extension in the vicinity of the fracture in the tension test; usually expressed as a percentage of the original gage length, as 25% in 2". Elongation may also refer to the amount of extension at any stage in any process that elongates a body continuously, as in rolling.

embrittlement - Severe loss of ductility of a metal or alloy.

endurance limit - The maximum stress to which material may be subjected an indefinitely large number of times without causing failure.

environment - The conditions surrounding a material including such factors as temperature, humidity, pressure, velocity and composition of surroundings.

Epon resin - A trade name for a series of epoxy resins.

Epoxy resins - Recently developed synthetic plastic like thermosetting resins formed as condensation products of the polyphenols and epichlorodins.

Erichsen test - A ductility or cupping test in which the depth of impression at fracture, made by forcing a cone-shaped, spherical-end plunger into the sheet specimen, is measured in millimeters.

erosion - Destruction of metal or coating by the abrasive action of liquid or gas. Usually accelerated by the presence of liquid or solid particles suspended in gases or liquids. Accelerated by increases in velocity. At times the abrasive medium is corrosive also and produces a combination of erosion and corrosion.

etching - Roughening by the attack of reagents on a metal surface.

exfoliation - The spalling or scaling off of a surface in flakes or layers.

fatigue failure - A fracture starting from a nucleus where there is an abnormal concentration of cyclic stress and propagating through the metal. The surface is smooth and frequently shows concentric (sea shell) markings with a nucleus as a center.

fatigue limit - The maximum stress that a metal will withstand without failure for a specified large number of cycles of stress. Usually synonymous with endurance limit.

fatigue strength - The range of stress to which an elastic material may be subjected a stated number of times in succession without fracture.

film - A thin, not necessarily visible layer of material.

fissures - Narrow openings, cracks or crevices.

flaking - Internal fissures in large steel forgings or massive rolled shapes. In a fractured surface or test piece they appear as sizable areas of silvery brightness and coarser grain size than their surroundings.

flash deposit - A thin deposit on a surface in a short period of time. In electrodeposited coating, usually a thickness of less than 0.00001".

fluxing - Applying a solid or gaseous material to molten metal in order to remove oxide dross and other foreign materials.

fretting corrosion - Corrosion at the interface between two contacting surfaces accelerated by slipping motion between them.

frit - In ceramics, an imperfectly vitrified and granulated glass like material used for the making of ceramic coatings.

fused metallized coating - A metallized coating that has been fused in place after being sprayed.

galling - The damaging of one or both metallic surfaces by removal of particles from localized areas during sliding friction.

galvanic cell - A cell made up of two dissimilar metals or conductors in contact with an electrolyte.

galvanic corrosion - Corrosion associated with the current of a galvanic cell made up of dissimilar electrodes. Also known as couple action.

galvanizing - Applying a zinc coating by dipping in a bath of molten zinc (hot dip galvanizing) or by electrodeposition of zinc (electrogalvanizing).

galvannealed - Galvanizing metal (zinc) applied to a surface after which the article is passed through an oven at about 1200°F. The resulting coat is dull gray without spangle.

general corrosion - Uniform corrosion attack over the entire exposed surface.

grains - Crystals in metals.

grit blasting - An airblasting operation using various grit materials, as distinguished from sand, for cleaning a surface.

heat treatment - An operation or combination of operations, involving the heating and cooling of a metal or alloy in the solid state, for the purpose of obtaining certain desirable conditions or properties.

high alloy steel - An alloy steel containing over 7% of alloying elements.

high frequency induction - The process of local heating by electrical induction using high frequency current as the primary.

high speed plating - Electroplating at high current densities to deposit a metal at an accelerated rate.

holiday - A hole or vacancy or uncovered area in a coated surface.

honing - Finishing a surface by means of rubbing with fine abrasives. Liquid honing, finishing a surface by blasting with a slurry of fine abrasives in a liquid.

hot short range - The range of temperature in which a normally plastic material becomes brittle.

humidity test - A corrosion test in an atmosphere of relatively high humidity (moisture content).

hydrogen embrittlement - Embrittlement caused by entrance of hydrogen into the metal as for example through pickling or electroplating.

hydrolyses - A dual decomposition reaction involving the separation of water and its ions and the formation of a weak acid, or a weak base or both.

immersion coating - A coating formed by deposition of a metal from a solution of its ions on another metal with or without replacement.

impingement attack - Corrosion associated with turbulent flow of a liquid or gas. For some metals the action is considerably accelerated by entrained bubbles in the liquid or entrained droplets of liquid in the gas.

inhibitor - A chemical substance or mixture which when added in small concentrations to an environment or a coating material effectively decreases corrosion.

interface - The mating surface of two closely adjacent parts.

intergranular corrosion - Preferential corrosion at grain boundaries of a metal or alloy. Also called intercrystalline corrosion.

intermelting - Simultaneous melting of two or more metals in contact with each other.

lapping - Producing a smooth surface by means of a fine abrasive in oil or water and a disk or flat block of wood, leather or soft metal.

lattice structure - An arrangement of points in space, representing the relative positions of corresponding atomic, molecular, or ionic centers in the elementary cells or structure units of a crystal.

lifting - As applied to coatings, peeling in large areas with the peeled coating remaining intact.

local action - Corrosion caused by local galvanic cells on a metal surface.

low alloy steel - An alloy steel containing less than 7% of alloying elements.

low hot hardness - Low hardness when at an elevated temperature.

macroscopic - Visible either with the naked eye or under low magnification (up to about 10 diameters).

macrostructure - The structure and internal condition of metals as revealed on a ground or polished (and sometimes etched) sample, by either the naked eye or under low magnifications (up to about 10 diameters).

matte surface - A surface with low specular reflectivity.

metallizing - The process of spraying a surface with a metal.

metal replacement - The deposition of a metal from a solution of its ions or from a vapor compound on another metal accompanied by an interchange of ions of the two metals.

microhardness - The hardness of microscopic points within an alloy.

mill scale - The heavy oxide film that forms on the surface during the hot processing or heat treating of metals, especially on iron and steel products.

molten salt bath - A salt or mixture of salts at a temperature sufficiently high to be in the liquid (molten) state.

monel metal - A native alloy of 67% nickel, 28% copper, 1-2% manganese and 1.9-2.5% iron.

mud blasting - Cleaning with a suspension of fine sand in water projected at a surface at a high velocity.

Neoprene - Chloroprene rubber formerly sold under the trademark "DupPrene".

nitriding - A process of case hardening in which an alloy is heated in an atmosphere of ammonia or in contact with nitrogenous material to produce surface hardening by the absorption of nitrogen, without quenching.

oxidation - The reaction of a metal with oxygen to form an oxide. Clean surfaces of many metals oxidize very rapidly when exposed to the oxygen in air. The rate of oxidation decreases as protective oxide films are formed. The oxide films formed in air at room temperatures are usually invisible. When formed at higher temperatures they may build up in thickness so as to pass through several orders of interference colors. Prolonged heating at high temperatures usually will produce thick surface layers of oxide or scale which may or may not be adherent.

oxygen concentration cell corrosion - Cell corrosion where the e.m.f. is due to variations in oxygen concentration in the electrolyte.

package stability - Ability to maintain a satisfactory condition during time while in a packaged condition.

pack chromizing - Chromizing by packing or embedding in a granular chromizing material in a retort or box and heating the retort or box to the desired temperature.

pack siliconizing - Siliconizing by packing or embedding in a granular siliconizing material in a retort or box and heating the retort or box to the desired temperature.

passivating - The process of inhibiting corrosion by changing the potential of a metal surface to a more cathodic value.

peeling - The lifting and loss of coatings from areas of appreciable size.

peen plating - The process of applying a metallic coating of a metal onto a metallic object by tumbling or ball milling the object in powder or flake metal.

pH - A symbol for the logarithm of the reciprocal of the hydrogen-ion concentration. It denotes the true acidity or alkalinity of a solution.

Phenolic resin - A generic term applied to the entire group of thermosetting phenol-formaldehyde plastic resins.

phosphate coating - A chemical conversion coating produced on a metal by immersion or wetting with a solution containing phosphoric acid plus metal salts.

pinhole porosity - Very small holes scattered through a coating.

pit - A depression in the surface of metal.

pitting corrosion - The type of localized corrosion causing pits.

Polyethylene - A synthetic plastic consisting of a polymer of ethylene.

Polymerization - A reaction in which two or more molecules of the same substance combine to form a compound, from which the original substance may or may not be regenerated; the new molecular weight being a multiple of that of the original compound.

precipitation hardening - A process of hardening an alloy in which a constituent precipitates from a supersaturated solid solution.

preplating - An initial electro or immersion plate applied to a surface before the application of an additional coating.

prime coat - A first coat of paint applied to improve adherence of the succeeding coat. Frequently containing a corrosion inhibitor.

pyrolytic decomposition - Decomposition due to elevated temperature.

refractory - A heat resistant material, usually non-metallic, used in ceramics.

relative humidity - The ratio, expressed as a percentage, of the amount of water present in a given volume of air or gas at a given temperature to the amount required to saturate the air or gas at that temperature.

replacement coating - See metal replacement.

Rockwell hardness - A hardness number on a special scale corresponding to the increase in depth of penetration of a given indentor under a given increase in load.

rusting - Corrosion of iron resulting in the formation of products on the surface consisting largely of hydrous ferric oxide.

sacrificial metal - A metal which is anodic to the metal to which it is applied and thus offers cathodic protection by being sacrificed in an electrolytic corrosion cell.

salt spray test - An accelerated corrosion test in which the metal specimens are exposed to a fine mist of salt water solution either continuously or intermittently.

sand blasting - Cleaning a surface by blowing sand at it with a blast of air.

scaling - The formation at high temperatures of partially adherent layers of corrosion products on a metal surface.

seal treatment - A process used to fill the pores of porous coatings.

seizing - Damaging of a metal surface by rubbing with another metal. Similar to galling.

sensitization - In stainless steels, carbide precipitation at grain boundaries creating susceptibility to intergranular corrosion.

Sherardizing - A zinc coating process in which the metal object to be coated is tumbled in a zinc powder mixture under a non-oxidizing atmosphere and at a temperature below the melting point of zinc.

Silicone - A complex polymer consisting of a mixture of various organo silicon oxide polymers.

Silicone-Alkyd Copolymer - A polymer of silicone-alkyds as distinguished from a polymer of silicon-monoxide (silicones).

Silicone base - A coating made up of polymers of silicon-monoxide.

siliconizing - Adding silicon to iron base alloys by heating the metal below its melting point in contact with silicon bearing solids, liquids or gases.

silver solder - Alloys of silver, copper, zinc and other metals, melting between 650 to 875°C, used for making joints.

"soft" condition - An annealed condition.

soft soldering - Soldering with lead base or tin base solders.

spalling - The chipping or fragmentation of a surface or surface coating caused, for example, by differential thermal expansion or contraction.

springback - An indicator of elastic stresses, frequently measured as the change in radius of curvature of a strip after removing it from the mandrel about which it was held.

staking - Fastening in place by means of prick punching.

stress corrosion - Corrosion of a metal accelerated by stress.

stress corrosion cracking - Spontaneous failure of metals by cracking under combined action of corrosion and stress, residual or applied.

stress raisers - Sharp changes in contour, notches, or surface defects in metal shapes that cause a concentration of stresses in a stressed member.

stress relief treatment - A process of reducing residual stresses in a metal object by heating the object to a suitable temperature and holding for a sufficient time.

strike - An initial electrochemical deposit; or sometimes the electrolyte from which such deposit is made.

stud welding - An arc welding process where heating is with an electric arc drawn between a metal stud, or similar part, and the work until the surfaces to be joined are properly heated, when they are brought together under pressure, and no shielding is used.

submerged arc welding - An arc welding process of the metal-arc type in which the filler metal is deposited beneath a shielding blanket of granular, fusible material.

surface activating solution - A solution which destroys, or tends to destroy, surface passivity of a metal.

tank plating - Electroplating of work in a still tank of solution as distinct from plating in a rotating or revolving container called "barrel plating".

tarnish - Discoloration of a metal surface due to formation of an adherent continuous film of corrosion products.

terne plate - Steel sheet, hot dip coated with terne metal (10-15% tin; 85-90% lead).

thermoplastic resins - A resin capable of being repeatedly softened by heat.

throwing power - The ability of an electroplating solution to deposit metal uniformly on a cathode of irregular shape.

thermosetting resins - A resin capable of being hardened by heat. It cannot be resoftened.

tin embrittlement - Embrittlement caused by tin in an iron base alloy or by the penetration of molten tin along grain boundaries of the iron base alloy when it is under stress at a temperature above the melting point of tin.

tuberculation - The formation of localized corrosion products scattered over the surface in the form of knoblike mounds.

underfilm corrosion - Corrosion that occurs under protective coating systems in the form of randomly distributed hairlines or spots.

vapor deposited coating - A coating deposited from a vapor compound of a metal without a replacement reaction as described under "metal replacement".

vehicle - In paints, the medium or carrier with which pigments are mixed, as oil in paints.

Vickers hardness test - An indentation hardness test employing a 136° diamond pyramid indenter and variable loads enabling the use of one hardness scale from very soft lead to tungsten carbide.

Vinyl - A loosely used term to cover the various groups of vinyl resins. Generally, resins consisting of copolymers of vinyl chloride and vinyl acetate.

Vinylidene Chloride Copolymers - Monomeric form of polyvinylidene chloride resins.

wash primer - A phosphoric acid containing prime coat paint often containing zinc chromate and other corrosion inhibitors.

wet corrosion - Corrosion in the presence of plain water or aqueous solutions.

wetting - The adhesion of a liquid onto a surface.

wire gun - In metallizing, the apparatus that continuously melts the tip of a wire and blasts or sprays the molten metal away from the tip.

zinc embrittlement - Embrittlement caused by zinc in an iron base alloy or by the penetration of molten zinc along grain boundaries of the iron base alloy when it is under stress at a temperature above the melting point of zinc.

Appendix II

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