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CARBONYL METAL PLATED PRODUCT

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This invention deals with a method of plating metals, and particularly with a method based on the decomposition of gaseous metal carbonyls.

This application is a continuation-in-part of my co-pending application, Serial No. 85,941, filed April 6, 1949, now U.S. Patent No. 2,682,702, granted July 6, 1954, entitled "Carbonyl Metal Plated Product."

In coatings obtained from metal carbonyls, the disadvantage heretofore has frequently been encountered of the coating not sufficiently adhering to the base metal. Moreover, the metal coating would become blistered if the object so coated was raised to elevated temperatures, for example, a heat treatment process.

It is an object of this invention to provide a method by which the above mentioned disadvantages are overcome.

In particular, it is an object of this invention to provide a method for metal plating by which a firmly adhering metal coating is obtained.

It is another object of this invention to provide a method of producing metal coating which can withstand elevated temperatures without blistering.

It is still another object of this invention to provide a method of producing metal coatings which may be subjected to a heat-treatment process without thereby impairing the adherence of the coating.

It is still another object of this invention to provide a product whose base material is provided with a uniform deposited coat consisting of two separately deposited layers.

These and other objects are accomplished by carrying out the metal deposition in two states in between which the base metal and its coating are subjected to a de-gasification treatment carried out by subjecting the material to heat.

In the first or initial step, only a very thin porous film is applied to the metallic base by decomposing gaseous metal carbonyl. A layer of 0.00001" to 0.00025", preferably of 0.00005" to 0.00015" in depth, was found most satisfactory for this initial coating. However, the invention is not restricted to this particular range.

After this first layer has been applied, the coated article is heat treated. While applicant does not wish to be bound by theory, it is believed that the heat-treatment step effects desorption of gas while the coating is still in a porous state.

Since the porosity of a coating varies inversely as to thickness, and since heat treatment of thick coatings applied at one time blisters and deforms the coating, it is believed the theory developed from discoveries giving rise to the instant invention presents an explanation accounting for a portion if not the entire basis for non-adherence of coatings encountered heretofore.

The heat-treatment in no way involves heating to temperatures which cause formation of alloys between the base and the metal coating. Microscopic examinations show no penetration into, for example, a copper base by a nickel coating heated to 800° F.

The various methods of cleaning a base metal surface as by acid, alkali, buffing, and the like, apparently differ little in effect as regards the adherence of the coating. If the base to be coated is clean, the coatings will have an adherence characteristic quickly determinable by simple tests showing whether the single coating method or the

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double coating method of this invention was the plating system utilized.

In addition to grease, metal oxide films must be removed from bases such as copper and aluminum. This film may be removed in the cleaning or by contact within the plating chamber with reducing gases, for example, hydrogen, prior to introduction of decomposable carbonyl gases.

Inasmuch as identical cleaning steps have been used for identical bases which have been coated in one step and by the two step method of this invention, the pre-coating cleaning is not accountable for the difference in the adhering character of the deposits.

Gases may be desorbed from the thinly coated bases by heating to a temperature in the range of 500° F. to 1200° F. depending upon the temperature which can be applied to the base without softening or destroying some characteristic such as temper or can be applied to the coating.

For example, lead patterns should not be heated much above 550° F. while, on the other hand, alloy steels withstand temperatures in excess of 1200° F. At the lower temperatures the heating is continued for a longer time in order to effect comparative completeness of desorption.

Heating periods of 2 to 30 minutes have been found to be satisfactory. When heating a copper base covered with an initial coating of nickel, a treatment at a temperature of 800 to 900° F. for about 15 minutes was found most advantageous.

The intermediate heat-treatment may be carried out in a chamber under non-oxidizing, but preferably under reduced atmosphere conditions. Nitrogen, carbon monoxide, carbon dioxide, hydrogen, natural gas, commercial brazing furnace gas, or mixtures of the above gases or other gases known in the art are suitable for this purpose.

One of the features of well bonded coatings is their ability to withstand compression and expansion without breaking free from the base. Thus, any metal base which will withstand gas desorbing temperatures may be coated by this carbonyl decomposition process.

Base materials which may be coated are, for example, copper, aluminum, magnesium, lead, cast iron, alloy steels, low carbon steels, non-ferrous alloys, such as bronze, brass, Monel metal and the like.

The process of this invention is applicable for plating with all metals which form gaseous carbonyls. Thus, plating with chromium, iron, tungsten, cobalt, molybdenum, tellurium, rhenium, and other metals may be successfully carried out by the method described.

Each of these metal carbonyls has a temperature at which decomposition is complete. However, decomposition does take place slowly at lower temperatures. For this reason it is preferred that the carbonyl be brought into contact quickly with the base metal heated to a temperature in the optimum decomposition range for each material.

In the case of tungsten, nickel, chromium, iron, we prefer to utilize a temperature in the range of 350° F. to 425° F., although temperatures below and above this range may be utilized and still accomplish plating by decomposition of carbonyl.

After the heat-treatment step a metal coating of the desired thickness is applied to the pre-treated base by decomposing metal carbonyls.

The product thus obtained is characterized by an excellent bond and a very uniform and smooth surface structure. After the deposition of the coating layer proper a second heat treating step may be applied. However, this is not obligatory. Sometimes an after-treatment is utilized to increase the ductility of the coating layer.

In the following, the process is described as applied to the coating of various metal bases with a number of metals deposited from volatile metal carbonyls.

Example I

A copper plate was first mechanically cleaned by sanding. Thereafter the copper metal was heated to approxi-

gaseous metal deposition in accordance with the present invention as compared with wet electroplating using electrolytic solutions are shown in the following tabulation.

Metal Panels of	Plated with	Approximate Plate Thickness, Inches	Type of Plating	Remarks
Steel-----	Nickel--	0.0004-----	Wet Electroplated--	This is typical wet electroplating practice to secure adhesion and properties. Wet plating is slow, troubled with hydrogen embrittlement, uses electricity, and is a cumbersome process.
Do-----	---do---	0.0004 deposited over initial heat-treated 0.00005 coating of nickel.	Nickel carbonyl gas plated over initial coating after heat-treating at 800° F.	The Gas Plating Process is not subject to hydrogen embrittlement, uses gases not solutions containing electrolytes, is rapid, continuous and complete utilization of metallic compounds may be effected.
Aluminum-----	---do---	0.0004-----	Wet Electroplated--	Coatings of typical electroplate are both porous and brittle. A typical specimen of nickel has a tensile strength of 85,000 p.s.i. and an elongation of 3% which may be increased to 9% by annealing.
Do-----	---do---	0.0004 deposited on initial heat-treated 0.00007 coating of nickel.	Nickel carbonyl gas plated over initial coating after heat-treating at 750° F.	Coatings prepared by Gas Plating are more ductile. For instance, a specimen of nickel prepared by Gas Plating has a tensile strength of 93,000 p.s.i. and an elongation of 16% before annealing.

mately 375° F. in an atmosphere containing approximately 1.4 percent by volume of nickel carbonyl and diluted with carbon dioxide gas. The rate of gas flow was approximately 4 cubic feet per minute at a temperature of 78° F. and 125 mm. Hg. The copper was exposed to this atmosphere for about 2 minutes after which time a film of 0.00007" thickness had formed on the copper base. Thereafter the metal was heated in an atmosphere of natural gas to a temperature of about 800° F. for approximately 15 minutes.

After these preliminary steps the coating proper was performed by subjecting the metal to the same conditions and gases as in the preliminary film-forming step. This second step was carried out for about 15 minutes when a coating of 0.0004" had formed.

In order to increase the ductility of the coating, I subjected the metal to an additional heating step. This step consisted in heating for 15 minutes to a temperature of from 800° F. to 900° F. in an atmosphere of natural gas.

Example II

A lead pattern may be coated in the equipment utilized in the plating operation of Example I.

The lead pattern may be coated with iron deposited from iron carbonyl. The base may be heated to approximately 360° F. in an atmosphere of nitrogen containing about 2 percent by volume of iron carbonyl. After exposure of the pattern to this atmosphere for about 2 minutes, the temperature of the pattern may be raised to 525° F. and held there for 20 minutes.

After these preliminary steps the final film-forming step may be performed under the same conditions as is maintained in the preliminary coating step.

Example III

An aluminum radar antenna may be coated in the same equipment as is used in Examples I and II.

The aluminum may be treated with acid and then buffed to prepare clean surfaces. The aluminum may be coated with nickel by heating the base to approximately 375° F. in one minute with a feed rate of approximately 50 cubic feet per hour of nickel carbonyl vapor diluted with hydrogen.

The initially coated base may be heat treated at 750° F. for 20 minutes to desorb gas. Following the heat treatment, the final coating and heat treating may follow exactly the pattern of Example I.

Example IV

An SAE 1020 steel plate may be treated under similar conditions to Example I to plate the steel base with chromium deposited at a temperature of about 400° F.

Some of the important advantages and characteristic physical differences obtained by so-called dry plating by

The base metal panels in each case were subjected to cleaning by washing in a cleaner composed of three ounces of sodium phosphate in a gallon of water, the solution being heated to 200° F., and after washing the panels therein, rinsing the same in cold water.

The coatings obtained by the process of this invention on each of the bases of the examples are uniform in structure, free from blisters, and well adhering to the base metal. Heat-treatment does not form blisters and impair the firm bond between the coating and the base metal.

In addition, apparatus such as the radar antenna of Example III, have been subjected to special tests under which the base suffered a 15 percent elongation and withstood tensile strain of 90,000 pounds per square inch before breaking. Up to the breaking point, the adhering coating of nickel exhibited no checking or breaking tendency and the coating parted in line with the point of failure of the base material.

It will be understood that this invention is not to be restricted to the examples given in the specification, but that it is susceptible to various modifications and changes which come within the spirit of the disclosure and the steps of the appended claims.

I claim:

1. A multi-layer metal product which is resistant to blistering and separation of the layers upon heating the metal product at elevated temperatures comprising a first metal forming a base, a thin layer of a second metal adhered to said base by exposing the base to an atmosphere of gaseous carbonyl formed from said second metal and having a thickness of between about 0.00001 and 0.00025 inch, said thin layer being of greater porosity than said base metal, and having the gas therein desorbed therefrom, and a further layer of said second metal disposed over said thin porous layer by exposing said thin layer to an atmosphere of gaseous carbonyl formed from said second metal, said further layer being substantially greater in thickness and higher in density than said thin metal layer, and of a thickness of at least 0.0004 inch.
2. A multi-layer metal product which is resistant to blistering and separation of the layers upon heating of the metal product at elevated temperatures comprising a lead metal base, a thin layer of iron adhered to said lead base by exposing the base to an atmosphere of gaseous carbonyl formed from iron and having a thickness of between 0.00001 and 0.00025 inch, said thin layer of iron being of greater porosity than said lead metal base and having the gas therein desorbed therefrom, and having a second layer of iron disposed over said thin porous layer by exposing the thin layer to an atmosphere of gaseous carbonyl formed from iron, said second layer being substantially greater in thickness and higher in density than said thin layer of iron.

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3. A multi-layer metal product which is resistant to blistering and separation of the layers upon heating of the metal product at elevated temperatures comprising a steel base, a thin layer of chromium adhered to said steel base by exposing the base to an atmosphere of gaseous carbonyl formed from chromium and having a thickness of between about 0.00001 and 0.00025 inch, said thin layer of chromium being of greater porosity than said steel base, and having the gas therein desorbed therefrom and a layer of chromium dispersed over said thin porous layer by exposing said thin layer to an atmosphere of gaseous carbonyl formed from chromium, said second layer being substantially greater in thickness and higher in density than said thin layer of chromium.

4. A multi-layer metal product which is resistant to blistering and separation of the layers upon heating of the metal product at elevated temperatures comprising a Monel metal base, a thin layer of tungsten adhered to said Monel base by exposing the base to an atmosphere of gaseous carbonyl formed from tungsten and having a thickness of between about 0.00001 and 0.00025 inch, said thin layer of tungsten being of greater porosity than said Monel metal base and having all the gas desorbed therefrom, and a second layer of tungsten disposed over said thin porous layer by exposing the thin layer to an atmosphere of gaseous carbonyl formed from tungsten, said second layer being greater in thickness and higher in density than said thin layer of tungsten.

5. A multi-layer metal product which is resistant to blistering and separation of the layers upon heating the metal product at elevated temperatures comprising a first metal forming a base, a thin layer of a second metal adhere to said base by exposing the base to an atmos-

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phere of gaseous carbonyl formed from said second metal and having a thickness of between about 0.00001 and 0.00025 inch, said thin layer being of greater porosity than said base metal, and having the gas therein desorbed therefrom, and a further layer of said second metal disposed over said thin porous layer by exposing said thin layer to an atmosphere of gaseous carbonyl formed from said second metal, said further layer being substantially greater in thickness and higher in density than said thin metal layer, and of a thickness of at least 0.0004 inch, said first metal forming base being selected from the group consisting of steel, copper, aluminum, magnesium, lead and alloys thereof, and said second metal being selected from the group consisting of nickel, chromium, iron, tungsten, molybdenum, cobalt, tellurium and rhenium.

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