

Sept. 25, 1962

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3,055,089

GASEOUS METAL PRODUCT AND PROCESSES

Filed Aug. 6, 1958

2 Sheets-Sheet 1

Fig. 1.

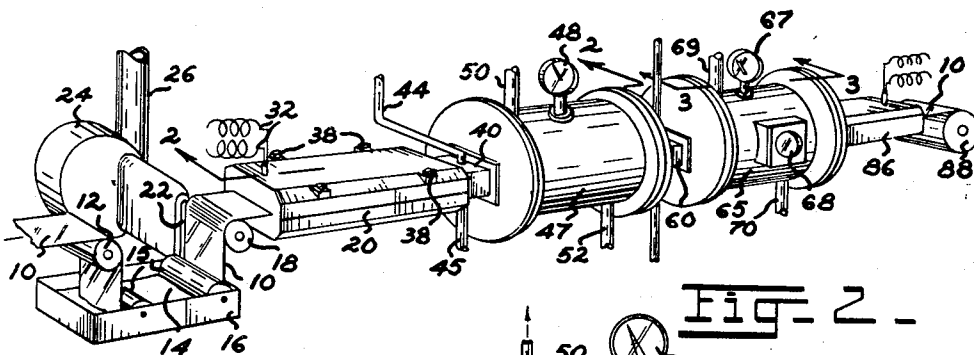


Fig. 2.

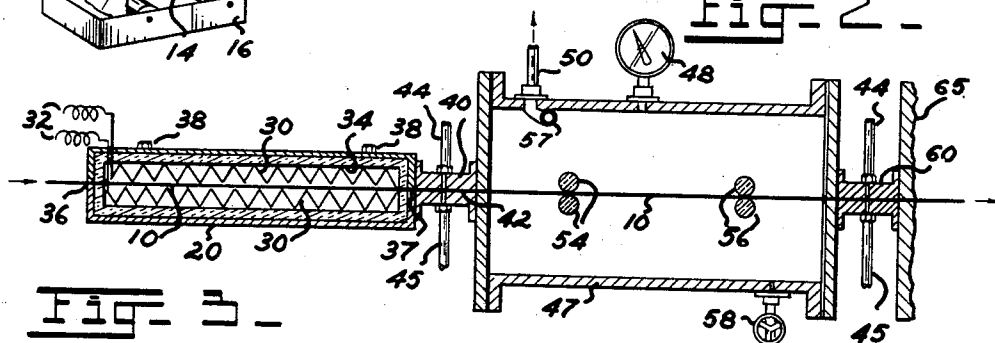


Fig. 3.

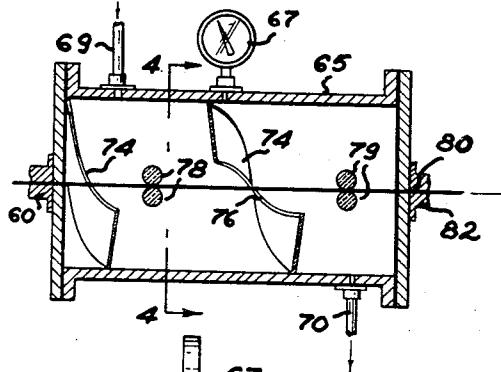


Fig. 5.

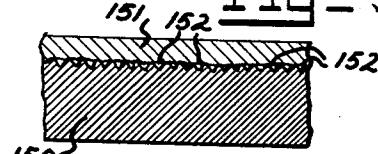


Fig. 6.

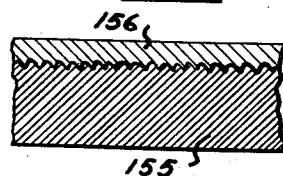
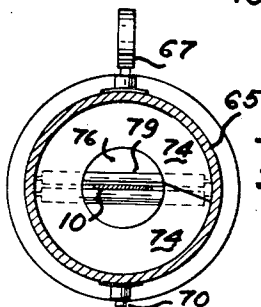


Fig. 4.



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2 Sheets-Sheet 2

Fig. 7

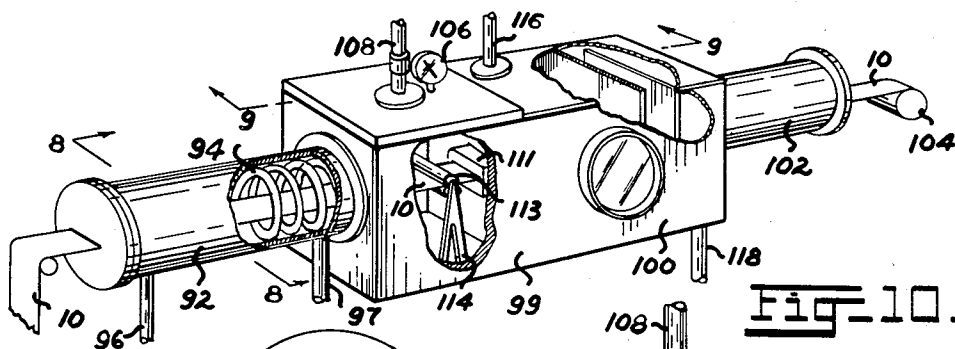


Fig. 8

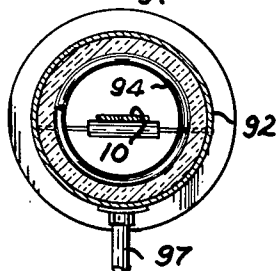


Fig. 10

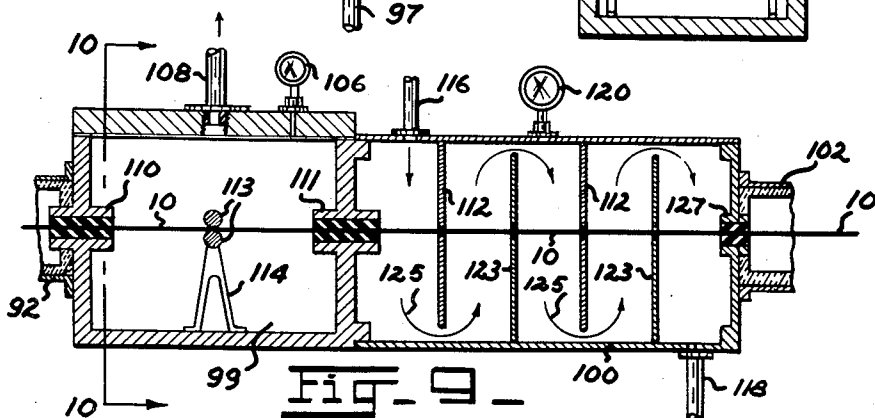
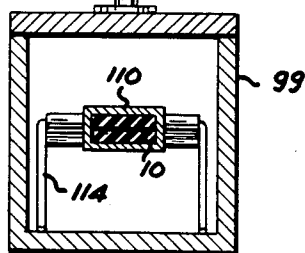


Fig. 9

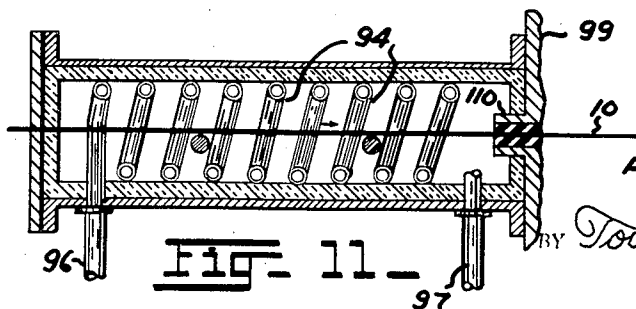


Fig. 11

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Filed Aug. 6, 1958, Ser. No. 753,567
7 Claims. (Cl. 29—196)

This invention relates to the art of gaseous deposition of metals. The invention more particularly is concerned with the preparation of gaseous plated metal products and improved processes for carrying out gaseous metal deposition.

In the preparation of coatings as obtained for example by gaseous metal deposition of metal carbonyls, it has been proposed to produce such metal coatings by treating the base metal, in the form of a strip or other article, which has been mechanically or chemically cleaned, to gaseous metal deposition by heating the material in an atmosphere containing the heat-decomposable gaseous metal compound and thereafter subjecting the gaseous metal treated article to heating to produce a relatively smooth, uniform, coherent continuous metal coating. The present invention distinguishes from the prior processes in that the metal base or material to be plated is subjected to a pre-treatment to produce a dry, deaerated metal surface for receiving the gaseous metal coating.

The invention thus makes it possible for the first time to produce a metal coating which is interlocked with the base metal in such a manner as to produce a substantially integral product. The product thus distinguishes from so-called wet-plating of metal surfaces, e.g., as in electroplating, in that there the plating produces a substantially laminated product and the plating is not interlocked and deposited in the bottom and wall surfaces of the pores or minute, substantially invisible depressions in the metal surface. Heretofore it has been known that such pores and submicroscopic depressions of the surface metal could not be plated utilizing the so-called "wet" processes, wherein solutions containing the salts of the metal to be plated are utilized with or without electrical means.

By the present invention a product is produced wherein the metal plate is carried out utilizing gaseous heat decomposable metals and whereby the metal to be plated is initially heated to drive off all occluded gases and while thus heated is subjected to vacuum or reduced pressure conditions so as to expunge the metal surface to be plated of all gases and permit the gases containing the gaseous metal to enter the pores and sub-microscopic depressions in the metal surface and deposit the metal therein to thus form an interlocked substantially integral metal product.

It is the principal object of the present invention to produce a gaseous metal coated product wherein the metal product produced is made up of a metal base and a coating which is substantially integral therewith.

Another object of the invention is to provide an improved method of plating utilizing gaseous metal compounds and wherein the gaseous metal deposition is carried out so as to produce an interlocking of the metal coating with the base metal and thus provide a substantially deeper penetration of the coating metal into the base metal than has heretofore been effected by wet and dry methods of plating.

It is another object of the invention to provide an improved method of producing metal coatings which can withstand elevated temperatures and bending stresses without causing blistering or peeling of the metal coating.

It is a further object of the invention to provide a method of producing metal coated articles having a co-

herent interlocked metal surface coating over the metal base.

It is a still further object of the invention to provide a product comprising a base metal material which is coated with uniformly deposited metal wherein the metal coated with uniformly deposited metal wherein the metal and diffuse therein so as to become substantially integral with the base metal.

These and other objects and advantages will become apparent as the description proceeds, and taken in conjunction with the drawings forming a part of this specification, wherein—

FIGURE 1 illustrates diagrammatically and pictorially an apparatus for carrying out the gaseous metal plating in accordance with this invention;

FIGURE 2 is a vertical cross-sectional view taken substantially on the line 2—2 of FIGURE 1, and looking in the direction of the arrows;

FIGURE 3 is a similar cross-sectional view as in FIGURE 2, taken substantially on the line 3—3 of FIGURE 1, and looking in the direction of the arrows;

FIGURE 4 is a cross-sectional view through the gaseous metal plating chamber, taken substantially on the line 4—4 of FIGURE 3, and looking in the direction of the arrows;

FIGURE 5 is an enlarged view showing a metal article plated by the wet plating method;

FIGURE 6 is a similar view illustrating a like cross-section of a metal strip plated in accordance with this invention;

FIGURE 7 is a similar view in perspective as in FIGURE 1, illustrating a modification of the apparatus and process therein, and wherein the metal strip to be coated is heated by means of a closed coil and the deaeration chamber is substantially integral with the gaseous deposition chamber, providing a more compact apparatus;

FIGURE 8 is a cross sectional view taken on the line 8—8 of FIGURE 1, and looking in the direction of the arrows;

FIGURE 9 is a somewhat enlarged cross sectional view taken on the line 9—9 of FIGURE 1, and looking in the direction of the arrows;

FIGURE 10 is a similar sectional view taken substantially on the line 10—10 of FIGURE 9, and looking in the direction of the arrows; and

FIGURE 11 is a similar sectional view on a somewhat enlarged scale taken on the line 11—11 of FIGURE 1, and looking in the direction of the arrows.

In the preferred process of the invention, and which will be described with particular reference to the plating of a continuous length metal strip, it is understood that the invention is not to be restricted to the shape or size of the base metal to be plated. For example, the gaseous metal plating may be carried out as a continuous or discontinuous process.

In the embodiment shown in FIGURES 1—4 of the drawings, a metal strip 10, which may comprise steel, aluminum, magnesium, copper, etc., or alloy metals, and which has been previously cleaned as by electrochemical or sand blasting or the like, is passed over the roll 12 and thence into the cleaning bath 14, being drawn under the spaced rolls 15 arranged in the bottom of the cleaning tank 16.

The cleaning bath 14 may comprise rinse water, organic volatile solvent, e.g., ethyl acetate, acetone, petroleum solvent, or mixtures thereof, to wash the strip and remove any grease and foreign particles or pre-cleaning solution. As the metal strip 10 is drawn upwardly and over the roll 18 it is subjected to an air blast 22 which preferably comprises hot air as supplied from the blower 24, the air being drawn into the blower 24 through the pipe line 26, as shown in FIGURE 1.

After passing the metal strip through the tank 16, it is drawn upwardly and over the roll 18 and thence into the heating chamber 20, the strip being moved along and centrally between the vertically spaced electrical heating elements, or resistance coils 30. The heating elements 30 are connected to a source of electrical current by suitable conductors 32. The heating chamber 20 comprises an elongated compartment having insulated inner walls 34 and a slot opening 36 for the entrance of the metal strip 10, and a similar exit opening 37 at the opposite end, the heating chamber being suitably fabricated from two halves which are bolted together, as at 38, as shown in FIGURES 1 and 2.

Joined to and communicating with the exit opening 37 of the heating chamber 20 is a gas lock gate means 40 which comprises an I-shaped member having a longitudinal slot opening 42 therethrough which is adapted to register with the exit opening 37 so as to accommodate the passage of the metal strip 10. Communicating with the opening 42 of the gas lock 40 are tubular conduits 44 and 45 through which is passed the inert gas to provide the gaseous gate interlocked between chamber 20 and the deaerating chamber 47.

The deaerating chamber 47, as shown, preferably comprises an elongated cylindrical chamber which is fitted with a pressure gauge 48 and conduits 50 and 52 for the admission and withdrawal of gas from within the chamber 47. Arranged within the chamber 47 are cooperating pairs of guide rolls 54 and 56 which are arranged to guide and support the metal strip 10 as the same is drawn therealong through the chamber. As illustrated, the conduit 50 is open at its inner end 57 and communicates with the chamber 47, the conduits being connected to a vacuum pump or the like to provide a vacuum or reduced pressure chamber for drawing off any occluded gases from the surface of the metal strip before subjecting the same to gaseous metal plating. The conduit 52 is provided for introducing inert gas or washing gases, such as nitrogen, helium, carbon dioxide, etc., where it is desired to introduce the same while subjecting the strip to reduced pressure conditions. In this manner a gaseous washing effect may be produced simultaneously with the low pressure conditions as effected by the vacuum pump. A valve 58 is provided in the line 52 so that the same may be sealed off where it is desired to use only the vacuum for low pressure treatment in chamber 47.

From the deaerating chamber 47 strip 10 passes through the gaseous gate interlock 60 which is of similar construction and operation as gas lock gaseous gate interlock 40.

The strip is thus passed from the chamber 47 into the gaseous metal plating chamber 65 which is preferably of similar construction as chamber 47, and is provided with a pressure gauge 67 and window 68 for viewing the interior of the plating chamber. Conduit 69 which communicates with the plating chamber at one end permits the introduction of the heat decomposable gaseous metal plating compound. At the opposite end a conduit 70 is provided. The gaseous metal compound is preferably introduced through the conduit 69 and after circulating through the chamber and in contact with the metal strip is withdrawn through the exit conduit 70.

To assist in the even distribution and circulation of the gaseous metal compound in the chamber 65, the same is provided with helical-shaped baffles 74 and 76. Guide rolls 78 and 79 are arranged in the chamber 65 and adapted to support and guide the strip 10 therealong similarly as guide rolls 54 and 56 of chamber 47.

After the metal strip 10 is passed through the gaseous metal plating chamber 65, it is drawn outward through the exit opening 80 and through the gaseous lock gate 82, which is of similar construction and operation as gas locks 40 and 60, and thence through the heat treating chamber 86 which is constructed and operated similarly as the heating chamber 20. The finished plated strip is

drawn from the heat treatment chamber 86, and after cooling in the air, is wound up on the storage roll 88, as illustrated in FIGURE 1.

In a modification shown in FIGURES 7-11, the metal strip being treated, as shown at 10, is passed through a heating chamber 92, which chamber in this instance is heated by the helical coils 94 through which heated fluid, such as steam, hot water or the like fluid, is passed. Strip 10 is supported and drawn centrally of the coils 94 so as to be evenly heated. Conduits 96, 97 are connected to the chamber 92 and the coil 94 for passing heated fluid through the coil.

After the strip 10 has passed through the pre-heating chamber 94 it is conducted into the vacuum or low pressure chamber 99 and thence into the gas plating chamber 100, and finally through the post heating or annealing chamber 102, after which the finished gas plated metal strip 10 is rolled up on the storage roll 104.

The low pressure chamber 99 is provided with a pressure gauge 106, and the conduit 108 which is in communication with the interior of the chamber is provided, the conduit being connected to a vacuum pump or evacuating prime mover whereby the chamber 99 is kept under reduced pressure. Provision is made at the inlet and exit of the strip for properly sealing the openings. In this instance the gates 110 and 111 comprise sponge rubber seals which function as a squeegee to seal the strip as the same moves into and out of the chamber 99. Appropriate guide rolls 113 are arranged on the standard 114 and which support and guide the strip 10 through the low pressure chamber.

In the gaseous plating chamber 100, conduits 116, 118 are provided through which the heat decomposable gaseous metal compound is introduced and discharged respectively, as shown more clearly in FIGURE 9. A pressure gauge 120 is provided for observing the fluid pressure in the gaseous plating chamber.

In order to circulate the gaseous metal compound in contact with the moving sheet or strip 10, suitable baffles 112, 123 are spacedly arranged longitudinally of the plating chamber, as illustrated in FIGURE 9. The gaseous metal compound is admitted through the conduit 116 at one end of the chamber 100 and passes downwardly and upwardly about the baffles 112, 123, as indicated by arrows at 125, the exhaust gases and unused decomposition products are drawn off through the conduit 118 at the opposite end of the gaseous plating chamber.

The strip 10 after passing through the gaseous metal plating chamber is drawn outwardly through the exit gate 127 and into the post heating chamber 102, and after cooling in the air is stored on the roll 104.

An important aspect of applicant's invention is the provision of a vacuum or low pressure pretreatment following the heating of the strip or metal article to be gaseous metal plated.

The vacuum pressures used may vary depending upon the particular metal being plated, in each instance being sufficiently high to produce a perfectly dry metal surface being free of moisture and water vapor and wherein the pores and sub-microscopic depressions in the metal surface are free of all occluded gases. This pre-heating and vacuum or low pressure treatment makes it possible to produce a greater depth of penetration of the gaseous metal plated layer into the surface of the base metal and thus bring about the production of a metal product having a metal coating layer which penetrates into the base metal to provide the same with a layer or metal which is interlocked with the base metal thus forming a substantially integral metal layer therewith.

The invention accordingly provides a method of dry plating metal articles in a manner to provide the same with a coating metal layer which adheres tenaciously to the base metal forming a coherent, substantially integral body. As is well known, in wet electroplating it has been the practice to apply a flash coating of metal such as

copper over the base metal to improve the cohesion of the plated metal. Such practice becomes entirely unnecessary with gaseous metal plating in accordance with applicant's invention.

In carrying out the gaseous metal plating in accordance with applicant's process, leakage of gas from one compartment to another is effectively prevented by the use of inert gas gate locks, such as shown at 40 and 60 in FIGURE 2, the inert gas medium used in this instance being carbon dioxide, nitrogen or the like, the pressure being maintained slightly higher than the chamber to be protected so as to cause leakage of the inert vapor into the chamber rather than leakage of the gas outwardly of the chamber.

In this process a stream of gaseous material is conducted into the gaseous plating chamber and circulated about the heated metal strip. The gaseous plating atmosphere may be formed by mixing an inert gas with the vapors of a volatile metal compound or by atomizing a liquid metal compound into a blast of hot inert gas or other equivalent method.

Carbon dioxide, helium, nitrogen, hydrogen, the gaseous product of controlled burning of hydrocarbon gases free of oxygen, and the like, have been utilized as a carrier medium or inert gas medium.

In some instances the use of hydrogen is preferred, as for example, in the cleaning anneal chamber where its ability to act as a reducing agent may be put to advantage to remove the oxide film or rust from iron or metal strip being plated.

Metals to be deposited may be introduced as gaseous metal carbonyls or vaporized solutions of certain of the metal carbonyls in readily vaporizable solvents (for example, petroleum ether), also nitroxyl compounds, nitrosyl carbonyls, metal hydrides, metal alkyls, metal halides, and the like.

Illustrative compounds of the carbonyl type are nickel, iron, chromium, molybdenum, cobalt, and mixed carbonyls.

Illustrative compounds of other groups are the nitroxyls, such as copper nitroxyl; nitrosyl carbonyls, for example cobalt nitrosyl carbonyl; hydrides, such as antimony hydride, tin hydride; metal alkyls, such as chromyl chloride; and carbonyl halogens, for example osmium carbonyl bromide, ruthenium carbonyl chloride, and the like.

Each material from which a metal may be plated has a temperature at which decomposition is complete. However, decomposition may take place slowly at a lower temperature or while the vapors are being raised in temperature through some particular range. For example, nickel carbonyl completely decomposes at a temperature in the range of 375° F. to 400° F. However, nickel carbonyl starts to decompose slowly at about 175° F. and therefore decomposition continues during the time of heating from 200° F. to 380° F.

A large number of the metal carbonyls and hydrides may be effectively and efficiently decomposed at a temperature in the range of 350° F. to 450° F. When working with most metal carbonyls we prefer to operate in a temperature in the general decomposition range of the volatile compounds.

If the metal is, for example, hot drawn strip, the hot strip upon cooling to the plating temperature range after deaeration may be led directly to plating chamber with or without an annealing stage therebetween. If an anneal is desired, the operation within the apparatus may be carried out in a manner similar to that used when starting with cold metal. The metal strip may be raised to and maintained at desired temperatures by causing the metal to conduct electricity or by induction heating.

The temperature in preheating and post heating chambers is considerably higher than plating temperatures, i.e., in the range of 400° to 1200° F.

Preparatory to coating the strip, the metallic material may be cleaned by employing conventional methods used

in the art, comprising electro-chemically cleaning by moving the same through a bath of alkali or acid electrolyte wherein the strip is made the cathode or anode.

Pickling of the metal with hydrochloric, sulfuric or nitric acid, or a combination of acids may also be made as a part of the cleaning process, and the strip thoroughly rinsed or washed prior to introduction into the plating apparatus.

However, if the metal strip is in good condition a cleaning anneal may suffice, in which event the strip may be heated just prior to entering the vacuum treatment chamber.

In a cleaning anneal any grease and the like will be burned away by bringing the strip to red heat.

The invention will be more clearly understood from the following description of one embodiment of the apparatus and its mode of operation.

By subjecting the metal to be plated to a pre-heating treatment prior to the vacuum or low pressure treatment, occluded gases are more readily removed and at a lower vacuum pressure. This vacuum deaeration treatment prior to gaseous metal plating constitutes an essential step of the process in order to produce an absolutely dry metal surface. The presence of hydrogen, oxygen or water vapor entrapped or occluded in the pores or irregularities over the surface of the metal is avoided by the present process and a thoroughly coherent metal coating produced.

The post heat treatment of the gaseous plated metal may be omitted if desired, but is preferred in most cases to produce a more even textured and smoother plating film or coating. The post heat treatment also is advantageous in preventing the entrainment of moisture. To further assist in this, it is preferable to carry out the post heat treatment in the presence of inert gas, e.g., helium, argon, nitrogen, carbon dioxide or the like. This may also be accomplished by allowing a controlled amount of gas leakage of waste gas to take place from the plating chamber or by circulating a small amount of the relatively spent or inert gases through the post heating chamber.

The post heating temperatures employed will vary for different metal platings and base metals treated as aforementioned. Generally the post temperature is the same or somewhat higher than the pre-plating heat treatment, the latter being governed by the temperature required to effect substantially complete removal of gas occlusions in the surface depressions of the base metal under the reduced pressure conditions. The post heating of the plated product in addition to degassing the strip may be controlled to effect annealing of the strip. The duration of heating in both pre-heating chamber and post heating chamber may be suitably varied to provide for a heat treatment of from ten to twenty minutes as desired.

The following examples are illustrative but not limitative of the invention.

EXAMPLE I

Nickel-Coated Steel Strip

A steel strip which is to be coated and which has been chemically cleaned in the conventional manner is passed through the rinsing bath and air dried by hot air blast. The strip is then moved along through the pre-heating chamber and subjected to a temperature of 525° F., the strip being moved along at a uniform rate and such that the plating time allowed is approximately two to three minutes. The heated strip then passes directly into the low pressure or vacuum chamber where it is subjected to a vacuum of approximately 1 mm. Hg after which the strip is passed along and through the gaseous metal plating chamber. Nickel carbonyl in the form of vapor and admixed with carbon dioxide carrier gas is fed to the plating chamber. Approximately five cubic feet of nickel carbonyl-carbon dioxide mixture per hour is fed through the plating chamber, the metal carbonyl being present in

the mixture of vapor is nickel carbonyl and carbon dioxide in the proportionate amount of about five ozs. of carbonyl per cubic foot of carbon dioxide. The temperature in the plating chamber and strip is approximately 400° F.

For a plating exposure of two and one-half minutes, this provides a coating of nickel of approximately 0.002 inch which interlocked and penetrated into the micro-pore surfaces of the metal is provided. After gaseous plating the strip is moved from the plating chamber through the post heating chamber where it is subjected to a temperature of approximately 700° F. in the presence of carbon dioxide.

EXAMPLE II

Nickel Coated Aluminum

Aluminum metal strip is substituted for steel strip material and processed as in Example I, except that both pre-heating and post heating treatments are carried out at about 500° F.

EXAMPLE III

Cobalt Coated Steel

Steel strip in this example is processed as in Example I, utilizing cobalt carbonyl as the heat-decomposable gaseous metal compound.

The cobalt carbonyl is introduced at a rate of approximately one pound of carbonyl (liquid) per minute. Gaseous plating temperature is maintained at approximately 425° F. and nitrogen gas used as the carrier in place of carbon dioxide.

EXAMPLE IV

Antimony Coated Copper Metal

Copper sheet is coated with antimony by first pre-heating copper strip material free of foreign matter in an atmosphere of helium at 525° F. The heat treated strip is then passed into a vacuum chamber where the hot metal strip is subjected to a vacuum pressure of 50 mm. Hg and in an atmosphere of carbon dioxide. The strip is then immediately passed to the gaseous metal plating chamber where it is subjected to a gaseous atmosphere of antimony hydride heated to 400° F. to effect decomposition and plating out of antimony metal onto the copper strip. The post heat treatment is carried out at a temperature of 475° F. to produce a final coherent antimony coating on the copper metal base strip, being integrally united with the copper metal.

EXAMPLE V

A steel sheet is gas plated with molybdenum metal similarly as described in Example I, and using molybdenum carbonyl in place of nickel carbonyl. A temperature of approximately 450° F. is used in the gas plating chamber.

While the foregoing examples are given to more particularly point out how the invention may be practiced, it will be understood that the invention is not to be specifically limited thereby. The essence of the invention is the provision of a pre-treatment so as to deaerate or de-gas the metal to be gaseous plated so as to provide a perfectly dry, water-vapor and hydrogen free metal surface for receiving the gaseous metal plating. The process provides a finished product as aforementioned, wherein the plating or metal coat is interlocked with the base metal so as to form a substantially integral metal product.

In this connection, FIGURES 5 and 6 illustrate in enlarged section, the essential difference in structure between wet plated metal products and gaseous or dry plated metal products. As illustrated in FIGURE 5, metal coating is applied over conventional treated metal as generally indicated by the reference character 150 which is wet plated by a metal coating as indicated at 151, there is invariably a discontinuous layer or plurality of microscopic gas pockets or bubbles 152 in between the metal coating layer 151 and base metal 150. In extreme

cases where these gas occlusions become large enough or continuous, the metal coating peels away from the base metal.

Referring to FIGURE 6, there is illustrated in enlarged section a gaseous metal coated structure as produced in accordance with this invention. In this instance, as shown, the base metal 155 and metal coating 156 are interlocked to provide a substantially integral structure. The microscopic pores at the surface of the metal are freed of gas occlusions and gaseous metal allowed to enter and thus penetrate into the body of the base metal, deposition of metal taking place to thus provide an interlocking of the metal coating or plating with the base metal.

The foregoing description of a method of gaseous metal plating and product obtained thereby is accordingly distinguished from conventional wet plated products and methods. Whereas the method and apparatus disclosed herein are susceptible to various changes and modifications without departing from the principle and spirit of this invention, it is intended that such modifications as are required to adapt the invention to different conditions and uses are contemplated as within the scope of the invention except as restricted in the appended claims.

This application is a continuation-in-part of my application Serial No. 439,075 filed June 24, 1954.

What is claimed is:

1. A method of producing metal articles having a layer of metal interlocked with the surface of the article by the deposition of metal from heat-decomposable metal compounds wherein the article to be plated is pretreated to clean and deaerated and moved along through a plating chamber containing a heat-decomposable gaseous metal compound, and wherein the temperature within the plating chamber is sufficient to cause decomposition of the heat-decomposable metal compound and plating out of the metal onto the article, the improvement which consists in the step of subjecting the cleaned metal article to be plated to a pre-heat and vacuum treatment to deaerate the pores of the surface of the article to remove occluded gases, and immediately thereafter subjecting the same to gaseous metal plating, and circulating said gaseous metal compound about said article in a helical shaped path to cause said metal compound to penetrate deeply into the surface of said article and diffuse in the pores and then thermally decomposed to cause the metal constituent to be deposited into said pores, said vacuum treatment being conducted at a temperature between about 400 to 1000° F.

2. A method of producing a metal article having a layer of metal interlocked with the base metal and forming a substantially integral body of metal, which comprises thoroughly cleaning the surface of the base metal including rinsing and air drying to remove foreign matter, heating the metal and while thus heated subjecting the same to reduced atmospheric pressure conditions to deaerate the pores of the metal surface of occluded gases, and then subjecting the resultant deaerated metal to gaseous metal deposition by intimately contacting said deaerated metal with a heat-decomposable metal compound of molybdenum and circulating said gaseous metal compound about said article in a helical shaped path to cause said metal compound to penetrate deeply into the surface of said article and diffuse in the pores and then thermally decomposed to cause deposition of the metal constituent thereof into the pores and sub-microscopic depressions of the base metal to produce a molybdenum metal plated product having integrally united layers of metal, said heating of the metal in a reduced atmosphere being conducted in the presence of non-oxidizing conditions.

3. A method of producing a metal article having a base metal and continuous layer of metal interlocked with said base metal and forming a substantially integral body of metal, said method comprising cleaning the surface of the base metal including rinsing and air drying to remove foreign matter, heating the metal and while thus heated subjecting the same to reduced atmospheric pres-

sure conditions to deaerate the pores of the metal surface of occluded gases and produce a dry, deaerated base metal surface, subjecting the thus deaerated metal to gaseous metal deposition by contacting said deaerated metal with a heat-decomposable gaseous metal compound at a temperature sufficient to cause thermal decomposition of the gaseous metal compound and circulating said gaseous metal compound about said article in a helical shaped path to cause said metal compound to penetrate deeply into the surface of said article and diffuse in the pores and then thermally decomposed to cause deposition of the metal constituent thereof into the pores and sub-microscopic depressions of the base metal, and thereafter heating the plated material to a temperature between about 475° F. and 700° F. to effect degassing and annealing of said plated material and produce a finished product, said last-mentioned heating being conducted in the presence of inert carbon dioxide gas.

4. A product made in accordance with the method of claim 1, wherein the base metal is aluminum and the outer metal layer is nickel.

5. A product made in accordance with the method of claim 1, wherein the base metal is steel and the outer metal layer is cobalt.

6. A product made in accordance with the method of

claim 1, wherein the base metal is copper and the outer metal layer is antimony.

7. A product made in accordance with the method of claim 1, wherein the base metal is steel and the outer metal layer is molybdenum.

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